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Project A-389

X-RAY DIFFRACTION STUDIES OF THERMAL
MOTIONS IN CRYSTALS

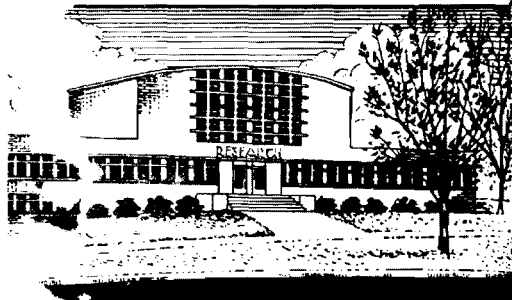
by

R. A. Young

June 1, 1958 to May 31, 1959

Contract No. NOnr 991(00) and 991(06); NR 017-623

Placed by the
Office of Naval Research (Physics Branch)
Washington 25, D. C.



Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
OF THE GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

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ABSTRACT

The general problem is the study, by x-ray means, of thermal vibrations of the atoms in crystals and their interactions with other phenomena of interest in crystal physics. The first experimental studies deal with the temperature dependences of the motions in AgCl as revealed by their effect on the Bragg intensities. Extended consideration has been given to the background of the problem as found in the theory of and the literature on thermal motions of atoms, or lattice vibrations, as related to x-ray measurements of Bragg intensities.

A method for determining temperature factors (and hence Debye- Θ 's) from temperature dependences of x-ray intensities is derived and experimentally illustrated. A second method is suggested.

Possible effects on the data of such things as (1) thermal diffuse scattering (TDS), (2) temperature dependence of primary extinction, and (3) defect concentration are considered in some detail. Possibilities for assessing or studying the same factors through their effects on the apparent Bragg peaks are noted.

Equipment design and performance, design of experiments, experimental techniques, and characteristics of the specimen, etc. are discussed in detail, especially in connection with accuracy and reproducibility.

Particular attention has been given to means for shaping the specimens without distorting them. Economical use of personnel time and materials has been considered.

A conceptual device referred to as the "acceptance region" model has been developed and utilized to determine the requirements on and the factors affecting the x-ray beam geometries.

Intensity data were collected for (hhh), (hh0), and (h00) reflections of AgCl at 10-degree intervals over the temperature range 90°K to 300°K.

Variations in diffraction peak breadths with temperatures were observed and are discussed.

Reproducibility in the intensity vs. temperature measurements was of the order of 1/2 to 3/4%.

The amplitudes of thermal motions of the silver and chlorine atoms were found to be quite similar, in agreement with observations by others. This result is interpreted to mean that the acoustic (rather than optical) modes of lattice vibrations have dominant importance to x-ray observations of the present type in AgCl.

An inflection in the semi-log plot of intensity vs. temperature was found in the case of the (111) reflection. The possibility that the inflection may indicate a temperature induced change in bond character will be investigated.

The errors introduced by TDS and α -doublet separation (both of which are temperature dependent) in the measures of Bragg intensities vs. temperature were partially overcome by a technique involving extrapolation to $\sin \theta = 0$.

Evidence for anisotropy in the thermal motions of the atoms in AgCl was not conclusive; further effort will be expended definitely to support or to reject present indications of anisotropy. Existence of anisotropy would probably indicate anharmonic thermal vibrations.

Approximate Debye- Θ 's have been determined from the intensity vs. temperature data which are in reasonable agreement with literature values obtained by other means.

The general technique of extracting crystal-physics information from careful measurements of the temperature dependence of the Bragg intensities continues to show promise. Contemplated applications of the results includes preparation of detailed electron density maps (for which the temperature factors will be determined from their temperature dependences), first of AgCl and then of other materials. The study of various kinds of lattice defects and crystal imperfections will follow.

SECTION 1

INTRODUCTION

I. INTENDED FUNCTIONS OF THIS REPORT

This report has been written with the intent that it shall be of continuing use in the actual conduct of the project as well as a report to the sponsor. Thus an attempt has been made to discuss here much of the literature, the theoretical background, and the experimental considerations and techniques which are and will continue to be relevant to the work of this project on studies of thermal motions in crystals (particularly AgCl) by means of observations of Bragg intensities. Further, an attempt has been made to present the generally applicable material in sufficient detail and logical consistency so that this report may serve both as a manual and, at times, something of an introductory text on x-ray studies of thermal motions (by studies of Bragg intensities). It is hoped that it may be read with understanding by, for example, first year graduate students in physics or chemistry who have only rudimentary training and experience in x-ray diffraction.

It is believed that the availability of a manual, such as this report is intended to be, will have special value in acquainting new staff members with the work of the project and in otherwise enhancing the continuity and unity of project activities.

II. GENERAL PROBLEM AND BACKGROUND

A. Statement of the General Problem with Some Background Information

As indicated by the title, this project is for the studies of thermal motions in crystals by x-ray diffraction. It is intended to include, when

appropriate, studies of the thermal motions themselves, methods for determining them, and applications of the measures and methods to other problems in crystal physics. Examples of such other problems are radiation damage mechanisms and detailed electron density distributions.

The thermal motions, or lattice vibrations, are of fundamental interest in a variety of problems. They are involved in and to some extent may be determined from specific heats, elastic constants, infrared and Raman spectra, the temperature dependence of thermal expansion, the temperature coefficient of electrical resistivity, and thermal conductivity, among other things. The inelastic scattering of cold neutrons, which is closely related to x-ray thermal diffuse scattering, allows determination of the entire elastic spectrum. An extraordinarily long time is required to collect the data, however, and only a very few places have the neutron flux even to attempt it (principally Brookhaven and Chalk River).

Much of the basic x-ray theory involved in the present project is covered by James¹, particularly in his Chapter Five which considers the influence of temperature on the scattering of x-rays. There are two principal effects: (1) The intensities of the Bragg peaks are reduced; the half-widths of the peaks are not changed as long as the vibrations are approximately harmonic. (2) Interaction of the x-ray photons with the lattice phonons gives rise to thermal diffuse scattering (TDS) which appears as extra scattered intensity distributed nonuniformly throughout reciprocal space.

While TDS measurements can in principle yield the entire elastic spectrum they are in fact tedious to make, subject to large correction terms, such as that for Compton scattering, and are somewhat difficult to analyze.

While the TDS method is by no means being overlooked in the present work, nor is its value being underestimated, it is the intent here, at least at first, to compromise the completeness of the thermal vibration information for the sake of easier attainability. Attention is first directed, therefore, to the method by and the extent to which thermal vibration information may be obtained from the effect of these vibrations on the Bragg intensities. Correlations of results and comparisons of methods with those reported in the literature will be made where possible. It is hoped finally to introduce defects into the crystals and to note their effect on the thermal vibrations as measured here. It is also expected that the thermal motion determinations made here will be used to increase the detail that may be obtained in determinations of the electron density distribution in the crystal study.

To the extent that the lattice vibrations are harmonic and the Debye-Waller theory applies, the effective scattering factor, f , of an atom in vibration is related to the scattering factor, f_0 , of the same atom at rest by

$$f = f_0 e^{-M} \quad (1)$$

where

$$M = B \frac{\sin^2 \theta}{\lambda^2} = 8\pi^2 \overline{u^2} \frac{\sin^2 \theta}{\lambda^2} \quad (2)$$

M is the Debye-Waller temperature factor,

$\overline{u^2}$ is the mean square displacement of the atom from its rest position (parallel to the scattering vector),

θ = the Bragg angle,

λ = the x-ray wavelength, and

B, often called simply the "temperature factor," depends in general upon the atom type, the direction of the scattering vector, and the temperature.

Individual anisotropic temperature factors have frequently been determined from sets of isothermal x-ray data. In the general case B is assumed to have ellipsoidal symmetry and the dependence of M on $\frac{\sin^2 \theta}{\lambda^2}$ is then employed to determine the principal axes of B. The values of B so determined may be in error for a variety of reasons which are not encountered if B is determined from its temperature dependence. Very few determinations of B have been made in this way and, insofar as the writer is aware, these were made only by the determination of the ΔB between two fixed temperatures. Methods for the determination of thermal vibration parameters (B , $\overline{u^2}$, Debye- Θ) from intensity versus temperature data are being investigated in the present work. Both the slopes at various temperatures and the values of the parameters required in a curve fitting procedure are measures from which the desired quantities, and possibly their temperature dependence, may be determined. Investigations based on the temperature dependence of intensities are attractive at this point because, with counter methods, the temperature dependence of the intensity of a particular reflection can frequently be determined with greater accuracy than can the intensity of one reflection relative to another.

Because the values of the methods used are expected to depend heavily upon the accuracy of the measurements, one of the major problems of the

current investigation is the determination of relative intensities and changes in intensities with near-maximum precision in a reasonable length of time. A considerable portion of the following report is, therefore, devoted to a discussion of the factors affecting accuracy. These include such things as absorption, extinction, and the contribution of TDS to apparent Bragg intensities as well as the various instrumental factors and matters of technique.

B. Choice of Specimen Material

Since the thermal motions and the techniques for studying them were of interest, rather than any particular crystal, some choice of specimen was possible. A balance between simplifying and complicating factors was attempted as follows. It was felt that all atomic positions should be fully determined by symmetry so that no part of the observed changes in intensity would be due to changes of atomic positions. It was thought that two atom types should be present in order that (a) ionic as well as covalent bonding should be possible, (b) two different amplitudes of thermal motion would be expected, and (c) any results might be more readily transferable to crystals of interest for themselves than would be the case if the studies were done on even more elementary crystals. It was felt, however, that more than two atom types would be excessive. The NaCl-type structure was chosen because of the simple way in which the structure factors are compounded from the individual scattering factors. Because of the possible usefulness of the information to be gained, on thermal motions, for the determination of the details of electron density distributions, a simple series of crystals

which would show varying degrees of covalency was sought. It was also desired to search for a possible introduction of anisotropy in B due to covalency. Because of the possibility of connecting changes in thermal vibrations with radiation damage, specimens in which the defect concentration could readily be changed were also desired. The silver halides seemed to satisfy all of these requirements.

The particular member of the group chosen for first investigation is AgCl. This choice was guided by availability in high purity and by the fact that a TDS study had been done on it.

C. Statement of Initial Problems

The Debye characteristic temperature, whatever the shortcomings of the Debye theory, is a widely used computational quantity. As such, it provides a convenient point for comparison of some of the results of various methods for studying thermal vibrations. The first studies of AgCl are therefore directed toward the determination of Debye- Θ values both as a function of direction and as a function of temperature, from the temperature dependence of Bragg intensities, and are also directed toward comparison of these results with the Debye- Θ 's determined by other means. The next step will be the determination of Debye- Θ 's as a function of direction at one temperature from relative intensities of reflections which correspond to each of several directions in reciprocal space. Comparison of the two sets of results will constitute a partial check on the validity of the assumptions which are different in each of the two methods. When these initial studies are completed, it is expected that, on the one hand, detailed electron density maps will be prepared; and, on the other hand, the defect concentration in the

specimens will be varied by variations in the impurity content. Investigations will then be extended to the members of the series which have different degrees of covalency in their bonds and different ionic-radius ratios.

III. LITERATURE

The literature abounds with studies of the silver halides and with x-ray diffraction topics of peripheral interest. Of the x-ray papers only a very few of those which are most directly relevant to the immediate problem are discussed below. Similarly, only those papers dealing with AgCl, and particularly those which are on topics relating to lattice vibrations are discussed. A much more extensive literature search has been made and will be drawn upon as appropriate in future reports.

A. Temperature Factor, TDS, and Elastic Spectrum

Laval² is generally credited with having first recognized the origins of and having developed the theory of TDS. Lonsdale, in a more readily available publication³, has given a full account of work on diffuse scattering and extra reflections up to 1942. Laval has continued his work on TDS^{4,5}. One of his conclusions is that the elastic coefficients have in fact a lower symmetry than they do in the Voigt formulation. The lower symmetry arises from relaxation of the requirement that the stress tensor be symmetric.

Blackman⁶ goes into more detail than does James¹ in considering the effect of the actual vibrational spectrum upon the x-ray temperature factor when more than one type of atom is present. He notes that, because of the existence of peaks in the vibrational spectrum at low frequencies, the Debye- Θ as determined from x-ray measurements is always less than that to be expected from elastic measurements. Combining formulae (21) and (22) of

Blackman⁶ gives the following relations among the Debye temperature, Θ_x , determined from Bragg intensities; the vibrational frequency spectrum, $p(\nu)$, the masses, m , and the mean square displacements, $\overline{u^2}$, (perpendicular to the Bragg planes) of the two atom types in alkali halide type crystals:

$$\frac{3h^2 T}{4\pi^2 k_x^2} = \frac{1}{4\pi^2} \frac{\int \rho(\nu) \bar{\epsilon} \nu^{-2} d\nu}{\int \rho(\nu) d\nu} = \frac{1}{2} (m_1 \overline{u_1^2} + m_2 \overline{u_2^2}) \quad (3)$$

where

h is Planck's constant,

k is Boltzmann's constant,

T is the absolute temperature,

and

$\bar{\epsilon}$ is the mean energy of a linear harmonic oscillator given by

$$\bar{\epsilon} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \quad (4)$$

Because we are particularly interested in the temperature dependences of Bragg intensities, and because increasing temperature causes an increase in TDS and a simultaneous decrease in the Bragg intensity, the contribution of TDS to the apparent Bragg intensity is of considerable importance to us. The one-phonon contribution is especially important because it reaches a maximum at the Bragg position. Paskin and Chipman¹³⁻¹⁶ have made both theoretical and experimental investigations of the contributions of TDS to the apparent Bragg intensity, particularly the one-phonon and two-phonon contributions. They have derived a graphical method for correcting for the

TDS contribution¹⁵ to powder measurements. Paskin¹⁶ has considered the effect of using separate wave velocities for the longitudinal and transverse modes and finds that this better approximation to reality gives a larger rather than a smaller TDS contribution to the apparent Bragg intensity. Nilson¹⁷ has noted that the error in the determination of the x-ray temperature factors from single crystal data at a single temperature largely cancels the error due to TDS; thus, crystal structure determinations may not be significantly affected by TDS. Any thermal vibration information deduced from the temperature factors obtained during an isothermal crystal structure refinement certainly would be in error, however, and possibly, very badly so. Nilson has reworked the data of Renninger¹⁸ on NaCl to account for the TDS contribution and thereby changes the value of the x-ray Debye- Θ from 319°K to 302°K. The specific heat value is 281°K, and the value obtained from elastic constants is 303°K. In this case, at least, it is clear that a correction for the TDS contribution to the Bragg intensities considerably improved the agreement of the elastic and the x-ray values.

B. Determination of Deformation or Defects by Studies of Temperature Factors

Anything which is capable of causing any distortion of the lattice (such as foreign atoms or defects, including those produced by radiation damage) may be expected to affect the thermal motions by effecting changes in the force constants. It would also affect the x-ray temperature factors by increasing the apparent zero point motion (i.e., by introducing random displacements which exist even at absolute zero). A Russian paper¹¹ entitled "X-ray Investigation of the Deformation and Bond Strength in the Crystal Lattices of Metals and Alloys" distinguishes four such distortions and

discusses the separation of the static and dynamic distortions by means of their effect on the Bragg intensities. That work involves principally the comparison of the relative intensities of selected reflections. In study of boron carbide Tucker and Senio¹² have done a full crystal structure determination. From the anisotropic temperature factors (all at one temperature) obtained, they have deduced that the central carbon atom in the three-carbon chain in this structure is selectively removed by neutron bombardment. The above are two of the best examples of deformation or damage studies by x-ray diffraction.

C. Bonding Detail in Electron Density Maps

As was stated above, it is intended finally to make detailed electron density maps for some of the crystals. Work done on α -quartz by the writer⁷ is of interest in this connection as well as in connection with the general problems of accuracy and of thermal motions. The work of Wagner, Witte, and Wölfel⁸, which has appeared in a series of articles, probably represents the most careful electron density determinations that have been published. They have reduced the probable error in the structure amplitude to the order of 1 to 2%. Peters⁹, who worked with Brill and Hermann on x-ray investigation of chemical bonding during the years around 1940, has set down some criteria for detecting chemical bonding detail in electron density distributions. He points out that in order to measure electron distributions with an accuracy of about ± 0.1 electrons/ \AA^2 , for crystals containing light atoms, it is necessary to determine the intensities over a range of 1 to 10,000. The strong reflections should have an accuracy of $\pm 1\%$ and the weakest 20 to 30%.

The form factors ordinarily used in crystal structure analysis are spherically symmetric. It would be expected, of course, that bonding would destroy the spherical symmetry. McWeeny has provided a mathematical formula¹⁰ which recasts the form factor in such a way as to take into account a variable degree of deformation due to bonding. McWeeny's technique may be extremely useful in the final stages of fitting calculated to observed electron density distributions.

D. AgCl - Photolytic Effects and Purity

We shall now turn our attention specifically to AgCl. The bulk of the work that has been done on AgCl has been done on powders, emulsions, or single crystals of only moderate purity. Since the photolytic effects are greatly influenced by impurities, by static deformations, and by particle size, it is important that all work be referred to unstrained single crystals of high purity. Nail, et al.¹⁹, have described the preparation of very high purity silver halide crystals. In these crystals of AgCl and AgBr the concentration of the more important impurities (e.g., divalent metals) is less than 10^{-7} .

Seitz²⁰ has made an extensive review of the properties of silver halide crystals. He reviewed the electronic properties and the nature, formation, and annealing of defects. Below 300°C Frenkel defects predominate. These defects provide an interstitial silver ion; colloidal darkening occurs from coalescence of these silver ions to give colloidal specks of silver not larger than about 100 Angstroms. Such darkening is not expected to be reversible. So-called molecular darkening, which precedes the colloidal stage, is reversible by bleaching.

Seitz notes that the quantum yield of photo electrons is nearly independent of temperature. This indicates that we might expect that the rate of production of defects in our specimens by our investigatory x-ray beam should also be approximately independent of temperature.

Seitz lists a number of desirable experiments, one of which is low temperature x-ray investigation of AgCl to see if the diffuse scattering observed by Burgers and Hiok²¹ is of thermal origin or if it is due to permanent distortions. The work of this project will bear on that point. Seitz notes that the darkening depends heavily on dislocation density and hence on plastic flow; moving dislocations are especially important because they form clusters of vacancies. Kooij and Burgers²² have presented x-ray evidence for the formation of an actual silver lattice structure in irradiated AgCl single crystals. However, it seems certain that their crystals could not have had such high purity as do those described by Nail, et al.¹⁹. Extensive investigations of the silver halides, particularly in regard to defects and latent image formation, have, of course, been carried out by persons such as Chester Berry²³ at the Kodak Research Laboratories.

Nail, et al.¹⁹, also of the Kodak Research Laboratories, note that the high purity crystals do not darken upon irradiation. Moser, Nail, and Urbach²⁴ note that the darkening of pure AgCl is sub-visible, but even 5 ppm of copper have a profound influence and cause visible darkening in light. They note that the darkening is reversible by annealing.

Some of the high purity single crystal material described by Nail, et al.¹⁹, was kindly supplied by the Kodak Research Laboratories for the present investigation. F. Moser²⁵ points out that the expected photolysis in these specimens is less than 10^{13} silver atoms per cubic centimeter and can be regressed by annealing.

Thus, while the principal reason for the wide general interest in the silver halides is the photochemical effect which they show, it was to be expected at the outset of this project that the photolysis of specimens by our investigatory x-ray beam could be held to negligible levels by the use of sufficiently high purity materials.

E. AgCl - X-ray Studies

No references were found to x-ray determination of electron density distributions or temperature factors in AgCl. No x-ray studies were noted that took place at more than one temperature. Many other studies, particularly those relating to emulsions of mixed crystals, were noted. These latter studies will not be discussed further here, however, as it is felt that they generally are not relevant to the present work.

The lattice constant of silver chloride has been given by Barth and Lunde²⁶ as 5.545 kX units. More recent determinations by electron diffraction are probably no more accurate; the Barth and Lunde value will be used for the present work.

The one paper in the literature which has the greatest immediate relevance is that of Cole²⁷ in which he has determined the approximate elastic spectrum of the acoustic waves in silver chloride from TDS measurements. He used an assumed set of vibrational frequencies for the optical branch based on the Reststrahlen frequency. He determined dispersion curves for waves in the acoustical branch traveling in the [100], [110], and [111] directions. He showed that the velocities at infinite wavelength agreed fairly well with those given by the static elastic constants. The existence of this paper is extraordinarily useful to us because it allows comparison

of the two x-ray methods of studying thermal motions, viz., TDS and variations of Bragg intensities. Further, Cole's determinations of the wave velocities allow computations of Debye- Θ values which may be compared with those determined in the present work.

F. Debye- Θ ; AgCl - Debye- Θ

The literature contains, in addition to Cole's paper, a number of papers in which the Debye- Θ of AgCl has been determined or which give data from which the Debye- Θ may readily be calculated. Debye- Θ 's may in principle be determined from

1. specific heat data
2. elastic constants
 - a. as determined by mechanical methods
 - b. as determined by ultrasonic methods
3. thermal diffuse scattering measurements of the elastic spectrum
 - a. by x-ray means
 - b. by neutron scattering
4. Reststrahlen (ionic crystals only)
5. temperature coefficient of resistance
6. temperature variation of the thermal coefficient of expansion.

Of these methods, the two of least value are the temperature coefficient of resistance and the thermal coefficient of expansion methods. The determination of a Debye- Θ from the Reststrahlen frequency probably should not be taken seriously because it depends only on the optical frequencies and ignores the existence of acoustical modes. However, the Debye- Θ 's determined from the Reststrahlen frequency are often surprisingly close to those determined from specific heat measurements.

Blackman, who has devoted many papers to the subject of Debye- Θ 's, says²⁸ that no agreement should be expected between Θ_D and Θ_R , the specific heat and resistivity values, respectively. On the Bloch theory one should expect Θ_R to depend on the longitudinal vibrations only. Since, even in a cubic crystal, the longitudinal wave velocities are quite different from the transverse wave velocities, one would expect Θ_R and Θ_D to be quite different. Blackman has discussed the effect of the break-down of assumptions such as that of elastic isotropy on the Bloch theory and concludes that they are not responsible for the fact that empirically Θ_R is often approximately equal to Θ_D for a large number of metals. The point remains unresolved, but it seems clear that Θ_R values should not be regarded in the same light as Θ_D values. Kelly and MacDonald²⁹ have investigated the relationship between the Θ_R and Θ_D values in a variety of metals and have pointed out the general utility of Θ_D as a computational quantity even in cases where it is known that the Debye theory of elastic vibrations represents a gross approximation.

Lonsdale³² quotes $\Theta = 130^\circ\text{K}$ for AgCl from application of the T^3 law to the data of Clusius and Harteck³³. Stepanov and Eidus³⁴ have investigated the temperature dependence of elastic constants of silver chloride above room temperature and state that their room temperature elastic constants are in agreement with those determined by Arenberg³⁵. We have, therefore, used only Arenberg's data in calculating room temperature Debye- Θ 's from elastic constants for present purposes.

Present interest is more in a directionally dependent evaluation of the Debye temperature than in a mean characteristic temperature. However,

it is noted that Sutton³³ (and previously Quimby and Sutton) have presented an improved, "accurate" method for determining a mean Debye temperature from elastic constants.

Blackman³⁷ has given a comprehensive discussion of his work on the Debye- Θ up to 1941. In an earlier paper³⁸ he quotes the optically determined Debye- Θ values for AgCl as 150°K from absorption and 168°K from reflection. The source of these data is not clear, perhaps it is Dr. Clusius of Clusius and Hartek³³. He discusses the temperature dependence of Debye- Θ values and shows that they are expected to decrease with increasing temperature at high temperatures. At low temperatures, on the other hand, they may first decrease and then increase as absolute zero is approached. In the case of sodium chloride there seems to be about a 3% decrease from 100°K to a minimum at about 35°K followed by an increase to a value at 0°K which is about 5% above the 100°K value. It would appear at first glance that this dip followed by a rise would occur in silver chloride at a temperature well below the lowest temperature ($\sim 90^\circ\text{K}$) obtained in our current measurements.

Paskin³⁹ has formulated the temperature dependence of the Debye temperature in terms of an explicit volume dependence. He has shown that a Debye-Waller factor which takes account of this explicit volume dependence of the Debye- Θ allows a much better fit of intensity versus temperature data in the literature. This formulation of the volume dependence of the Debye- Θ promises to be useful in the present investigation. However, the use of Paskin's formulation requires knowledge of thermal expansion coefficients and the Grüneisen constant over the temperature range investigated. The thermal expansion coefficients of silver chloride have been investigated by

Strelkov³⁰ from room temperature to the melting point and by Sharma³¹ from room temperature to 325°C. No attempt has been made to derive Debye- Θ 's from these data. The Gruneisen constant is ordinarily considered to be rather temperature independent, but Sharma states³¹ that the Gruneisen constant calculated for AgCl above room temperature varies markedly with temperature. We have so far not been able to locate data on the thermal expansion coefficients nor on the Gruneisen constant over the temperature range from 300°K to 100°K, the temperature range currently under investigation.

IV. DETAILED STATEMENT OF IMMEDIATE PROBLEM

The immediate problem is the determination of the x-ray temperature factors, and, from them, the Debye characteristic temperatures and the root mean square displacements of the atoms in thermal vibrations. The temperature factors are to be determined both from the temperature dependences of Bragg intensities and from the temperature factor assignments found necessary for best fit in the refinement of "full" relative intensity data, at a single temperature, by one or more of the following techniques:

- (1) Fourier syntheses (i.e., electron density maps or Patterson diagrams),
- (2) differential syntheses, and
- (3) least squares procedures.

The measures of thermal motions obtained by these methods will be compared with each other and with the measures obtained by other techniques. The Debye- Θ is a convenient quantity for such comparison because it is obtainable from each of several techniques, e.g., specific heats, elastic constants, and so so. The x-ray temperature factors and the relative intensity

data (presumably of high precision) will be used to prepare electron density maps of AgCl of sufficient detail, it is hoped, to display electron density in any bond with appreciable covalent bond character. Since the value of the present investigation depends heavily upon precision in the data, considerable attention must be given to all factors affecting the precision and accuracy. These factors include instrumental factors, techniques in using the equipment, and factors associated with the specimen itself such as absorption, extinction, and the contribution of TDS to the apparent Bragg intensities.

The x-ray temperature factor effectively measures the average thermal motion in a direction perpendicular to the Bragg planes in question. Any anisotropy in such motion in a cubic crystal would itself be of interest. It is possible that the results for the thermal motions obtained from the temperature dependences of Bragg reflections will differ from those obtained by comparison of relative intensities at one temperature. Such a difference, if real, might be attributable to break-down in the assumptions of the Debye theory and may even be useful in investigating the nature of the break-down and in testing the range and degree of applicability of the Debye theory in any specific case.

In order to compare the measures of thermal motions obtained here with those obtained by other techniques it is necessary to understand the relationship between the actual lattice vibrational spectrum and the thermal motion parameter measured in each case.

Because it is desired that the results shall be definitive for AgCl, rather than for a particular specimen, it will be necessary to make measurements on a number of specimens from a number of different sources.

However, the possible influence of a photochemical effect on the results (through creation of defects with consequent distortion of the lattice and change of the atomic restoring forces and hence elastic spectrum) must always be borne in mind. When studies have been completed on specimens in which the photochemical effect can be neglected they will then be extended to specimens in which the degree of photolytic activity is deliberately varied by the addition of selected impurities.

THEORY

I. GENERAL COMMENTS ON LATTICE VIBRATIONS, DEBYE- Θ , AND ATOMIC VIBRATIONAL DISPLACEMENTS

A. Lattice Vibrations

The motions of the atoms in a lattice are, of course, coupled to one another. To the extent that the motions of the individual atoms may be assumed to be harmonic, it is both possible and desirable to express the motions in terms of the $3N$ (actually $3N-6$) independent normal modes, where "N" is the number of atoms in the lattice. Each normal mode is associated with a plane wave traveling through the lattice. Associated with each permissible wave direction there are one longitudinal and two transverse modes. The longitudinal and transverse waves usually have quite different velocities, even though they may have the same propagation vector. The fact that the waves travel in a lattice, instead of a continuum, gives rise to dispersion even within one type of mode (i.e., longitudinal or transverse). The variations in the wave velocities and lack of knowledge of the distribution function, $\rho(v)$ (from which one may obtain the number of normal modes in the frequency range dv), present grave problems in the study of lattice vibrations.

B. Debye Model and Debye- Θ

In order to make an attack on the problem, Debye assumed that all of the waves had the same velocity and that the function $\rho(v)$ would be the same as that which would occur in an isotropic continuum, i.e., proportional to v^2 . This is the oft-mentioned parabolic distribution of states in k space (the magnitude of k is $\frac{2\pi}{\lambda}$). In order to obtain the internal energy of the

crystal due to lattice vibrations, it is necessary simply to sum over the mean energies of the individual modes. The mean energy of a quantum mechanical oscillator of frequency ν is given by equation (4). Since the number of atoms, N , is very large, the sum over N discrete states may be replaced by an integral over the distribution function $\rho(\nu)$. In the Debye model, this gives

$$U \propto \frac{1}{V_0^3} \int_0^{\nu_m} \frac{h\nu^3 d\nu}{e^{\frac{h\nu}{kT}} - 1} \quad (5)$$

where

U is the internal energy

V_0 is the common velocity of the lattice waves, and

h and k have their usual meanings.

The upper limit, ν_m , of the integral is determined by the condition that the total number of modes shall be $3N$. The Debye characteristic temperature, Θ , is defined as the temperature corresponding to this maximum frequency, ν_m , by the relation

$$\Theta = \frac{h\nu_m}{k} \quad (6)$$

Thus, the higher the maximum frequency allowable in a particular crystal, the higher the Θ . This frequency may be increased either by shortening the minimum distance between atoms (i.e., increasing the radius of the first Brillouin zone) or by increasing the interatomic force constants. Since the

minimum interatomic distances do not vary greatly from crystal to crystal, the observed differences in Θ may be expected to be due to interatomic force constant differences. In general, then, it may be expected that the harder (less compressible) a crystal is, the higher its Debye- Θ will be.

There are several major weaknesses in the above approach which should be pointed out: the very fact that crystals do have a thermal coefficient of expansion shows that the lattice vibrations are not entirely harmonic; the normal mode analysis is, therefore, not entirely justified. Much more important weaknesses, however, are the assumption of a single wave velocity and the assumption of the parabolic distribution of states in "k" space. Later investigators have sometimes replaced Debye's single distribution function by two or more parabolic distribution functions, each with its own cut-off frequency. But use of a sharp cut-off frequency is yet another weak point and one which has been widely criticized. In spite of all these obvious shortcomings, the Debye- Θ is an extremely useful computational quantity. It appears in many solid-state phenomena. It represents a simple, average, thermal parameter which may be measured many different ways. Further, the Debye theory of specific heats has enjoyed remarkable successes in accounting for the experimental data.

C. Relation of Atomic Displacements to Elastic Spectrum

A plot of $p(v)$ versus v is called the "elastic spectrum." The relationship between the individual waves which make up the elastic spectrum and the mean square displacements of the atoms is readily shown. Let \vec{Z} be a unit

vector in the Z-direction, which is not necessarily the crystallographic Z-direction. Since the lattice vibration waves are all independent of one another, the square of the displacement of a particular atom will be the sum of the squares of the displacements due to each of the many waves. Let \vec{A}_n be the vectorial displacement amplitude due to the nth wave, then the mean square displacement of the particular atom in the Z-direction is given by

$$\overline{u_z^2} = \frac{1}{2} \sum_{n=1}^{3N} (\vec{A}_n \cdot \vec{Z})^2 \quad (7)$$

where use has been made of the fact that the time average of the square of a sinusoidally varying function is one-half the square of the amplitude. This equation may be compared with equation (3) where the elastic spectrum has been indicated by the continuous distribution function $\rho(v)$.

II. EFFECT OF LATTICE VIBRATIONS ON X-RAY INTENSITY

We consider here only the intensity of the Bragg reflections and not that of the thermal diffuse scattering. For more detail and for the development and justification of the equations given in this section, the reader is referred to James¹, Chapter Five.

A. X-ray Temperature Factor - Physical Origins

The effect of thermal vibrations is to vary continuously the phase relations between the x-rays scattered from any two atoms. The effect of this on the observed Bragg intensities can be quantitatively accounted for by modifying the atomic form factor (scattering factor) for a stationary atom,

f_0 , by an appropriate temperature factor, e^{-M} , as has been done in equation (1). Equation (1) may be conceptually misleading, however, as it seems to imply that the effect of the thermal vibrations is to smear out the electron density distribution in a given atom and thereby to increase the average phase difference between different parts of the electron cloud surrounding the particular atom. Since the frequency of the lattice vibrations is very small compared to the frequencies of the x-rays and since the adiabatic assumption is made (i.e., that the electron cloud follows the motion of the lattice point without any lag), such a picture is wrong in concept.

B. X-ray Temperature Factor - Relation to Atomic Displacements

If a single kind of atom is present, the temperature factor, M , is related to the mean square displacements of the atom as is shown in equation (2) where the direction of u is parallel to the scattering vector, \vec{s} . In the Bragg case, this is a direction perpendicular to the Bragg planes. Thus, measurement of the x-ray temperature factor constitutes a measure of the mean square displacement of the atoms perpendicular to a particular Bragg plane.

If $\overline{u_z^2}$ is not isotropic, then the x-ray temperature factors will be anisotropic. Further, there may be causes other than thermal for the displacement of the atoms from their proper crystallographic positions. Residual strains, lattice vacancies, interstitial ions or atoms, substitution of atoms of different sizes at some of the atomic sites and displacements due to the proximity of crystallite or grain boundaries are some of the factors that can give rise to a mean square displacement of the atoms which is not of thermal origin and which is not, incidentally, particularly dependent upon temperature. Since the causes of the thermal and other displacements are

independent, the effective mean square displacement, $\overline{u^2}$, that can be obtained from measurement of x-ray temperature factors is given by

$$\overline{u^2} = \overline{u_t^2} + \overline{u_1^2} + \overline{u_2^2} + \dots + \overline{u_n^2} \quad (8)$$

where $\overline{u_t^2}$ is of thermal origin and the other terms are from the "n" possible other origins. It is clear at this point that the thermally induced displacements can be separated from the others through observation of the temperature dependence of the x-ray temperature factor. Measurements of the x-ray temperature factors at some very low temperature would not in themselves be sufficient as $\overline{u_t^2}$ does not go to zero at absolute zero (because of the zero point energy of an oscillator).

C. X-ray Temperature Factor - Relation to Debye - @

By expressing the mean kinetic energy of a particular mode in terms of its amplitude and frequency and also in terms of its mean energy as a quantum mechanical oscillator, it can be shown that the average value, $\overline{A_n^2}$, of the square of the amplitude of the nth lattice wave is given by

$$\overline{A_n^2} = \frac{2h}{mN\omega_n} \left(\frac{1}{\frac{h\omega_n}{e^{kT} - 1}} + \frac{1}{2} \right) \quad (9)$$

where m is the mass of the one kind of atom considered, N is the total number of atoms, ω_n is the angular frequency of the lattice wave, and $h = h/2\pi$. The additive term, 1/2, arises from the zero point energy.

A particular frequency distribution of normal modes must now be chosen before the total mean-square-displacement of the particular atom may be

obtained. When the Debye distribution is used, the result for the temperature factor is

$$2M = \frac{4kT}{m} \left[\sum_j \frac{1}{v_{mj}^2} \left\{ \phi(x) + \frac{x}{4} \right\} \right] \frac{\sin^2 \theta}{\lambda^2} \quad (10)$$

where

$$\phi(x) = \frac{1}{x} \int_0^x \frac{\xi d\xi}{e^\xi - 1} \quad (11)$$

and

$$x = \frac{h v_m}{kT} \quad (12)$$

In equation (10) each value of j refers to a different wave velocity. Corresponding to each wave velocity, provision is made for a different limiting frequency v_m . As is shown by equation (5), when more than one wave velocity is considered in the specific heat case, the different velocities contribute according to the reciprocals of their cubes. Equation (10) points out that in the x-ray case, on the other hand, different velocities (which are directly related to the frequencies) contributed according to the reciprocal of their squares. It is customary to consider two velocities as a first approximation, one for the longitudinal and one for the transverse modes. If we then define a Debye- Θ based on the maximum frequency for each mode, we find that the mean characteristic temperature for the specific heat case, Θ_D , is given by

$$\frac{3}{\Theta_D^3} = \frac{1}{\Theta_\ell^3} + \frac{2}{\Theta_t^3} \quad (13)$$

whereas the mean characteristic temperature for the x-ray case, Θ_x , is given by

$$\frac{3}{\Theta_x^2} = \frac{1}{\Theta_\ell^2} + \frac{2}{\Theta_t^2} \quad (14)$$

where Θ_ℓ refers to the longitudinal mode and Θ_t refers to the transverse mode. One result of this difference between the methods of averaging is that Θ_x is always larger than Θ_D by a few per cent. The exact amount depends upon Poisson's ratio in a manner reviewed by James¹. Dropping the subscript on the x-ray Debye- Θ for the moment, we have, for the temperature factor, by equations (10), (6), and (14)

$$M = \frac{6h^2 T}{mk \Theta^2} \left\{ \phi(x) + \frac{x}{4} \right\} \frac{\sin^2 \Theta}{\lambda^2} \quad (15)$$

With equations (2) and (15) we are prepared to relate the measured x-ray temperature factors either to the mean square displacement of the atoms or to the Debye temperature, Θ , as we choose. Many of the assumptions involved in the development of these two equations are certain to be violated in any real case. This circumstance detracts significantly from the physical meaning of the numeric results that may be obtained. The numbers obtained, however, will still have considerable value for comparison with others as a function of direction in the crystal, as a function of specimen treatment or

preparation. Further, (particularly in the case of the Debye- Θ) the numbers so obtained may be compared at least semi-quantitatively with the numbers obtained by totally different techniques.

D. X-ray Temperature Factor - The Constant, B

It is often convenient to consider explicitly that part of M which does not depend on $\sin \Theta/\lambda$. It is to be expected that this quantity, B, will always be a constant for a given direction and a given atom in the crystal. By equations (2) and (15), we see that we may express B either of two ways

$$8\pi^2 \overline{u_z^2} = B_z = \frac{6h^2 T}{mk \Theta_z^2} \left\{ \phi(x) + \frac{x}{4} \right\} \quad (16)$$

where the subscript z indicates that we have a particular direction in mind (not necessarily the crystallographic Z-direction). Knowing B we may obtain either the mean square displacements or the Debye- Θ from equation (16). Further, equation (16) shows a relationship between the Debye- Θ and the mean square displacements.

III. DETERMINATION OF B FROM $\frac{\sin \Theta}{\lambda}$ DEPENDENCE OF M

A. Determination of a Single, Overall B Value

According to the kinematical theory of x-ray diffraction, the observed intensity, I, is proportional to the square of the absolute value of the structure factor, F, which in turn is given by

$$F = \sum_j f_j e^{-M_j} e^{-2\pi i(hx_j + ky_j + lz_j)} \quad (17)$$

where h , k , and l are Miller indices and x_j , y_j , and z_j are the fractional coordinates of the j th atom in the unit cell. In the case of a simple cubic, monatomic lattice, made up of spherical atoms, there is but one value of B . The assumption of a single, isotropic B is often used as a first approximation in a more complicated case, too. In this event, one may write

$$I = I_0 e^{-2M} = I_0 e^{-2B \frac{\sin^2 \theta}{\lambda^2}} \quad (18)$$

where I is the actually observed intensity, and I_0 is the intensity which would have been observed if there were no thermal motions. B may be determined from a plot of $\ln(I/I_0)$ versus $\frac{\sin^2 \theta}{\lambda^2}$, which has slope $-2B$. If B is isotropic, this is a simple graphical method; in the present and more complicated cases the individual anisotropic values can be determined by more complicated means.

B. Weaknesses of the Angle-dependence Method

The I_0 's used in this determination are to be obtained from equation (17) with $M = 0$. Thus, the calculated I_0 and, consequently, the determination of B depend upon a knowledge of the atomic form factors and the atomic coordinates, x , y , and z . In simple crystals, such as those with the NaCl type structure, the atomic coordinates are fixed by symmetry requirements and hence are known precisely. The atomic form factors are never completely known, but are probably almost always known to within a few per cent. Since in general the various f_j 's will combine in different ways for the different reflections, the lack of precise knowledge of the atomic form factors is not necessarily detrimental to the determination of B from a plot of equation (18).

Much more serious is the lack of knowledge of the factors which relate the intensity to the square of the structure factor. For a given experimental arrangement and a given specimen, the diffracted intensity I is given by

$$I = C^2 \frac{1 + \cos^2 2\theta}{\sin 2\theta} AE |F|^2 \quad (19)$$

where

θ = Bragg angle

A = absorption factor

E = extinction factor

C = constant

$|F|$ = structure amplitude

Equation (19) holds if the necessary extinction correction is not too large. The extinction correction is a measure of the degree to which the kinematical theory fails to apply to the crystal because the crystal is not perfectly mosaic. The absorption factor, A , may easily be the cause of the largest error in the present experiments and is the subject of a separate discussion later in this report.

C. Determination of Individual, Anisotropic B Values

In some cases the uncertainties in A and in E may be made small enough to be ignored, and sufficiently accurate values of B may then be obtained from equation (18). In the event that B is anisotropic, separate plots of equation (18) may be made; and, consequently, separate B values may be obtained for each direction in reciprocal space.

For a sodium chloride type crystal it is, in principle, possible to determine individual B values for the two types of atoms present. The structure factor in this case is given by

$$F = 4(f_1 e^{-M_1} \pm f_2 e^{-M_2}) \quad (20)$$

where the plus sign is to be used if the Miller indices are all even and the minus sign if they are all odd. If the Miller indices of a reflection in this structure are neither all odd nor all even, the structure factor is identically zero for that reflection. When the absolute value of F has been determined by the use of equation (19), it is to be plotted against $\frac{\sin^2 \theta}{\lambda^2}$. Two curves should then be drawn through the data; one connecting the all-even indexed reflections and one connecting the all-odd indexed reflections. This plot should look something like Figure 1.

Curves like those in Figure 1 allow interpolation so that, for example, one may determine the value that an odd indexed reflection would have had, had it been possible for it to occur at the same $\frac{\sin \theta}{\lambda}$ value as an even indexed reflection has. Then we can combine the F_+ (from all even indexes) with the F_- evaluated at the same $\frac{\sin \theta}{\lambda}$ to give

$$CF_+ + CF_- = C 8f_1 e^{-M_1} \quad (21)$$

and

$$CF_+ - CF_- = C 8f_2 e^{-M_2} \quad (22)$$

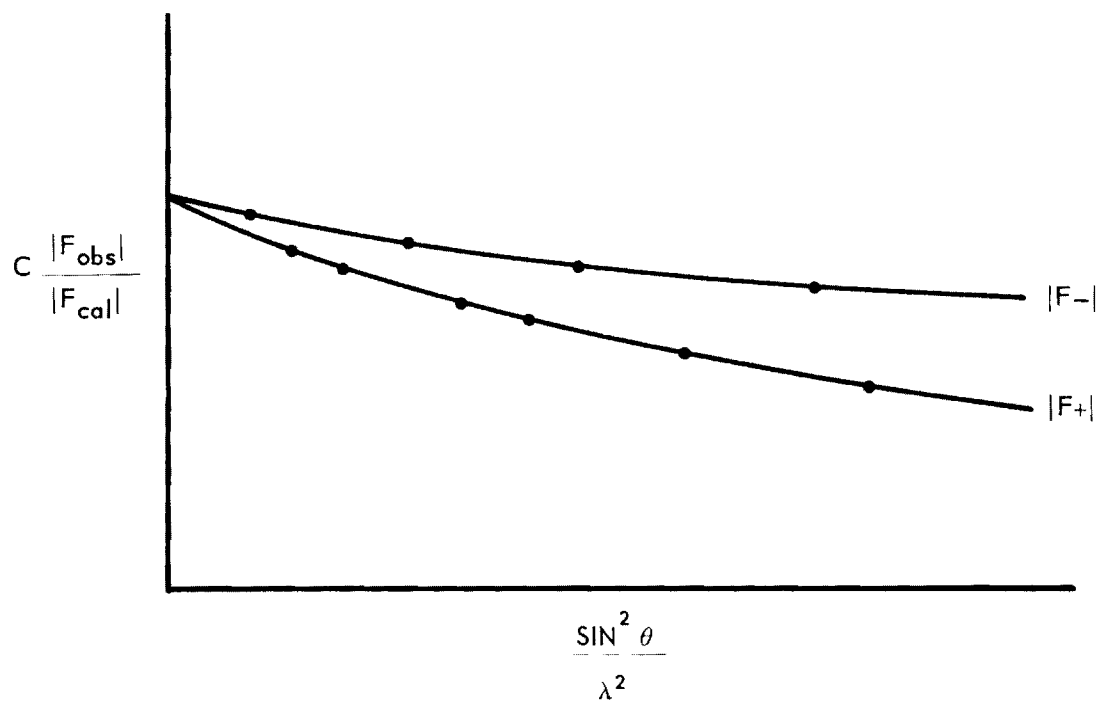


Figure 1. Idealized $\sin \theta$ Dependence of $|F|$.

Each of these equations may now be evaluated at several values of $\frac{\sin \theta}{\lambda}$; and, when they are divided through by the appropriate form factor (which is itself a function of $\frac{\sin \theta}{\lambda}$), the slope of the resultant log plot of this quantity versus $\frac{\sin^2 \theta}{\lambda^2}$ will give the value of B for the particular atom. This technique has been used by others for determination of isotropic B values¹. It can be applied in the determination of anisotropic B values, however, providing that there is a succession of even indexed and odd indexed reflections available which pertain to a particular direction in reciprocal space. In NaCl type crystals the (hhh) reflections satisfy this condition. The (h00) and (hh0) do not, however, as only the even indexed reflections of this type are observable.

No direct use has yet been made of this graphical technique in the present work. The possibility of its use has had some effect in the planning of the experiments. The details of the technique, particularly for the anisotropic case, have been worked out as indicated above; and it is expected that the technique will be applied as soon as good relative intensity data are available.

IV. DETERMINATION OF TEMPERATURE FACTORS FROM THE TEMPERATURE DEPENDENCES OF INTENSITIES

A. Some Desirable Features of this Method

As will be shown below, it is possible to use the temperature dependence of the intensity of a particular Bragg reflection to obtain, without reference to any others, the temperature factor that applies to that reflection. It is frequently experimentally possible, as it is in the present

case, to determine the temperature dependence of the structure amplitude of a particular reflection with better accuracy than the relative structure amplitudes of more than one reflection may be determined. This circumstance arises partly because of the uncertainty in the factors A and E in equation (19) and partly because of the experimental ease with which the intensity of a particular reflection may be continuously observed as the temperature is changed.

B. Derivation of Required Relationships

1. Assumptions

In the following discussion, the possibility that the extinction factor may itself be a function of temperature is ignored. The possibility and significance of such an occurrence are discussed separately, later.

It is further assumed that the change in the Bragg angle, θ , is small enough so that the thermally induced changes in the Lorentz and polarization factor ($\frac{1 + \cos^2 2\theta}{\sin 2\theta}$) may be neglected. In the case in which this assumption is not justified, the following discussion may be corrected for it simply by replacing "the intensity at each temperature" by "the quotient of the intensity with the L. P. factor." As is shown by equation (19), the temperature dependence of the intensity under these assumptions is just the temperature dependence of $|F|^2$. By equation (17) we see that the temperature dependence of the structure factor, F, may have several parts: one due to the form factor, one due to the atomic positions, and one due to the temperature factor M. Use of crystals so simple that all of the atomic positions are fixed by symmetry eliminates the contribution to the temperature dependence of F of otherwise possible variations in atomic positions. It is also assumed in

what follows that the atomic form factors are not temperature dependent, excepting to the extent that they are affected directly by thermal vibrations. While this assumption is obviously not wholly justified, it seems doubtful that the bonding would change markedly over the temperature ranges we are currently investigating (100 to 300°K). In any event it is the outer electrons that would be affected; thus, the assumption is better justified for heavy than for light atoms and for high order than for low order reflections.

With the foregoing assumption, the only temperature dependence of F , and hence of the observed intensity, that need be considered for present purposes is that due to temperature dependence of the various M_j 's.

1. Case of a Common Temperature Factor for all M_j 's

a. The parts of M . We consider first the simple case in which a common temperature factor applies to all atoms. From equation (18) we see that

$$\frac{d}{dT} \ln(I/I_0) = - 2 \frac{dM}{dT} \quad (23)$$

where it will be recalled that M is given by equation (15). The temperature dependence of M has four parts: the factor T , the temperature dependence of the quantity in the braces, the temperature dependence of the Debye- Θ , and the temperature dependence of $\frac{\sin^2 \theta}{\lambda^2}$ due to the effect of thermal expansion on the Bragg angle. For $x = 0$ the quantity in the braces is exactly one; for $x = 1$ the quantity in the braces is about 1.03. For the temperatures above the Debye temperature the variations in the quantity in braces may ordinarily be neglected. However, this is not the case for temperatures below Debye temperature.

b. Temperature dependence of the Debye- Θ . The temperature dependence to be expected in the Debye- Θ has been discussed briefly in the preceding discussion of the literature. It was pointed out that a plot of the Debye- Θ versus temperature was expected to show a "wiggle" at very low temperatures and to fall off monotonically at high temperatures. Paskin³⁹ explicitly considered that part of the temperature dependence of the Debye- Θ which is due to its volume dependence and found that the expression

$$\Theta = \Theta_0 \left(\frac{V_0}{V} \right)^2 \quad (24)$$

gave a considerable improvement in agreement between theoretical and experimental temperature factors of KCl in the high temperature region. In equation (24), Θ_0 is the Debye temperature at absolute zero. Its value is determined by extrapolation from the high temperature values without the "wiggle" previously mentioned. V_0 is the volume at absolute zero and V is the volume at temperature. The Gruneisen constant, γ ,

$$\gamma = \frac{V\beta}{C_V K} \quad (25)$$

is generally quite independent of temperature. However, this independence has been questioned²⁸ for the case of AgCl above room temperature. In equation (25) β is the thermal coefficient of expansion, K is the compressibility, and C_V is the specific heat at constant volume.

For present purposes it is assumed that γ does not depend upon temperature. While this assumption may not be justified, it is still to be expected

that the use of equation (24) will represent a partial correction. Substitution of equation (24) in equation (15) gives

$$M = \frac{6h^2}{mk \Theta_o^2} \left(\frac{v}{v_o} \right)^{2r} T \left\{ \phi(x) + \frac{x}{4} \right\} \frac{\sin^2 \theta}{\lambda^2} \quad (26)$$

c. Expressions for dM/dT and their validity. The derivative of equation (26) with respect to temperature is

$$\frac{dM}{dT} = \frac{6h^2}{mk \Theta_o^2} \left(\frac{v}{v_o} \right)^{2r} \left[f(x) + (2r - \frac{2}{3})\beta T \left\{ \phi(x) + \frac{x}{4} \right\} \right] \frac{\sin^2 \theta}{\lambda^2} \quad (27)$$

where

$$\beta = \frac{1}{v} \frac{dv}{dT} \quad (28)$$

and

$$f(x) = 2\phi(x) - \frac{x}{e^x - 1} \quad (29)$$

In equation (27) the term in "2r" arises from Paskin's factor for the Debye- Θ variation and the term in "2/3" arises from variation in $\frac{\sin^2 \theta}{\lambda^2}$. It is clear that in equation (27) the f(x) term, which is shown in Figure 2, will be dominant, particularly at low temperatures. In fact, if the temperature is low enough so that the temperature coefficient of expansion has essentially disappeared, equation (27) reduces to

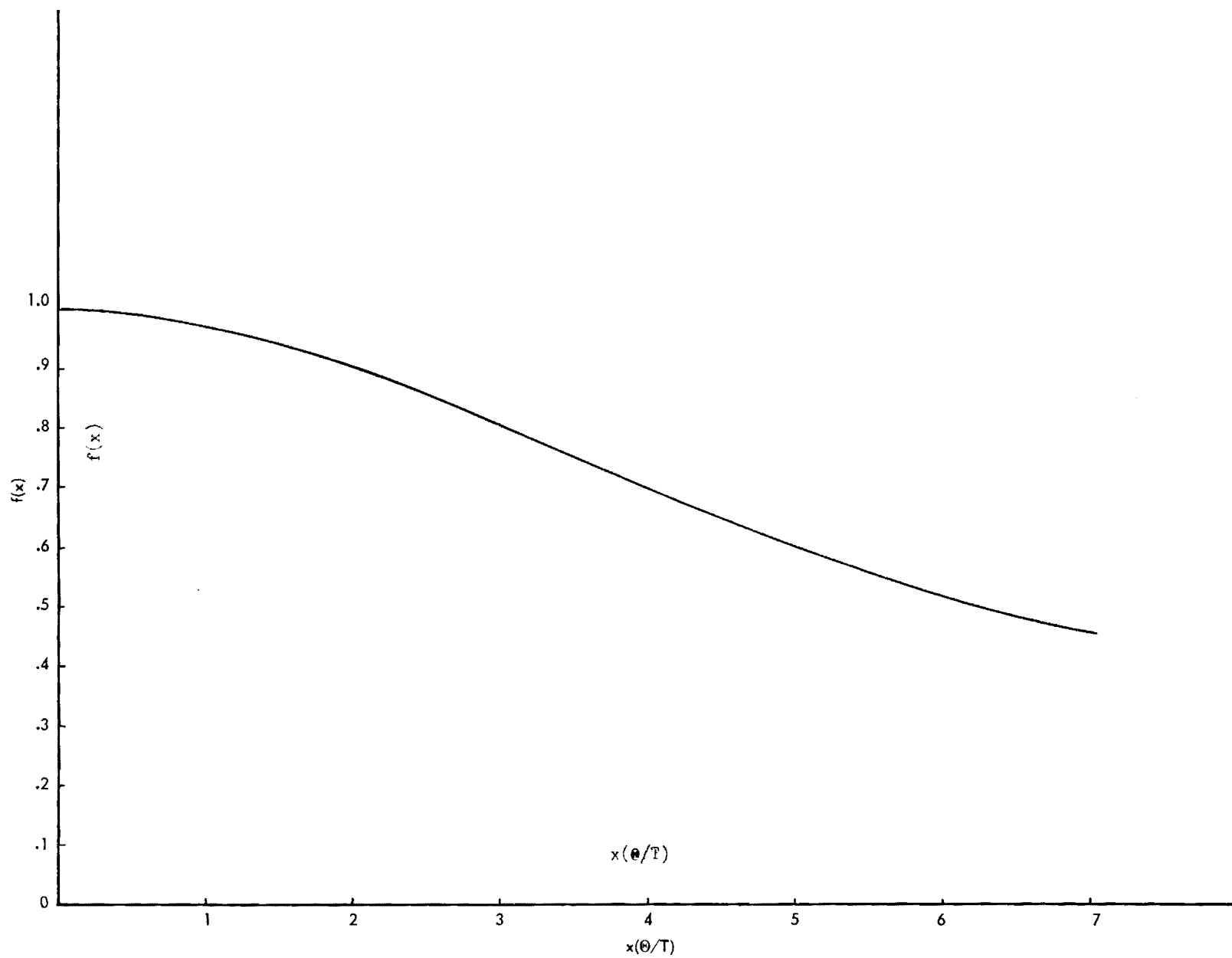


Figure 2. The Function $f(x)$.

$$\frac{dM}{dT} = \frac{6h^2}{mk\Theta_o^2} f(x) \frac{\sin^2 \Theta}{\lambda^2} \quad (30)$$

At high temperatures on the other hand, $f(x)$ becomes very nearly one, and equation (27) becomes

$$\frac{dM}{dT} = \frac{6h^2}{mk\Theta_o^2} \left(\frac{v}{v_o} \right)^{2\gamma} \left[1 + (2\gamma - \frac{2}{3})\beta T \right] \frac{\sin^2 \Theta}{\lambda^2} \quad (31)$$

As is shown by Figure 2, the function $f(x)$ is a slowly varying function of x ; it changes only from 1 to 0.6 as x changes from 0 to 5. Since $f(x)$ is actually a function of the Debye- Θ , an iterative solution for Θ is necessary in equation (30) whereas iteration is not necessary in using equation (31). However, it is in the range where equation (30) applies that the assumption of harmonic oscillations is best met. Since the harmonic assumption is essential to the whole treatment of lattice vibrations, it might be difficult within the range of equation (31) to distinguish between a breakdown of the normal modes' representation and a breakdown of the Debye distribution of normal modes. In the range of equation (30) on the other hand, the normal mode analysis should apply quite well so any anomalous behavior must be ascribable to a breakdown of the Debye distribution assumption.

Since 2γ is larger than $2/3$, equations (23) and (27) show that a plot of $\ln(I/I_o)$ versus T should have a slope which decreases at low temperatures, may be reasonably constant over a mid-range of temperatures, and increases with increasing temperatures in the high temperature region.

d. Debye- Θ from change in slope. If the slopes can be measured with sufficient accuracy an interesting possibility arises for determining a Debye- Θ directly from the change in slope of Log I versus T with temperature and from the character of f(x) in the low temperature region. The assumption, for the moment, is that there is a single, constant Debye- Θ over this region. From equation (30) it is clear that

$$\frac{\left(\frac{dM}{dT}\right)_{T_1}}{\left(\frac{dM}{dT}\right)_{T_2}} = \frac{f(x_1)}{f(x_2)} = \frac{\frac{d}{dT} (\ln I/I_o)_{T_1}}{\frac{d}{dT} (\ln I/I_o)_{T_2}} \quad (32)$$

This is one of a pair of simultaneous equations in x, the other of which is

$$\frac{x_1}{x_2} = \frac{\Theta/T_1}{\Theta/T_2} = \frac{T_2}{T_1} \quad (33)$$

These two equations may readily be solved graphically by placing f(x) on a log-log plot. We have tried this method of determining a Debye- Θ directly from a change in slope in the case of two or three reflections from NaCl. The results were of the right order of magnitude but were not thought to be reliable because the slopes were not sufficiently well determined. When we have succeeded in making least squares fits of our data to the best smooth curves, we shall attempt to make use of this method again. Some further investigation of the significance of the Debye- Θ determined in this way will also be undertaken. A very interesting aspect of this determination

is that the result is independent of the choice of any particular method of averaging over the masses involved; in fact, the masses of the various atoms do not enter into it at all. An obvious shortcoming of the method is that it assumes that the same Θ_0 applies at each of two temperatures which may be fairly widely separated. This assumption in turn depends upon the parabolic distribution by Debye as being a satisfactory approximation to the real distribution, a circumstance which may often not occur.

e. Discussion. The use of equation (27) or one of the approximations to it [i.e., equation (30) or equation (31)] allows determination of Θ and, hence, of B and of $\overline{u^2}$ directly from the temperature dependence of the intensity of a single given Bragg reflection and allows this to be done as a function of temperature. We do know of past studies wherein the difference between the intensities of a particular reflection at two temperatures has been used to determine a temperature factor; we are not aware of any case in which the actual slope at a given temperature has been used, either to determine the temperature factor as a function of temperature or even at a single temperature, and we are not aware of any previous suggestion concerning the possibility for determining a Debye- Θ from the change of slope of the intensity versus temperature curve.

Up to this point the discussion has assumed that all atoms have the same temperature factor in a given direction. Even in the case in which this is not true, the number obtained by such an assumption may have considerable usefulness; for example, it could be followed as a function of specimen preparation, impurities, radiation damage, etc. Anisotropy, or changes in the anisotropy, in the thermal motions could be detected by these measurements

based on the temperature dependence of Bragg reflections. Further, the numerical value for the x-ray Debye- Θ which is obtained by ignoring the differences between atoms and which, thereby, has the effect of averaging over the various atoms, is the Debye- Θ value which should be compared with specific heat determinations.

3. Case of Individual Temperature Factors in NaCl-type Structures

More detailed information concerning the motions of the individual atoms may be obtained, however. In the case of the simple NaCl-type structure, which AgCl has, it is noted that equation (20) may be written

$$\frac{F}{4f_1} = e^{-M_1} (1 \pm f e^{-\Delta M}) \quad (34)$$

where

$$f = \frac{f_2}{f_1} \quad (35)$$

and

$$\Delta M = M_2 - M_1 \quad (36)$$

Taking the temperature derivatives of the logs, one obtains

$$\frac{d}{dT}(\ln I^{1/2}) \propto \frac{d}{dT}(\ln \frac{F}{4f_1}) = -\frac{dM_1}{dT} \mp \frac{\frac{d\Delta M}{dT} f}{1 \pm f e^{-\Delta M}} \quad (37)$$

It is clear that if the temperature factors for the two atoms are not the same the temperature dependence of the even reflections should be different

from that of the odd reflections. It is possible that a graphical solution may be obtained for M_1 and M_2 from the temperature dependence data. Perhaps they can be found in a manner somewhat analogous to that described above for the determination of temperature factors from their $\frac{\sin^2 \theta}{\lambda^2}$ dependence. Such a possibility has not yet been fully explored. Instead, the approach being currently investigated, and which is expected to be the one most used, involves a least squares fit of experimental data to a theoretical curve of intensity versus temperature. The theoretical curve is to be based on equations (17), (19), and (26). The adjustable parameters in the least squares fit will be one Θ_0 value for each type of atom present. It is anticipated that this least squares procedure will be programmed for a high speed digital computer (either the IBM 650 or the Datatron 220) and that it will be routinely used as a primary tool in the analysis of the intensity versus temperature data.

V. CONTRIBUTION OF TDS TO APPARENT BRAGG INTENSITY

A. Angular and Temperature Dependent Characteristics of TDS

It is well known^{1-3,13-17,40} that TDS contributes some intensity to the apparent Bragg intensity. The one-phonon TDS contribution is actually peaked at the Bragg position. The contribution of TDS to the apparent Bragg intensity, particularly for a crystal with a low Debye- Θ , such as AgCl has, may easily run as high as 30%^{15,16}. Since the temperature dependence of TDS and of the Bragg intensities are of opposite signs, a correction for TDS is doubly important when the temperature dependence of Bragg intensities is being studied. Methods have been offered (Nilsen¹⁷, Chipman¹⁵ among others) for the correction of the Bragg intensities, observed at one temperature, for the

TDS contribution. The analytic method depends upon the measurement of TDS at points away from the Bragg peak and subsequent computation from these measurements of the contribution at the Bragg peak. As Paskin¹⁶ has shown, the computed result depends heavily upon the wave velocities assumed. Chipman's graphical method¹⁵, being a wholly empirical method, is probably to be preferred to the analytic methods in the absence of detailed knowledge of the elastic spectrum. One-phonon and two-phonon contributions to TDS are ordinarily all that are considered. At a given temperature, the ratio of the one-phonon to the two-phonon contribution depends on the distance from the observation point to the nearest reciprocal lattice point and on the distance from that reciprocal lattice point to the origin of reciprocal space. The ratio of one-phonon to two-phonon scattering is infinite precisely at the reciprocal lattice point, i.e., right under the maximum of the Bragg peak. At a given position the ratio of two-phonon to one-phonon scattering is directly proportional to temperature⁴⁰. Equation (2) of Ramachandran and Wooster⁴⁰ indicates that the one-phonon scattering at any particular point in the neighborhood of a reciprocal lattice point is proportional to the temperature, the square of the structure amplitude at that temperature, $\frac{\sin^2 \theta}{\lambda^2}$, and the reciprocal of the square of the distance of the point in question from the actual reciprocal lattice point. Thus, we might expect the total one-phonon contribution over some small region in the neighborhood of the reciprocal lattice point to be given by

$$I_{TD1} = \frac{kT}{R^2} |F|^2 \frac{\sin^2 \theta}{\lambda^2} \quad (38)$$

where k' is an appropriate constant and \bar{R} is the properly weighted average distance of the region in question from the reciprocal lattice point. Equation (38) may be assumed to represent the total one-phonon contribution to the Bragg peak actually observed with the method used. Then, the observed intensity "I" will be given by

$$I = I_o e^{-2M} + \frac{k T I_o e^{-2M}}{\bar{R}^2} \frac{\sin^2 \theta}{\lambda^2} \quad (39)$$

or

$$I = I_o e^{-2M} \left(1 + \frac{k T \sin^2 \theta}{\lambda^2} \right) \quad (40)$$

where k is the appropriate constant.

B. Possible Graphical Correction for and Measurement of TDS Contribution

The actual situation is, of course, not this simple. For one thing, the contribution of two-phonon scattering has been totally ignored. Secondly, the concept of averaging over the various values of "R" is questionable. However, equation (40) does serve to point out that the relative contribution of the TDS to the apparent Bragg intensity might be expected to depend upon $\frac{\sin^2 \theta}{\lambda^2}$, that it would become zero at $\sin \theta = 0$, and that the temperature dependence of the apparent Bragg intensity would be influenced by TDS by an amount which also goes to zero at $\sin \theta = 0$. These observations on thermal diffuse scattering suggest that the B values obtained from the temperature dependence of Bragg intensities may be corrected for the TDS contribution graphically. If the error due to TDS actually does go to zero at $\sin \theta = 0$,

then a plot of the various B values, as obtained, versus $\frac{\sin^2 \theta}{\lambda^2}$ should extrapolate to a B value free of TDS error at $\frac{\sin^2 \theta}{\lambda^2} = 0$. Experimental tests of this possibility are not yet complete. If this method of correcting for TDS can be shown to be valid, however, it may also be possible to go back and, with knowledge of the correct temperature factor, to estimate the actual percentage TDS contribution to the apparent Bragg intensity for each individual reflection. If such a correction proves to be possible, it will be a valuable aid in improving the accuracy of the relative intensity data which are to be gathered later on.

VI. SIGNIFICANCE OF ANISOTROPY OF THERMAL MOTIONS IN CUBIC CRYSTALS

The assumption that the lattice vibrations are harmonic so that they may be represented by the independent normal modes also implies that the mean square displacements of a given atom type may be expressed in terms of independent mean square displacements along each of three, mutually perpendicular, principal directions. This property is employed to write the temperature factor "M" in tensor form as

$$M = \beta_{ij} h_i h_j \quad (41)$$

where h_i and h_j are each one of the Miller indices of the reflection considered (i.e., $h_1 = h$, $h_2 = k$, etc.). The symmetry of the cubic crystal requires that the thermal ellipsoid (the ellipsoid for which the principal axes are defined by the root mean square displacements of the atom in the three principal directions) degenerate to a sphere. In equation (41) this requires β_{ij} to have spherical symmetry. Therefore, if any anisotropy in the thermal

displacements is found it must mean that either (1) the crystal is not actually cubic or (2) the assumption of harmonic vibrations is not justified and, consequently, the description of the thermal motions in terms of a thermal ellipsoid and the analytic expression of a temperature factor as 2nd rank tensor [equation (41)] is no longer justified. Inability to use an expression like equation (41) would greatly complicate a crystal structure refinement in which the temperature factors were variables.

In such a case it would seem to be necessary to determine the temperature factors individually for each reflection from separate experiments; perhaps experiments of the type described here would suffice.

SECTION 3

EXPERIMENTAL PART

I. EQUIPMENT DESCRIPTION

A. Standard Commercial Items

The x-ray equipment being used in this work includes a Philips x-ray generator, scintillation counter, and associated scaling and recording circuits. A molybdenum anode tube has been used for all work so far; a silver anode tube has just been received; copper and iron anode tubes are also on hand. The x-ray generator and the associated circuits are supplied with a regulated voltage ($\pm 1/4\%$ or better) and a separate beam current stabilizer is used. A geiger counter is also available, but the scintillation counter is preferred because of its larger range of linearity, because of the uniformity of response across its window, and because its quantum counting efficiency, particularly for short wavelengths such as MoK, is much higher than that of the geiger counter.

The equipment includes precession and Weissenberg cameras of Supper Manufacture. The film cassette of the Weissenberg is ordinarily not used; the Weissenberg is instead used as a base for the scintillation counter holder.

B. Special Spindle Drives on the Weissenberg

The standard motor drive for the spindle on the Weissenberg camera was much too fast for present purposes. A motorized drive system in which the existing worm gear is coupled directly to a small synchronous (Haydon) motor was substituted. It is shown in Figure 3. Drive speeds are changed by

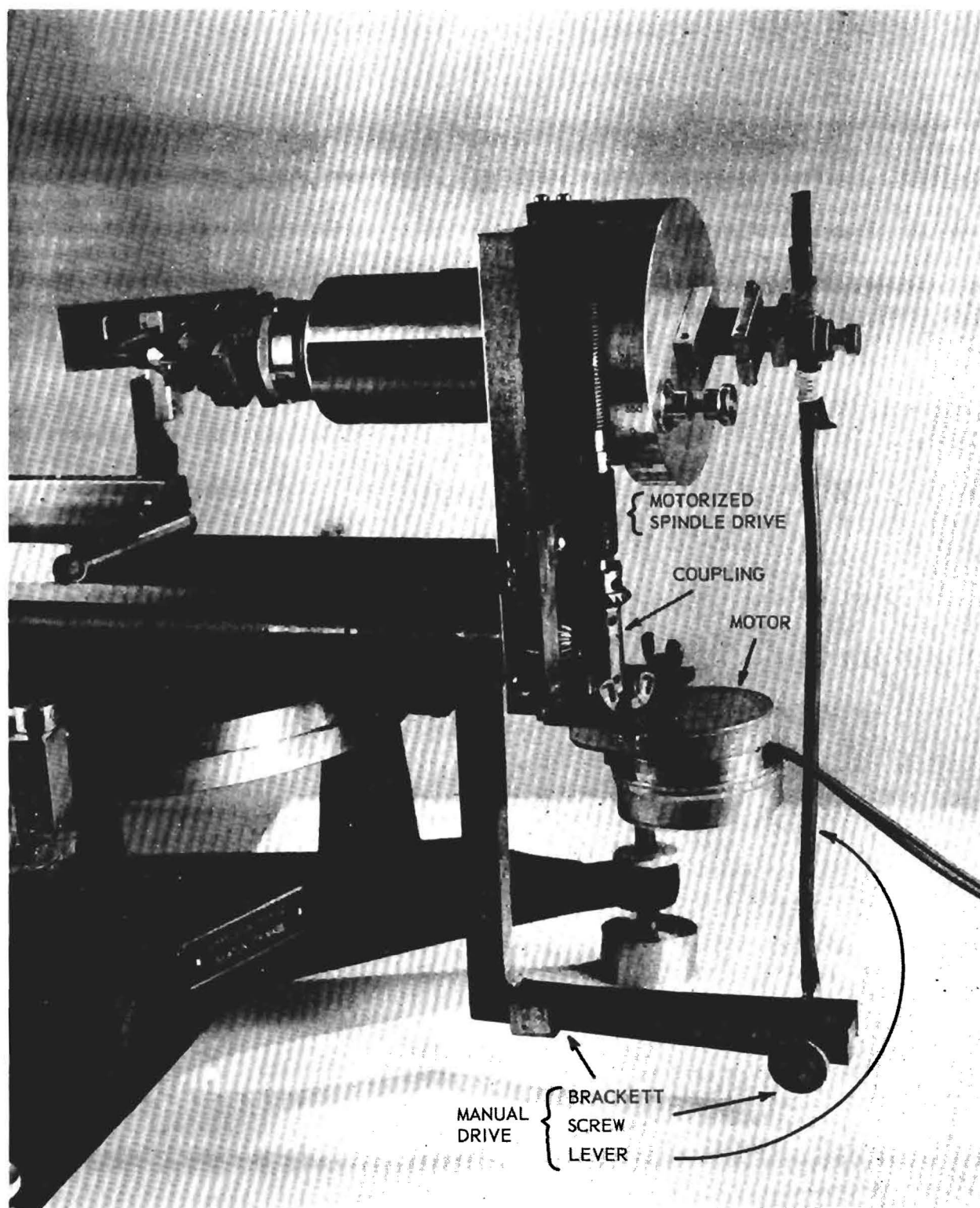


Figure 3. Special Spindle Drive.

changing the Haydon motors. One-half, one-tenth, and one-thirtieth rpm motors have been found useful. Since the drive shafts of these motors are only friction coupled to the motor in the reverse direction, they may be manually advanced.

A simple attachment was made to the spindle to permit fine manual control of the spindle position. The device is also shown in Figure 3. It consists essentially of a metal lever which is friction fitted to the outer end of the spindle and which extends down to a position near the work surface of the x-ray generator where it is driven by a tangential screw. One complete revolution of this tangential screw rotates the Weissenberg spindle by about 12 seconds of arc.

C. Equipment for Control of Radiation Character

Three items of equipment have been used for control of radiation character. They are a pulse height analyzer, a monochromator, and a differential (Ross) filter. The pulse height analyzer is Atomic Model 510, slightly modified to reduce considerably the resolution time. The modification consists of a change in the value of one resistance at one of the inputs to the anti-coincidence circuit.

The monochromator used to date consists simply of a flat piece of sodium chloride held in the monochromator housing made by Philips Electronics, Inc., for use with their powder cameras. Future monochromator arrangements are expected to employ quartz crystals and holders that are more suitable for use with the Weissenberg arrangement. The purpose which was served by the monochromator, as used, was to show the difference between control of the radiation character by crystal monochromatization and control by other means.

The device that has been most used in the present work for control of the radiation character has been the differential filter. This consists of two filters whose absorption edges are on opposite sides of the characteristic wavelengths being employed. A convenient holder for the filter pair, shown schematically in Figure 4 and photographically in Figure 7, is based on a cap which fits over the front of the scintillation counter. The two filters are mounted in a bar which slides in a groove in the cap. The change from one filter to the other is accomplished by sliding this bar until the spring loaded ball riding on the edge of the bar falls into an indentation and thereby positions the bar. It was found convenient to line the interior front surface of the holder with lead (excepting for a small central hole). This reduced the background due to scattered radiation and particularly due to proximity of the main beam when the counter was at low angles.

The two filter materials usually used with molybdenum radiation are zirconium and either yttrium or strontium. Since the pure metals are not sufficiently stable in air, some compound, such as the oxide, must be used in the case of yttrium and strontium. We have prepared suitable filter material from Y_2O_3 by mixing it with acetone-thinned "Duco" cement and allowing it to harden into a slab. The slab was then shaped to fit the holder and was carefully thinned as needed by scraping or sanding. Care was taken to insure that the sides remained parallel during the thinning period. A standard thickness of zirconium metal filter was used for the other filter, and the two were balanced with the aid of a Norelco Diffractometer. A single crystal was mounted as the specimen in the diffractometer and the scintillation counter with the attached filter holder were mounted on the diffractometer

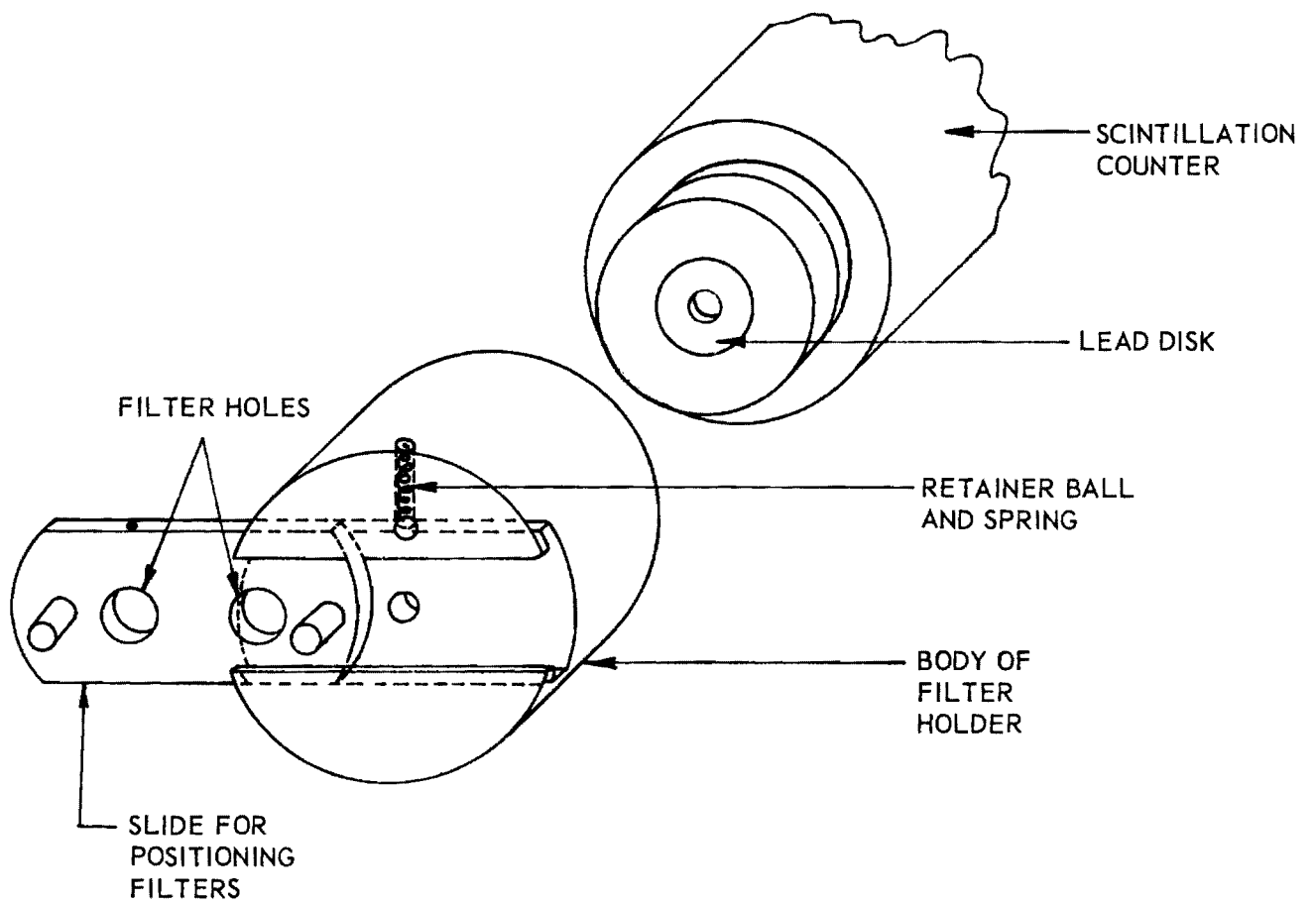


Figure 4. Holder for Filter Pair.

arm. Kirkpatrick⁴² has discussed the conditions for balance in filters of this type. Aluminum foil and the emulsion free backing of photographic film were used as the third materials mentioned by Kirkpatrick. An experimentally perfect balance could not be achieved. The effect of this unbalance will be discussed later at some length.

D. Low Temperature Apparatus

The crystal is held on the end of a fine glass fiber and is cooled by a stream of cold gas as is indicated by Figure 5. This arrangement is due to Post, Schwartz, and Fankuchen⁴³. The "nozzle" provides a central cold stream and an annular stream of dry air at room temperature. The inner conductor in this nozzle has double walls with an evacuated space between them. Hence we often refer to this whole device as a "Dewar nozzle." As is indicated in Figure 5 there are three gas streams associated with the nozzle. The outer stream is the annular sheath of dry air. The cold stream carries gas at the lowest temperature attainable. The mixer stream carries dry gas at room temperature and is used to control the temperature by diluting the cold stream.

Figure 6 shows the cold gas train. Dry nitrogen first passes through coils immersed in a dry ice and alcohol bath and then is bubbled through the liquid nitrogen. The escaping bubbles plus the nitrogen vaporized by cooling the incoming gas are collected by the transfer tube before they go into the neck of the liquid nitrogen bottle. The liquid nitrogen bottle is a standard 25 liter, metal type. Collecting the cold gasses at the bottom of the neck, as shown, instead of at the top of this neck made the difference between -130°C and -180°C at the outlet of the Dewar nozzle. The transfer

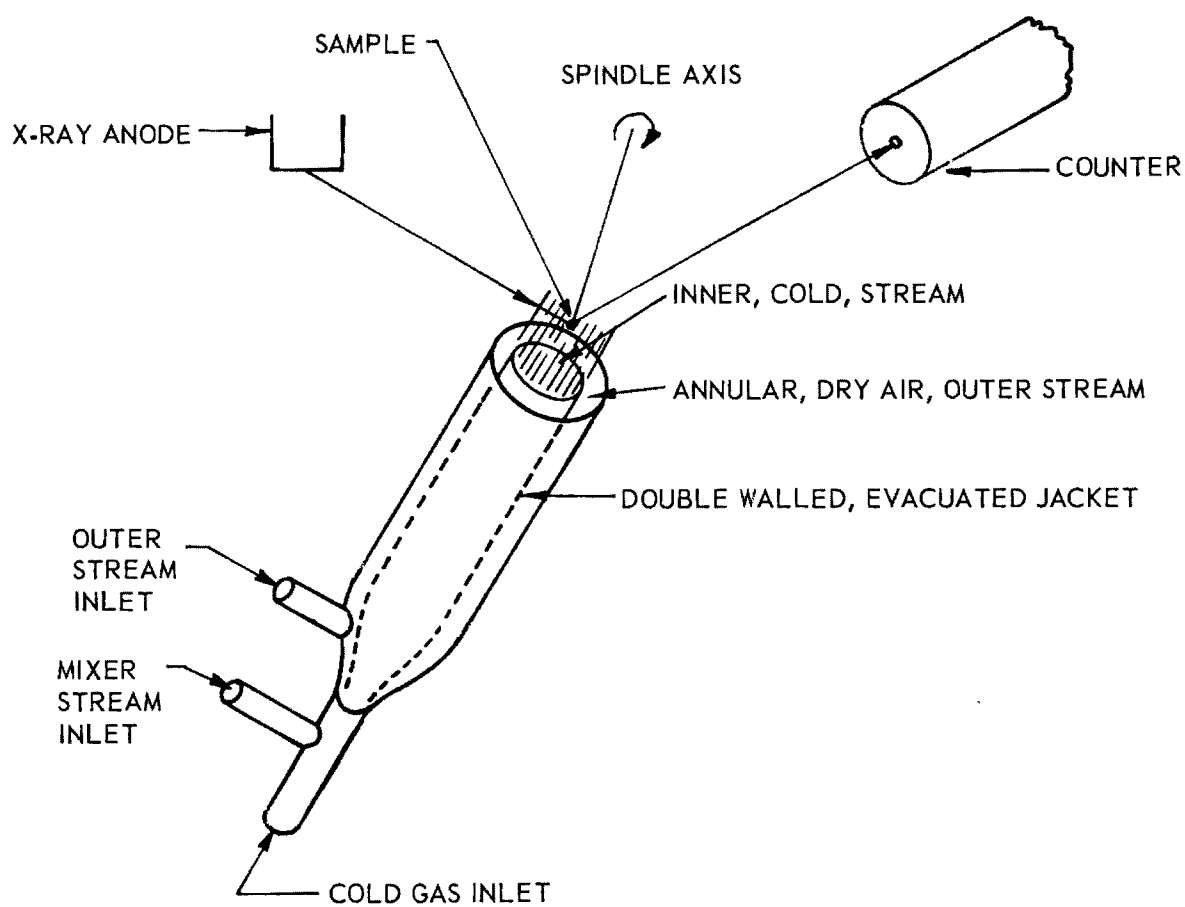


Figure 5. Low Temperature Arrangement.

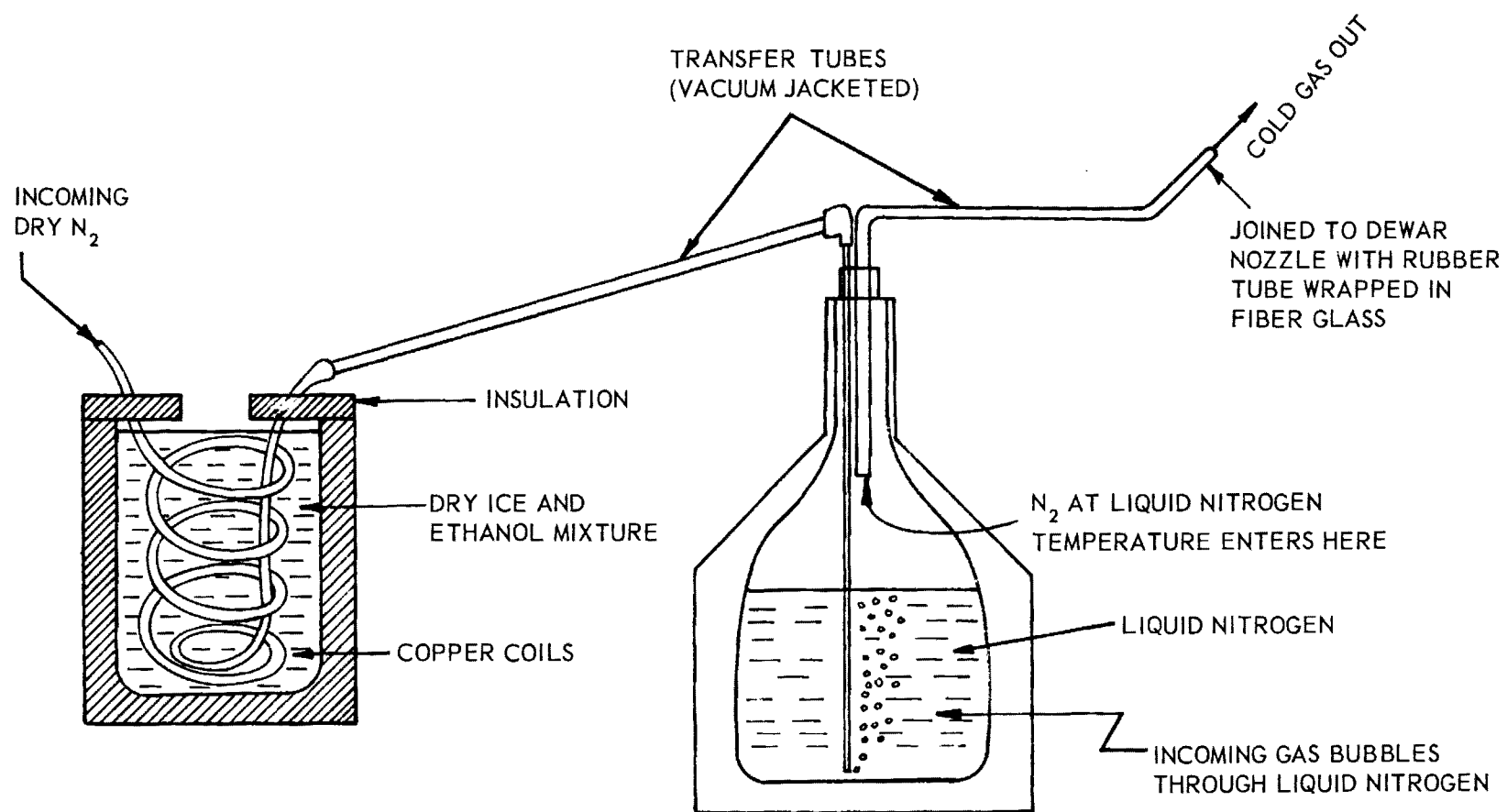


Figure 6. Cold Gas Train.

tubes are double walled glass tubes in which the space between the walls is evacuated. These tubes are not silvered or insulated any further. During operation some moisture occasionally collects on the outside of the second transfer tube -- it is not enough to form drops; no frost ever forms.

The temperature of the crystal is not measured directly; instead, the temperature of the cold stream at the outlet of the Dewar nozzle is measured by a thermocouple arranged so that its junction is in the center of the cold stream. The thermocouple was calibrated at the boiling point of liquid nitrogen (-195.8°C), the melting point of isopentane (-159.6°C), the melting point of ether (-116.3°C), the sublimation point of dry ice (-78.5°C), and the melting point of mercury (-38.9°C).

When it is not intended to work at temperatures below about -73°C , the liquid nitrogen bottle is dispensed with and the last transfer tube is connected directly to the copper coil in the dry-ice bath. In this case the gas used for the cold stream is dry air from the same source as that used at all times in the outer stream. A continuous supply of dry air is furnished by two banks of silica gel dryers which are automatically switched in and out of the line (without surges) and regenerated by heating. Constant flow velocities in the dry air stream are assured by two pressure regulators and about five cubic feet of ballast volume. Flow velocities in the cold stream are on the order of 30 to 45 liters per minute. Each stream is provided with a flow meter.

E. Counter Adaptor for Weissenberg Camera

The counter holder, shown in Figures 7 and 8, is of Georgia Tech design and construction. It provides a stable mounting for the counter with both

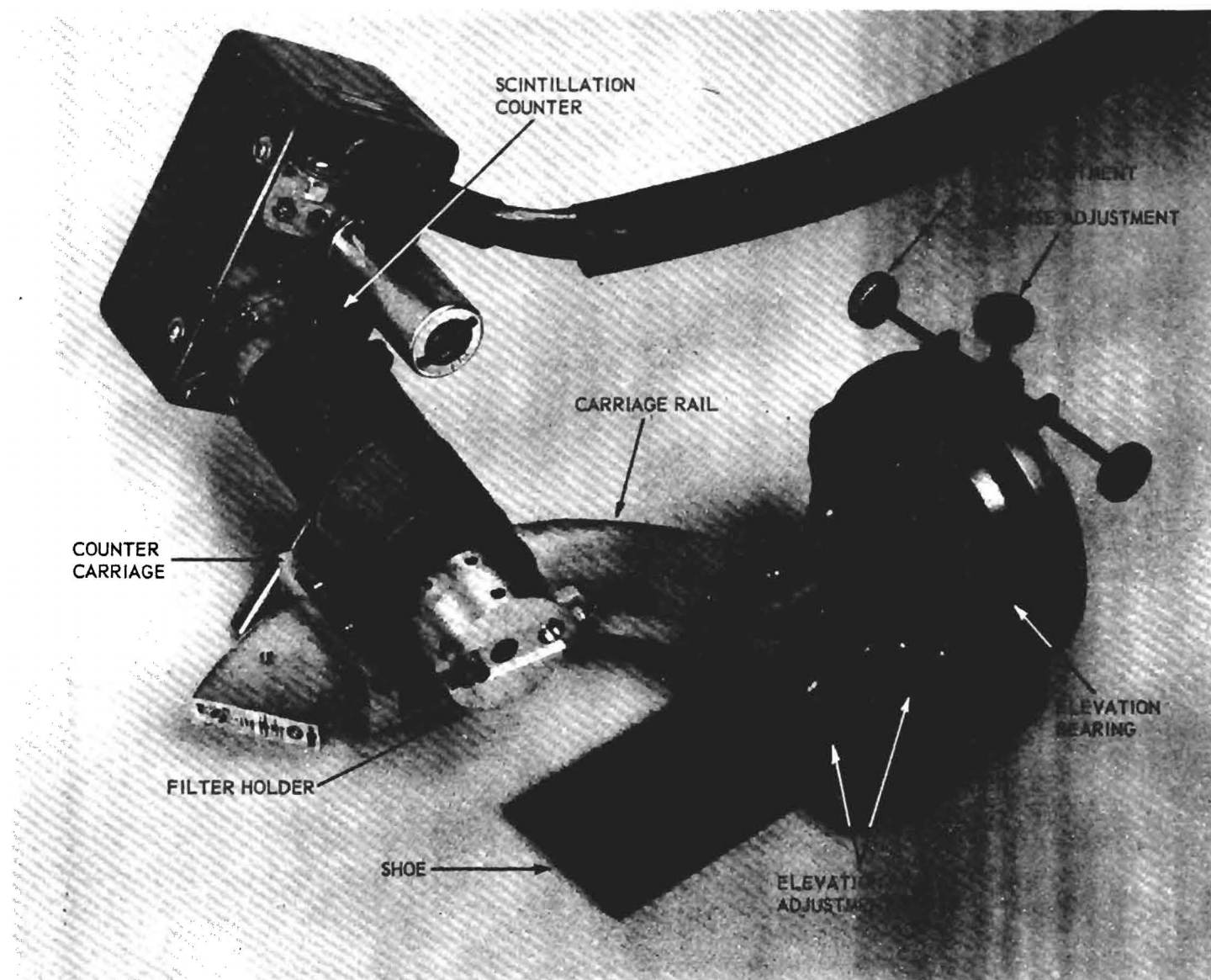


Figure 7. Counter Holder.

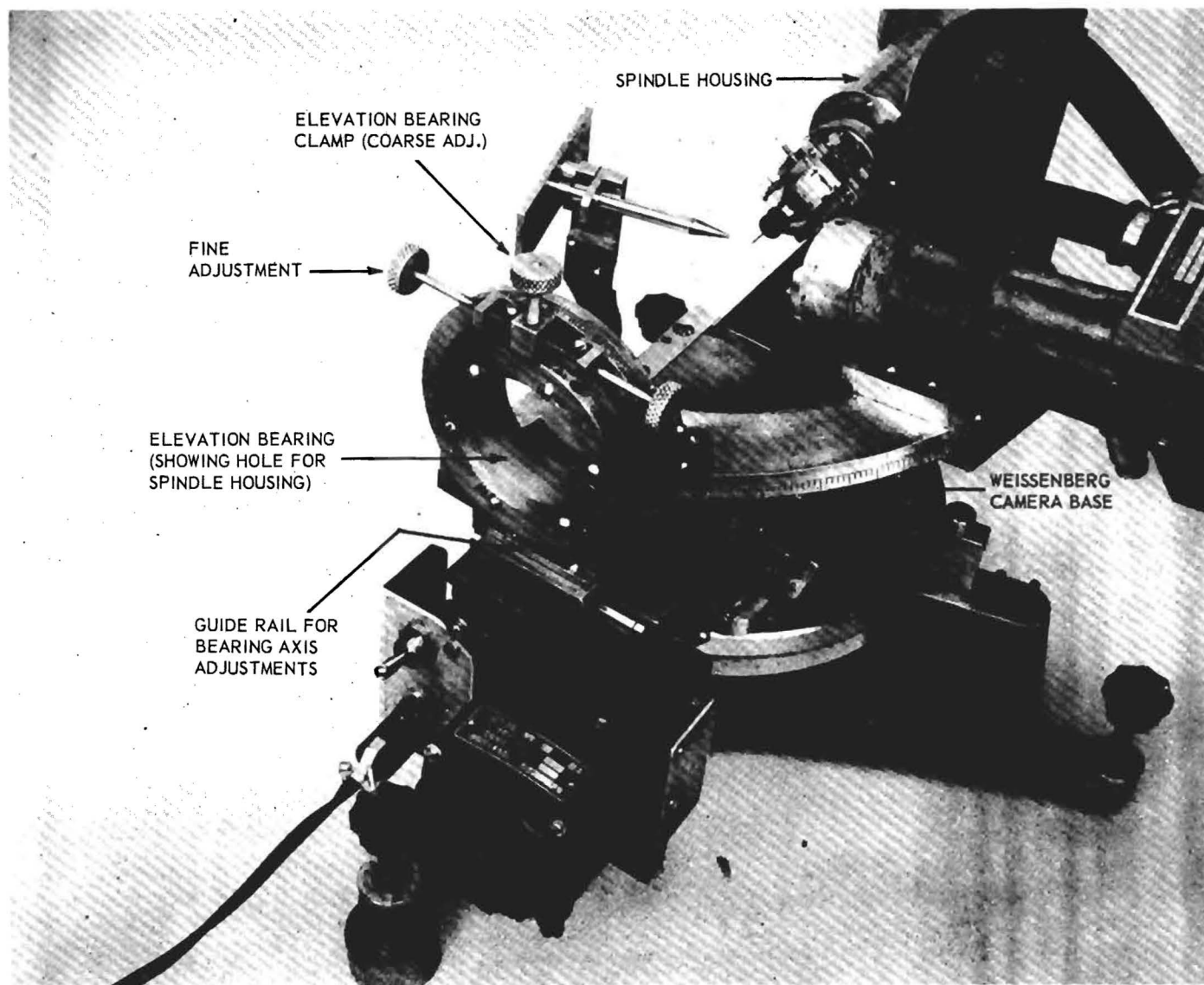
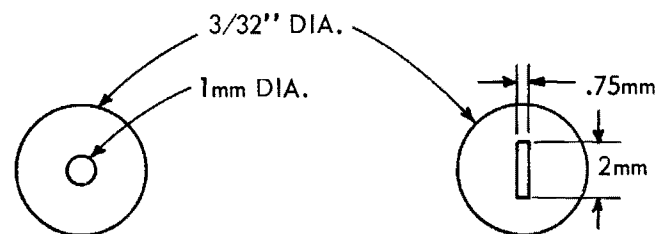
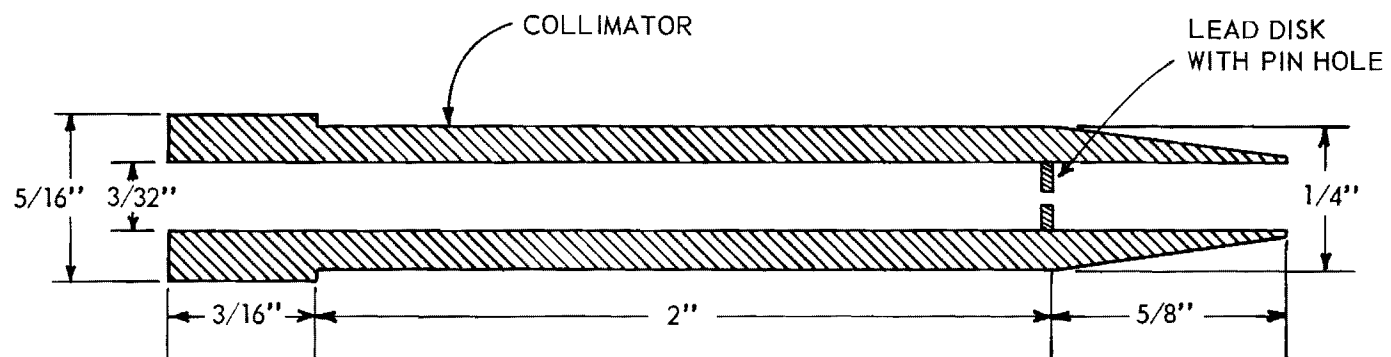


Figure 8. Counter Holder in Place on Weissenberg.

quick release and fine adjustments in azimuth and elevation about the crystal position as center. It is found to be considerably more stable and easier to use than one which is commercially available. It is also more flexible as the open center in the elevation bearing is large enough to slip over the spindle mounting of the Weissenberg. It thus allows the rail, which actually carries the counter, to be supported at either the left or the right of the Weissenberg camera base. The counter holder is always supported by the cassette carriage so that no forces or torques are applied to the Weissenberg spindle as a result of mounting the counter. The construction of the counter holder is such that ring and worm gears may be readily attached at the elevation bearing to provide a motorized drive in elevation angle. This has not so far been done.

F. Collimators

Two different "collimators" have been employed. Both have the same body dimensions; the dimensions for the "pinholes" are given in Figure 9. In each case only one pinhole was employed and was at the position shown in Figure 9. The pinhole was a circular hole of 1 mm diameter in a lead plug. The "rectangular collimator" employed a rectangular hole in a lead plug at the pinhole position shown in Figure 9. The dimensions of this hole were .75 mm by 2.0 mm and some care was taken to see to it that the sides of the rectangular hole were parallel and that when in use the sides of this hole were perpendicular to the spindle axis on the Weissenberg.



FRONT VIEW OF LEAD DISKS SHOWING PIN HOLES

Figure 9. Collimator Design.

II. THEORETICAL CONSIDERATIONS REGARDING EXPERIMENTAL PROCEDURES

A. Radiation

1. Wavelengths Desired

The wavelengths readily available for use in x-ray diffraction range from about 0.5 to about 2.0 Å. It is desirable to make observations on reciprocal lattice points remote from the origin because (a) there the magnitude of the effect of the temperature factor is enhanced by the large value of $\frac{\sin^2 \theta}{\lambda^2}$ (see the discussion of M in the Theory Section), (b) the statistical error in any final result may be reduced by making more independent observations, i.e., observations of the intensities associated with a larger number of reciprocal lattice points, and (c) the general trend in structure factors is that they become smaller with increasing distance, d^* , from the origin of reciprocal space; the further out observations are made the smaller will be the error that may be introduced by neglect of observations still farther out. All observations are limited by the wavelength used to a sphere in reciprocal space which is centered about the origin and has a radius equal to twice the reciprocal wavelength. Thus the total number of reciprocal lattice points that may be observed, insofar as the wavelength limitation is concerned, is proportional to the inverse cube of the wavelength. Consequently, even a relatively small change in the wavelength may make a significant change in the number of observations possible. In general, it is also desirable that absorption be minimized. These two reasons, absorption and d_{\max}^* , are arguments for the shortest wavelength possible.

If a crystal monochromator is to be used simply to separate the α -doublet from the rest of the radiation, the strongest reflection from the monochromatizing crystal will be used. This reflection will occur at low angles where the Lorentz and polarization factor will be much more favorable for the short than for the long wavelength so that the intensity loss due to crystal monochromatization will be minimized for the short wavelength.

However, under the usual operating conditions, the shorter the characteristic wavelength concerned the more nearly it falls in the maximum intensity region of the white background. The result is that the peak to background intensity ratio may suffer when the shorter wavelengths are used. Also to be considered are the angular separation of the diffracted rays (which is smaller with shorter wavelengths) and the spectral response of the detector. These considerations of background, resolution, and detector response may make a long wavelength more desirable than a short one. However, if (1) the unit cell is small (as is the case in the present work), (2) either a crystal monochromator or a differential filter is used, and (3) a scintillation counter which has a 100% detection efficiency over the range of wavelengths being considered is used, then all of these objections to a short wavelength are overruled.

From the above it would seem that the best choice would be the shortest possible wavelength. However, it is desirable to have a range of wavelengths available in order that the data may be compared as a function of wavelength, particularly when investigating extinction and absorption experimentally. There is the additional consideration of the output intensities obtainable in x-ray tubes with different anodes. Radiations that have been chosen for

use here are AgK_α (0.5 Å), MoK_α (.71 Å) and CuK_α (1.54 Å) radiation. The advantages of the silver tube are apparent from the above. The disadvantages of it in comparison to a molybdenum tube are its high initial price and its low permissible target loading.

2. Spectral Distribution and its Control

The spectral distribution of intensity in the output from an x-ray diffraction tube is partly that of the usual white spectrum, the position of whose maximum depends upon the excitation voltage used. On this white spectrum there are superimposed certain peaks due to the characteristic radiation from the target material. These are ordinarily the K_α and K_β characteristics. A single filter with an absorption edge between the β and α wavelengths can successfully discriminate against the β without reducing the intensity of the α by more than 1/2. This single filter also discriminates to some small extent against some of the short wavelength part of the continuous, or white, background. In general it may be said that the single filter has little value in discriminating against the general white background. A pulse height analyzer (PHA) can discriminate quite successfully against the parts of the white background that are far removed from the desired characteristic wavelength, but the response of the PHA and counter combination is not sufficiently sharp to discriminate against β in the presence of α . Thus, the combination of a single filter and a PHA backing up the scintillation counter successfully discriminates against the β and also improves markedly the general peak-to-background ratio, especially when the shorter wavelength characteristics are used. In this case, though, only about 40% of the characteristic α that is emitted by the tube can be effective (50% lost in the filter, an additional 10% in the PHA).

The best possible peak-to-background ratio is obtained by monochromatizing either the incident or the detected x-ray beam by diffracting it from another crystal. The spectral width of the monochromatized beam may be exceedingly narrow (it depends on the choice of crystal and reflection used in the monochromator) and it is even possible by this means to select only one component of the α -doublet for use. Such selectivity requires the use of high angle reflections, however, for which the reflection efficiency is very small. It is usual practice to use a lower angle reflection which has a higher reflection efficiency and, consequently, not to separate the components of the α -doublet. This maintains an excellent peak-to-background ratio in the diffraction pattern, but the reflection efficiencies for the monochromatizing reflection are still ordinarily a few per cent at best. Thus the principal objection to crystal monochromatization is that too much intensity is lost in the monochromatizing process. An interesting feature of crystal monochromatization is that the divergence of the beam may thereby be changed and focusing may be accomplished; when a flat, monochromatizing crystal is used the divergence in the beam is ordinarily reduced. A flat monochromatizing crystal has been used from time to time and probably will be used in the future to show the degree to which the results obtained with other techniques approach those obtained with crystal monochromatized radiation.

The differential filter seems to offer a compromise between spectral "cleanness" and intensity. In the case of molybdenum radiation, zirconium and yttrium filters have been used. The absorption edges of these materials are at 0.689 \AA and 0.727 \AA , respectively. If the filters are perfectly balanced, the differences in two diffraction patterns, each of which was

taken with a different filter, should be due to the narrow range of wavelengths between the absorption edges. The procedure is to subtract the diffraction pattern obtained with the yttrium filter from that obtained with the zirconium filter. If the two filters are not perfectly balanced, it would seem in principle to be possible to multiply the diffraction pattern taken with yttrium filter by some constant factor before subtracting it and yet to obtain essentially correct results. Of course if the unbalance were in opposite directions, but of the same magnitude, on the two sides of the region between absorption edges, then this constant factor technique would not be able to provide correction.

When the diffraction pattern has to be run separately with each filter, as is the case when the total count is measured over a certain angular range, the extra time required may be objectionable. However, if a certain total number of counts above background is to be obtained this may be accomplished much more quickly with the differential filter than with the crystal monochromator. These considerations plus the experimental convenience of making two peak height measurements with the differential filter have caused us to make considerable use of the differential filter technique. An unforeseen difficulty was encountered in the use of differential filter with a stationary counter. It will be discussed later.

3. Alpha-doublet Effect

The fact that the K_{α} radiation is composed of two wavelengths rather than one presents a difficulty in all measurements where the breadths of the diffraction peaks are of interest or where the functional form of the distribution of scattered intensity from a single wavelength is desired. Present

interest is in the changes in the observed breadth, B_0 , of the diffraction peaks due to changes in the α -doublet separation, d , due to temperature changes. In the intensity vs. temperature data for this project it is the integrated intensity that is desired yet it is most convenient to measure the peak height. Since B_0 is defined as the ratio of integrated intensity to peak height, the changes in B_0 are of considerable importance. As will be discussed later, it has been shown that the observed B_0 changes with temperature are in at least qualitative agreement with the changes to be expected from the α -doublet effect. Unfortunately, the relationship between the change in B_0 and the change in d depends in a complicated way on B , the breadth of the diffraction peak observed with truly monochromatic radiation. This subject has not been investigated fully yet; an analysis which is basically similar to that needed here has been made by persons interested in crystallite size determination from diffraction broadening. It is discussed by Klug and Alexander⁴⁴, among others. While analytic relations between d and B_0 are desired, they seem not to be available. Perhaps it will be possible to meet present needs with the plot of B/B_0 versus d/B_0 given by Klug and Alexander. The magnitude by which the effect may change the peak-height-to-area relation as the temperature is changed in the present studies seems to be on the order of a few per cent.

B. X-ray Beam Geometries^{*}

The following discussion involves considerations of specimen size and shape; target size, shape and inhomogeneity; detector window size and shape; and collimator design.

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^{*} Up to the time the following was written the author had not been able to find any similar discussion in the literature. It has since been brought to his

1. Acceptance Region

Understanding of the relationships between these various factors is aided by discussion of the "Acceptance Region," a phrase coined by the author in previous discussions of this same topic⁷. The present discussion is clearer than previous discussion⁷ and represents some extension of and additions to the ideas of it. Each particular set of Bragg planes (or reflection) has its own acceptance region; it is the region in which the source of any ray must lie if a corresponding diffracted ray is to be received by the detector. It is most easily described for a spherical, mathematically perfect crystal and for the case of monochromatic x-rays. Figure 10 is drawn for this hypothetical case. The acceptance region is bounded by the lines a, b, c, and d. It is formed from the region between two limiting cones, of apex angle $180^\circ - 2\theta$, which are coaxial and are separated by the specimen diameter. The lateral limits of the acceptance region, indicated by g and h in Figure 10 are set by the lateral limits of the detector window (g' and h') and the size of the specimen; only if the specimen is of zero size will these lateral limits be set by the width of the detector window alone. We define the limits g and h as the limits of position for a point source of x-rays such that all diffracted

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attention, principally by Dr. Furnas, that many of the points discussed here plus others relating to the topic of x-ray beam geometries have been discussed by Dr. Furnas in the manual which he prepared for distribution and use with the Single Crystal Orienter (Goniostat) offered commercially by the General Electric Company.

It is expected that a review of the General Electric manual will appear shortly in the usual literature. Discussions between Dr. Furnas and the present writer revealed no disagreements on any of the points which both had covered.

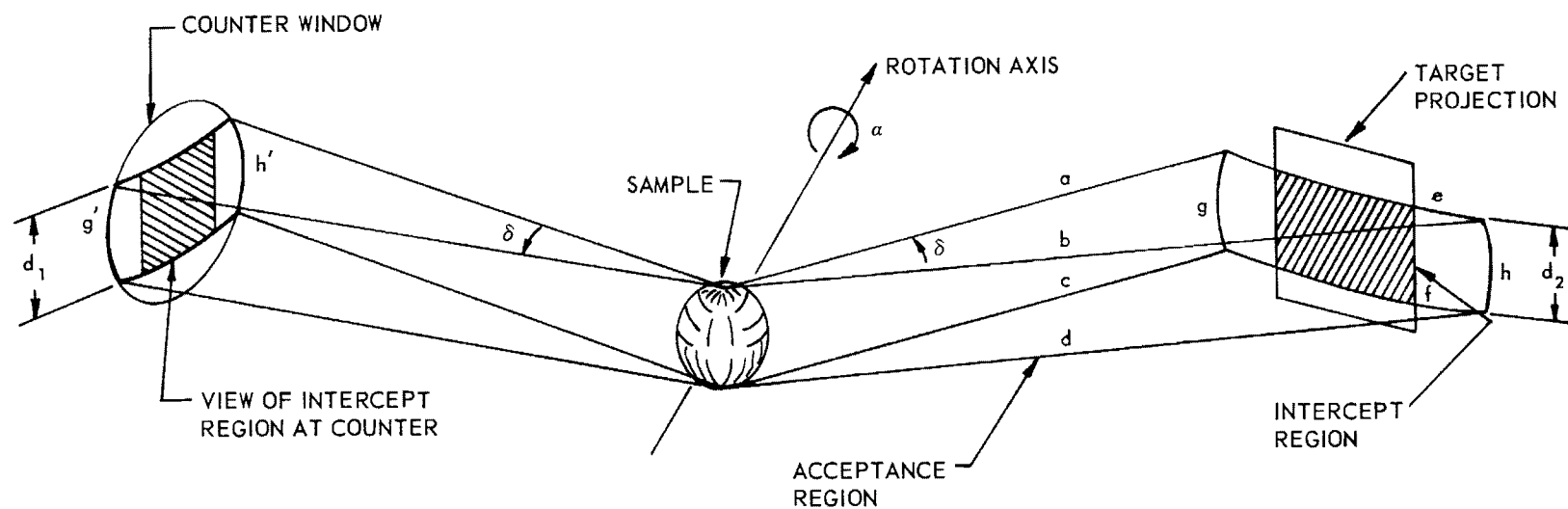


Figure 10. Acceptance and Intercept Regions.

x-rays can enter the detector window no matter from what part of the specimen they are diffracted. Thus, if the size of the detector window is kept constant, the limits g and h draw closer together as the specimen size is increased. For the case of a perfect crystal and perfectly monochromatic radiation the limits e and f are set by the maximum dimension of the specimen in the direction perpendicular to the Bragg planes giving rise to the reflection. In this idealized case there is no ambiguity in the definitions of g and h; if the specimen is allowed to have some mosaic character and/or the radiation is not perfectly monochromatic two definitions are useful.

- 1- The first definition, which is analogous to that given for g and h, is that e and f are the limits of position for a point source of x-rays such that all diffracted x-rays may enter the window no matter from what part of the crystal they are diffracted.
- 2- The second definition is that e and f are the limits of position for a point source such that any ray diffracted by any part of the crystal can enter the detector window.

In what follows these two definitions of e and f, with the definition given for g and h, will be referred to as the first and second definitions of the acceptance region. Clearly the vertical height (separation of e and f) of the acceptance region in definition (1) increases with increasing specimen size and decreases with increasing mosaic character and increasing wavelength spread. The acceptance region described by definition (2), on the other hand, increases in vertical height with an increase in specimen size, mosaic character, or wavelength spread.

2. Detector Window Size

The criteria for the size of the detector window are easily established. The minimum width, that is the minimum distance between g' and h' , is the sum of two parts: (1) the maximum width of the specimen (or, later on, the maximum length of the specimen which can receive any radiation) and (2) the arc length which subtends the same angle at the specimen as does the maximum lateral dimension of the target. The vertical dimension of the detector window is the sum of three parts: (1) the maximum specimen height as viewed from the detector, (2) a length which subtends at the specimen the same angle as does the maximum height of the target, (3) the length which subtends at the specimen an angle equal to the $\Delta 2\theta$ brought about by the wavelength spread. Specimen shape enters this picture by making the minimum required vertical dimension depend on the lateral position on the detector window and vice versa. As the crystal is rotated about the spindle axis (rotation angle " α ") the region, hereafter called the intercept region, which is common to the target and to the acceptance region may sweep over the target. The corresponding diffraction image (see Figure 10) will move over the detector window but will not overlap it if the window has been designed according to the preceding criteria. If the detector is not to be stationary but is to be moved at twice the angular velocity of the crystal, the "maximum height of the target" may be replaced by "the maximum height of the intercept region."

There is one additional consideration in the choice of the detector window size; it should not be any larger than necessary both to meet the above criteria and to give adequate tolerance in positioning the window. Further enlargement of the windows simply adds to the background level observed.

3. Divergence and Convergence

A pinhole type collimator can serve three functions: (1) to limit the specimen's view of the target, (2) to prevent some of the air scattered radiation and that scattered from the inside of the x-ray tube and the tube window from reaching the detector, and (3) to limit the amount of divergence, or convergence, in the incident beam.

A logical system for distinguishing between the convergence and the divergence in an x-ray beam is the following. Radiation from any part of the target takes place in all directions. If both the specimen and the target are of infinitesimal size, then all of the rays which leave the target and strike the specimen are necessarily parallel, and, consequently, the beam has neither convergence nor divergence ("beam" is meant to include only those rays which leave the target and actually strike some part of the specimen). As the specimen is given finite size, the rays will diverge from the point target to reach all parts of the specimen; the angle of maximum divergence will be the angle subtended at the target by the maximum dimension of the specimen. If, on the other hand, the target is given finite size while the specimen is retained as a point, rays from all parts of the target will converge to the point specimen; the maximum angle of convergence will be the angle subtended at the specimen by the maximum dimension of the target. It is clear, then, that if both the specimen and the target have finite size the incident beam has both a convergent and a divergent character. The convergence is determined by the target size, the divergence is determined by the specimen size; whether the incident beam is predominantly convergent or divergent depends upon the relative size of the target and specimen. In

the event that a collimator, such as a two pinhole collimator, is used, the words "specimen" and "target" in the discussion just preceding should be replaced by the phrases "specimen as seen from the target" and "target as seen from the specimen," respectively.

4. Flat-topped Rocking Curves

The curve obtained by plotting diffracted intensity versus spindle position (α) as the crystal is rotated through the Bragg position is hereby designated the "rocking curve." One often hears it said that if the rocking curve can be made to have a flat top, the height of this top above background will be proportional to the integrated intensity. This statement is true only if the rocking curve is made flat-topped in a particular way. That way is as follows: Let the target be uniformly illuminated or at least have no illumination gradient perpendicular to the lines e and f in Figure 10. Further, let it have parallel sides and let its vertical extent be larger than the vertical extent of the acceptance region according to definition (2). Then as the crystal is rotated there will be an angular region of rotation wherein the distribution of intensity in the intercept region does not change though the acceptance region is sweeping over the target. This will cause the rocking curve to have a flat top. Further, since the vertical height of the acceptance region is completely filled with radiation, radiation is incident simultaneously upon each part of the crystal from all directions for which any diffraction is possible. Since diffraction over the whole possible angular range in the neighborhood of the Bragg angle is thereby simultaneously and uniformly provided for, the intensity received at the detector must be strictly proportional to the integrated intensity that would be obtained by

rotating the crystal in a strictly parallel beam. (A perfectly spherical specimen is assumed in the above.)

It is to be noted that it is possible to obtain a flat-topped rocking curve in which the height of the top is not proportional to the integrated intensity. If the vertical height of the target (refer to Figure 10) is smaller than the vertical height of the acceptance region according to definition (1), then (for the perfectly spherical specimen) while the crystal is being rotated so that the entire target lies between e and f the height of the rocking curve will not change. Yet, during this rotation not all parts of the crystal are receiving radiation from all of the directions for which diffraction is possible (for this particular Bragg reflection, of course). Thus, in this case, the height of the flat-topped region of the rocking curve is not proportional to the integrated intensity. Actually, in this case the rocking curve would probably not have a top that was really flat for two reasons: (1) As the target position moved between e and f the region of the specimen effective in diffracting the x-rays would move from top to bottom of the specimen. Since not all parts of the specimen have the same thickness as viewed from the target, and since (on the kinematical theory) the diffracted intensity is proportional to the volume irradiated, the diffracted intensity would be constantly changing. (2) Differences in absorption due to varying path lengths in the specimen, as the effective region moved through the specimen, would also prevent the top of the rocking curve from being entirely flat. However, this "wrong" way of providing a flat top on the rocking curve could very easily provide a gently rounded top which might be mistaken for a flat top. It is important to distinguish

between the two sources of nearly flat-topped character in the rocking curves in order to avoid the false assumption that just because the rocking curve has a nearly flat top, the height of this top must be proportional to the integrated intensity.

5. Specimen Size

We have so far determined criteria for the size of the detector window and have determined that the specimen should be smaller than the target. Since both the wavelength spread and the mosaic character of the real crystal cause d_2 in Figure 10 (the separation of the limits e and f) to be considerably larger than the specimen dimension; and since the difference between d_2 and the specimen dimension will depend on the Bragg angle, there is probably little point in trying theoretically to determine the proper specimen size. Experimental measurements of the mosaic spread and the wavelength spread would have to be made in any event; it is simpler to start with the largest target that is practical from other considerations and then to reduce the size of the specimen until, if possible, the rocking curves take on a flat top character.

6. Collimator Design

The role of the collimator has yet to be determined. If true rocking curves are desired, the incident radiation must be rendered parallel by crystal monochromatization. If the desirable flat top curve is to be obtained either no crystal monochromator or one which provides convergent radiation, and hence is rather elaborate, will be used. It is clear that the vertical dimension of the slits or pinholes in a collimator must be greater than the vertical dimension of the acceptance region at the position

of the slit or pinhole (2nd definition of the acceptance region is used here) or the flat top region of the rocking curve will be lost. Since it is desirable to use the full maximum height of the target, in order that flat top curves may be obtained at as large Bragg angles as possible, the collimator should not touch either the line drawn from the top of the specimen to the top of the target or from the bottom of the specimen to the bottom of the target (Figure 10). Another way of saying this is that the collimator should not limit, in the vertical direction, the view that any part of the specimen has of the target. It may be necessary in the case of a specimen such as a long cylinder to limit the irradiated length of the specimen. This should be done with slits whose edges extend in the vertical direction (assuming a horizontal cylinder axis) and are parallel in order that the same length of the specimen shall always be irradiated even though it may move up and down slightly as it is rotated on the spindle axis. Clearly, if no other considerations are involved, it is preferable to use a specimen short enough (in length along the spindle axis) so that it all may be irradiated. Then the stringent requirements on the collimator construction may be dropped.

7. Value of Acceptance Region Model

The discussions based on Figure 10 show the criteria which must be met by the things which determine the x-ray beam geometries. Whether or not these criteria have been adequately met may be determined by experiment. The discussions indicate something of the relative sizes desired for the target, the specimen, the detector window, and the pinhole diameters or slit widths in a collimator. The discussions have also provided a model

(acceptance region and intercept region) which will be useful in the discussions of other things, e.g., required precision in crystal alignment, effect of target shape in comparing zero layer to upper layer data, and effects of the actual nonuniform illumination of the target and a symmetric specimen shape.

8. Target Illumination Gradients and Specimen Shape

It is clear that if there are illumination gradients perpendicular to e and f in Figure 10 the radiation falling on different parts of the specimen at the proper angle for diffraction will not be all of equal intensity. Since the total intensity emitted from the intercept region would change as the intercept region moved over the target (due to the aforementioned gradients) then the diffracted intensity would change as the crystal was rotated even though the crystal might have been arranged to have uniform thickness as viewed from the target and even though there were no absorption. The combination of nonuniform specimen thickness and nonuniform intensity in the intercept region could very well cause the top of the rocking curve to show more than one maximum. The usual result is that the rocking curve has a single maximum and no flat region at the top. Visualization of the interaction between inhomogeneity in target illumination and nonuniformity of specimen thickness (as viewed from the target) is aided by consideration of the case of the perfect crystal and the perfectly monochromatic x-rays. In that case x-rays emanating from a point at distance x down from e in the intercept region of Figure 10 will be diffracted only from portions of the specimen which lie at distance x below the top of the specimen.

It is clear that in relation to the comparison of relative intensities of reflections which occur at different Bragg angles, one effect of non-uniform target illumination is to make desirable a specimen shape which is symmetric about the spindle axis. Since, as has been stated above, it is generally desirable that the extent of the specimen along the spindle axis should be short enough so that the whole specimen may be irradiated, the choice of specimen shapes is practically restricted to short cylinders or spheres. Possible difficulties in squaring off the ends of the short cylinders and keeping these ends accurately perpendicular to the spindle axis makes a spherical shape the usual practical choice.

There are some additional experimental reasons for preferring the sphere. If the specimen has a cylindrical shape, the actual shape and breadth of a given diffraction peak is affected by the angular divergence between the cylinder axis and the rotation axis. Variations in peak shape will affect the relationship between peak height and peak area, which, it will be noted, must be known if use is to be made of peak height measurements alone.

9. View of Target

a. Upper layer error. It is clear from Figure 10 that unless the target, as viewed from the specimen, is symmetric about the incident beam as axis, the intercept region will have different shapes or different distributions of intensity (or both) according to how far the scattering vector, \vec{S} , is rotated from the vertical. (The vector \vec{S} may be considered to be perpendicular to the Bragg planes giving rise to the particular reflection.) It is clear that only in the zero layer could all reflections have the same view of the target. Consider for the moment the case in which the (00 l)

planes in a cubic crystal are aligned perpendicular to the spindle axis, and consider the Weissenberg camera to be used in the equi-inclination manner. Then when a $(00l)$ reflection is being observed the scattering vector, \vec{S} , will lie parallel to the spindle axis and the acceptance region will be 90° rotated from that shown in Figure 10. The intercept region will be a vertical band on the target instead of being a horizontal band as is shown in Figure 10. Again, the simplest case which will show the effect under consideration is that of the perfect crystal and monochromatic radiation. If the target extends out of the acceptance region at all, as it does in Figure 10, it is clear that the length of the intercept region along lines e and f will change as the \vec{S} vector is rotated from the vertical. This has the effect of increasing the total radiation power that lies in the intercept region, and consequently, increases the diffracted intensity that will be measured. Thus, it would be necessary to correct the observed intensity of any upper layer reflection relative to the zero layer reflection, or one upper layer reflection relative to another upper layer reflection, for a "view of target" error. In principle it would seem possible to calculate this correction; in practice it may be quite difficult to make the calculation because of inhomogeneities in target illumination, because of unknown and varying divergence of the acceptance regions for different reflections, and because the exact size and shape of the target and of the acceptance regions are unlikely to be sufficiently well known. The correction can be made experimentally through comparison of the sets of relative intensities obtained with two different crystal mountings, or it may be avoided entirely by bringing all reflections into the zero layer for measurement. The well known "Goniostat,"

designed by Dr. D. Harker and Dr. T. Furnas of the Polytechnic Institute of Brooklyn, is specifically designed to accomplish this with a single mounting of the crystal on its fiber. A. R. Lang⁴⁵ has described his concept of a device which combines the simplicity of Weissenberg geometry with a means for rotating the "Weissenberg," about an axis coincident with the incident beam, so that every reflection may readily be brought into the zero layer for measurement.

It might seem at first glance that if the target were small enough to be wholly included in the acceptance region this "view-of-target" error would not occur. It would not if only peak heights were being measured, but, as has been discussed above, peak heights of this type have little meaning. Meaningful measures could only be obtained by obtaining the total area under a "rocking curve." (Equi-inclination Weissenberg geometry is assumed throughout this discussion.) Relative motion of the target and the acceptance region caused by rotation about the spindle axis (see Figure 10) is always in the vertical direction. Thus, as the acceptance region becomes tilted with respect to its position in Figure 10, the path traveled by the small target through the acceptance region becomes lengthened. The amount of this lengthening is a simple cosine function of the angle by which \vec{S} deviates from the vertical so corrections for the view of target error should be simple in the event that the specimen had a high degree of symmetry.

b. Specimen shape considerations. The present discussion of view of target also bears on desirable specimen shapes. If the specimen is symmetric about the incident beam then the distance between e and f in Figure 10 will remain constant, insofar as it is determined by specimen dimension,

as the \vec{S} vector is rotated out of the vertical. However, if the specimen is a cylinder whose axis is parallel to the spindle axis the distance between e and f, which depends upon the maximum specimen dimension in the direction of the \vec{S} vector, will first increase and then decrease as the \vec{S} vector is rotated from the vertical to the horizontal (i.e., parallel to the spindle axis). Thus, there is an additional "view of target" error introduced into the relative intensities by a lack of symmetry of the specimen about the incident beam. It has previously been established that symmetry about the spindle axis is required (and it is also required for absorption correction reasons). Both of these symmetry requirements can be satisfied simultaneously only by spherical specimens. Thus, it appears that the collection of the best relative intensity data, even from non-absorbing specimens, requires the use of spherical specimens. It is to be noted that the view of target error introduced by variations of the distance between e and f through use of a specimen which is not symmetric about the incident beam cannot be corrected for by a Goniostat nor by Lang's instrument. It is further to be noted that the view-of-target error discussed here applies to peak height measurement as well as to integrated measurements.

c. Magnitude of Error. The view-of-target error is not necessarily large. Previous work done by the author⁷ showed that a final R factor ("reliability index" in a crystal structure determination) of 8 per cent could be obtained even when this view-of-target error was neglected. Since a large part of this 8 per cent (which amounts to 16 per cent variation in intensity measurements) was due to other factors, the view-of-target error in that one case did not exceed a few per cent. The specimens were

approximately spherical and the product of the absorption coefficient times the specimen diameter was about 0.4 in the case just cited.

C. Specimen Dependent Accuracy Factors

1. Absorption

a. Absorption factors for simplest cases. Unknown variations in the absorption factor, A , in equation (19), may be the principal source of error in a set of structure amplitudes, $|F|$, which have been determined from intensity measurements. If the absorption coefficient and the specimen shape and orientation are accurately known, the absorption factor applicable to each reflection may be calculated. Such calculations are extremely laborious for all but a few specimen shapes. For those specimens which do not intercept the entire beam, the sphere and the cylinder represent the simplest cases. The absorption factor for a cylinder aligned parallel to the spindle axis is a function of the Bragg angle, of the layer of the reflection, and of the product μR where μ is the linear absorption coefficient and R is the radius of the specimen. The absorption factor for a spherical specimen depends only on the Bragg angle and on μR . Tables are available for both of these cases. If the specimen shape is not symmetric about the spindle axis, then the absorption factor will be a complicated function of spindle rotation angle as well as of the parameters mentioned.

b. Criteria for accuracy in specimen shaping. Some considerable effort, therefore, may profitably be spent in shaping the specimens. The accuracy with which the specimens must be shaped depends upon the linear absorption coefficient, μ , for the particular specimen and radiation used. The required accuracy of specimen shaping may be discussed in terms of the

deviations of the actual specimen surface from that of an equivalent sphere (or cylinder), shapes for which the appropriate absorption corrections are tabulated. The radius, R , of the equivalent sphere is to be such that the absorption produced by the whole sphere, for a particular reflection, is equal to the average absorption produced by the actual specimen as it is rotated about the spindle axis. Absorption corrections actually applied to the data will be those appropriate to a sphere of the size estimated to be that of this equivalent sphere. The actual specimens, assumed to be spheres, are probably well approximated by ellipsoids. We discuss the factor by which the absorption correction so made will be in error because the specimen is not actually spherical. One of the extreme cases is represented by the ray shown in Figure 11. In this case the extra distance that the ray has to travel because of the nonspherical shape is δ . The total pathlength is then $2R + \delta$ and the reduction of intensity due to absorption is indicated by equation (42).

$$I = I_0 e^{-\mu(2R+\delta)} = I_0 e^{-\mu 2R} e^{-\mu \delta} \quad (42)$$

It is clear that the additional absorption due to the misshaping of the crystal depends upon the absolute value of the misshaping and not on the per cent deviation of the real from the desired surface. In the worst possible case the ray might both enter and leave the specimen at the points where there was a maximum deviation of the specimen surface from the ideal surface. In this case " δ " in equation (42) should be replaced by " 2δ ". It is to be noted that " δ " may be either positive or negative. The most extreme case then

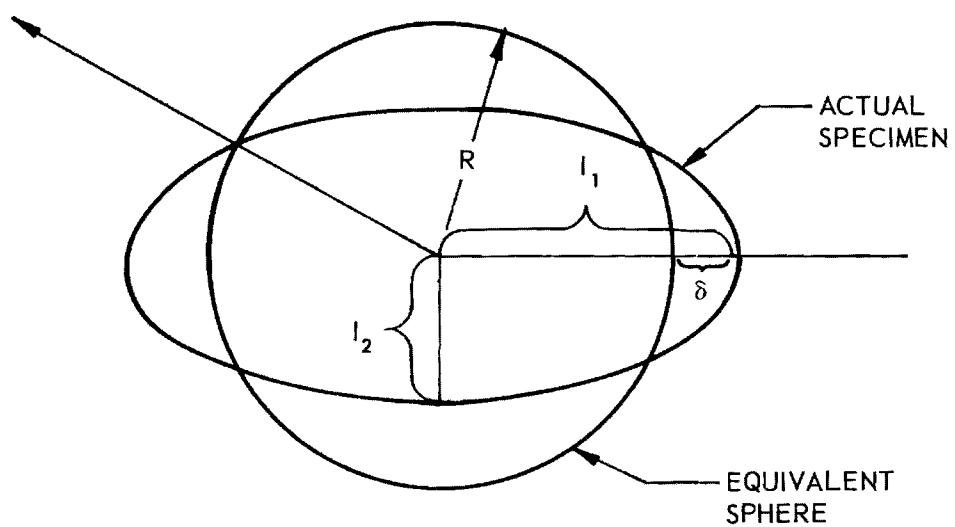


Figure 11. Equivalent Sphere of Ellipsoid.

compares a ray passing along the minor axis of the ellipsoid with one passing along the major axis. By use of equation (42) and by letting the subscripts 1 and 2 stand for the major and minor axis, respectively, the ratio of these intensities is

$$I_2/I_1 = e^{-\mu(\ell_1 - \ell_2)} \quad (43)$$

where ℓ is the total length of the specimen along the particular ellipsoid axis. Since the value of the exponent will always be small for any case of interest, only the first two terms need be retained in an expansion; and the error due to the use of the absorption factor for a sphere of radius equal to either the major or minor axis of the actual ellipsoid describes the specimen's shape obeys the inequality.

$$\% \text{ error} < \mu(\ell_1 - \ell_2) \times 100\% \quad (44)$$

If the radius of the sphere is chosen to lie midway between ℓ_1 and ℓ_2 the error is immediately cut in half. For the case of silver chloride and molybdenum radiation the linear absorption coefficient is 135/cm. Thus, if the maximum absorption error is to be 1% the difference between the maximum and minimum dimension of the ellipsoidal specimen must be 7.4×10^{-5} cm. This represents a rather stringent requirement on specimen shaping even though it is calculated for a set of extreme assumptions. The actual situation is not this bad because the additional volume also diffracts. The absorption coefficient for silver chloride in silver radiation is about one-half of that used above, so the use of silver radiation relaxes these

requirements somewhat. In any event, however, it is clear that a high premium is to be placed on accurate shaping of the specimen.

c. Absorption factor for general ellipsoid. It would seem in principle to be possible to use quantitative knowledge of the ellipsoidal character of the specimen, of the absorption coefficient, and of the relation of the ellipsoidal axis to the crystallographic axis to calculate the absorption factor applicable to each individual reflection.

The integrations encountered, however, are cumbersome and probably must be accomplished numerically. Thus, this one problem would call for the use of a very large-scale computer. According to the advance program for the American Crystallographic Association meeting to be held on July 20-24, 1959 (at Cornell University), D. R. Fitzwater of Iowa State College will present a paper which apparently is concerned with just such a program. If Dr. Fitzwater has indeed solved this problem his solution will probably be of great value to us in our future determinations of relative structure amplitudes from observed intensities.

d. Experimental techniques for avoiding, for detecting, and for partially correcting for absorption errors. Recognition of the absorption problem and of the fact that it had not yet been overcome contributed to the decision to observe first the temperature dependencies of single reflections. As has been noted elsewhere the absorption factor cancels out of the comparison of the intensities of the same reflection at different temperatures.

There are several ways of detecting experimentally the variation in absorption factors due to specimen shape asymmetry and at least one way of attempting to correct for it. If, for the equi-inclination Weissenberg

geometry, a reflection is observed for which the S-vector is parallel to the spindle axis, the diffracted intensity should be independent of spindle rotation. Dependence of detected intensity, in this case, upon spindle position indicates that the specimen shape is not symmetric about the spindle axis (it is assumed that all alignment adjustments have been completely made).

Since the Bragg angle for a particular reflection varies with the wavelength used, then the x-ray beams will follow different paths through the crystal for different wavelengths. If there is an absorption factor error due to specimen shape-asymmetry, two different sets of relative intensities, taken with different wavelengths, will not reduce to the same relative structure amplitudes. This is not a clear-cut test, however, as extinction effects would also make the two resulting sets of structure amplitudes differ, though not in the same way.

Under certain circumstances it may be possible to make corrections for shape asymmetry on the basis of the observed intensities themselves. The author has previously been able to accomplish this with a quartz specimen⁷. The crystal symmetry requires certain reflections to be equivalent. A lack of such equivalence in the observed intensities indicates a specimen shape error. Polar plots of the intensities vs. crystal position may be used to determine the magnitude of this effect as a function of crystal position and Bragg angle. Frequently, as many as eight members of a set of equivalent reflections may be brought successively into diffracting positions simply by rotating the spindle. In the previous work mentioned⁷, the author was able to reduce the specimen shape error from about 4% to less than 1% by application of this technique.

2. Extinction

a. Origins and usual correction methods. In the kinematic theory of x-ray diffraction it is assumed that there is no re-scattering of once scattered radiation. The diffracted intensity is proportional to the square of the structure amplitude. Re-scattering of the once scattered radiation within the same mosaic block of the crystal leads to the effect known as primary extinction. Re-scattering from a different mosaic block leads to the effect known as secondary extinction. Both of these effects are related to some power of the structure factor in such a way that the strongest reflections have their intensities most reduced by extinction. The degree of extinction also depends upon the wavelength, upon the size of the mosaic blocks, and, in the case of secondary extinction, upon the spread in the angular orientations of the mosaic blocks. In the case of a large, perfect crystal the conditions of the dynamical theory are satisfied and the intensity is proportional to the first power of the structure amplitude. It is to be expected that no real crystal wholly satisfies the assumption of either theory. The kinematic theory is usually assumed, and the extinction effects are taken into account as corrections to be applied to the observed intensities. There is no suitable theoretical way of making these corrections. Numerous experimental means have been devised.

Vand⁴⁶ has investigated the functional form of the extinction correction, has proposed a convenient exponential approximation to the more rigorous form, and has discussed a graphical method of making approximate corrections with plots which involve intensity ratios and assumed structure amplitudes. It would seem to be a useful method when the structure

amplitudes are fairly well known, such as they are in the later stages of the crystal structure refinement. Vand's approximation (which applies best for small crystals completely bathed in the incident radiation and for diffraction at small angles) shows the exponent of the exponential correction to be proportional to the square of the structure amplitude, to the square of the wavelength, and to the square of the effective linear dimension of the mosaic block, and to be inversely proportional to the square of the volume of the unit cell. For secondary extinction the angular dispersion of the blocks, and an additional power of the linear dimension of the crystal, also enter.

Gatineau and Mering⁴⁷ made use of the wavelength dependence of extinction to propose a correction based on the extrapolation of a plot of $\ln I$ vs. λ^2 to zero wavelength. Chandrasekhar⁴⁸ has proposed a method of correcting for extinction, whether secondary or primary, which is based on the variation of the extinction effect with variation in the direction of polarization of the incident beam. Chandrasekhar's method has the advantages that it is confined to a single wavelength and to a single reflection at a time; thus, there are no errors due to uncertainties in the absorption correction.

In a determination of the relative structure amplitudes at a given temperature the above discussion means that it would be well to make provision for the use of different wavelengths and different polarization directions.

b. Possible temperature dependences. A more immediate concern is the possibility that the extinction effect may be temperature dependent. One effect of primary extinction is to increase the height while reducing

the area of a true rocking curve. Since primary extinction presumably depends upon $|F|^2$, which in turn is temperature dependent, it would seem possible that the diffraction peaks corresponding to the strongest reflections might become sharper as the temperature was reduced. In this event, following the peak height alone as a function of temperature would not give a true indication of the dependence of integrated intensity upon temperature.

Extinction might also be affected indirectly by temperature through temperature dependence of the equilibrium populations of defects, e.g., color centers. Since these defects are produced by the x-ray beam at a rate which is essentially independent of temperature and since they anneal at a rate that does depend upon temperature, the equilibrium populations should be greater at the lower temperatures. This effect would make the extinction less pronounced at the lower temperatures, in contrast to the effect just mentioned.

If the temperature range or the rate of change of temperature was such that the mosaic block's size would be changed, either by annealing or by breaking up, the extinction would be changed as an indirect result of the temperature change. The possibility of changes in extinction due to changes in the block size can be virtually eliminated by keeping the specimen temperature below the annealing temperature and by avoiding thermal shock to the specimen.

No matter what the cause might be, a temperature dependence of the extinction correction is undesirable in connection with thermal motions measurements; though it may be of considerable interest in studies of imperfections. Experimental tests for significant temperature dependence of

extinction may be carried out in at least two ways: (1) in the absence of extinction changes the integral breadth (the ratio of the total area to the peak height) of a reflection observed with strictly monochromatic radiation will not depend upon temperature and (2) in the absence of extinction changes the same temperature dependence should be observed with two different wavelengths. Measurements of the breadth of reflections as a function of temperature have been carried out in several cases and measurements of the temperature dependence of the same reflections with different wavelengths will be undertaken shortly. The search for extinction effects through the temperature dependence of the integral breadth is complicated by the effect of the varying α -doublet separation upon the integral breadth. Further, if the experimental arrangement is such that the observed peak height is proportional to the integrated area of a true rocking curve then the ratio of the peak height to integral breadth of such an observed peak would not be expected to be changed by changes in extinction.

3. TDS

In the section on "Theory" the contribution of TDS to the apparent Bragg intensity was discussed. It was suggested there that the dependence of the TDS contribution upon scattering angle might make it possible for one to eliminate the error due to TDS by noting the dependence of the results on scattering angle and extrapolating to zero angle. The possibility has also been noted of using Cole's data²⁷ to correct our apparent Bragg peaks for the TDS contribution.

The fact that the TDS peaking under the Bragg peak is much less sharp than that of the Bragg peak itself leads to two possible methods of detecting

experimentally the existence of a TDS contribution to the apparent Bragg intensity. The two peaks are shown schematically in Figure 12; the observed or apparent Bragg peak is found by the superposition of these two. It is clear that one effect of the TDS contribution will be to increase the integral breadth of the apparent Bragg peak. Since the intensities in the Bragg and TDS peaks change oppositely with changes in temperature, the integral breadth of the apparent Bragg peak should be temperature dependent if the TDS contribution is significant. As has been pointed out elsewhere, however, the integral breadth may also be temperature dependent for other reasons. It is clear from Figure 12 that the most noticeable effect of TDS will be that of extending the wings of the apparent Bragg peak. If measurements of the intensity of the wings were to be made at points far enough removed from the exact Bragg angle, such as at point "a" in Figure 12, the intensity observed should be due entirely to TDS and the temperature dependence of the intensity observed there would be opposite to that observed for the true Bragg peak. Thus, a decreasing intensity at point "a" with decreasing temperature would indicate the presence of a significant TDS contribution to the apparent Bragg intensity. In principle it would seem to be possible actually to measure the TDS contribution from (1) the temperature dependence of the intensity at a point such as point "a" in Figure 12, and (2) the knowledge of the functional form of the TDS. In practice, however, it is doubtful if the measurements could be made with sufficient accuracy to allow quantitative determinations of the TDS contribution.

4. Defect Concentration

One effect of defect concentration upon apparent Bragg intensity will be to produce an apparent temperature factor due to the static atomic

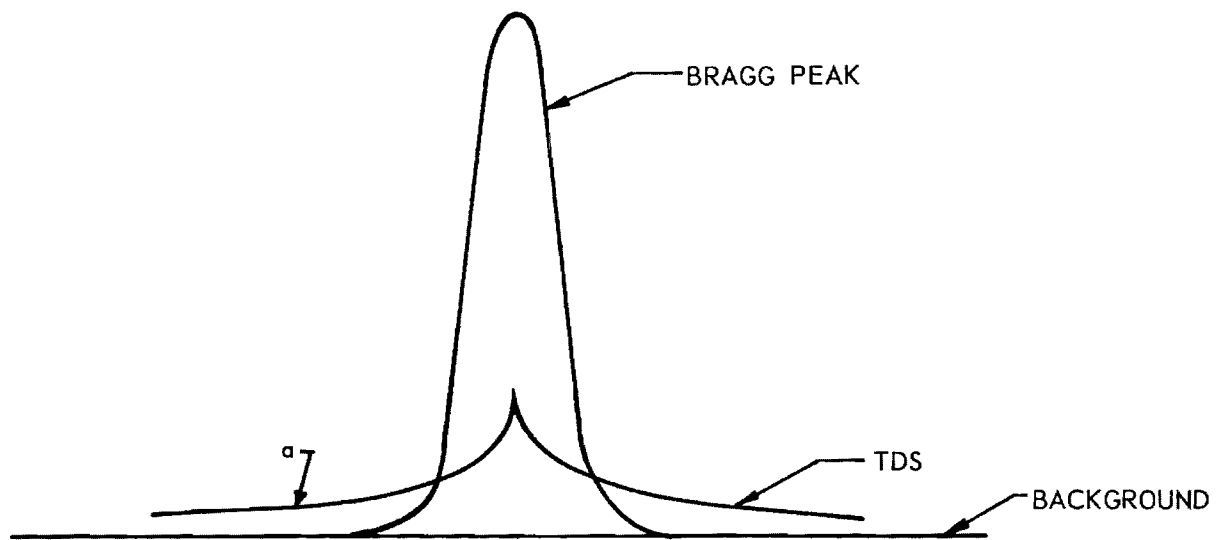


Figure 12. T.D.S. and Bragg Peaks.

displacements caused by the defects. This would provide one of the additive terms, such as $\overline{u_1^2}$ in equation (8). A second effect is to change the elastic constants. This would result in a change in the temperature dependence of $\overline{u_T^2}$ in equation (8). The first effect would not influence the determination of Debye- Θ 's from the temperature dependences of intensities; the second would, though possibly only very slightly. If the defect concentration changed with temperature, as would seem to be probable in many cases, both the first and second effects named here would themselves be temperature dependent and an additional temperature dependence of the observed intensities would be brought about thereby.

In the case of reflections which exhibited extinction the change of defect concentration with temperature would be expected to produce an inversely related change in the magnitude of the extinction effect and thereby to make it, in turn, temperature dependent. In the case of silver chloride, the production of Frenkel defects by the incident x-ray beam is expected to be independent of temperature. The rate at which the defects anneal depends upon temperature. The concentration of Frenkel defects in our experiment is, therefore, expected to increase with decreasing temperatures. The effect of this on extinction can be experimentally noted in either of two ways. (1) The integrated intensity of a reflection so affected would be found to increase abnormally with decreasing temperature. (2) The integral breadth of such a reflection would also be found to increase with decreasing temperature.

Changes in the integral breadth due either to the α -doublet effect or to a change in extinction due simply to the temperature dependent change in the structure factor would sharpen rather than broaden the peak with

decreasing temperature. Thus, it is experimentally possible to separate the several effects. It is apparent that these effects of the defect concentrations, and changes in them, provide possible means for the study of the defects themselves. This possibility will be borne in mind and may form the subject of future work, but will not be investigated in the immediate future.

D. Choice of Peak Parameters to be Measured

1. Area vs. Peak Height

It is assumed in the following discussion that the rocking curves are not sufficiently flat-topped so that the peak heights are strictly proportional to the integrated areas.

The integrated intensity, or the area under the diffraction peak, corresponds to the total power diffracted during one complete passage of the reciprocal lattice point either into or out of the sphere of reflection. Most formulae for intensity are based on this measure. However, it is much easier and quicker to measure the peak height alone. Whether the area is to be measured as a total number of counts obtained during a certain angular transit of the spindle or as the area under a peak on the recorder trace, it takes longer to measure areas than peak heights.

Measurements of peak heights might also be expected to suffer less from the TDS contribution to the apparent Bragg intensity, particularly if the reflection is fairly far out in reciprocal space. It is also noted that essentially only one phonon TDS scattering will contribute to the apparent peak intensity whereas two phonon scattering will contribute significantly to the measured area.

One of the large sources of error in measurements of integrated areas is the uncertainty in background placement. Small errors in placement of the background line will produce a much smaller percentage of errors in peak heights than in areas. On the other hand varying separation of the α -doublet, such as that due to temperature variation, will not affect the area measurements though they will affect the peak height measurements. The extra breadth of the upper layer peaks worsens the problem of background placement in area measurements.

The Lorentz factor for integrated intensities is well known. It depends only on the general arrangement of the experiment and not on the particular experimental specimen. The Lorentz factor that would apply to peak height measurements, however, would have to be calculated separately for each peak measurement and would be complicated. Such quantities as both angular and spatial distribution of energy in the incident beam and the angular spread of the mosaic block in the crystal would have to be known, possibly for each reflection, before such calculations could be carried out.

It may be possible for one to avoid the need for calculating Lorentz factors for peak heights by graphically converting peak heights to areas. The simple, well known Lorentz factor then applies. The required graph may be prepared from experimental measurements of the ratio, B_0 , of area to peak height, for the particular specimen, as a function of Bragg angle and possibly as a function of temperature. If there is no "view-of-target" error, all peak height measurements of a particular reflection will be the same no matter in what layer the measurements happen to be made. Thus, if B_0 may be assumed to have a simple dependence on Bragg angle, θ , (extinction and

shape asymmetry of an absorptive specimen would invalidate this assumption) then it should be necessary to measure only enough B_0 's to enable construction of a plot of B_0 vs. θ . Since changes in temperature will also affect B_0 due to the effect on the α -doublet separation, a separate B_0 vs. θ plot should be made for each of several temperatures, in the manner indicated schematically in Figure 13-a. Alternatively, a B_0 vs. T plot may be made for each of several θ 's necessary to cover the range of observation, in the manner indicated schematically in Figure 13-b. This general scheme has previously been used by the author with some success⁷.

2. Peak Height Times Width vs. Total Count or Recorded Area

Integrated intensities may be measured fairly directly in any of at least three ways: (1) Total counts may be obtained over a certain angular range which includes the peak. (2) The recorded area on a trace of intensity vs. angle may be measured. (3) Height and width parameters of the peak may be separately measured and then multiplied to obtain the area. Attention is directed here to the third possibility. The Bragg peaks are ordinarily considered to have the functional form of either

$$y = \frac{A}{1 + k^2 x^2} \quad (45)$$

or

$$y = Ae^{-k^2 x^2} \quad (46)$$

In each of these equations "A" corresponds to peak height and k is a measure of the breadth of the peak. The total area under a peak which has either of these functional forms is then proportional to the product of a height with a width measurement.

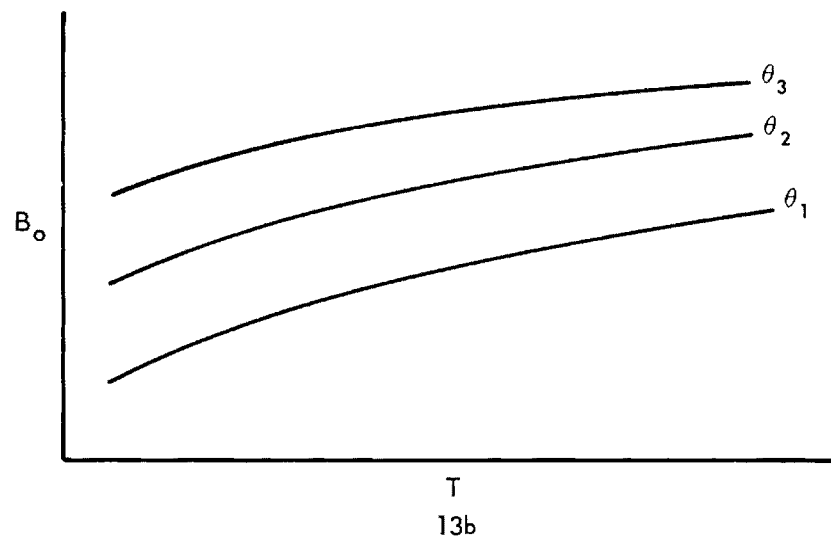
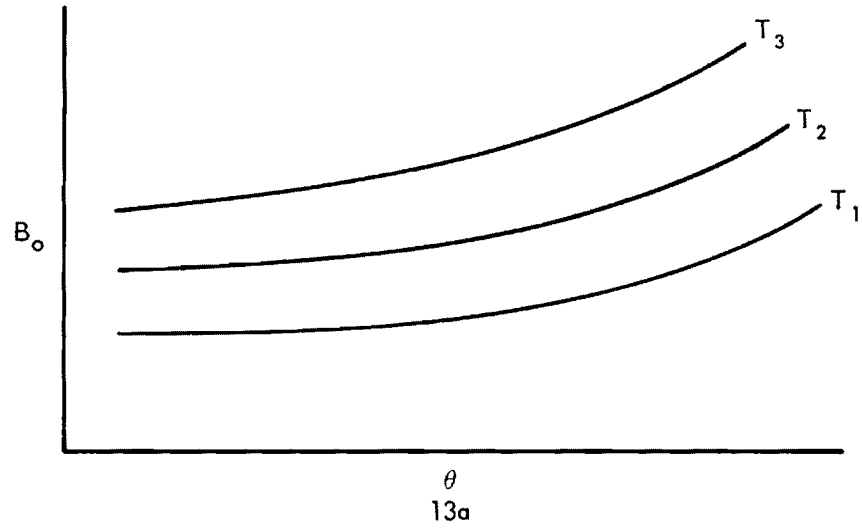


Figure 13. B_o vs. θ and T .

The width measurement, B_0 , may be either the integral breadth or the width measured at half height. If the integral breadth measurement is to be used, there will be no saving in time obtained by measuring the area as a product of the height and width parameters (instead of measuring the area directly). If, on the other hand, a width at half height may be used, a considerable saving of time is possible. Further, since the peak is widest at the base, a measurement of recorded area or of total count is more susceptible to errors in background placement than is a measure of area based on peak height times width at half height.

In principle it would seem possible that the peak heights and half widths could be determined more quickly than a direct total area measurement of comparable accuracy might be made. A technique used in the present work for determining the peak height in a reproducible fashion has been the following. The intensity was measured to the desired statistical accuracy at each of three equally separated points, near the top of the peak, so chosen that the central point showed the greatest intensity. The three points were then fitted by a parabola which was symmetric about a vertical line. The maximum of the parabola was taken to be the maximum of the peak. While it may be argued that the actual shape of the peak is not parabolic, the advantage of the method is that it is a simple way of obtaining reproducible results.

The peak widths at half height may, of course, be determined from a recorded trace of intensity vs. angle. The trace need not extend all the way into the background on either side, thus considerable time may be saved in obtaining the trace. However, better accuracy and greater speed may be

obtained by making measurements at 2 points, one above and one below half height, on each side of the peak with a predetermined statistical accuracy. The intensity measures at each of the points are plotted vs. diffraction angle and the two points on one side of the peak are connected by a straight line. A straight line is an adequate approximation to the actual shape of the curve describing the peak in this region if the points are not very far apart. When the two straight line segments have been constructed, the distance between them at half height may be measured with good reproducibility and sufficient accuracy. These procedures for determining the peak height and the width at half height are pictured in Figure 14.

The measure of integrated area as a product of peak height times width works best for strictly monochromatic radiation; the α -doublet separation introduces a third parameter not considered in equations (45) and (46). The effect of the α -doublet separation on the ratio of peak height to area depends on both the separation and the peak breadth. No simple analytic form for this dependence is known to the author. This effect has received considerable attention from others in connection with crystallite size determinations and, insofar as the author is aware, the best solution to the problem is a graphical one such as is described by Klug and Alexander⁴⁴.

E. Economical Use of Liquid Nitrogen

Since the local price of liquid nitrogen is \$0.90 to \$1.10 per liter and since the consumption may run as high as two liters per hour, the economics of the use of liquid nitrogen are important.

It is assumed that the crystal is to be cooled by a stream of cold gas. The comparisons to be made at the moment are those of various ways of providing a given volume of cold gas at a given temperature.

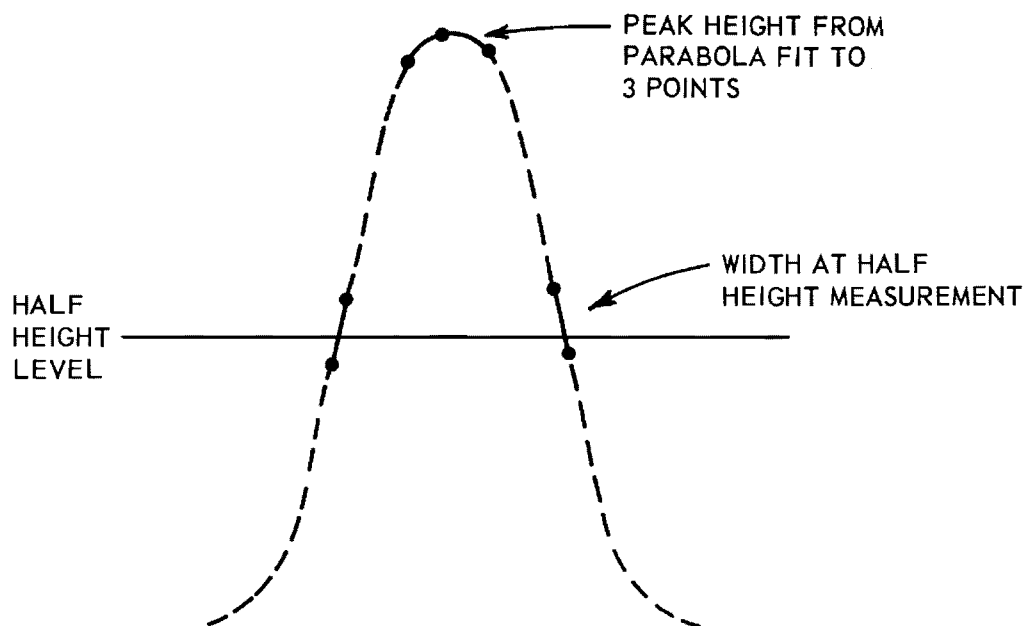


Figure 14. Fixed Count Methods for Peak Heights and Widths.

A stream of gas, possibly pre-cooled by dry ice, may be further cooled either by passing it through coils immersed in liquid nitrogen or by bubbling it through the liquid nitrogen (Figure 6). A continuous supply of air dried by silica gel is available. However, the vapor pressure of water in equilibrium with silica gel is so much higher than the vapor pressure at liquid nitrogen temperature that if the air were cooled by liquid nitrogen some water would be sure to condense in the coils or in the liquid nitrogen. Further, the oxygen fraction of the air would tend to condense in the coils or, in the event that the air was bubbled through the liquid nitrogen, in the bottom of the liquid nitrogen bottle.

Since nitrogen was chosen in the first place to avoid the dangers of liquid oxygen, the constant build-up of liquid oxygen either in the coils or in the liquid nitrogen is considered to be undesirable. Thus air, even dried air, is not a suitable gas for the cold stream. The cold gas stream is supplied with dry nitrogen from cylinders.

It is clear that it is much more efficient to bubble the gas through the liquid nitrogen than to circulate the incoming gas through and out of the liquid nitrogen in coils. In the former case both the incoming gas and the liquid that has been vaporized by cooling the incoming gas contribute to the exit cold stream whereas in the latter case the cold nitrogen gas that came from vaporization is lost.

A commonly used method of supplying a cold stream of nitrogen gas is that of immersing an electric heater in the liquid nitrogen and thereby boiling off the nitrogen gas. This is not as efficient a method of using the liquid nitrogen as is the method which involves bubbling the incoming

gas through the liquid nitrogen; the heat energy supplied by the heater in the one case is supplied by the incoming gas in the other case; the incoming gas which is thereby cooled, adds to the total amount of cold gas available from the consumption of a given quantity of liquid nitrogen. Results of some rough calculations follow: The vaporization of one liter of liquid nitrogen per hour will provide a flow rate of nitrogen gas (at liquid nitrogen temperature) of about ten liters per minute. But if the heat of vaporization of this one liter of liquid nitrogen is supplied by an incoming gas stream, fifteen liters per minute of dry nitrogen at -70°C may thereby be cooled to liquid nitrogen temperatures.

Thus, for the expenditure of one liter of liquid nitrogen approximately twenty-five, rather than ten, liters of nitrogen gas at liquid nitrogen temperature may be obtained. However, the cost of the incoming dry nitrogen and of the pre-cooling must also be considered. Our dry ice costs about \$2 per 50 lb. block and the dry nitrogen costs about \$4 per 220 cu. ft. tank. With this price structure, the economics favor pre-cooling an incoming stream of dry nitrogen. If the price of liquid nitrogen were as low as \$.50 per liter, however, the electric heater method would be preferable. In some localities, and providing that sufficiently large quantities are bought (100 liters or more at a time), liquid nitrogen may be bought at the same rate per unit mass as dry nitrogen. In that case the only advantage of pre-cooling by dry ice would be to make the trouble of changing liquid nitrogen bottles necessary less frequently. In such a case the electric heater method would probably be used because of its convenience, even though it would necessitate changing liquid nitrogen bottles about twice as often as would be necessary if dry nitrogen initially at room temperature were bubbled through the liquid nitrogen.

The greatest savings in consumption of liquid nitrogen could undoubtedly be realized by changing the method of cooling the crystal. However, it is felt that the advantages of cooling with the cold gas stream, as is currently being done, outweigh the cost of the wasted cooling capacity.

F. Choice of Direction of Temperature Variation

In measurements of thermal motions by means of their effect on the temperature dependence of Bragg intensities, room temperature is a natural dividing point between temperature ranges that might be considered.

Certain advantages accrue to either choice of temperature range, i.e., either above or below room temperature.

1. Advantages of Working in the Range from Room Temperature Down

The principal advantages of the low temperature range may be summarized as

- a. TDS is minimized with decreasing temperature.
- b. The vibrations become more nearly harmonic as the temperature is decreased; and, hence, the lattice wave theory applies better.
- c. The increased intensity at decreased temperature, due to diminution of the temperature factor, allows measurement of less intense diffraction peaks. Thus, more peaks can be measured. Peaks too weak to be measured directly at room temperature can be measured at the low temperature and corrected to room temperature by application of a temperature factor. They may then be included in a Fourier series presentation of electron density to reduce the series termination effects.

- d. If the temperature is reduced there is less chance that annealing and recrystallization will take place and thereby change the extinction and mosaic spread.

2. Advantages of Working in the Range from Room Temperature Up

The principal advantages of the high temperature range are:

- a. At least over the first few hundred degrees the temperature variation may be accomplished at less expense than is required to accomplish cooling.
- b. The quantity in braces in equation (26) becomes essentially constant as the temperature is increased, with the result that the temperature dependence of the temperature factor may be represented by equation (31). It will be recalled that the advantage of equation (31), which applies to the high temperature range, over equation (30), which applies to the low temperature range, is that equation (31) may be solved without iteration.

3. Conclusion

It is concluded that both temperature ranges may be useful, but that first studies should be made in the low temperature range because of the advantages cited above, principal among which is the better approximation to truly harmonic vibrations that may be expected.

G. Choice of Reflections to be Observed First

When the relative intensity data from which electron density maps will be prepared are gathered, it is expected that observations will be made on all reflections lying within a certain sphere in reciprocal space. However,

for the determination of Debye- Θ 's or temperature factors certain directions -- the principal directions in the crystal -- are more interesting than others. They are the [100], [110], and [111] directions. If any anisotropy exists in the temperature factors, measurements of the thermal vibrations along these three directions should have the maximum probability of detecting it. The physical reasoning which supports this contention is that no matter what the bond types, these three directions should include both the maxima and minima of the force constants.

Another consideration with respect to choice of reflections is that a selection of all-even and all-odd (indices) reflections should be observed in order that the thermal vibrations of the individual atom-types may be separated by comparison of the odd vs. even temperature factors.

H. Number of Background Counts Required to Obtain a Given Accuracy in the "True" Peak

It is well known that the statistical error in the counting of N random events in a given time is \sqrt{N} . One of the presently useful calculations based on this is the calculation of the number of background counts, C_B , which must be observed in order to obtain a given statistical accuracy in the true peak count, C_T , for a given gross peak, (C_p), to background ratio, a . Thus

$$a = \frac{C_p}{C_B} \quad (47)$$

and

$$C_T = C_p \pm \Delta C_p - (C_B \pm \Delta C_B) \quad (48)$$

The per cent error in C_T in equation (48) is given by

$$\frac{\% \text{ error}}{100} = \frac{\Delta C_p + \Delta C_B}{C_p - C_B} = \frac{\sqrt{C_p} + \sqrt{C_B}}{C_p - C_B} \quad (49)$$

which, by use of equation (47) can be reduced and rearranged to give the desired number of counts in the background as

$$C_B = \left(\frac{\sqrt{a} + 1}{a - 1} \right)^2 \left(\frac{100}{\% \text{ error}} \right)^2 \quad (50)$$

I. Calculations of Weissenberg and Counter Holder Settings

The Weissenberg geometry is particularly well-suited to easy calculation of the counter azimuth and elevation angle settings, the equi-inclination angle, and the relative spindle angle required for any given reflection. The counter adaptor for the Weissenberg that we use has been designed to carry out the Weissenberg geometry by providing rotation in elevation about an axis which remains coincident with the spindle axis and by providing rotation in azimuth, about the crystal as center, in a plane which contains the spindle axis and whose rotation about the spindle axis is a measure of elevation angle. Further, the direction from the crystal to the zero of azimuth is always maintained perpendicular to the spindle axis. Following Buerger⁴⁹ the azimuth angle is designated ν , the equi-inclination angle is designated μ , and the elevation angle is designated T . For the equi-inclination method the values of ν and μ are ideally the same. They may be readily calculated for each layer from the known distance (in reciprocal space) from the layer in question to the zero layer. The calculation of T reduces to a two dimensional problem which proceeds along exactly similar lines for each layer

excepting that the "circle of reflection" (appropriate slice of the Ewald sphere) decreases in diameter with increasing layer number. The procedure to be followed is adequately described by Buerger⁴⁹. It is to be noted that all of these calculations of settings need be made only with slide-rule accuracy as they will be experimentally optimized in each case in any event. A plot of a representative reciprocal lattice layer, probably the zero layer, is useful for the determination of relative settings of the spindle angle, α . A circle of reflection and a few reciprocal lattice points are shown in Figure 15. Let the reading of the spindle degree scale be α_0 when the position vector of the reciprocal lattice point R_0 is in the vertical. The angle by which the spindle must be rotated to bring a reflection from this vertical position into contact with the circle is $\frac{\pi}{2}$. If the reflection desired is not R_0 , but instead is that designated by the reciprocal lattice point R , whose position vector makes the angle β with the position vector of R_0 , an additional spindle rotation of β will be required to bring the point R into contact with the circle. Thus, the actual spindle reading, α , will be given by

$$\alpha = \alpha_0 + \frac{\pi}{2} + \beta . \quad (51)$$

It is to be recalled that α_0 is the spindle reading obtained when the position vector of the reference reciprocal lattice point, R_0 , is in the vertical position.

The elevation angles, π , are assumed to have been calculated already. The β angles may be calculated but may much more easily be determined with

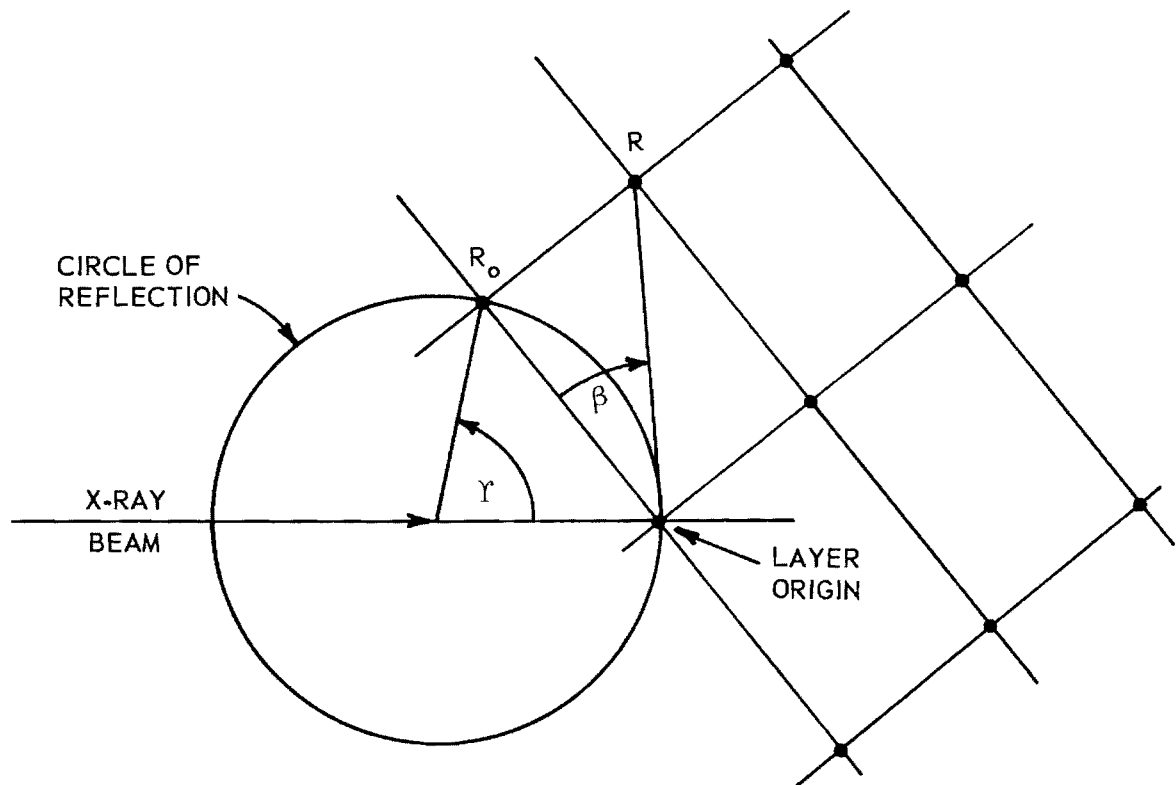


Figure 15. Determination of Spindle Settings.

sufficient accuracy with a simple drawing of the reciprocal lattice layer and a protractor. It is worth re-emphasizing that there is no point in attempting to calculate any of these settings with extreme precision as the applicability of the results would necessarily be tested experimentally in any event by experimental optimization of the settings.

It would appear that the calculations of the settings for the Weissenberg are far simpler than the calculations required for the settings of the "Goniostat."

III. EQUIPMENT PERFORMANCE

Several aspects of equipment performance have been checked and will be discussed individually.

A. Stability and Linearity

1. Stability

Long-term checks of the stability of the overall equipment were made. Proper settings were made so that a strong, diffracted beam was received by the counter. All settings were then left unchanged while the recorder was allowed to trace out the record of indicated diffracted intensity for periods as long as several hours. It was found that with no PHA (pulse height analyzer) and with the molybdenum anode x-ray tube operated at 45 kv and 20 ma there was a long period (one to two hours) drift of $\pm 2\%$ in the recorded intensity. When the beam current was reduced to 9 ma the drift was reduced to $\pm 1/2\%$ during a run of several hours duration. Changing the kv from 45 to 55 seemed to have no effect. With the PHA in the circuit and counting rates on the order of 20,000 counts per second (which is in the

linear range) the long-term drift amounted sometimes to $\pm 1/2\%$ but at other times to $\pm 1-1/2\%$. Often only one maximum in the recorded intensity would be observed in a four-hour period. The differences obtained in different checks of the stability with the PHA gave preference to leaving it out of the circuit.

However, it is suspected that there were unrecorded differences in the window widths in the two cases cited, so that with adequate window width the presence of the PHA in the circuit would not add any noticeable long-term drift. The only short-term instabilities observed in these tests were those due to the random counting process itself. The marked dependence of stability on beam current has caused us to use a 10 ma beam current routinely instead of the rated permissible value of 20 ma.

2. Linearity

The linearity of response of the overall detection equipment to counting rate was checked by the multiple absorber technique. Pieces of x-ray film, which are remarkably uniform, were used as the absorbers. It was found that even with the PHA in the circuit the response was linear within 1% up to counting rates of 32,000 counts per second. Without the previously mentioned modification in the PHA, deviations from linearity would have been expected at counting rates of about 5,000 counts per second. With a Geiger counter, deviations of 1% from linearity would have been expected at counting rates as low as 500 counts per second. Furthermore, the response of the Geiger counter is not uniform across the counter window as the scintillation counter response is.

B. Malfunction Rate

1. Binary Stages

The high-speed binary stages in the "scintillation proportional unit" have given a great deal of trouble. The most common malfunction is the intermittent failure, on the part of one of the binary stages, to divide. The intermittent nature of the malfunction and the continued operation in the presence of the malfunction make its presence, or absence, extremely difficult to detect. Replacing, or in some way interchanging, the 5964 electron tubes in these stages would usually correct the malfunction for a time. Unfortunately, the malfunction would occur and be discovered again after any period of time which ordinarily ranged from zero to about one week. It was finally established that this particular malfunction was extremely prevalent and that various circuit repairs or modifications that had been performed had failed to correct it, the unit was returned to the factory and a borrowed unit was used in its stead. The borrowed unit seemed to perform satisfactorily, and after its return from the factory the original unit also seemed to perform reliably. Unfortunately, the bad performance of the scintillation proportional unit makes it impossible to place quantitative dependence on any of the data collected before April, the time at which the borrowed unit was installed.

2. All Other Electronic Gear

All of the other electronic gear behaved normally during the year excepting the scintillation counter. The photomultiplier tube of this counter apparently became gassy after, at the most, a few hundred hours of use. A replacement was obtained and has been working satisfactorily.

3. Arcing

Some difficulty has been experienced with arcing in the x-ray tube well. The problem seems to be getting progressively worse. Neither dust nor condensed moisture, due to the cooling of various surfaces by the cold water used for x-ray target cooling, seem to have prime responsibility for the arcing. This problem has so far not been solved; attempts have been made to obviate it by operating the tube at less than the desired potential, by frequent cleaning of the insulating surfaces, and by keeping alert for either the smell of ozone or the sound which would indicate the presence of the arcing.

C. Tolerances in Weissenberg, Counter, and Crystal Settings

By "tolerance" is meant the amount by which a setting may be changed without affecting the diffracted intensity by a measurable amount ($< 1\%$). Tests which gave the results to be described were made by observing the peak intensity of a representative reflection. The settings to be considered on the Weissenberg camera base are μ (the equi-inclination angle), the spindle translation, and α (the spindle angle). The settings on the counter holder are T (elevation angle) and v (azimuth angle). The settings which determine the crystal alignment are the settings of the two arcs on the goniometer head which carries the fiber on which the crystal is mounted.

It was found that the "plateau" was $1-1/2$ to 2 degrees wide in T , 1 to $1-1/2$ degrees wide in v , and at least 0.5 mm wide in spindle translation for typical reflections observed in the present work. No "plateau" is to be sought in μ for this angle is strictly determined by the crystal parameters.

However, the position of the crystal along the spindle axis (spindle translation) and the experimentally determined μ are not independent. For a given spindle position the sharpness of the dependence of diffracted intensity on μ depends on the orientation of the \vec{S} vector relative to the plane which contains the incident beam and the spindle axis. If the \vec{S} vector lies in this plane, the dependence is as sharp as is the dependence of intensity on α when the observation is made in the zero layer (i.e., when the \vec{S} vector is perpendicular to the plane containing the incident beam and the spindle axis). For zero layer observations, however, any small errors in μ may be fully compensated for by changes in v and T .

The crystal alignment procedure usually used involves the use of a reflection for which the \vec{S} vector lies in the plane containing both the incident beam and the spindle axis. In this procedure the diffracted intensity is sensitive to goniometer arc adjustments as small as two or three minutes. However, for a zero layer measurement (and so, in principle, for any measurement for which the \vec{S} vector has any appreciable component out of the plane containing the incident beam and the spindle axis) a missetting of one of the goniometer arcs by as much as 1° can easily be compensated for by a change in α . This compensation may readily be understood by reference to Figure 10 and the discussion concerning it. The worst effect of the missetting of a goniometer arc would be to tilt the acceptance region on the target and to move it up or down (see Figure 10) slightly. The up or down variation is just what is corrected by a change in α . The 1° tilt would produce no noticeable effect on the intensity.

It is concluded that adequate tolerances and compensations in the settings are provided so that only ordinary care in the use of the instrument is required to insure that experimental errors due to missettings are insignificant.

D. Performance of Low Temperature Apparatus

The lowest temperature that has been obtained at the crystal position is about 90°K . The distribution of temperature in the cold stream near the crystal is sufficiently uniform so that slight displacements (1 to 2 mm) of the crystal with respect to the central axis of the cold stream would produce temperature differences of less than 1° . A similar situation applies with regard to displacements along the cold stream. Checking on the temperature distribution in the cold stream is not yet complete, but preliminary checks indicate that the temperature changes by less than 6° from a position at the center of the nozzle opening to an axial position $1\frac{1}{2}$ cm away. It is thought probable that this change is actually less than 1° .

The small size of the crystal, the strongly thermally insulating mounting (small glass fiber), the flow velocity in the cold stream, and the apparent immediacy with which intensity changes when the crystal temperature is changed lead to the assumption that the crystal temperature must be within 5°C of the cold stream temperature. Further checks on this point will be made, as appropriate, in future work.

Frosting of the specimen may sometimes be a problem. If, with the flow velocities that we use in both the inner and outer streams (> 30 l/min), the crystal is no more than 1.5 cm from the end of the dewar nozzle, noticeable frosting of the specimen will be avoided even for periods of several hours at the lowest temperatures.

One of the greatest advantages of the present cooling system is the ease with which the temperature may be varied. The temperature may be changed by 20°C and re-stabilized at the new temperature in a total elapsed time of two to four minutes. If the starting temperature is room temperature, the system may be stabilized at 90°K in less than 20 minutes. If one is willing to make further slight adjustments, the temperature may be held at $90^{\circ}\text{K} \pm 1^{\circ}$ within 10 minutes after commencing operations. Once stabilized, the temperature of the cold stream remains constant within less than 1° without further attention.

One 25 liter bottle of liquid nitrogen ordinarily lasts for about 25 data-taking hours. If the temperature of the cold stream were to be maintained at the lowest temperature, the one bottle of liquid nitrogen would last about 10 hours or less.

IV. THE SPECIMENS

A. Choice of Kind of Material

Sources of single crystal silver halide material were sought at the outset of the project. No sources were found for single crystals of AgF or AgI . Some efforts were therefore made to prepare AgF . However, AgCl and AgBr were both found to be available in single crystal form. Eastman Kodak Company kindly supplied specimens of very pure AgCl and very pure AgBr . Optical quality AgCl was purchased from Harshaw Chemical Company. The availability of these specimens and the availability of thermal diffuse scattering measurements on AgCl (Cole²⁷) led to the choice of AgCl for initial investigations. A further reason for the choice of AgCl (or AgBr) is that Eastman Kodak Company has offered to supply samples doped in various controlled ways.

B. Photochemical Effect

Although the literature indicated that the photochemical effect of visible light and of x-rays on high purity AgCl single crystals was negligible, our early work -- cutting, shaping, and mounting -- with the crystals was done either in a dark room or under a soft incandescent light. After the samples were mounted, they were coated with carbon black to protect them from the ultraviolet components of the fluorescent lights in the laboratory.

It was shown that any photochemical effect in the present samples was, in fact, negligible at room temperature; diffracted intensities were not measurably affected by bathing an unprotected sample in fluorescent light and x-rays for several hours. However, darkening of the samples does occur under the above conditions after about 15 minutes at approximately -70°C . The specimens bleach out shortly after being returned to room temperature even when dark for several hours. This low temperature darkening was found to have no measurable effect on current intensity observations.

C. Specimen Preparation and Mounting

1. Production and Checking of Shaped, Distortion-free Specimens

As has been mentioned previously, it is desirable to shape the specimens to small spheres a few tenths of a millimeter in diameter. Pure AgCl is so subject to plastic flow that considerable care must be taken in cutting and shaping it. At room temperature plastic flow is such that the crystal simply cannot be broken apart. It can be cut, for example, with a jeweler's saw and a kerosene lubricant or with a razor blade into which teeth has been filed, but these mechanical means still result in unnecessary distortion at the cut.

In order to avoid the distortion, the following method is now being used. A knife-edged steel disc about 1-1/2 inches in diameter and 5 mils thick is rotated with a small motor (Dremel "Moto-tool"). Photographic "hypo" solution is an excellent etchant for AgCl. The rotating steel disc is kept wet with the etchant as the crystal is advanced onto the disc slowly and carefully enough so that a cut is made solely by etching, and the disc itself does not actually touch the crystal. The 5-mil circular saw, which is available as a standard accessory to the "Moto-tool," is superior to a plain disc as the teeth in the saw help to hold a larger amount of hypo at the position of use. Small cubes are cut from the parent crystal by this controlled etching process.

Because of the desirability of the spherical shape in minimizing absorption problems in relative intensity measurements, some special effort has been expended in trying to make the cubes into spherical specimens. A commonly used method for preparing spheres consists of tumbling the specimens in an air blast on the inner periphery of an abrasive lined cavity. This method produced AgCl specimens which appeared to be very nearly spherical, but whose surfaces were darkened. Even though the darkened portion was etched off and even though the crystals were subsequently annealed at 760°F for three days, distortion of the crystals was still quite noticeable in Laue patterns.

Before a sample is finally used for collection of data, a precession or Laue picture, or both, is taken to check possible distortion as indicated by doubled or badly smeared spots. A polarizing microscope has also been used in an attempt to detect a stress field associated with distortion, but precession and Laue pictures are more suitable.

At present all sample shaping is being done by etching with hypo. The crystal to be shaped is fastened to a spindle shaft rotated by a Dremel "Moto-tool" motor. The rotating crystal is brought into contact with a blotter placed on end in a beaker half filled with hypo, as is indicated in Figure 16. With this arrangement, any portion of the crystal can be given a fairly circular cross section; the high spots are etched off by contact with the hypo-soaked blotter. No spherical samples have yet been produced by this technique. The variation in intensity of the reflection used for alignment varies by about 25% as our most symmetrical crystal is rotated on the Weissenberg spindle axis. A truly spherical sample should yield a variation of this type of less than 1%. Since our present measurements of intensity vs. temperature are not put in error by lack of knowledge of the absorption correction, we have postponed further attempts to make spherical samples. It is hoped that in the future undistorted spherical samples will be made by some as yet untried technique. Grinding in the sphere grinder at a temperature near the Debye- Θ (which is less than 130°K) will be tried in the hope that the distortion due to plastic flow will thereby be minimized.

2. Mounting

a. Technique. The shaped crystals are mounted on glass fibers with any one of several adhesives. The glass fiber is first affixed, with wax, to a brass plug which fits the goniometer head. A particular orientation of the nearly spherical specimen may be maintained, while it is mounted on the glass fiber, with the following technique: The sample is held in the desired orientation by placing it on the adhesive side of a piece of Scotch tape. This piece of Scotch tape is taped with other pieces to a glass

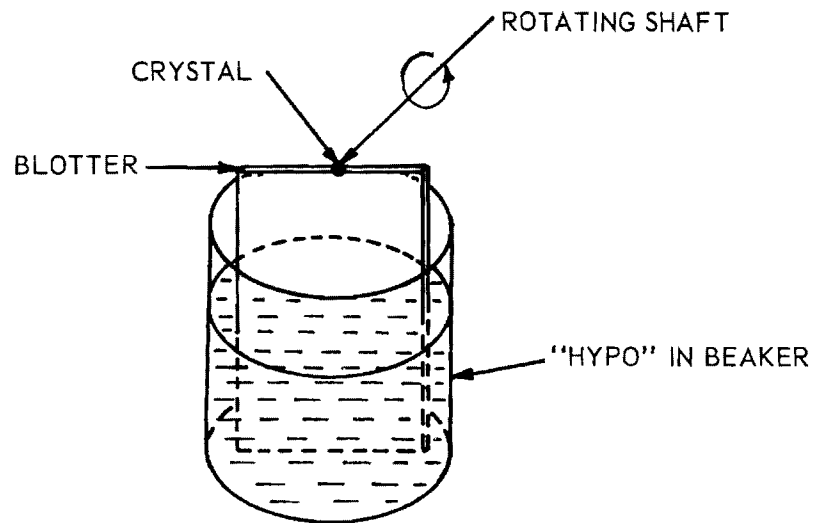


Figure 16. Controlled Specimen-Etching Arrangement.

microscope slide which in turn is taped to a rectangular metal weight. This arrangement is placed on a laboratory microjack positioned so that the specimen lies directly under the end of a glass fiber. The glass fiber is held in a vertical position by attaching the brass plug, with clay, to the vertical side of any convenient object. With a second fiber the adhesive is applied to both the specimen and to the mounting fiber. The jack is then raised cautiously to bring the fiber and the specimen into desired contact. The whole operation is monitored through a stereomicroscope. Care is taken to see that no excess adhesive is applied to the specimen and to see that a symmetrical joint is formed. A symmetrical joint is desirable so that as the specimen is cooled the contracting adhesive will not twist the sample out of its proper alignment.

b. Remounting for alignment; adhesive pairs. When the sample has been shaped by any of the methods described above, there are no cleavage faces which could aid in mounting the crystal in a desired orientation. Since the crystal is cubic, polarizing optics are of no help. A trial and error method is used which consists of (1) arbitrarily orientating the crystal before it is glued to the fiber; (2) aligning the crystal initially with the use of precession "setting" pictures; (3) remounting and re-aligning with the precession camera if necessary, and (4) making final alignment on the counter-adapted Weissenberg as is described in the next section. A crystal is usually remounted if neither the [100] nor the [110] direction can be brought parallel to the axis of rotation.

To facilitate remounting of a crystal, a series of 3 pairs of adhesives has been selected. Either member of a pair is insoluble in the solvent of the other member. The following table lists the adhesives.

<u>Adhesive</u>	<u>Soluble In</u>	<u>Insoluble In</u>
Polyvinyl Alcohol	H ₂ O	Amyl Acetate and Ethylene Dichloride
Formvar	Ethylene Dichloride	H ₂ O and Amyl Acetate
Zapon Acquinat "A" (not available at this time)	Amyl Acetate	Ethylene Dichloride
Formvar	Ethylene Dichloride	H ₂ O and Amyl Acetate
Carboxymetholcellulose	H ₂ O	Amyl Acetate and Ethylene Dichloride
Collodion	Amyl Acetate and Ethylene Dichloride	H ₂ O
Mucelage	H ₂ O	

If remounting of the crystal is required, it is placed under a brass plug and fiber as usual, but it is now held in a known orientation by the goniometer head. The second member of the adhesive pair is then used to make a symmetrical joint between the new fiber and the sample. When the second adhesive dries, the first fiber is removed by dissolving the first adhesive. Remounting is sometimes done several times before a satisfactory orientation is obtained.

D. Table of Specimens

All of the specimens that have been employed to date are listed in Table I along with their approximate dimensions.

TABLE I
LIST OF SPECIMENS

<u>Sample</u>	<u>Approximate Shape</u>	<u>Size</u>	<u>Source Material</u>
5	Rod	2 mm long, .5 mm dia.	HARSHAW #1
6	Ellipsoid	.6 mm long, .4 mm dia.	HARSHAW #1
7	Ellipsoid	.3 mm long, .2 mm dia.	HARSHAW #1

V. DATA COLLECTION

A. Data Collection Procedures

1. Crystal Alignment

A crystal alignment with the $[220]$ direction parallel to the spindle axis was usually desired in the present work because with this orientation the zero layer contained all three principal directions, $[h00]$, $[hh0]$, and $[hhh]$. It was often found to be advantageous to make the initial, gross alignments with the precession camera. Final alignment was made by a technique described by I. Fankuchen (private communications). It makes use of the fact that if the d^* vector of a particular reflection is aligned exactly parallel to the axis of rotation (i.e., the spindle axis) and the reciprocal lattice point is placed on the sphere of reflection, the diffracted intensity will not change as the crystal is rotated through a full 360° about the spindle axis (provided that the crystal is spherical). This alignment procedure is carried out in practice as follows: ω and ν are set for the desired reflection. T is set at zero. The crystal is properly

centered by the use of the telescope (supplied with the Weissenberg) and the spindle and goniometer head translations. One arc of the goniometer head is then set parallel to the incident beam and is adjusted until a maximum diffracted intensity is observed. The goniometer head is turned 180° and the arc is again adjusted for maximum intensity. If the arc position required the second time differs from that required in the first adjustment, an adjustment is made in the equi-inclination angle, μ . Correctness of the setting of ν (the azimuth angle of the counter) is experimentally checked as well. When sufficient adjustments have been made so that the two positions of the arc required for maximum intensity at spindle positions 180° apart are not different by more than about $1/4^\circ$, the second arc is set parallel to the beam and the process is repeated. It is not to be expected that μ will be changed when working with the second arc. By working back and forth between the two arcs the alignment is refined until it is accurate to within less than 5 minutes.

Re-alignment is sometimes necessitated by the temperature changes. When one is first working with any given sample, it is always desirable to re-check the alignment, with the procedure outlined above, at the lowest temperature and at each of several intermediate temperatures. This is required in order to be sure that the adhesive joint on the crystal is sufficiently symmetrical so that no major de-alignment is caused by the temperature change. Such checks have sometimes shown it to be desirable to remount the specimens.

It has been found necessary from time to time to "touch up" the alignment. Ordinarily, if the adhesive joint is fairly symmetrical, such touching

up of the alignment is not necessary during any one day's run, even though the temperature may be changed frequently by the maximum possible amount.

2. Experimental Optimization of Calculated Settings

The equi-inclination angle, μ , is pre-calculated, but it is experimentally optimized in the manner described above as a part of the alignment procedure. The width of the counter window was chosen in advance so that it was more than wide enough to receive all of the diffracted beam at any one time. The counter elevation angle, Υ , and azimuth angle, ν , are pre-calculated approximately but are experimentally optimized for each reflection. This optimization is accomplished by changing the setting first in one direction and then in the other until the intensity observed drops off by a given amount, e.g., 10%. The settings required to produce this diminution of intensity are noted; the optimum setting is half way between the two.

3. Procedures in Making Intensity Measurements

a. Total count and area measurements. Records made with crystal-monochromatized radiation of the intensity vs. spindle position indicated that the intensity continued to fall off slightly for as much as 5° on either side of the precise Bragg position (at room temperature). In principle then, a measurement of integrated area or of total count under the peak should extend over an angular range larger than 5° on either side of the peak. The time consumed in making such a measure would be excessive. In the measurements actually made a total range of no more than about 6° was covered. Since the spindle was driven at constant velocity by a synchronous motor, the time elapsed in driving over a peak could be measured with much better accuracy than could the actual angular range covered. Therefore, when the

differential filter was used both traces over the peak were made for the same length of time. While such a measure of integrated area probably left out some area (outside of this 6° range) which should have been included, it was felt that the amount left out would not significantly affect our measures of the temperature dependence of the Bragg intensities. As it has turned out, the reproducibility in all of our total count measures of intensity vs. temperature made so far has been so poor that none of the data have actually been useable. One reason for this is that the electronic circuits were behaving in an unreliable fashion, as has been discussed earlier. Another possibility, which has not yet been fully explored, is that the drive system used does not actually drive the spindle at a sufficiently uniform angular velocity. This particular point will be checked further in the near future.

In using the differential filter, it was known that the two filters were not perfectly balanced. It was planned that a measure of the degree of unbalance could be made and that the background obtained with the one (appropriate) filter could then be multiplied by this constant correction factor before subtracting the corrected background measurement from the total measurement. It was hoped that the measure so obtained would be a sufficiently accurate measure of the true intensity. Because of the marked angular dependence of this correction factor, which was discovered very recently (April) and which is discussed later in this report, it is now believed that the background measurements obtained for the total count measurements with the differential filter technique are not reliable.

b. Peak height measurements. Three different methods of making measurements of the peak height have been considered:

(1) The spindle angle may be set with the manual lever-and-tangential screw arrangement to give maximum intensity as indicated by the recorder. Finding of the proper position may be facilitated by deliberately missetting the angle enough so that the intensity falls off slightly, first on one side and then on the other of a peak; the "proper" setting is half way between the two incorrect settings. If the peak has any tendency toward flatness at the top, this technique would be expected to give reproducible results. The author has found previously that this technique gives results which are generally reproducible to 1/2% for the peak shapes usually obtained with spherical crystals less than 1/2 mm in diameter⁷ (MoK_α radiation; $\theta < 45^\circ$).

(2) The motor drive may be used to rotate the spindle over the range of angles in the immediate vicinity of the maximum of the diffraction peak. A best smooth curve may then be drawn through the recorded trace and the maximum of the peak may thereby be obtained with a reproducibility (unless the peak is very weak) of 1/2% or better.

(3) Fixed counts may be taken at each of three points near the peak and the data may be fitted with a parabola; the maximum of the parabola locates the peak maximum in a reproducible fashion. This technique has already been discussed in Part II, D 2 of Section 3.

c. Comparisons of intensity measurement procedures. Since other sources of error tend to make it pointless to attempt peak height measurements with a reproducibility of much better than 1/2%, there is no particular advantage of the fixed count method over either of the other methods;

and the fixed count method usually takes longer. The method which involves motor-driving the spindle has the advantage that a continuous record of the approach to the peak maximum and the recession from it is made; there are fewer chances for mistakes to be made in finding the peak maximum with this technique than with the wholly manual technique. Further, it was found that in actual practice the wholly manual technique was usually no faster than the motor drive technique. The bulk of the peak height measurements have, therefore, been made by motor-driving the spindle over a small angular range which includes the maximum of the peak. The spindle was then reset, manually, to a position at least very close to the maximum, the other member of the differential filter pair was placed in front of the counter, and the background measurement was thereby made at that point. It is believed that, with the differential filter, such measurements of the background can be more successfully corrected for unbalance by a simple multiplying factor than can measurements of the background under the whole peak area. When measurements were made as a function of temperature, the background measurements were not repeated at every temperature; the changes in background were immeasurably small. Instead, the background measurements were obtained at the lowest and highest temperatures and, at most, one or two intermediate temperatures.

4. Low Temperature Procedures

Approximately constant flow velocity was maintained in the cold stream at all temperatures including room temperature. The temperature of the cold stream was varied by mixing in varying amounts of room temperature gas with the gas at liquid nitrogen temperature. The crystal temperature

was monitored by a thermocouple placed in the cold stream at the outlet of the dewar nozzle. Because it was so easy to change the temperature of the specimen, intensity vs. temperature data were ordinarily taken on but one reflection at a time. The intensities were checked at 20° intervals, both during cooling and during warming; the intervals were mismatched so that the completed data contained measurements at every 10° . Actually two equivalent reflections, which occurred 180° apart in spindle position, were followed as a function of temperature in every case. During the first few runs with a given specimen, the alignment was rechecked at the lowest temperature and again at room temperature. If readjustments of the goniometer head arcs larger than about $1/4^{\circ}$ were required to optimize the alignment at either temperature, the crystal was ordinarily remounted. When it had been demonstrated that readjustment of the arcs of no more than $1/4^{\circ}$ were required for a given specimen, the realignment was no longer performed at each temperature. In a discussion of the acceptance region shown in Figure 10 and in the discussion of the tolerances permissible in the various counter settings, it was pointed out that crystal misalignments as large as 1° produced no measurable change in the maximum peak intensity.

5. Validation Procedures

When measurements of the intensities of various reflections relative to one another are measured, certain reflections will be chosen as standards and their intensities will be checked periodically throughout the measurements. For example, the intensity of at least one standard reflection will be checked at the beginning and the end of each data collection

period. If the beginning and ending intensities do not agree within a reasonable margin, say 1%, the data collected during the time between measurements of the standard reflection will be discarded.

In the present case in which intensity vs. temperature measurements are made on a single reflection, the corresponding criterion is that the intensity measured at the beginning of a run (ordinarily at room temperature) must agree with that measured for the same reflection at the end of the run (i.e., at the beginning temperature) within 1%. The technique of taking the warming and cooling data at 20° intervals which are "out of phase" by 10°, so that the data are "interlaced," is a validation procedure designed to point up the existence of any errors due to changes in the characteristics of the x-ray generation or detection equipment. The measurement of the two equivalent reflections, 180° apart in spindle rotation, is another validation procedure. In at least one case two observers, on different days, made measurements of intensity vs. temperature for the same reflection. These types of validation procedures will be carried out periodically in the future as they have been in the past. Finally, in order that the results shall be definitive for AgCl rather than for a particular specimen, a variety of different specimens is to be used. Some of these specimens will come from the same parent crystal; some will come from other sources.

B. Experience with Devices for Control of Radiation Character

1. Pulse Height Analysis

Pulse height analysis, crystal monochromatization, and a differential filter pair have all been used to control the radiation character. The pulse height analyzer (backing up the scintillation counter) is useful

only for eliminating wavelengths very far from the desired characteristic wavelength. It is good for eliminating background noises which originate in the circuits themselves.

2. Crystal Monochromatization

The crystal monochromator gives essentially zero background because it is so highly selective in passing the desired radiation wavelength. However, as has been pointed out, considerable intensity is lost in the crystal monochromatization process and the possible divergence and convergence in the beam are sharply limited. As was noted in the discussion of the acceptance region and the x-ray beam geometries, it may at times be highly desirable to have considerable convergence in the incident beam. One noticeable result of using the crystal monochromator is that the diffraction peaks are thereby much sharpened.

The only crystal that has been used for monochromatization so far was a sodium chloride crystal that happened to be at hand in the laboratory. More serious use will be made of crystal monochromatization in the future. At that time the crystals will be more carefully chosen, quartz crystals will probably be used, and the monochromatizing crystal will be cut according to some predetermined design. Curved crystal monochromators may, of course, be used but such use is not now contemplated. One design for a flat face crystal monochromator that will be tried is one which has the face cut at a slight angle to the Bragg planes being used. According to how this crystal is oriented, it will either produce a narrow pencil of rays from a fairly broad incident beam or will, on the other hand, broaden and somewhat homogenize the incident beam.

3. Differential Filter

The differential filter seems, in principle, to be the most desirable means of controlling the radiation character. If a filter pair could be perfectly balanced, the difference between two patterns, taken one with one filter and one with the other, would be due to the narrow band of radiation wavelengths which lie between the two absorption edges. This is a particularly desirable method for measuring peak heights as nothing need be moved except the filters themselves in order to measure both gross peak height and background. Thus, measurements of the backgrounds under peaks are really much more easily made with a differential filter than with no filter at all; in the second case it is necessary to turn the spindle until the crystal is no longer in a diffracting position. It is, of course, a practical impossibility to obtain a perfect balance between the two filters, particularly if one expects the balance to be maintained over any range of wavelengths. It was initially thought that the two filters could be first balanced as well as could easily be done, and then the degree of unbalance could be measured. The measurement of unbalance would then lead to a correction factor. All background measurements would be multiplied by the factor in order to correct for the fact that the two filters were not perfectly balanced. However, it was found that the degree of unbalance varied considerably over relatively small angular regions in the neighborhood of the Bragg peak. If a moving, rather than a stationary, counter technique had been used, these variations would not have been nearly so marked. The variations and at least a plausible explanation for them are discussed in the results and conclusion section (Section 4, Part II). As it is, it is

felt that the correction factor which was obtained for use precisely at the Bragg peak is good enough so that it will not put the true peak heights, measured with the differential filter technique, in error by as much as $1/2\%$ (due to this one cause alone).

C. Data Gathered

Many data were gathered expressly for the determination of reproducibility. It was initially attempted to obtain reproducibilities, in intensity measurements, better than $1/2\%$ -- preferably $1/4\%$. For that reason measurements were made with total count techniques. However, as has been pointed out, various instabilities and malfunctions in the equipment made it impossible to obtain such reproducibilities. The total count procedures were abandoned and measurements of peak heights were made from recorder traces. The traces may be read to within about $1/2\%$.

The only reflections which have been observed so far are those which correspond to one of the three principal directions, $[h00]$, $[hh0]$, $[hhh]$.

Data were taken to allow experimental comparison of the several methods of measuring B_0 : (1) The wholly manual method of counting the number of turns of the tangential screw required to change the intensity, as observed with the recorder, from half maximum on one side of the peak to half maximum on the other. (2) The method of making fixed counts at 2 points on each side of the peak and connecting these points as has been described. (3) The method of measuring directly on a recorder trace the width of the diffraction peak at half height. (4) The method of dividing either the total count or the total area recorded on a trace by the peak height.

Data were also gathered on B_0 vs. T for several reflections and will be discussed in the section on results.

Peak height vs. temperature data from one specimen were collected down to about 90°K for all of the strongest reflections in each of the three principal directions. Parts of such data were collected for other specimens. The first data at temperatures below dry ice temperature were collected on April 21.

Several records were made of diffracted intensity as a function of time of irradiation of the specimen. If the photochemical effect in the specimen were large enough to affect the x-ray results, then bathing the specimen in the incident beam for several hours would be expected to produce a noticeable change in the diffracted intensity. No such changes were noted after several hours exposure at either room temperature or at -73°C , even though the crystal became very noticeably darkened after four hours at -73°C . Upon warming to room temperature, the coloring disappeared. It was concluded that any photochemical effect present did not affect our diffracted intensity measurements by as much as $1/2$ of 1%.

SECTION 4

RESULTS AND CONCLUSIONS

I. REPRODUCIBILITY

A. Reproducibility in Peak Height

The reproducibility in the wholly manual method of determining peak height was assessed by making successive measurements of the peak intensity of a given reflection at a given temperature. The mean deviation from the mean was found to be 1/2%.

The reproducibility in the determination of peak heights by the motorized method (spindle driven over a small angular range by the synchronous motor, maximum peak intensity read from recorded trace) was determined, from a total of seven measurements on three different peaks, to be 1/2% (mean deviation from the mean).

The mean deviation from the mean in comparing the intensity of a particular reflection at room temperature before and after the specimen had been cooled was found to be 1.25%. This value was based on 74 separate observations, some of which were not made under the best conditions of equipment behavior. It is expected that in the future this type of reproducibility will be consistently somewhat better.

B. Reproducibility in Total Count Measurements

Insufficient data are available at present to determine the reproducibility in total count measurements of a particular diffraction peak. While many measurements were made, it was the lack of expected reproducibility that pointed up the existence of recurring, intermittent malfunctions in the counting equipment. Since these malfunctions have been corrected, no further data of this type have yet been taken.

C. Reproducibility in the Measurement of the Peak Breadth, B_0

Several measurements of B_0 were made by dividing the total counts in the diffraction peak by the peak height. The data were collected with the (440), (444), and (600) reflections of sample #6 and are shown in Figure 22. The scatter of the points about these curves yields a mean deviation from the mean of 3.3%. Undoubtedly, a part of this large mean deviation from the mean was due to the malfunctions previously mentioned. It is to be expected that this error may be reduced in future measurements.

Several measurements of B_0 were made by measuring, on the recorded trace of intensity vs. spindle angle, the width of the peak at half height. Comparison of the width after the cooling of the specimen to the width before cooling gave a mean deviation from the mean of 1.1%. However, the error in reading the width from the trace is on the order of 2% for the widest peak measured, so perhaps the value 1.1% is somewhat fortuitous.

Several manual measurements of B_0 were attempted by noting the number of screw turns required to change the recorded intensity from half maximum on one side of the peak to half maximum on the other side. The reproducibility in these measurements was determined by comparing the half widths after cooling to those before cooling. For the one reflection with which the reproducibility was investigated the mean deviation from the mean was about 2%. The operation of the manual device can easily be improved by a slight modification if it becomes desirable. This 2% figure could probably be thereby reduced to < 1%.

D. Reproducibility in the Temperature Readings

The uncertainty in a recorded temperature reading due to the combined effects of the inaccuracy in reading the scale on the potentiometer and to temperature drifts during the various intensity measurements is estimated to be of the order of ± 0.05 mv. For the chromel-alumel thermocouple used this amount to $\pm 1^{\circ}\text{C}$ at room temperature and about $\pm 2^{\circ}\text{C}$ at 100°K .

E. Reproducibility in the Temperature Dependence of Peak Heights

As is shown in Figures 24-26, the experimental points fit the smooth curve remarkably well. A quantitative estimate of the degree to which the smooth curve fit the experimental points was obtained by considering only the I-axis component of the perpendicular displacement of the experimental point from the curve. The mean deviation from the mean so obtained for four curves, chosen to represent the range of fitting qualities that we might expect, ranged from .41% in I to 1.0% and averaged .76%. The four curves were the I vs. T curves for the (333), (600) (two reflections), and the (800) reflections of sample #7.

In another experiment on reproducibility the same reflection of the same crystal was observed on different days by different observers. Two observations (at spindle positions 180° apart) were made by each observer of the intensity change caused by changing the temperature from room to dry-ice temperatures. The mean deviation from the mean of the observed changes was 1.9%. The observed change was itself 83% of the room temperature intensity.

The measured intensity change, due to a 100°K or 200°K temperature change, of each reflection in all of the compiled data was compared with the measured change in the intensity of the equivalent reflection. The mean

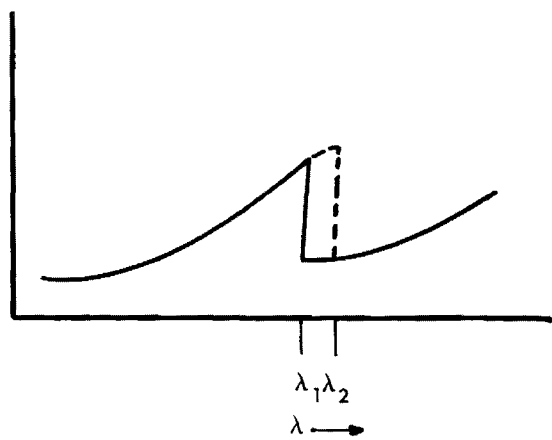
deviation from the mean change in intensity so obtained was 3.3%; the individual changes varied from 5 to 250% of the room temperature intensities.

Specimen to specimen differences in a change in intensity with temperature were assessed briefly by comparing the (600), (444), and (440) reflections of samples #6 and 7 over the temperature range from room to -73°C . The mean deviation from the mean change in intensity was found to be 3.1%.

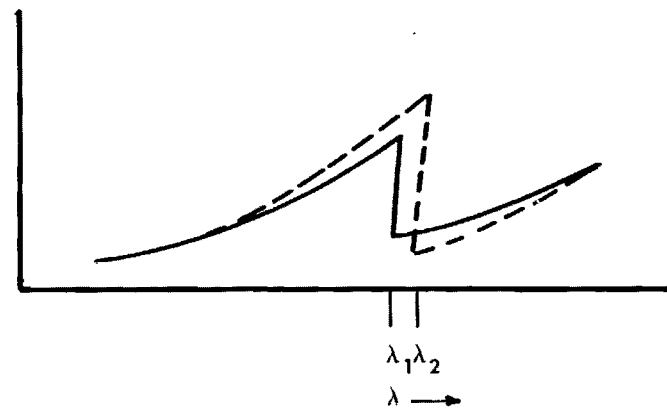
II. BEHAVIOR OF THE DIFFERENTIAL FILTER

A. Deviations from Perfect Balance

The differential filter technique seems to afford a means of giving monochromatic results without the intensity losses associated with crystal monochromatization. If the two filters are balanced, the difference between the diffraction patterns obtained with each separately will be due only to the narrow range of wavelengths lying between their absorption edges. The desired situation is shown in Figure 17-a. Here the thicknesses of the filters have been so arranged that the absorptions of the two filters everywhere outside of the range of wavelengths between λ_1 and λ_2 are the same. It is, in fact, not possible to get a perfect balance, partly because the relative sizes of the absorption jumps differ for any two filter materials and partly because the wavelength dependences of the absorption in regions away from the edge are not identical. Kirkpatrick⁴² has discussed this problem and has pointed out the improvement that can be obtained in the balance by the addition to one of the filters of a third material whose absorption edge is far away from λ_1 and λ_2 . The addition of the third material does improve the balance considerably but still does not make it



17A. DESIRED



17B. USUAL

Figure 17. Filter Pair Absorptions.

perfect over all wavelengths outside of the region between absorption edges. The situation normally encountered then is more nearly like that shown in Figure 17-b than like the idealized case shown in Figure 17-a.

B. Dependence of Radiation Character at Stationary Detector on Crystal Rotation

The difference between the balances at the long and short wavelength sides of the absorption edges can be very serious because the character of the radiation received at a stationary detector continually changes, as the crystal is rotated, so that the bulk of the received wavelengths lie first on one and then on the other side of the absorption edges. A clearer picture of the situation is given by the following discussion.

Consider zero layer geometry, Figure 18, in which the crystal rotation axis is perpendicular to the paper. The detector position is initially set for a particular hkl and λ and is then kept stationary. If the crystal is rotated so that any other set of planes ($h'k'l'$) makes equal angles with the incident and detected rays, it will diffract into the detector a wavelength commensurate with $d_{h'k'l'}$, providing only that that wavelength is present in the incident spectrum. The various possibilities are readily shown by the use of a particular layer of a reciprocal lattice. Figure 19 shows the (hkl) layer for a face centered cubic crystal. For the sake of simplicity, and without loss of generality, we discuss a particular case.

Consider the instrument initially to be set up for the (444) reflection. A line from the origin in Figure 19 through the (444) relp (reciprocal lattice point) shows the direction along which the position vector of any relp must lie if it is to be capable of diffracting any wavelength whatever

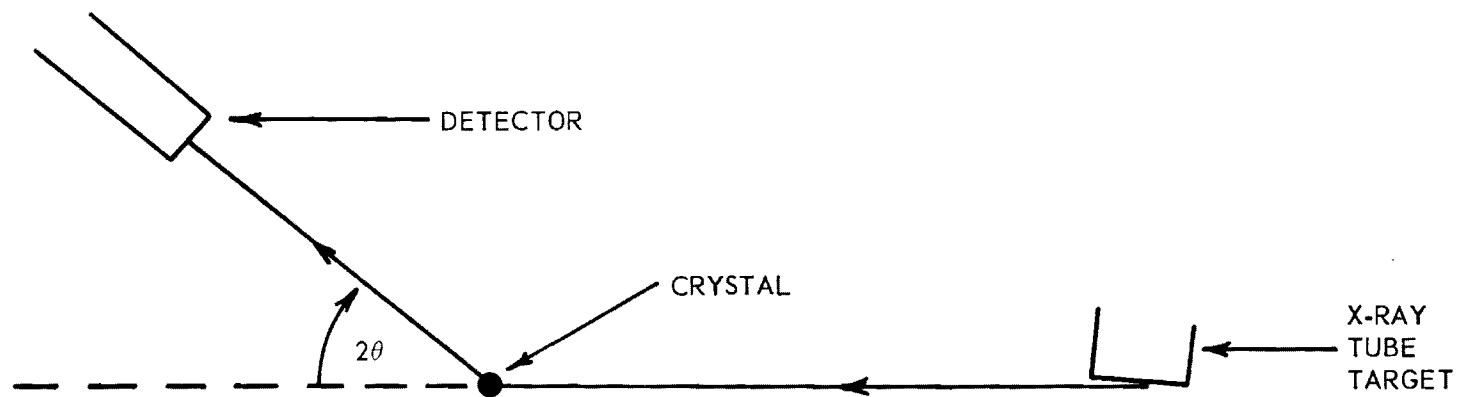


Figure 18. Zero Layer Geometry.

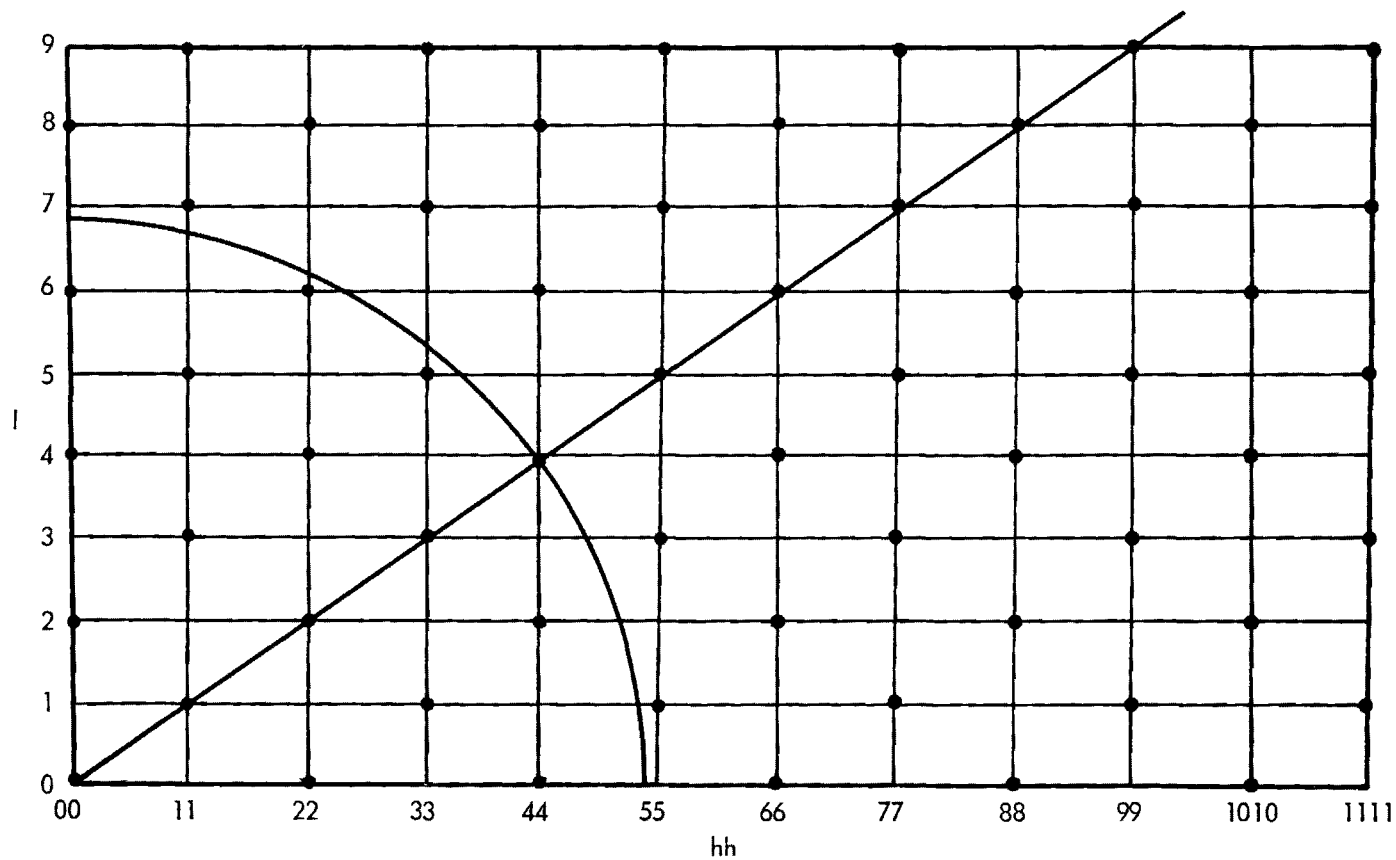


Figure 19. Reciprocal Lattice, FCC Crystal, $\{hhl\}$ Layer.

to the detector. Thus, if a straight edge is laid along the origin to the (444) relp and Figure 19 is then rotated under the straight edge (about the origin of reciprocal space) the various relps will be in the proper position for diffraction as they come in contact with the straight edge. The wavelength received by the counter is governed by the fact that any relp will diffract a wavelength which is inversely proportional to its d^* .

In Figure 19 a circle is drawn about the origin and through the (444) relp. It is assumed that the filter pair has been chosen so that the characteristic radiation from the x-ray target lies between the two absorption edges and that, further, the detector has been set in position to receive the characteristic radiation from the (444) reflection. A circle drawn about the origin through the (444) relp then corresponds to the dividing line between diffracted (and detected) wavelengths (a) longer than and (b) shorter than the region between λ_1 and λ_2 (in Figure 17). As the crystal is rotated so that Figure 19 revolves clockwise it is clear that, after the (hhh) reflections, the (hh, h+2) reflection which corresponds to the shortest wavelength observable will be the first reflection to contribute observable intensity in the direction of the detector. Because of the distribution of intensity in the incident spectrum, those relps which lie closest to or slightly farther out than the circle passing through (444) will contribute the greatest intensity. When the crystal has been rotated about 11° , the (446) will be in a diffracting position and will diffract a wavelength shorter than the characteristic. Another 3 degrees of rotation brings the (335) into a diffracting position, but this diffracts a wavelength longer

than the characteristic. In a rotation of only 3 degrees the character of the radiation received at the detector has changed from being predominantly shorter to being predominantly longer than the wavelength between the absorption edges of the filter pair. Thus, if the balance of the filter pair at the short wavelength side differs at all from that at the long wavelength side of the absorption edges, one would find that the ratio of the background as obtained with one filter to that obtained with the other filter would be an oscillating function of crystal rotation.

C. Effect of Radiation Character Variations on Background Measurements

The widely used working assumption is that the proper background reading may be obtained by rotating the crystal a few degrees off the position in which it diffracts the characteristic radiation. It is clear from the above discussion that this assumption is not valid; the "background" measured will depend upon which planes are in diffracting or near diffracting position, what wavelengths they are diffracting to the detector, the relative intensity of that particular wavelength in the incident spectrum, and the absorption of the filter for that particular wavelength. Stated more simply, the usual method of obtaining background measurements with a stationary counter is not reliable because the character of the radiation received by the detector depends in detail upon the amount of rotation of the crystal away from the Bragg peak. It is clear also that unless a filter pair were to be used which was perfectly balanced over all wavelengths outside the absorption edge, the differential filter technique could not compensate for this variation in radiation character.

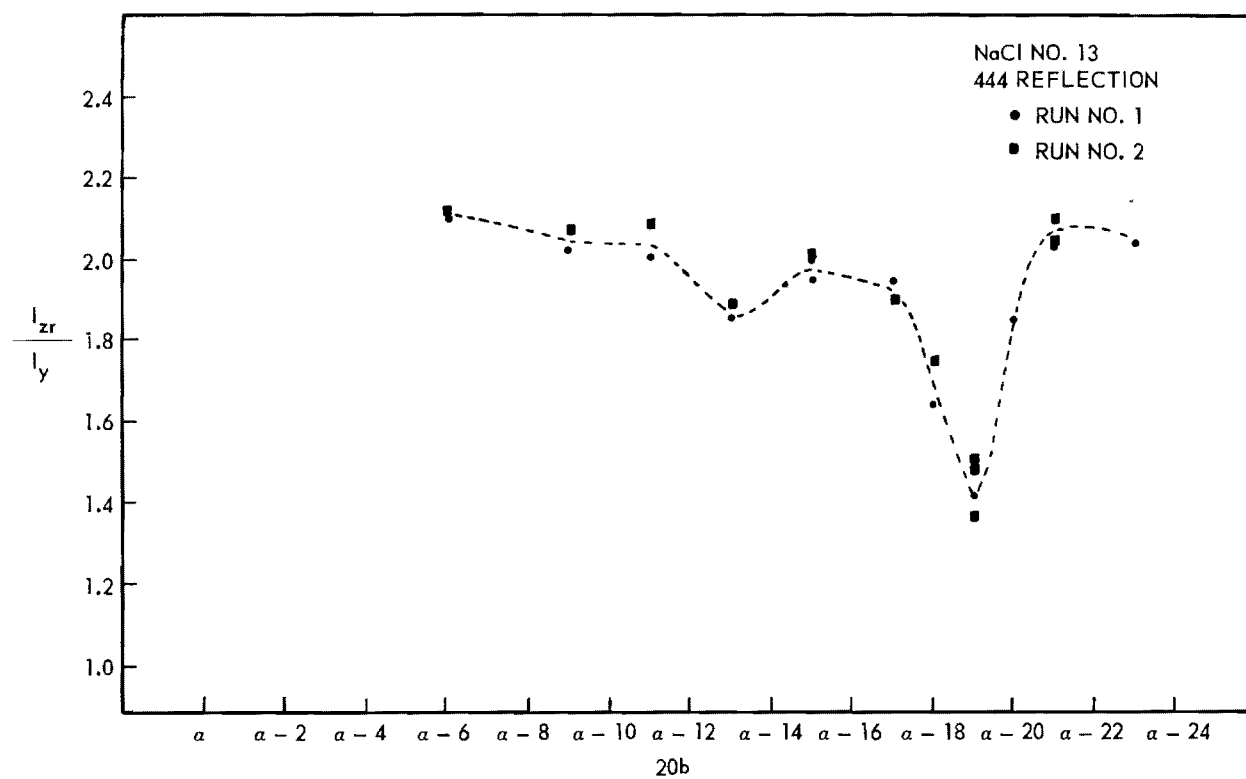
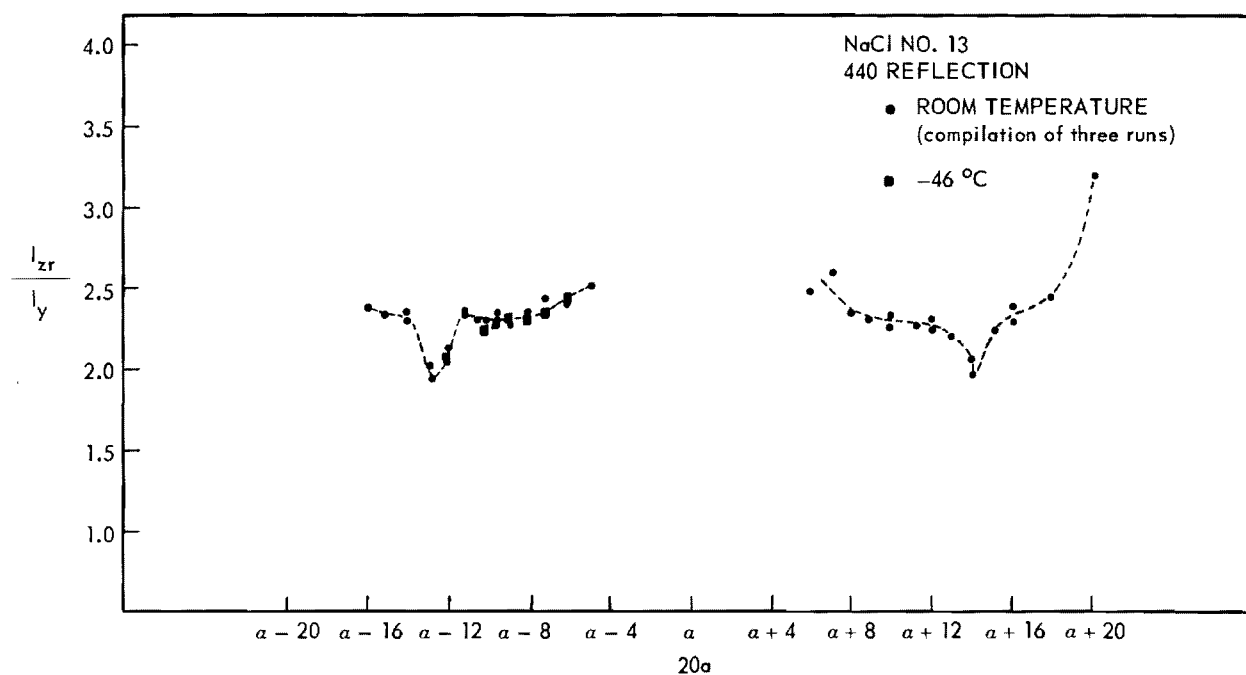


Figure 20. Measurements of I_{zr}/I_y with Stationary Counter.

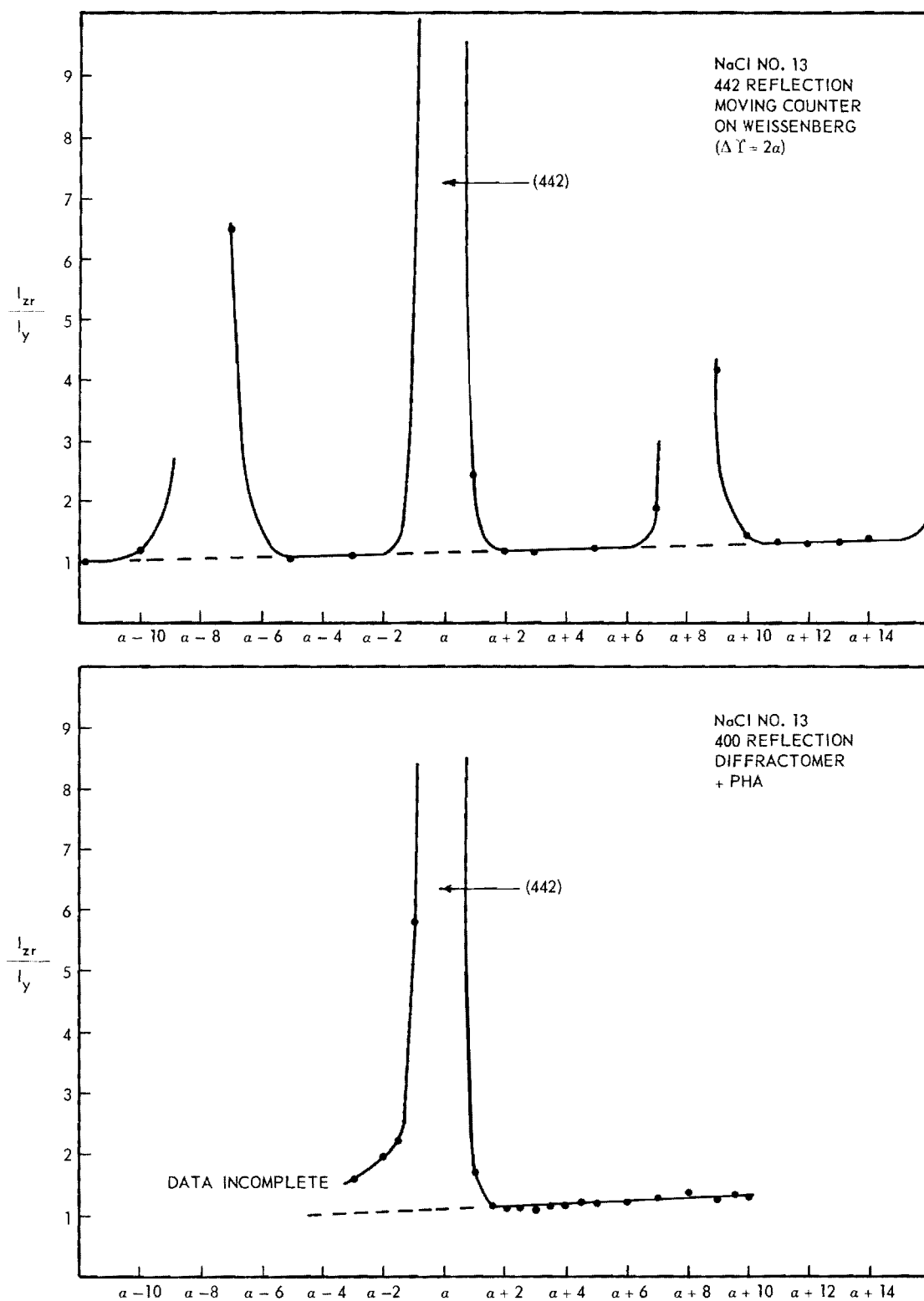


Figure 21. Measurements of I_{zr}/I_y with Moving Counter.

examination of Figure 20 above. Further, the difference in balance at long and short wavelength sides apparent in Figure 21 is actually fairly small. Thus the situation described by Figure 20, the explanation of which has just been given, presents a serious limitation to the usefulness of the balanced filter technique, even though the filters may be thought to be fairly well balanced.

E. Some Conclusions About the Use of the Differential Filter Techniques

While the unbalance of the filter used in this case was greater than it needed to be, nonetheless, several things are made clear by this experiment.

1. Since a perfect balance is not to be expected in any case, some of the variation shown in Figures 20 and 21 must always persist. Possibly it can be made small enough to ignore, at least for some purposes.
2. If a stationary detector is to be used, then the arguments set forth here indicate that crystal monochromatized radiation should be used for either peak area or background off the peak measurements and should be backed up with pulse height discrimination or some other means for removing the harmonic content.
3. If the detector is not stationary but is moved at twice the angular velocity of the crystal, the differential filter crystal technique works much better. In that case, the character of the radiation received by the detector shows monotonic rather than oscillatory changes with crystal rotation. Slight unbalance in the differential filters is then both more easily corrected and less important.

4. Larger scale plots of Figure 21-a indicated that the ratio of the intensity with the Zr filter to that with the yttrium filter was about 1.155 at the Bragg peak. Precisely at the Bragg peak it is not to be expected that other relps are contributing any "foreign" wavelengths to the detected radiation. (A possible exception to this is that other orders of the relp nominally under investigation could be making contributions. However, the higher frequency harmonics can be blocked by the pulse height analyzer.) Consequently this correction factor was used in obtaining true peak heights from measurements of gross peak heights with the Zr filter and from the intensity measured at the peak position with the yttrium filter. In those few cases in which it was necessary, for the present data, this same correction factor was applied to total area counts.

III. DEPENDENCE OF THE DIFFRACTION PEAK BREADTH, B_0 , ON DIFFRACTION ANGLE AND ON TEMPERATURE

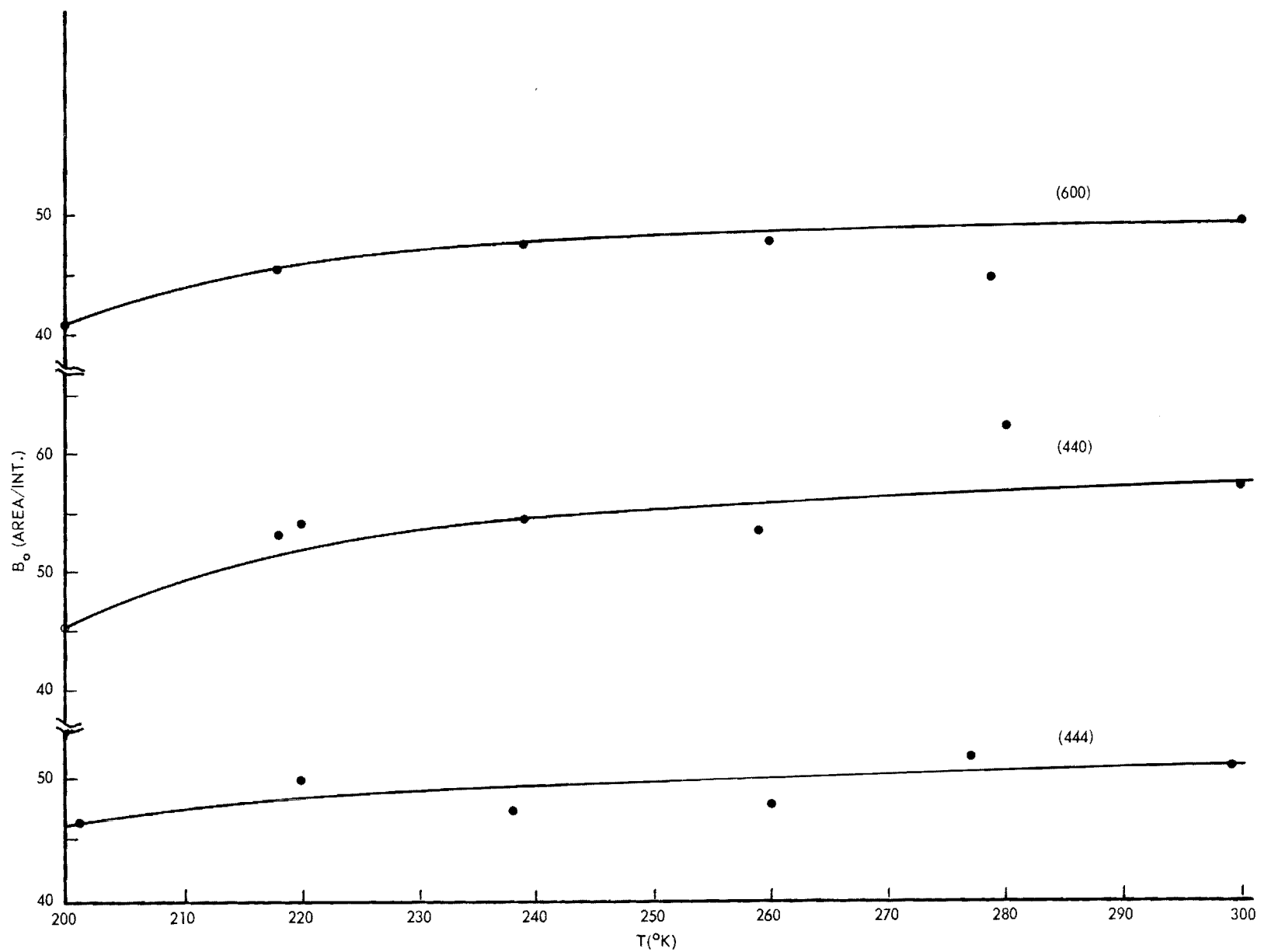
A. Integral Breadths

Several determinations of B_0 as a function of temperature and also as a function of diffraction angle were made on samples #5 and #6. Similar data will, of course, be taken on sample #7 and all future samples. The angle and temperature dependences of the B_0 's of sample #5, which was a rod, were similar to those of sample #6. All of the B_0 data reported here were collected with the total count method, but were, as has been mentioned before, subject to unnecessarily large errors because they were taken before the intermittent malfunctioning of the counting equipment had been eliminated. However, the data do serve to show a trend.

Figure 22 shows the measured B_0 values for three reflections of sample #6 as a function of temperature. All three reflections show a "sharpening up" with decreasing temperature such as might be expected either from the effect of thermal expansion on the α -doublet separation or from the reduction of TDS with increasing temperature. The scatter of the points in Figure 22 about the corresponding smooth curves is an indication of the errors in the B_0 measurements. It is believed that the largest part of these errors was due to equipment malfunction.

Figure 23 shows the dependence of B_0 on Bragg angle for several reflections of sample #6 at two temperatures. Again the form of the curves is qualitatively in agreement with that to be expected from the effect of α -doublet separation or from the TDS contribution. Either of these factors would tend to make B_0 increase both with increasing temperature and with increasing angle. It is thought probable, however, that the α -doublet effect predominates in these data. It will be noted that the abscissa of Figure 23 is actually tangent θ rather than the Bragg angle, θ , itself. The purpose of making the plot this way is to account partially for the variation in dispersion, and hence in the α -doublet separation, with angle.

It will be noted that in Figure 23 the B_0 at small angles does not change particularly with temperature. Figure 23 is at least a partial experimental justification of the extrapolation technique used later to eliminate or in any event to minimize the errors, due to the temperature dependence of B_0 , in results based at once on experimental measurements of peak heights and on theoretical analyses based on areas.

Figure 22. Temperature Dependence of B_O .

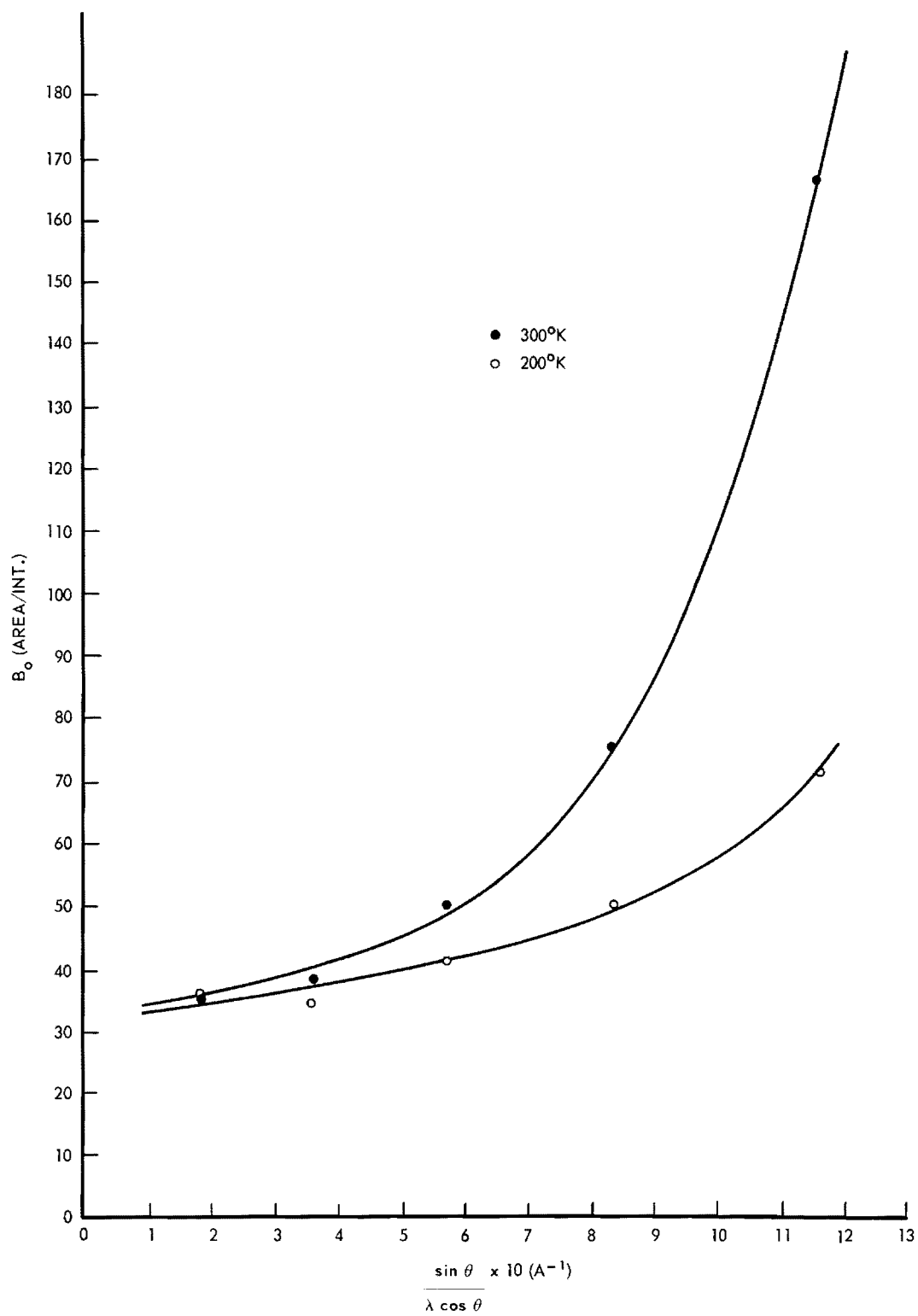


Figure 23. Dependence of B_0 on Diffraction Angle.

B. Temperature Dependence of Wings on Apparent Bragg Peaks

As was mentioned earlier, in connection with Figure 12, measurements on the wings of the apparent Bragg peaks at positions corresponding to point "a" of Figure 12 might be expected to reveal the presence of TDS through its temperature dependence. A rough measurement of this type was attempted over the temperature range from room temperature to -73°C without result. However, it is intended to repeat this experiment with more care and over a larger temperature range. The absence of a pronounced effect, however, does indicate that the principal temperature dependence of B_0 is probably due to changes in the α -doublet separation rather than to changes in the TDS contribution to the apparent Bragg peak.

IV. PRESENTATION OF INTENSITY VS. TEMPERATURE RESULTS

In Figures 24-26 the experimentally measured intensity is plotted against temperature for each of several reflections from sample #7, the smallest sample used to date. By equations (18) and (27) the slope of any such curve will yield the temperature factor corresponding to the assumption of equal amplitudes of thermal motions for both the silver and chlorine atoms. It is to be noted that the curves are not straight lines; this is primarily because $f(x)$ in the low temperature approximation given by equation (30) shows significant variation over the temperature range employed.

In Figures 24-26 the crosses indicate data taken on cooling the crystal; the circles indicate data taken on warming. The symbols, α_1 and α_3 , refer to equivalent reflections which occur at spindle positions which are 180° apart. For the sake of clarity in the presentation, all of the intensities

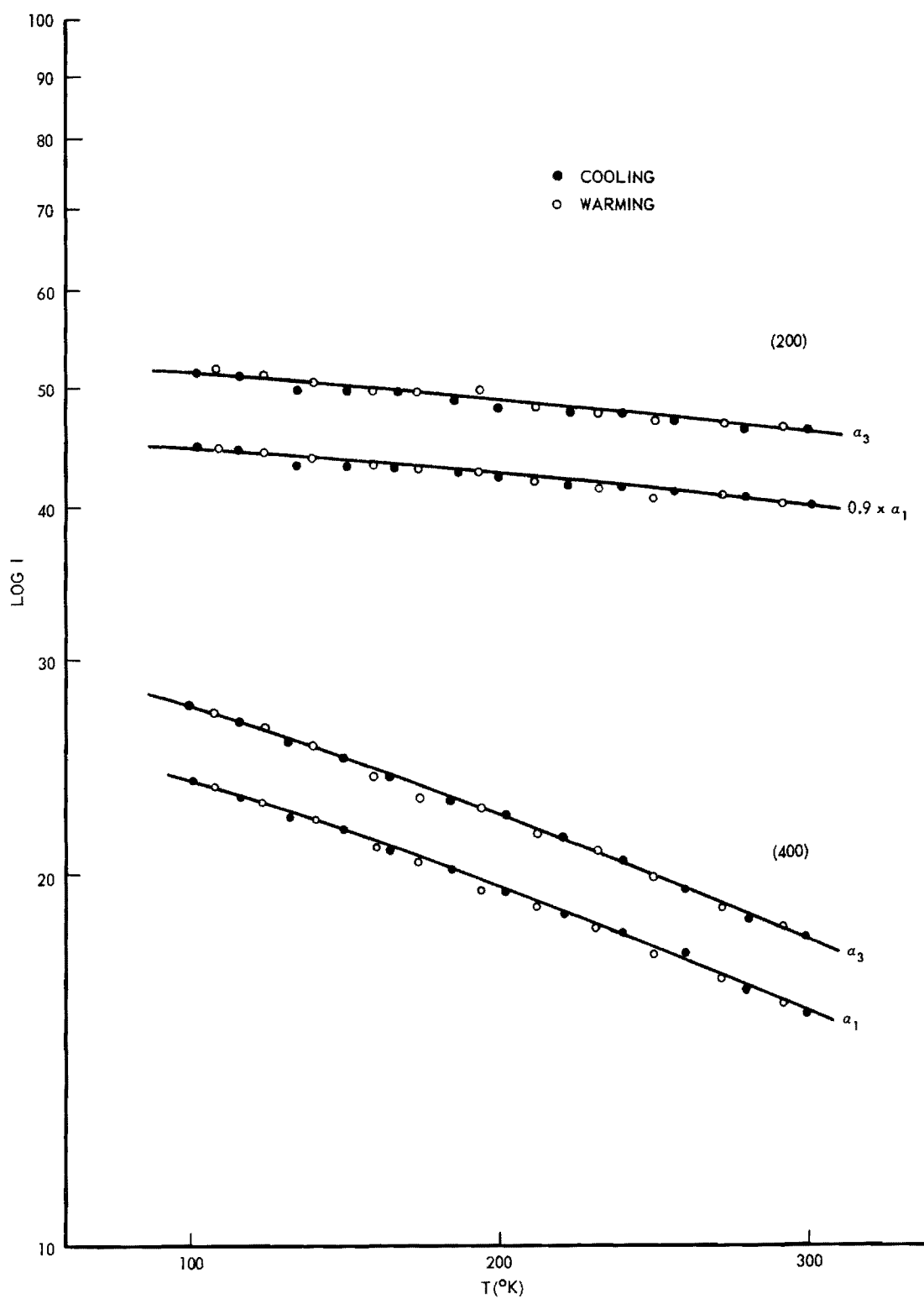


Figure 24. Temperature Dependence of Intensities.

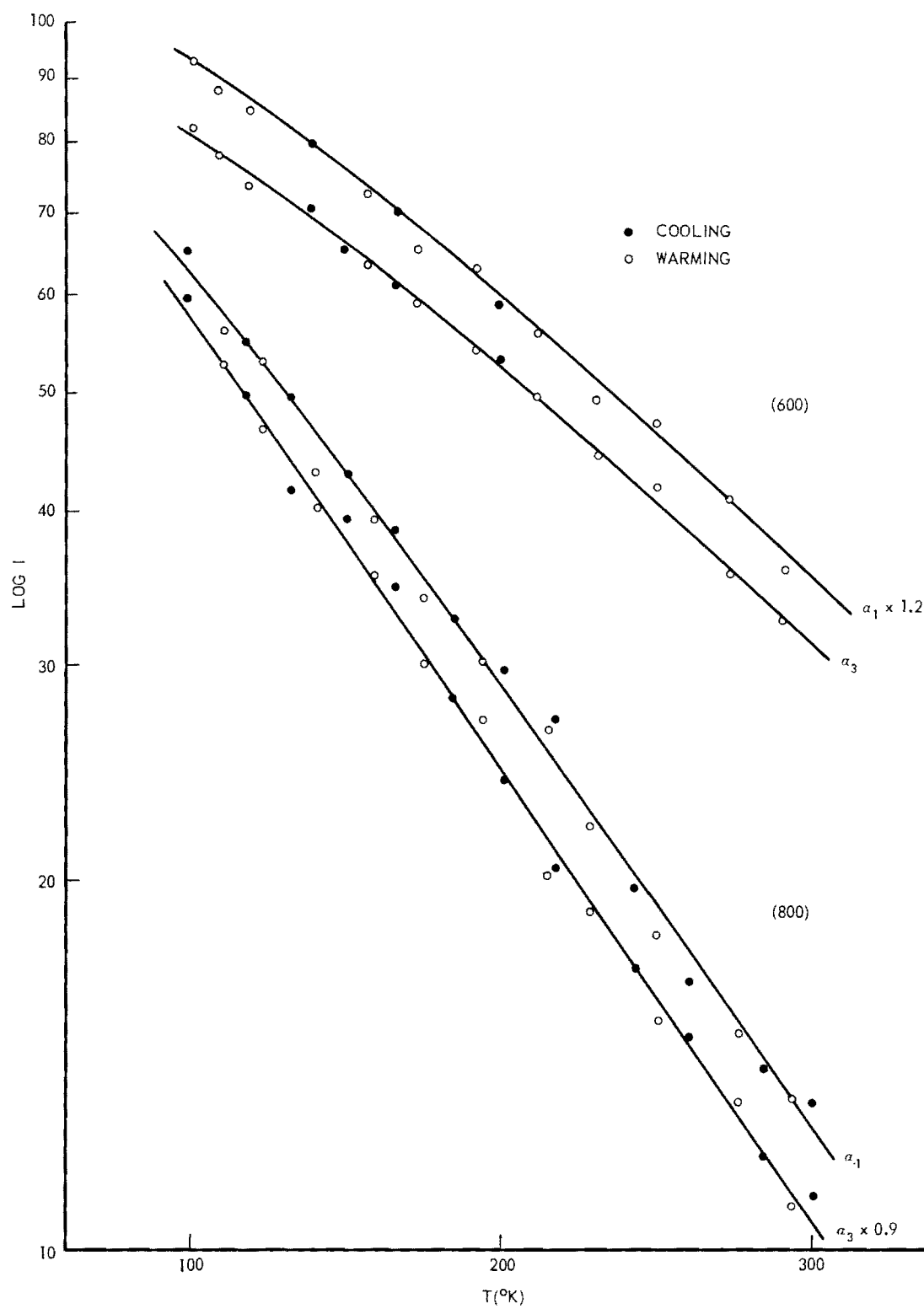


Figure 25. Temperature Dependence of Intensities.

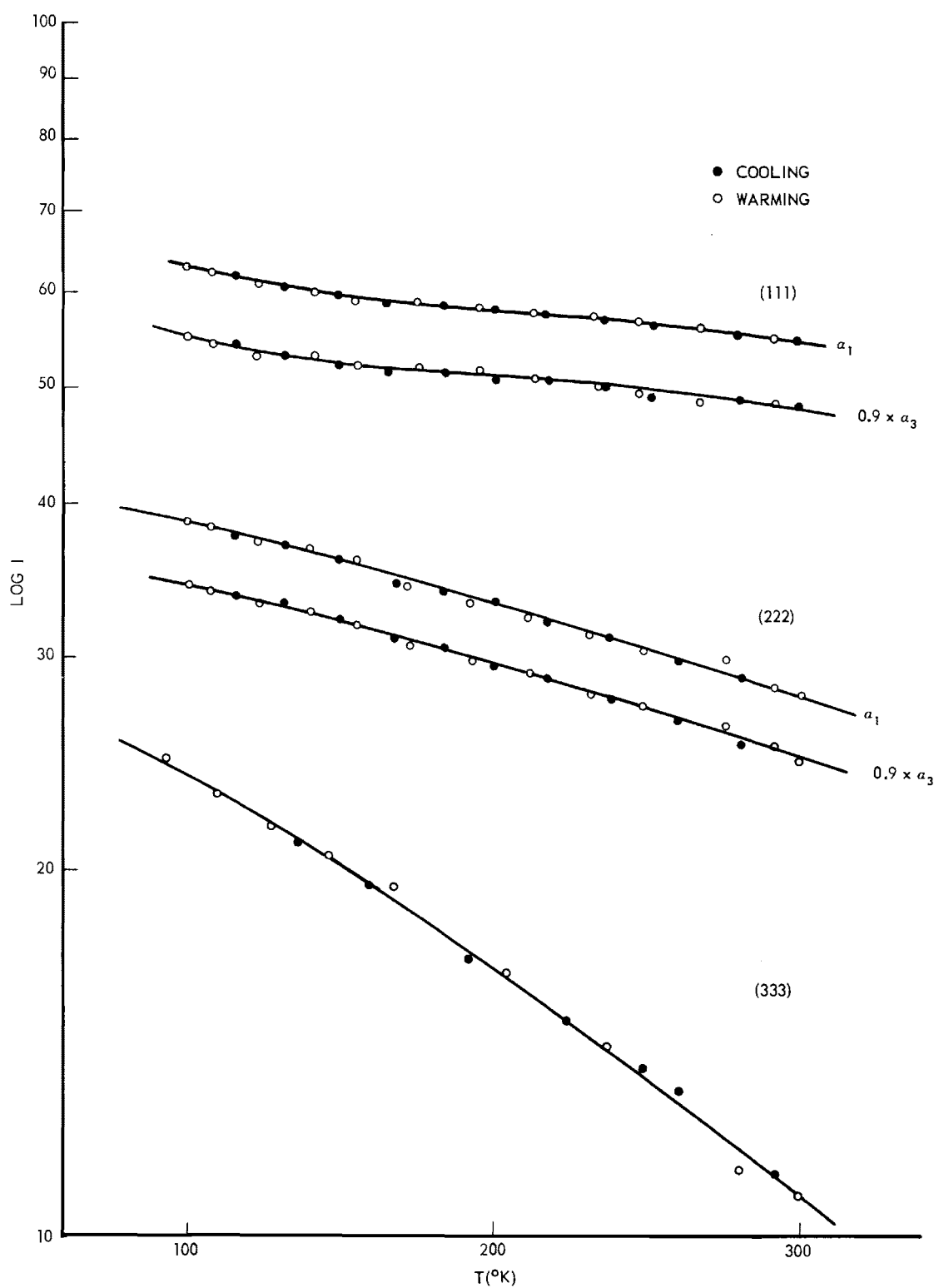


Figure 26. Temperature Dependence of Intensities.

from one of these reflections have been, in most cases, arbitrarily multiplied by 0.9 in order that the two curves may be shown individually.

On the assumption that the thermal expansion may be neglected [equation (30)] a slope, A, which should have the same value for all reflections may be obtained through use of the definition of A given by equation (52).

$$A = \frac{2 \, dM/dT}{\sin^2 \theta / \lambda^2} = \frac{d/dT(\ln I/I_o)}{\sin^2 \theta / \lambda^2} \quad (52)$$

However, the A values so obtained were not all the same,* and in Figures 27-29 the experimentally determined A values are plotted vs. $\frac{\sin^2 \theta}{\lambda^2}$. In Figure 27, the A values from just one type of reflection, (h00), from a particular crystal are plotted at two temperatures. In Figure 28 separate plots are made, at one temperature, for the A values from each type of reflection.

The A values in Figure 29 were determined two ways, but in both cases experimental measurements were made only at room temperature and -73°C; a straight-line relationship between log I and T was then assumed. In one case, the observations were based entirely on peak heights, as they were for Figures 27 and 28; in the other case they were based on actual measurements of diffraction peak area.

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* Because of the angular dependence of the error introduced by the α -doublet and by the TDS contributions.

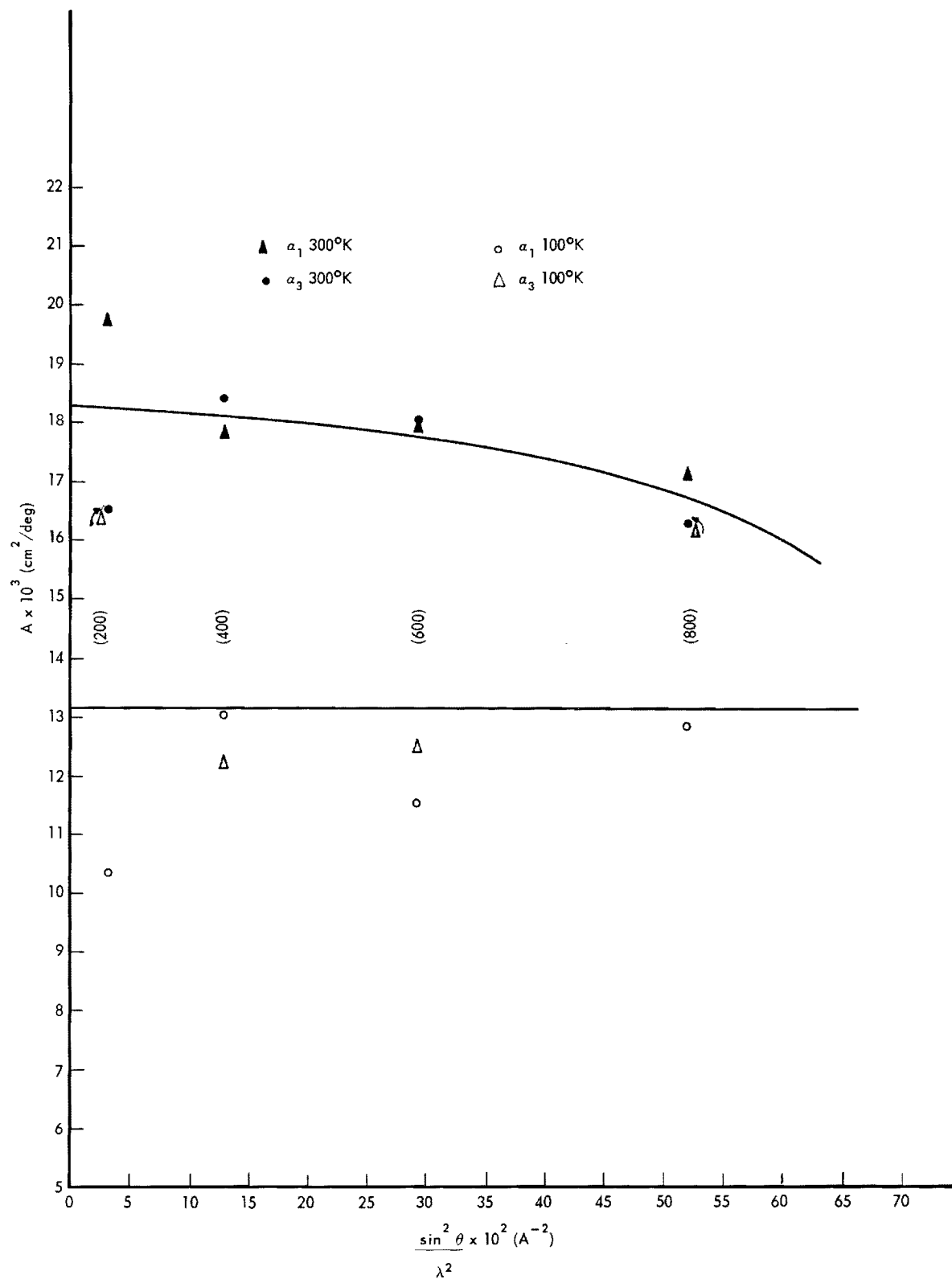


Figure 27. Dependence of Slope, A, on Diffraction Angle, Sample No. 7.

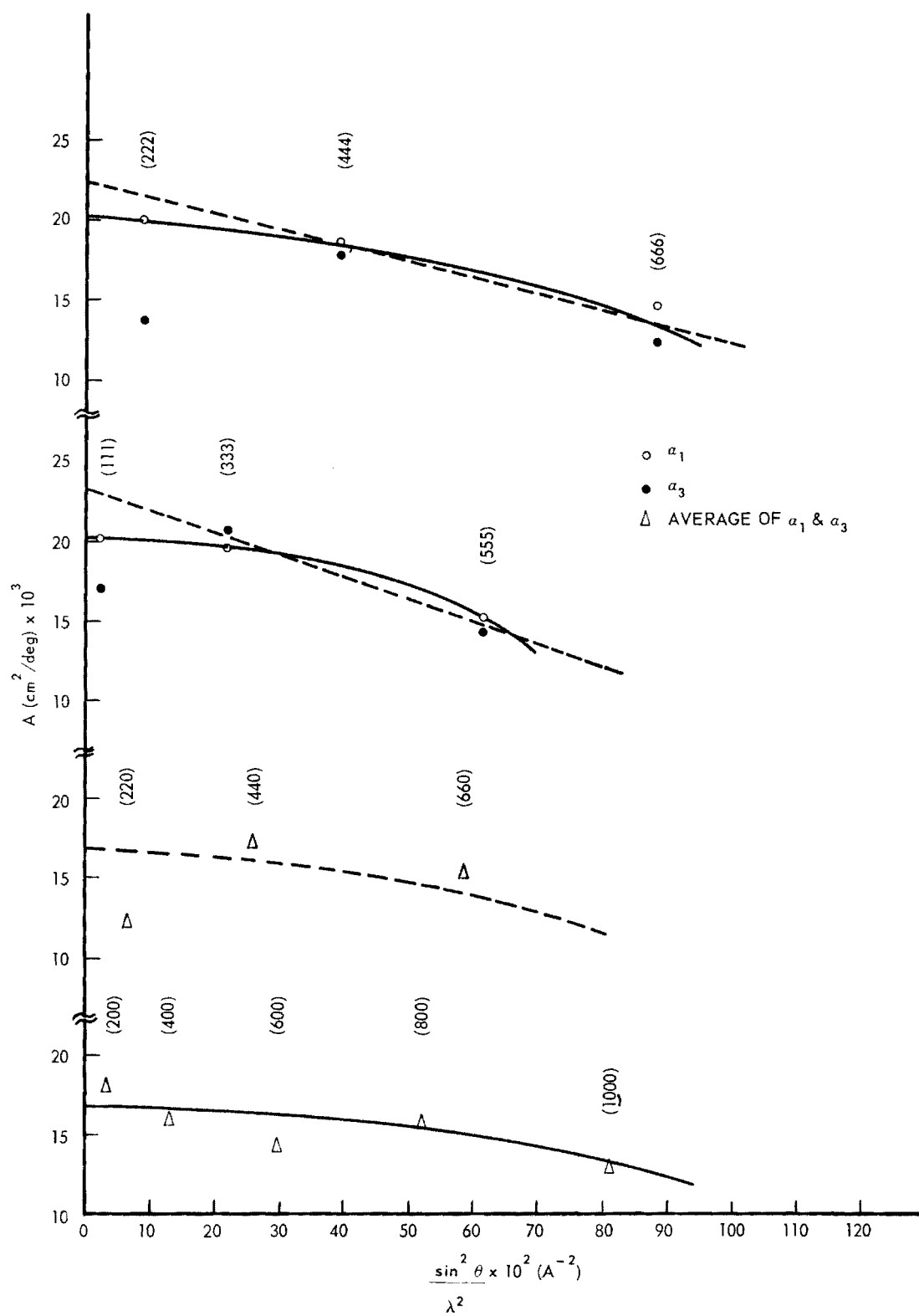


Figure 28. Dependence of Slope, A , on Diffraction Angle, Sample No. 6.

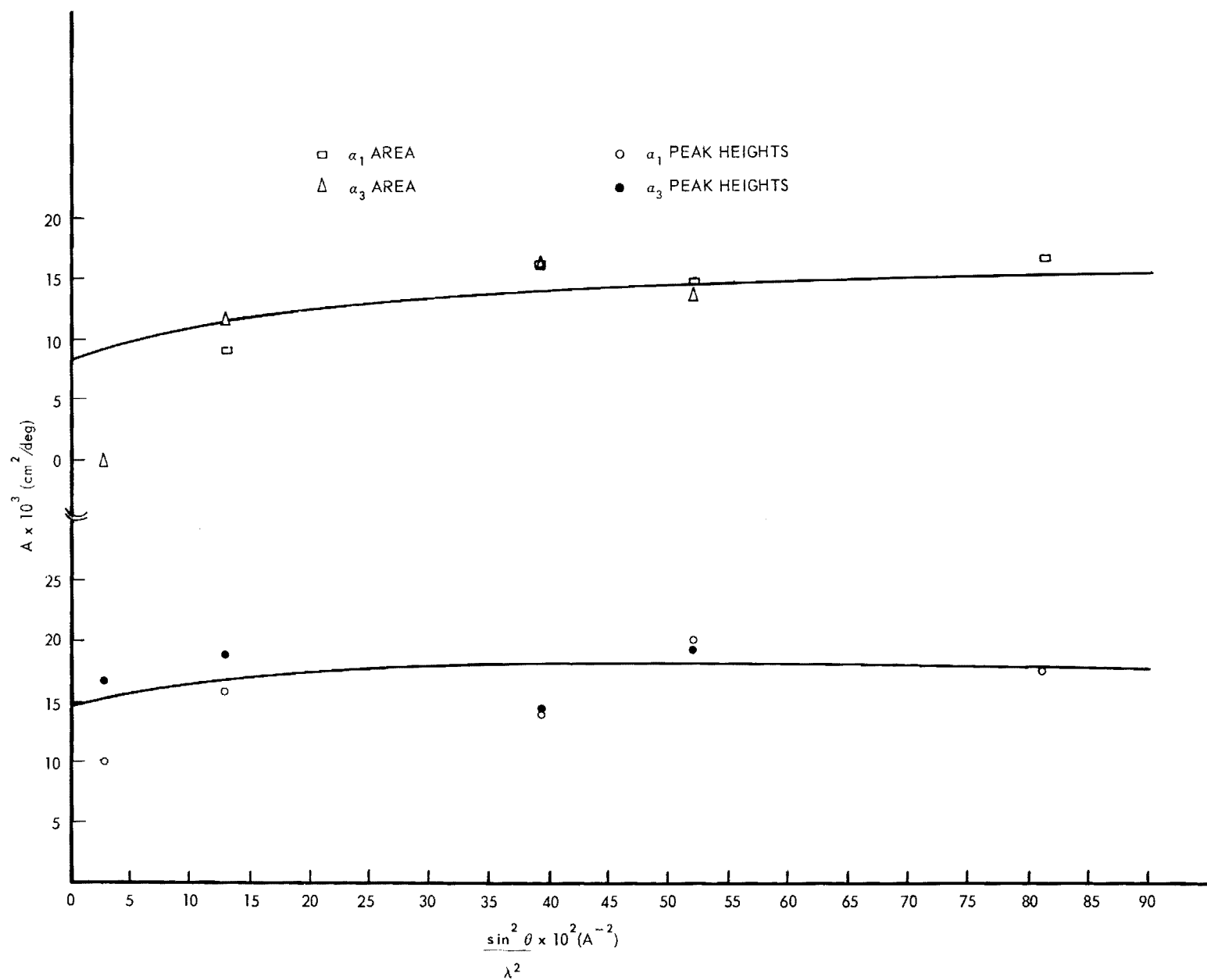


Figure 29. Dependence of Slope on Diffraction Angle, Sample No. 5.

V. DISCUSSION OF INTENSITY VS. TEMPERATURE RESULTS

A. Significance of Similarity of Even and Odd Results

It is clear from equation (37) that if the temperature factors for the two kinds of atoms are not the same then the slope of log intensity vs. temperature should be different for different parities in the indices of the reflections. The temperature factor B [see equation (18)], and consequently the slope A [equation (52)] must be different for reflections with odd parities in the indices from that with even parities in the indices unless ΔM is zero, i.e., unless the individual atoms have the same amplitudes of thermal motions.

Because our measurements of peak height may be affected by a varying α -doublet separation with changes in temperature and because of the temperature dependence of the TDS contribution, both of which are functions of $\frac{\sin \theta}{\lambda}$, it is not expected that exactly the same A values will be obtained for all reflections. However, the variation in A values from reflection to reflection, due to α -doublet separation and TDS contributions, should be a smooth function of $\frac{\sin \theta}{\lambda}$. Plotting A values vs. some factor such as $\frac{\sin^2 \theta}{\lambda^2}$ and extrapolating to $\sin \theta = 0$ should give results which are independent of the α -doublet error and the TDS error.

The fact that, for the (hhh) reflections of sample #6, the values of A obtained by extrapolation are essentially identical for both even and odd parities shows that either the amplitudes of the thermal motions of the silver and chlorine atoms, or at least that part of them which we measure with this technique, are very nearly the same. This, in turn, implies that the acoustical modes rather than the optical modes of lattice vibrations

are the ones which are important and are measured in our x-ray experiment, for it is only in the acoustical modes that one expects to find equal amplitudes of vibrations. Since the Debye- Θ 's obtained by our experiment seem reasonable, as will be discussed later, it appears that not only are the acoustical modes the ones whose changes are measured by our temperature-varying experiment, but that they are in fact dominant in providing the whole temperature factor; the optic modes apparently are not sufficiently excited in this crystal to contribute significantly to the total amplitude of thermal vibrations. This observation is in agreement with Cole's²⁴ statement to the effect that the temperature factors for Ag and Cl are essentially identical at room temperature.

B. Anomalies

The temperature dependence of the (111) reflection seems different from all of the others in that there appears to be a point of inflection in the intensity vs. temperature curve, as is shown in Figure 26. To date (June 1959) only the two equivalent reflections from one crystal have been measured so it is not possible to say whether or not this inflection is real. However, it seems plausible that it might be. It has been assumed that the atomic form factors, and hence the bonding, are not temperature dependent. Any change in bonding that did occur, however, would be expected to affect that part of the form factor which occurs at smallest values of $\frac{\sin \theta}{\lambda}$. Such changes in the form factor would, in turn, be most observable for the reflections which occur at the smallest value of $\frac{\sin \theta}{\lambda}$; in this case that is the (111) reflection. Further, if the change in bonding amounted to a change in the degree of ionization, as would seem possible, this would mean

that the form factor of one atom would be increased while that of the other would be decreased; such an effect would be most noticeable in reflections which depended upon the differences of the scattering powers of the two atoms: i.e., those with odd parity, such as (111). If the inflection in the (111) intensity vs. temperature curve really is due to electron transfer, the technique used here is certainly an interesting and relatively simple way of detecting it. Because of the possible significance of this apparent inflection in the (111) data checking its reality is of first importance and will be accomplished in the very near future*.

C. Utility of Extrapolation to $\sin \theta = 0$

Figures 27-29 show that in general there is a monotonic dependence of A on $\frac{\sin^2 \theta}{\lambda}$. The scatter of the points about the best smooth curve is larger than might be desired, but it is apparent that such a plot does accomplish at least a partial correction for the α -doublet and TDS errors. In making these extrapolations it is to be noted that the values of A determined at small values of $\frac{\sin \theta}{\lambda}$ are subject to much larger measurement errors than are those at the larger values, and hence should be weighted less heavily.

D. Anisotropy

As has been pointed out in the theory section, if the temperature factor is to be represented by a second order tensor, then in this cubic crystal the temperature factor must be spherically symmetric. Deviations

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* Note added in proof: The inflection in the log intensity vs. temperature curve of the (111) reflection has now been observed with another crystal.

from spherical symmetry, i.e., anisotropy in the temperature factor, would mean either that the crystal is not actually cubic, or that the "thermal ellipsoid" is not actually an ellipsoid but is a more complicated geometric figure. Directed bonds in the crystal might be expected to produce such deviations from the simple ellipsoid. Comparison of the extrapolated values of the slope, A , corresponding to each of the three principal directions in crystal #7 (Figure 28) seems to indicate a real difference between the $[hhh]$ and the $[h00]$ directions. The scatter of the few $(hh0)$ points about the best smooth curve through them is uncomfortably large, but it does seem probable that any reasonable extrapolation through these points would give an A value, corresponding to the $[hh0]$ direction, which would be intermediate between that for the other two directions. It is not possible to say, on the basis of so few data, whether or not any real anisotropy exists. More and, hopefully, better data will be collected on this point during the next year. If this apparent anisotropy in the actual temperature factor (at room temperature in the above discussion) is indeed real, it indicates that the $[111]$ direction is an easier direction of vibration for the atoms than is the $[100]$ direction; and the very existence of such differences in a cubic crystal implies the existence of an anharmonicity in the vibrations. The anharmonicity must arise from something besides simple ionic bonding, e.g., partially covalent character in the bonds. The point of interest here is not the character of the bonds in AgCl , which can be supposed from lattice energy calculations⁵⁰ to show partially covalent character, but is the fact that the present technique can detect such deviations from ionic character.

If the scatter in the measurements of A can be reduced or if enough more measurements are made to give the extrapolated value statistical significance, the comparison of extrapolated A values corresponding to different directions in cubic crystals might be used to indicate relatively small amounts of non-ionic character in the bonds of various crystals.

It is encouraging to note, with respect to the reality of the directional differences in A , that there is less difference between the two A values corresponding to the same direction in two different crystals (samples #5 and #6, see Figure 29 for sample #5) than between the extrapolated values for two directions in the same crystal ([111] and [100] directions in #6, Figure 28).

E. Debye- Θ 's

Debye- Θ 's were determined from the extrapolated A values by use of equation (30) with an iterative procedure for the determination of $f(x)$. Before the Debye- Θ can be determined from equation (30) it is necessary to make some decision as to how the masses of the two kinds of atoms are to be averaged. A simple arithmetic average was used in order to obtain some numbers for initial comparisons. The results are shown in Table II.

The Debye- Θ 's calculated from the data of Cole were based on the wave velocities which he reported; those calculated from Arenberg's data were based on the elastic constants which he reported. In neither case was any averaging procedure used, so these "Debye- Θ 's" are not quite comparable to the single Debye- Θ that would be obtained for the crystal by averaging over all directions, as is usually done when Debye- Θ 's are reported. While both the elastic constants and the wave velocities may be related to

TABLE II

Comparison of Debye- Θ 's

<u>Reported by or Based on Data From:</u>	<u>Reflections or Methods</u>	<u>Sample #</u>	<u>Temperature</u>	<u>Debye-Θ</u>
Present work	(h00)	6	300°K	139
		7	300°K	132
		7	100°K	155
	(hhh)	7	300°K	126
Cole ²⁷	TDS		300°K	132-206
Arenberg ²⁵	Elastic Constants		300°K	129-163
Lonsdale ³²	Sp. Ht.			130
Blackman ³⁷	Optical			150,168

direction, the directional relationships between these quantities and the Debye- Θ 's as determined in the present experiments are not simple; no attempt has been made to make these directional correlations in Table II. It is apparent from Table II that the Debye- Θ determined by the present method is fairly reproducible from crystal to crystal and that it does depend upon temperature, as is shown by the increase in the Debye- Θ measured for the same reflections in sample #7 at 300°K and again at 100°K. The agreement of the Debye- Θ 's as obtained by the present method, based on the temperature dependence of diffracted intensities, are qualitatively in agreement with those obtained by other methods. Investigation of the quantitative agreement must await the method-to-method directional correlations just mentioned

and must also await a more physically justifiable method of averaging masses than the simple arithmetic method used here.

VI. GENERAL CONCLUSIONS ABOUT INTENSITY VS. TEMPERATURE TECHNIQUES

It is clear from the preceding that the technique of measuring diffracted intensities as a function of temperature is capable of yielding considerable information. Reproducibility in the measurements has been almost surprisingly good. Debye- Θ 's may be determined, deviations from the Debye model may be detected, numbers may be determined which can be related to other parameters such as the pretreatment the crystals have received, it seems probable that anisotropy in the temperature factors may be detected, and it is possible that changes in bond character with temperatures have been detected. Other exploitation of the technique is possible, and it is expected that some of the further possibilities will be investigated in future work. For example, the effect of defects has not yet been explored in even a preliminary manner.

SECTION 5

FUTURE WORK

Work will continue to be directed toward finding out what information can be extracted from the temperature dependence of Bragg intensities, the possible applications of this information, and the experimental techniques required. Among the several specific problems that will be attacked in the immediate future are the following:

(1) Attempts will be made to determine separate temperature factors for the Ag and the Cl atoms. The primary means for doing this will be a least squares curve-fitting procedure, carried out with the help of a high-speed computer, in which the individual Debye- Θ 's are the variable parameters.

(2) Future investigations will be made of the causes and the degree of the dependence of B_0 on temperature. It is possible that some temperature dependence of the B_0 's of the strongest reflections will be found to be due to changes in primary extinction; if so, an attempt will be made to relate the variations in primary extinction to defect concentrations.

(3) The existence, the reproducibility, and the significance of the inflection in the intensity vs. temperature curve for the (111) reflection will be investigated. In particular, the possibility that this inflection indicates electron transfer will be carefully examined. Literature data on the temperature dependence of other physical properties that are closely dependent on bond character will be examined. Some measurements of the temperature dependence of the dielectric constant may be undertaken.

(4) Sample-to-sample differences in the temperature dependence of intensities will be sought. In the event that any real differences are found, an attempt will be made to correlate them with other known physical differences between the samples, e.g., source and impurity-content.

It is expected that at some time during the next year a full set of relative intensity data (on AgCl) will be collected at some appropriate temperature and detailed electron density maps will be prepared from them.

By use of the temperature factors determined from the intensity vs. temperature technique, it is hoped that the electron density maps will be made to reveal more information about the electron density in bonds than they would otherwise yield.

It is expected that most of the work indicated just above will be performed with AgCl crystals. However, AgBr and other crystals will be used as appropriate. It is desired eventually to make detailed intercomparisons of the electron density distributions in the various silver halides.

Respectfully submitted,

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Project Director

Approved:

21 October 1959

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Head, Physics Branch
Physical Sciences Division

BIBLIOGRAPHY

1. James, R. W., The Optical Principles of the Diffraction of X-rays, London: G. Bell and Sons, Ltd., 1958. (The Crystalline State II, edited by Sir Lawrence Bragg.)
2. Laval, Jean, "Étude expérimentale de la diffusion des rayons x par les cristaux," Bulletin de la société française de mineralogie, 137-253 (1939).
3. Lonsdale, Kathleen, "Experimental Study of X-ray Scattering in Relation to Crystal Dynamics," Reports on Progress in Physics 9, 256-293 (1943).
4. Laval, Jean, "Intensité des rayons x diffusés par l'agitation thermique de atomes," Academie de science des seances de l'academie des sciences 236, 1765-7 (1953).
5. Laval, Jean, "L'agitation thermique des atomes dans les cristaux. La diffusion des rayons x par les ondes élastiques et l'élasticité du milieu cristallin," Bulletin de la société française de mineralogie et de cristallographie 77, 219-27 (1954).
6. Blackman, M., "A Note on the Debye-Waller Theory," Acta Crystallographica, 734-37 (1956).
7. Young, R. A., "Electron Density and Thermal Effects in α -Quartz," Ph.D. Thesis in Physics submitted at the Polytechnic Institute of Brooklyn, 1959.
8. Wagner, B., Witte, H., and Wölfel, E., "Röntgenographische Bestimmung der Elektronenverteilung in Kristallen I," Zeitschrift für Physikalische Chemie 3, 273-95 (1955).
9. Peters, Cl., "Anwendung der röntgenographischen Fourier-Analyse auf Fragen der chemischen Bindung," Zeitschrift für Elektrochemie und Angewandte Physikalische Chemie 46, 436-43 (1940).
10. McWeeny, R., "X-ray Scattering by Aggregates of Bonded Atoms. III. The Bond Scattering Factor: Simple Methods of Approximation in the General Case," Acta Crystallographica 6, 631-7 (1953).
11. Kurdyumov, G. V., Il'ina, V. A., Kirtzkaya, V. K., and Lysak, L. I., "X-ray Investigation of the Deformation and Bond Strength in the Crystal Lattice of Metals and Alloys," Izvestiya Akad. Nauk. S.S.S.R. 17, No. 3, 297-312 (1953). Translated by J. Adam, Harwell, Berks. (1957).

12. Tucker, Charles W., and Senio, Peter, "X-ray Scattering by Neutron-Irradiated Single Crystals of Boron Carbide I," Acta Crystallographica 8, 371-378 (1955).
13. Paskin, Arthur, "Contributions of One- and Two-Phonon Scattering to Thermal Diffuse Scattering," Acta Crystallographica 11, 165-8 (1958).
14. Chipman, D. R., and Paskin, Arthur, "Temperature Diffuse Scattering in Cubic Powders I. Comparison of Theory with Experiment," MRL Report No. 49, Ordnance Materials Research Office, Watertown Arsenal, ASTIA Document No. 154006, July 1958.
15. Chipman, D. R., and Paskin, Arthur, "Temperature Diffuse Scattering in Cubic Powders II. Corrections to Integrated Intensity Measurements," MRL Report No. 50, Ordnance Materials Research Office, Watertown Arsenal, ASTIA Document No. 154007, July 1958.
16. Paskin, Arthur, "Elastic Wave Velocity Effect on Temperature Diffuse Scattering in Cubic Powders," MRL Report No. 54, Ordnance Materials Research Office, Watertown Arsenal, ASTIA Document No. 154010, September 1958.
17. Nilson, Nanny, "On the Corrections of the Measured Integrated Bragg Reflections due to Thermal Diffuse Scattering," Arkiv för Fysik XII, 247-257 (1957).
18. Renninger, M., "Zur Elektronendichte-Verteilungim Steinsalzgitter," Acta Crystallographica 5, 711-722 (1952).
19. Nail, N. R., Moser, F., Goddard, P. E., and Urbach, F., "Preparation of Silver Halide Crystals of High Purity," Review of Scientific Instruments 28, 275-278 (1957).
20. Seitz, Frederick, "Speculations on the Properties of the Silver Halide Crystals," Reviews of Modern Physics 23, 328-52 (1951).
21. Burgers, W. G., and Tan Koen Hiock, "Diffuse Bands on Laue Photographs of Silver Chloride Crystals," Nature 159, 845-6 (1947).
22. Kooij, J. N., and Burgers, W. G., "Disintegration of Silver Halide Crystals by Irradiation with Ultraviolet Light," Recueil des Travaux Chimiques des Pays-Bas 67, 21-8 (1948).
23. Berry, Chester R., "Physical Defects in Silver Halides," The Physical Review 97, 676-9 (1955).
24. Moser, F., Nail, N. R., and Urbach, F., "Note on the Darkening of Silver Chloride," The Physics and Chemistry of Solids 3, 153-155 (1957).

25. Moser, F., Private communication.
26. Barth, T., and Lunde, G., "Lattice Constants of the Cuprous and Silver Halides," Norsk Geologisk Tidsskrift 8, 281-92 (1926).
27. Cole, H., "Approximate Elastic Spectrum of Acoustic Waves in AgCl from X-ray Scattering," Journal of Applied Physics 24, 482-7 (1953).
28. Blackman, M., "On Θ Values in the Resistance of Metals," The Proceedings of the Physical Society London A64, 681-683 (August 1, 1951).
29. Kelly, F. M., and MacDonald, D. K. C., "On Θ Values in Metals," Canadian Journal of Physics 31, 147-164 (1953).
30. Strelkov, P. G., "The Dependence of the Thermal Expansion Coefficients of Silver Haloids on Temperature," Nature 139, 803-4 (1937).
31. Sharma, S. S., "Thermal Expansion of Crystals," Proceedings of the Indian Academy of Science 32A, 268-74 (1950).
32. Lonsdale, Kathleen, Acta Crystallographica 1, 144 (1948) quotes $\Theta(\text{AgCl}) = 130^\circ\text{K}$ from T^3 plot of K. Clusius and P. Harteck, Zeitschrift für Physikalische Chemie A134, 243 (1928).
33. Clusius, K., and Harteck, P., "Über die spezifischen Wärmen einiger fester Körper bei tiefen Temperaturen," Zeitschrift für Physikalische Chemie A134, 243-263 (1928).
34. Stepanov, A. V., and Eidus, I. M., "Temperature Dependence of the Elastic Constants of Monocrystals of Sodium Chloride and Silver Chloride," Soviet Physics JETP 2, 377-82 (1956).
35. Arenberg, D. L., "Determination of Elastic Constants in Single Crystals with Especial Reference to Silver Chloride," Journal of Applied Physics 21, 941-2 (1950).
36. Sutton, Paul M., "Computation of Mean Debye Temperature of Cubic Crystals from Elastic Constants," Physical Review 99, 1826-30 (1955).
37. Blackman, M., "The Theory of the Specific Heat of Solids," Reports on Progress in Physics 8, 11-30 (1941).
38. Blackman, M., "Contributions to the Theory of the Specific Heat of Crystals I - Lattice Theory and Continuum Theory. II - On the Vibrational Spectrum of Cubical Lattices and its Application to the Specific Heat of Crystals," Royal Society of London. Proceedings. London A148, 365-383, 384-406 (1935).

39. Paskin, Arthur, "A Reformulation of the Temperature Dependence of the Debye Characteristic Temperature and its Effect on Debye-Waller Theory," Acta Crystallographica 10, 667-669 (1957).
40. Ramachandran, G. N., and Wooster, W. A., "Determination of Elastic Constants of Crystals from Diffuse Reflexions of X-rays. I. Theory of Method," Acta Crystallographica 4, 335-344 (1951).
41. Chipman, D. R., and Paskin, Arthur, "Contributions of Temperature Diffuse Scattering to Wings on Bragg Peaks," Journal of Applied Physics 29, 1608 (1958).
42. Kirkpatrick, Paul, "Theory and Use of Ross Filters. II," The Review of Scientific Instruments 15, 223-229 (1944).
43. Post, Benjamin, Schwartz, Robert S., and Fankuchen, I., "An Improved Device for X-ray Diffraction Studies at Low Temperatures," Review of Scientific Instruments 22, 218-219 (1951).
44. Klug, Harold P., and Alexander, Leroy E., X-ray Diffraction Procedures, New York: John Wiley and Sons, Inc., 1954.
45. Lang, A. R., "Suggested Necessary Conditions for Successful Use of the Stationary Crystal Integrated Reflection Measuring Method with the Counter Spectrometer," Norelco Reporter V, 105 (September-December 1958).
46. Vand, Vladimir, "Methods for the Correction of X-ray Intensities for Primary and Secondary Extinction in Crystal Structure Analysis," Journal of Applied Physics 26, 1191-1194 (1955).
47. Gatineau, Lucien, and Mering, Jacques J., "Une methode de correction des effets d'extinction affectant les intensites des rayons x réfléchis par un cristal unique," Academie des Sciences Paris. Comptes Rendus 242, 2018-2021 (1956).
48. Chandrasekar, S., "A First-Order Correction for Extinction in Crystals," Acta Crystallographica 9, 954-956 (1956).
49. Buerger, M. J., X-Ray Crystallography, New York: John Wiley and Sons, Inc., 1949.
50. Huggins, M. L., "Transitions in Silver Halides," Phase Transformations in Solids (edited by R. Smoluchowski, J. E. Mayer, and W. A. Weyl), New York: John Wiley and Sons, Inc., 1951, 238-256.

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SECOND ANNUAL REPORT

Project A-389

X-RAY DIFFRACTION STUDIES OF THERMAL

MOTIONS IN CRYSTALS

by

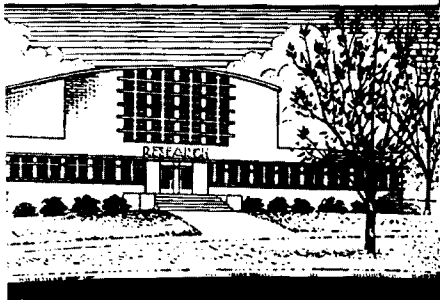
R. A. Young



June 1, 1959 to May 31, 1960

Contract No. NONr 991(00) and 991(06); NR 017-623

Placed by the
Office of Naval Research (Physics Branch)
Washington 25, D. C.



Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
OF THE GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

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ABSTRACT

Research has been continued on the general investigation of what can be determined by x-ray means, particularly from the temperature dependence of Bragg (x-ray) intensities, about thermal vibrations in crystals and their interactions with other phenomena of interest in crystal physics.

Most of the problems concerning experimental techniques in making the precision measurements had been dealt with in comprehensive (though not always conclusive) form in the last annual report. Attention to working out experimental techniques during the year centered mostly on shaping the crystals and on difficulties encountered in the use of balanced filters.

Intensity vs. temperature measurements were extended to additional AgCl crystals including one doped specimen and, for a few reflections, to additional x-ray wavelengths.

One result is that the inflection previously found in the semi-log plots of intensity vs. temperature for the {111} reflection was found to be reproducible in both Eastman and Harshaw specimens. Both the inflection and a marked λ dependence of the intensity vs. temperature measurements for the {111} reflection are tentatively concluded to be due to defects.

Some attempts have been made to obtain an analytical expression for " A_v " the normalized temperature slope of apparent Bragg intensity, which

includes EDS (thermal diffuse scattering) effects and which might make possible the separate evaluation of the one-phonon and two-phonon contributions to the intensity vs. temperature measurements (and hence, also to individual apparent Bragg intensities). A preliminary expression indicates that EDS contributions to A can be eliminated by extrapolating A to $\sin \theta = \infty$. An extrapolation of this kind at 100° K has yielded a Debye Θ which is in excellent agreement with those calculated from published elastic constants and elastic wave velocities determined by EDS measurements of AgCl. The underlying validity of this $\frac{dI}{d\theta}$ method of obtaining information about thermal vibrations is felt thereby to be demonstrated, though many problems of the analysis are yet to be resolved.

The Debye Θ calculated from a temperature factor obtained by the usual isothermal x-ray method (based on change of apparent structure amplitude with $\frac{\sin \theta}{\lambda}$), was much higher, as would be expected as a result of a large EDS effect.

A number of points have been touched on sufficiently to indicate the potential interest they may hold, but, so far, have not been dealt with conclusively. These include the dependence of A on λ , on doping, and on temperature (relative occupation of acoustic and optic branches, anharmonicity, and the temperature dependence of the Debye Θ are of particular interest here), reflection to reflection differences (in A) which exceed sample to sample differences, possible anisotropy of A (both anharmonicity and anisotropic EDS effects are possibilities to be considered here), and improved methods of reducing and analyzing the data.

Solutions to many of the problems can be greatly aided by the accumulation of more data on more crystals so that statistically significant conclusions can be made about AgCl in general rather than only about particular specimens. The additional data plus added understanding of the expected functional form of I (apparent) vs. T , A vs. T , and A vs. $\frac{\sin \theta}{\lambda}$ should bring more success than has so far been encountered with analytic curve-fitting procedures.

While many of the problems remain unsolved, it has been possible to point out and in some cases to demonstrate many of the possibilities of the method used for investigating thermal motions. Furthermore, the additional exploratory experimental and analytic work done during the year has made it possible to indicate rather definitely and in some detail a program for future work aimed at bringing to conclusions the initial studies of many of the facets mentioned above.

A determination of the thermal coefficient of expansion of AgCl over the range 100°K to 300°K is being made, by an x-ray method, concurrently with and complementary to the I vs. T studies. A paper describing these preliminary measurements, which was presented by Mr. Nicklow at the April 1960 meeting of the Georgia Academy of Sciences, is included as Appendix A. Work continues on this determination to increase the temperature range, to assess the effect of x-ray produced defects, and to make more detailed comparisons with published and otherwise expected results.

The proposal for the Ph. D. dissertation of Mr. Nicklow which was accepted by the faculty of the Georgia Tech School of Physics is included as Appendix B.

X-RAY DIFFRACTION STUDIES OF THERMAL MOTIONS IN CRYSTALS

I. STATEMENT OF GENERAL PROBLEM

The general problem is the study, by x-ray means, of the thermal motions in crystals and their interactions with other phenomena of interest in crystal physics. Particular attention is directed to the temperature dependences of Bragg intensities.

II. SUMMARY OF FIRST YEAR EFFORTS

During the first year of the project, the necessary general literature search was made, specific initial problems were chosen and the method of attack, i.e., the method of basing analyses first on the slopes of Bragg (x-ray reflection) intensities versus temperature data and the principal methods to be used in collecting these data, were largely decided on. Exceptionally pure, single-crystal AgCl was chosen as the first specimen material. The general background of x-ray studies of thermal motions in crystals was investigated at some length. A considerable amount of effort was expended on both theoretical and experimental considerations regarding the choice and preparation of samples, the choice and operation of equipment, and the data collecting procedures to be used. A large number of possible sources of error were recognized and considered in some detail and experimental tests of some were made.

The attainable reproducibility of the measurements was shown to be excellent, some analytic and experimental devices for circumventing certain sources of error were suggested. The particular problem of determining a Debye- Θ from the temperature dependences of Bragg intensities was se-

lected as a first goal (because the results could so readily be compared with the results of totally different methods) and the possibility of obtaining a reasonable value for the Debye Θ in this way was demonstrated.

The above and various other topics were dealt with, in a frequently pedagogic form, in Annual Report No. 1. It was felt that there was a need for connecting and setting forth in one place and in some detail (1) discussions of relevant sections of the literature (including some textbooks) specially prepared from the point of view of x-ray studies of thermal motions in crystals, (2) developments and expositions of ideas that had accumulated as a result of the project director's previous experience with precision and temperature-dependence x-ray measurements but which had previously not been written down systematically, and (3) the results of the efforts of the first year's work in regard to precision measure of x-ray intensities, their temperature dependences, and the problem and methods of interpretation of those data. The first annual report was used as a convenient vehicle for fulfilling this need. As a result, a large part of the organization and writing effort on Annual Report No. 1 was actually a part of the second year's activity. The report is fulfilling its intended functions very well within our laboratory and several requests for copies have been received from persons in other parts of the country.

III. SUMMARY OF SECOND YEAR EFFORTS

A. Introduction

During this second year of the project, research was continued on the questions of (1) what information can be obtained from the temperature

dependences of the intensities of Bragg (x-ray) reflections, (2) how the data can and should be gathered and analyzed, (3) how the results compare with crystal physical and crystal chemical information obtained by other techniques, and (4) how these temperature dependences may be used in various studies of crystal physical phenomena.

The principal type of data collected was, again, the apparent maximum intensity of Bragg reflections as a function of specimen temperature. A stationary counter, stationary crystal method was used.

The principal instrumentation involved a scintillation counter mounted on a Weissenberg camera base. Ag, Mo, and Cu target x-ray tubes were used with and without differential filters and a pulse height analyzer.

Sample materials were restricted to single crystals of AgCl (both doped and "pure") and NaCl.

The various facets of the second year's activity are summarized below. The treatment of the various topics is generally brief; technical detail and much of the arguments are left, when appropriate, to be covered in a technical report which is expected to appear within the next year.

B. Instrumentation and Technique Factors

Several relatively minor points regarding instrumentation and technique were investigated.

By comparing I_p vs T (maximum or peak intensity, I_p , of a Bragg reflection vs specimen temperature, T) data collected with MoK_β radiation to that collected with MoK_α radiation for the same reflections ($\{600\}$ and $\{400\}$ of AgCl #7), it was shown that the temperature induced variation in the α -doublet separation produced no measurable effect on the I vs T data collected with this x-ray beam geometry.

It was shown that all of the peaks (i.e., plots of intensity as a function of diffracting angle at and near the Bragg angle) routinely observed with a typical AgCl specimen (# 7) were at least approximately flat at their maxima, but that the approximation to flatness seemed to depend on crystallographic direction. No further investigation of this point has yet been made.

With the aid of a rotation photograph of a typical specimen (AgCl # 7), it was shown that each of the diffracted beams observed was small enough to fall entirely within the counter window.

A "new" method of preparing spherically shaped crystals of AgCl was used with some success. The method consists of packing the usual sphere grinder, described in Annual Report # 1, in a dry-ice and alcohol bath while supplying nitrogen gas at near liquid nitrogen temperature to do the blowing. While the method is slow (bathing the sphere grinder in liquid nitrogen made the process even slower), it does seem to produce well shaped crystals free from significant distortion. One crystal of approximately 0.15 mm diameter prepared this way (AgCl # 11), after first being pre-shaped by controlled etching with photographic "hypo", was spherical to within ± 10 microns.

Some difficulties concerning the balancing and use of balanced filters were discussed in Annual Report No. 1. Additional difficulties were experienced this year, particularly in connection with attempting to balance a Ni-Co (actually Ni - Co_3O_4) pair for use with CuK_α . These may be fairly well balanced on the diffractometer, using a large NaCl crystal as a specimen. When this pair is used on the counter-adapted Weissenberg, with a small spherical specimen of NaCl, the results indicated in Figure 1 are

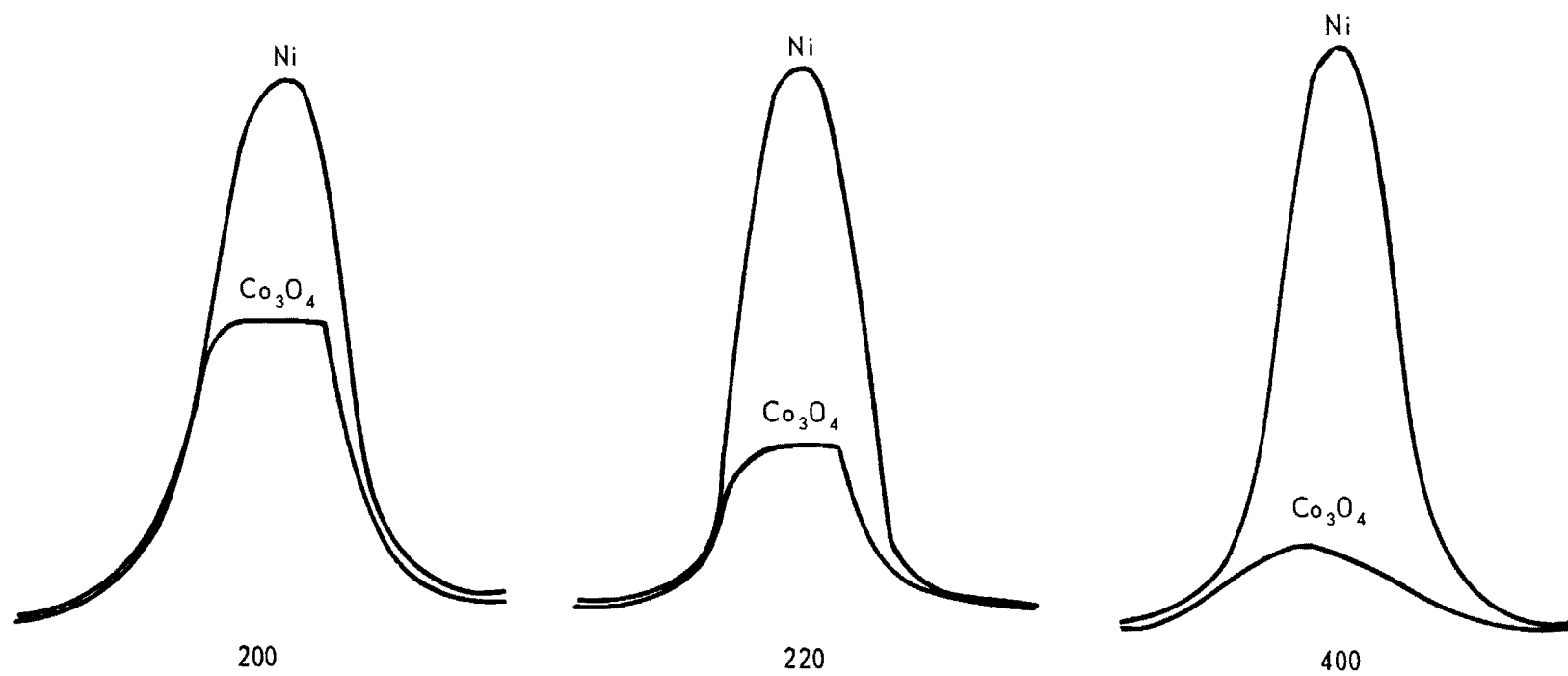


Figure 1. Peak Characteristics with "Balanced Filters" and Cu Radiation.

typical. A similar effect was observed with the (111) of AgCl.

The {400} result is about what one would expect as normal behavior. The use of a pulse height analyzer did not significantly change the character shown in Figure 1. While a number of possible causes for the unexpected behavior have been considered, both Compton scattering and a $\lambda/2$ contribution seem to be ruled out, even though lowering the applied voltage to the x-ray tube to 12 KV did make the (200) look approximately like the (400) in Figure 1. It is hoped that the performance of the several more tests now in mind will provide the basis for an adequate explanation of the unexpected behavior of the (200) and (220) with Co filtered Cu radiation.

C. Thermal Coefficient of Expansion of AgCl

The thermal coefficient of expansion of AgCl was determined as a function of temperature over the range 100°K to 300°K. The determinations were made with an x-ray method on the same materials used for the I vs T studies. Three papers ^{2, 3, 4} exist which deal with dilatometric measurements of the thermal coefficient of expansion of AgCl; none have been found which deal with x-ray measurements of this coefficient. Mr. Nicklow, the graduate student associated with the project, reported on our results and their comparison with theory and the work of others above room temperature^{3,4} at the April, 1960 meeting of the Georgia Academy of Sciences. The paper dealing with the low temperature region² did not become available to us until later. The text of the paper as Mr. Nicklow delivered it is presented in Appendix A. Some further data are being collected on more crystals, on a doped crystal, and at temperatures above room temperature. The collected x-ray results and comparisons of them with the dilatometric

results^{2,3,4} in the literature will probably be offered as a note to a scientific journal.

D. Specificity of I vs T data

As is exemplified by Figure 2, the I vs T data for a particular reflection were shown to be quite reproducible from specimen to specimen even though the specimens came from different sources. (Specimen 10 came from the very pure Eastman material, Specimens 7 and 11 came from commercially available Harshaw material.) This reproducibility is such that detailed behavior of the data, such as the temperature dependence not merely of I, but of dI/dT can be investigated as a function of specimen type.

The dependence of the I vs T data on x-ray wavelength and on specimen doping were investigated mostly with respect to the (111) reflections. The (111) studies will be discussed as a separate topic.

The (400) reflection of a doped (5 ppm of Cu) AgCl specimen seemed to show a slightly larger dI/dT than is typical for undoped specimens. However, since only this one reflection (besides the (111)) of one doped specimen has been examined so far, it is not yet possible to state whether doping actually affects the thermal vibration to an extent measurable by our technique. Many more measurements are planned.

The possible dependence of the I vs T data on x-ray wavelength was checked for two AgCl and one NaCl reflections besides the (111). For the (400) and (440) reflections of undoped AgCl, specimen # 7 there seemed to be little or no differences among the data collected with AgK_{α} , MoK_{α} , and CuK_{α} radiations. For the (440) of an NaCl crystal, however, dI/dT observed with CuK_{α} radiation in the range below 200°K was slightly smaller than that observed with AgK_{α} , though in the range from 200° to 300°K, the

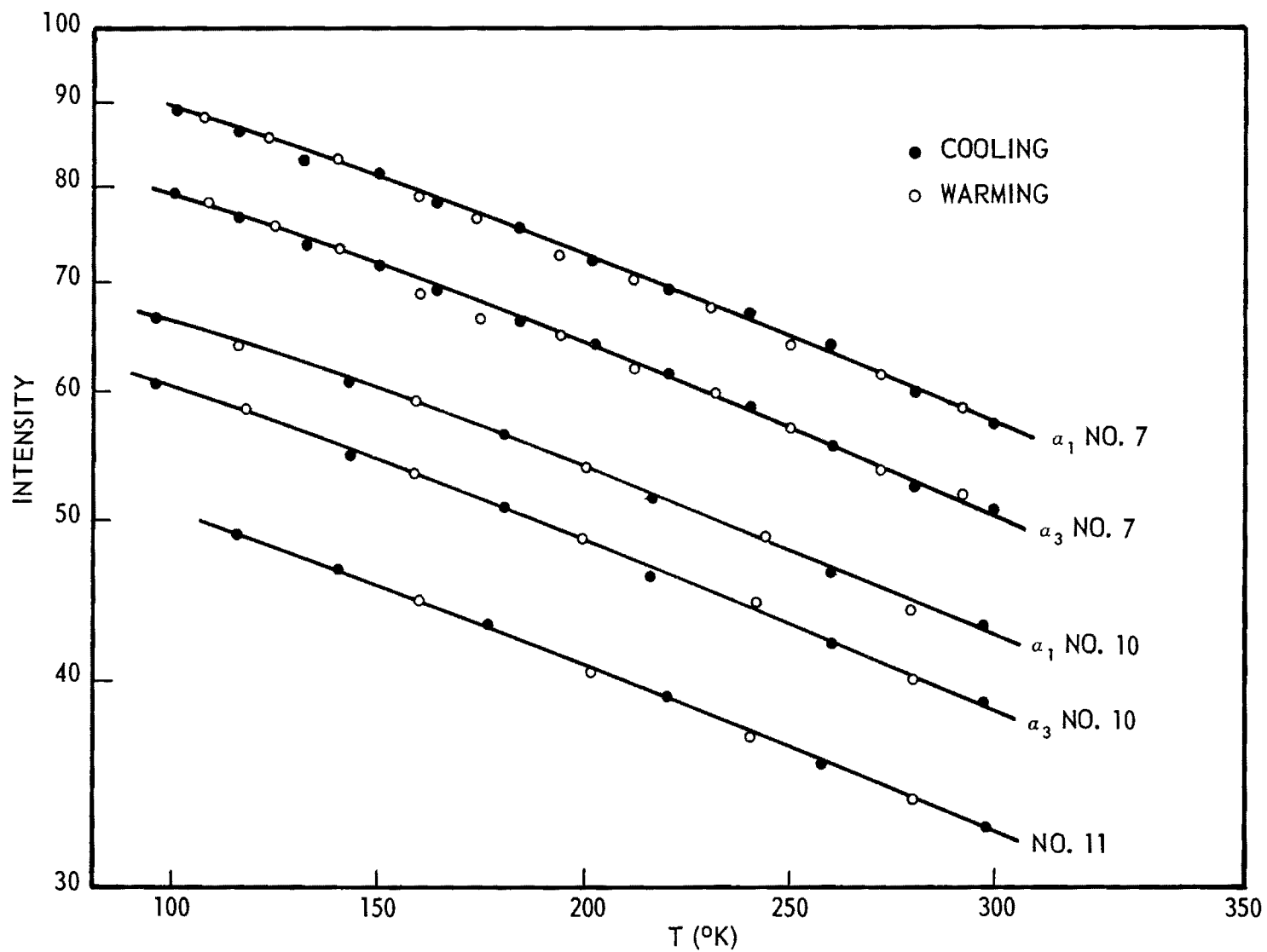


Figure 2. Temperature Dependence of Intensities, Sample to Sample Comparison of the (400) Reflection.

results differed by less than 3%. Further investigation of the wavelength dependence of the dI/dT results is planned.

E. Behavior of the {111} Reflection

The character of the temperature dependence of the (111) Bragg reflection has been investigated in some detail. The inflection in the I vs T data, reported for one crystal in Annual Report No. 1, was found to occur reproducibly with both Eastman and Harshaw specimens when MoK_α radiation was used. Two possible causes have seemed most likely: (1) the form factors were changing due to a temperature dependence of bond character or (2) the temperature dependence of the equilibrium population of the defects caused by the investigating x-ray beam was responsible. Directly pertinent information of other types, such as dielectric constant data, are desirable to determine if there is any significant temperature dependence of bond character. Less directly relevant quantities, the optical absorption⁵ and electron mobility⁶, show no unusual character in the neighborhood of the temperature at which the inflection in the (111) has been observed. No low frequency dielectric constant data for the temperature range of interest have been found.

I vs T measurements made with reduced intensity of the MoK_α , with AgK_α , and with CuK_α radiation and measurements made on a doped crystal did not, because of poorer counting statistics, definitely establish the presence or absence of the inflection in each case. However, the large slope obtained with CuK_α radiation, shown in Figure 3, the lack of x-ray wavelength dependence of the (400) and (440) data, and the fact that the longer wavelength is less penetrating (and therefore is expected to have a higher cross section for defect-producing interactions

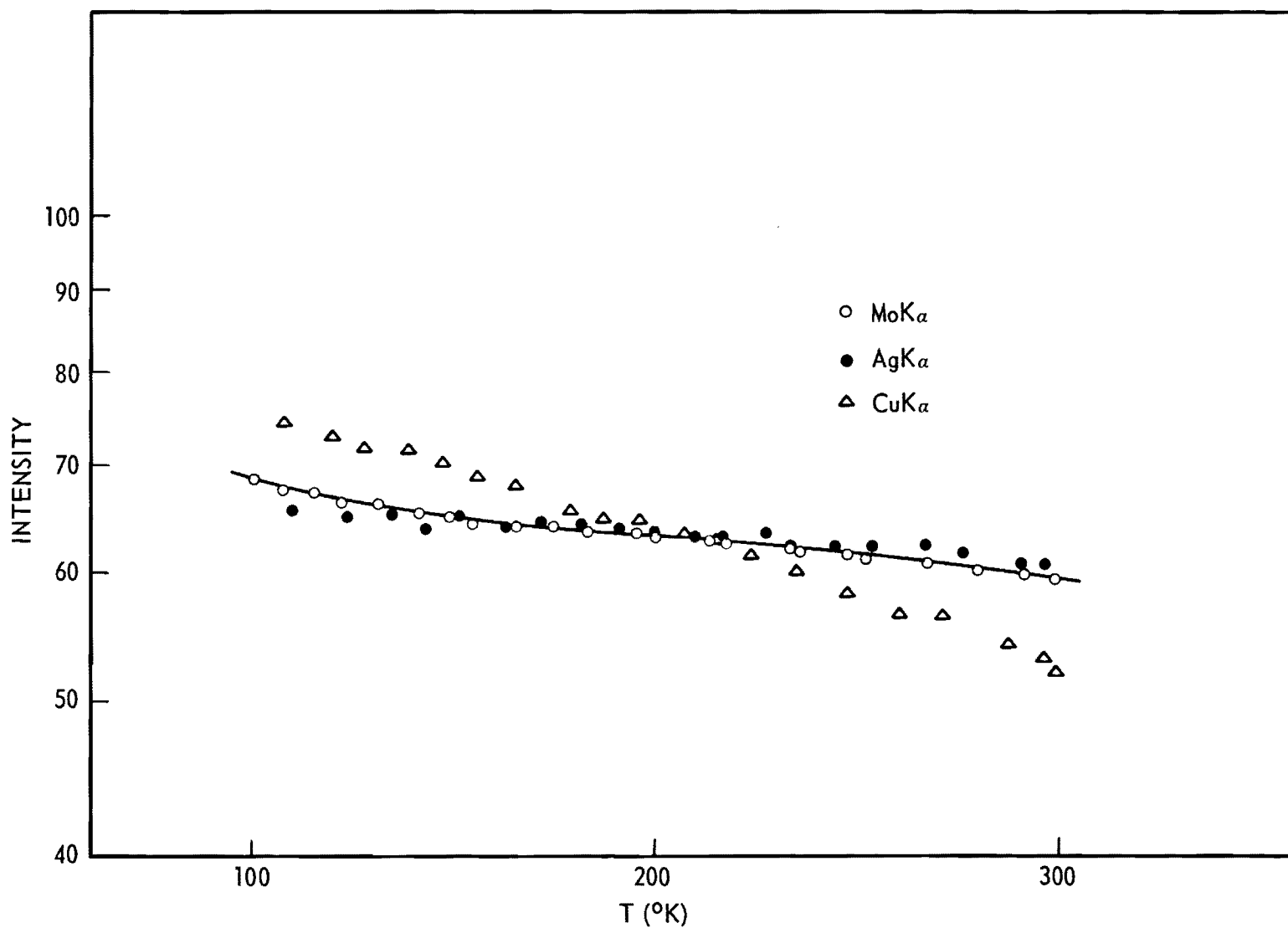


Figure 3. Dependence of Log I vs T Plot for the (111) Reflection on λ , Sample No. 7.

with the crystal) suggest that x-ray induced defects in a surface layer are responsible for at least some of the peculiarities of the (111) behavior. It seems most likely that the unexpected part of the (111) behavior is due to the effect of x-ray produced defects on the outer electron configuration; it seems unlikely that the relatively small difference in the effective thickness of the diffracting layer for the (111) and (400) could account for a surface thermal vibration effect being observed in the former case and not the latter. However, the origin of the difficulties encountered in attempts to balance filters for CuK_{α} radiation (shown in Figure 1) should be determined before any conclusions are based on the data collected with CuK_{α} radiation, whether or not collected with a balanced filter technique.

Further studies on these points are contemplated.

F. Studies of "A"

1. Introduction

Much of the work during the year dealt with the information obtainable from the slopes, dI/dT , of the I vs T data. In order to facilitate comparisons among reflections, it was convenient to use the normalized slope, A, defined in Annual Report No. 1 by

$$A = -\frac{1}{2} \frac{\frac{d}{dT} (\ln I)}{(\sin^2 \theta)/\lambda^2} \quad (1)$$

where θ is the Bragg angle and λ is the x-ray wavelength. In the first order approximation this is expected to be the same for all reflections of a cubic crystal. In many cases A is approximately equal to dB/dT where B is the usual, overall x-ray temperature factor (though it need not, in

this usage, be isotropic). All A values used in this report were determined graphically. Some results are shown in Figure 4.

While results are still statistically incomplete, it appears in Figure 4 that there are reflection-to-reflection differences which exceed sample-to-sample differences in the A values of pure AgCl, particularly at the higher temperature. A-values determined from measurements previously made in this laboratory on NaCl (Project E-173) also showed apparent differences among reflections. Further measurements of the reflection-to-reflection differences are planned (1) to put the present observations about AgCl on statistically firmer ground and (2) to ascertain whether similar differences occur with other materials.

2. TDS Contributions and Best Average A

A thermal diffuse scattering (TDS) contribution to the intensity data is recognized. Partially successful attempts have been made both to eliminate and to evaluate the effect of the separate TDS contributions by use of their expected $\frac{\sin \theta}{\lambda}$ dependence. The expected one-phonon and two-phonon contributions are given by the second and third terms, respectively in

$$I_A = I_B \left| 1 + k_1 T \frac{\sin^2 \theta}{\lambda^2} + k_2 \left(T \frac{\sin^2 \theta}{\lambda^2} \right)^2 \right| \quad (2)$$

where I_A is the apparent Bragg intensity, I_B is the true Bragg intensity, and k_1 and k_2 are very slowly varying functions of temperature and are expected to depend on $\frac{\sin \theta}{\lambda}$ only through the geometry of the particular experimental arrangement. Equation (2) is rewritten from one given by Ramachandran and Wooster⁷ and stated by them to apply to acoustic vibrations. Combining (1) and (2) gives A_c , the result expected for A in the presence of

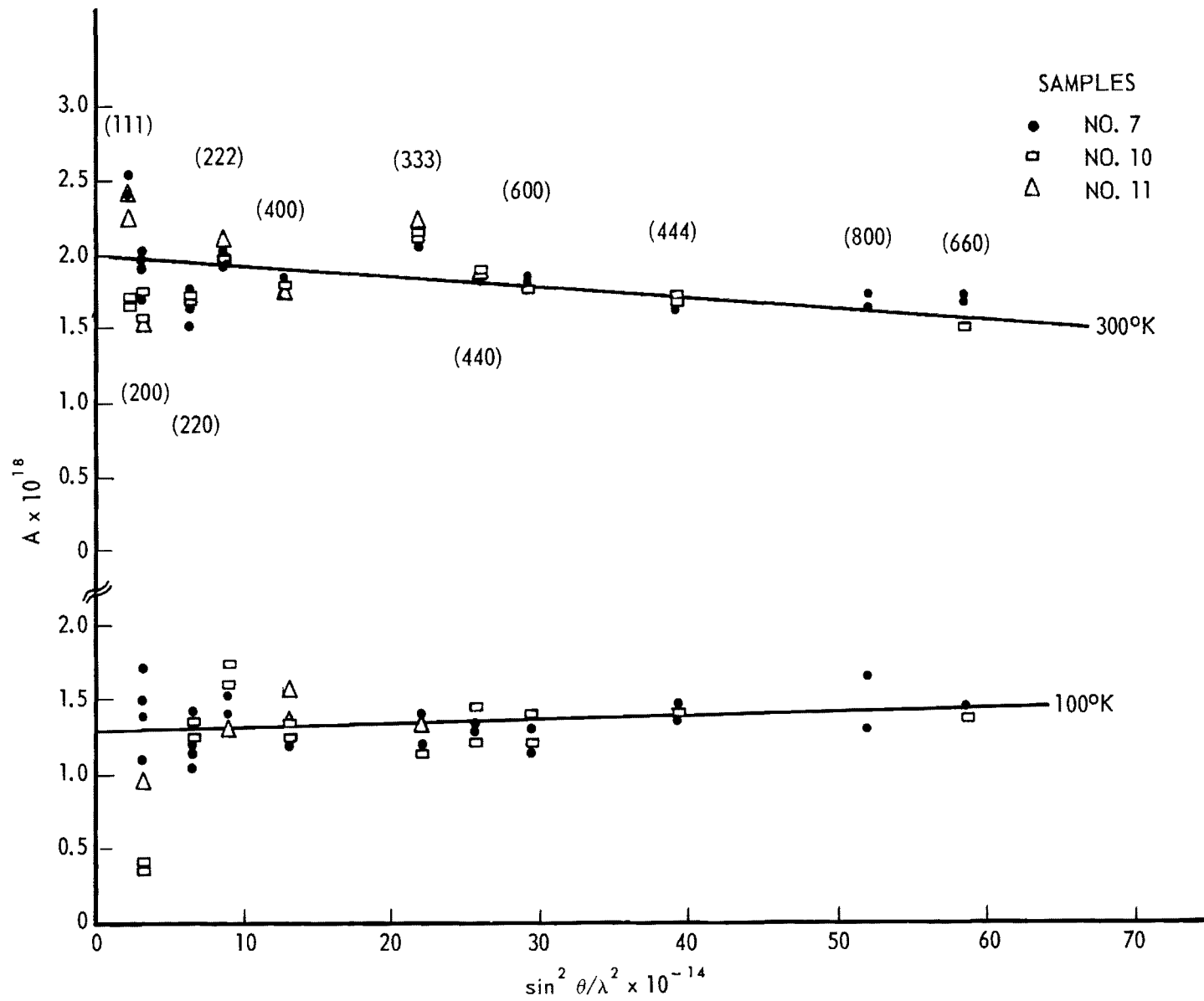


Figure 4. Dependence of A on $\sin^2 \theta / \lambda^2$.

one- and two-phonon contributions:

$$A_c = \frac{dB}{dT} = \frac{\frac{1}{2}k_1 + k_2 T \phi}{1 + k_1 T \phi + k_2 T^2 \phi^2} \quad (3)$$

where

$$\phi = \frac{\sin^2 \theta}{\lambda^2} \quad (4)$$

It was because of the type of dependences shown in Equation 2 that the A values from various reflections were plotted against $\frac{\sin^2 \theta}{\lambda^2}$. As is shown by Figure 4, trends with $\frac{\sin^2 \theta}{\lambda^2}$ do exist, even though real reflection to reflection deviations from a smooth monotonic trend also seem to exist. Equation (3) shows that the best average value of A exclusive of TDS contributions will be obtained by extrapolating the best curve through the various A values to $\frac{\sin^2 \theta}{\lambda^2} = \infty$. In Figure 5 the 100° K data of Figure 4 are replotted against $\left(\frac{\sin^2 \theta}{\lambda^2}\right)^{-1}$ in order to facilitate this extrapolation. To the degree to which Equation (2) accounts for the TDS contribution to the apparent Bragg intensity, and to which the extrapolated curve has the correct functional form, the effect of TDS has been eliminated by the extrapolation. Extrapolation to $\frac{\sin \theta}{\lambda} = 0$, on the other hand, leads to an average A in which there is a one-phonon, but not a two-phonon TDS contribution. This analysis indicates that it is possible, in principle, to obtain dB/dT, k_1 , and k_2 separately from the plots of A values, provided that the dependence, if any, of k_1 and k_2 on $\frac{\sin \theta}{\lambda}$ are known. The dB/dT term contains what is probably the principal thermal vibration information; the determination of k_1 and k_2 , allows calculation of both the one-phonon and the two-phonon contributions to the apparent Bragg intensities. These are also of interest for themselves

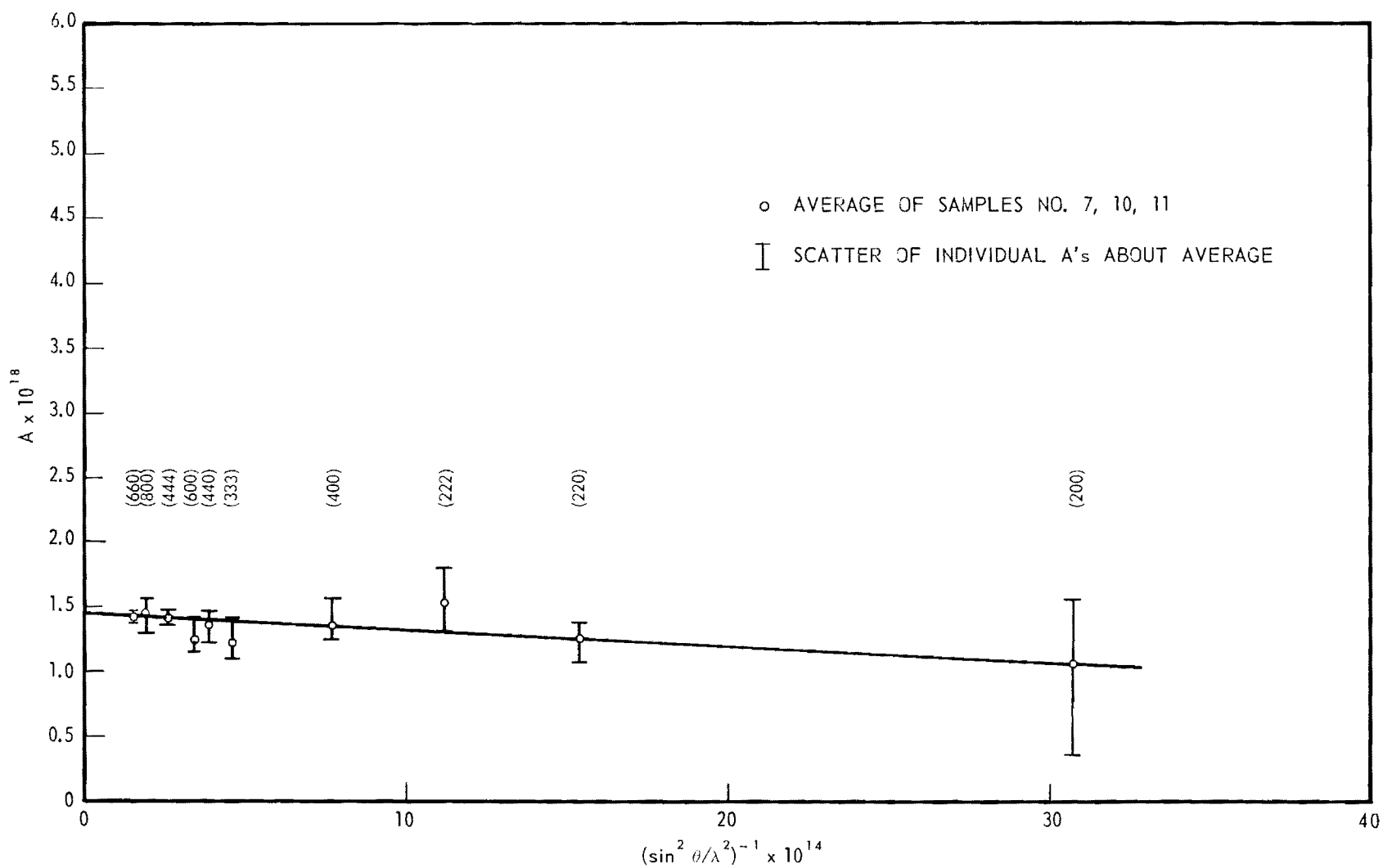


Figure 5. The Dependence of A on $(\sin^2 \theta / \lambda^2)^{-1}$ at 100° K.

because of their origins in thermal vibrations. Further, a means of making corrections for the TDS contribution to apparent Bragg intensities is of considerable importance in all studies in which accurate structure factors must be deduced from observed relative intensities. This is a requirement which takes on increasing importance as studies are carried out at higher temperatures and as more crystal structural detail and crystal physical information are sought by x-ray means. Given sufficient reflections, the procedure could be carried out as a function of direction - an interesting point in itself. Though the point has not been examined, it seems on the face of it that knowledge of k_1 and k_2 for our method should allow calculation of the equivalent quantities for integrated intensity measurements on both single crystals and powders.

At the moment the weakest point in the method described for handling the TDS contribution has to do with the scatter of the A values about a simple smooth curve. It may be that something in the geometry of our experimental arrangement causes k_1 and k_2 to depend on the particular reflection. A critical analysis of this point is planned. It may be that there are other factors, not yet considered, which cause the reflection to reflection deviations from a simple curve. Perhaps an analytic means of determining A from the I vs T data will substantially reduce the scatter. It may be that a better functional form for A vs $\sin^2 \theta / \lambda^2$ (or its reciprocal) can be used for fitting the experimentally determined A values. These points are to be examined. To some extent, the value of the method, even as used, is attested to by the good value for the Debye Θ that was thereby obtained. The Debye Θ determination will be discussed separately, where the sizeable effect of the TDS contribution on the value obtained by the usual, isothermal x-ray method will also be pointed out.

3. Temperature Dependence

The observed temperature dependence of the normalized slope, A, Figure 4, has not been wholly explained on the basis of the theory applied so far. As was shown in Annual Report No. 1 (P. 39), $\frac{dB}{dT}$ is expected to decrease with decreasing temperature. (The temperature dependence of the Debye Θ , which depends in part on the volume expansion of the crystal, makes a small contribution to $\frac{d^2B}{dT^2}$ at low temperatures.) Thus it is to be expected that A at 300°K is larger than A at 100°K. The expected difference $\left[\Theta (100^\circ\text{K}) - \Theta (300^\circ\text{K}) \right]$ due to volume expansion has not yet been calculated, because of lack of knowledge of the thermal coefficient of expansion. It is estimated that this factor alone will produce no more than a 10%, and probably only about a 5%, increase in A (300°K) over A (100°K). The observed difference at $\sin \theta = 0$ is about 20%. Part of the difference between 10% and 20% may be due to an explicit temperature dependence of the Debye Θ , part may be simply experimental error, part may be due to occurrence of more anharmonicity in the thermal vibration at 300°K, and part may be due to changes in the relative amplitudes or energies of the Ag and Cl thermal vibrations.

The observed temperature dependence of $\frac{dA}{d(\sin^2 \theta / \lambda^2)}$ has not yet been explained. Investigation continues of the application of the dependence predicted from Equation (3)

$$\frac{dA}{d\phi} = \frac{k_1^2 T \left\{ \frac{2k_2}{k_1^2} (k_1 T \phi + k_2 T^2 \phi^2 - 1) + 1 \right\}}{2(1 + k_1 T \phi + k_2 T^2 \phi^2)^2} \quad (5)$$

where again we have written ϕ for $\sin^2 \theta / \lambda^2$. Lack of knowledge of the magnitudes of k_1 and k_2 and in particular, of whether or not they are effectively the same for all reflections, has so far hampered our investigation of such

questions as whether the apparent 300°K to 100°K change in sign of $dA/d\phi$ is to be expected.

It is noted that the fact that the A vs ϕ slope at 100°K in Figure 4 appears to be positive may be due to errors in obtaining the data and drawing the curve. As more data are gathered and better curve fitting procedures are used, it is quite possible that $dA/d\phi$ at 100°K will be shown to be zero or even slightly negative.

G. Debye Θ

1. Debye Θ for AgCl

It was shown in Annual Report No. 1, that with certain assumptions a "Debye - Θ " could be obtained from dI/dT of a single reflection at a single temperature.

A Debye- Θ for AgCl has been determined from the best extrapolated A (Figure 5) so far obtained at 100°K. It is believed that the result, shown in Table I, is essentially free of TDS contributions.

The arithmetic average of the Ag and Cl masses was used. As is shown in the table, our Debye- Θ is in good agreement with those calculated from Arenberg's elastic constants⁸ (by the method of Quimby and Sutton¹⁰, and Sutton¹¹), and from Cole's elastic wave velocities⁹ determined from x-ray TDS measurements.

For comparison purposes, the x-ray temperature factor, and hence a Debye- Θ , were determined from the dependence of relative integrated intensities (all at room temperature) on $\frac{\sin^2 \theta}{\lambda^2}$. The reduced data are shown in Figure 6 where the slope of the best straight line yields the temperature factor. It is noted that, except for the (111) and the (333), the r.m.s. deviation from the straight line is no greater than about 1%. There do not

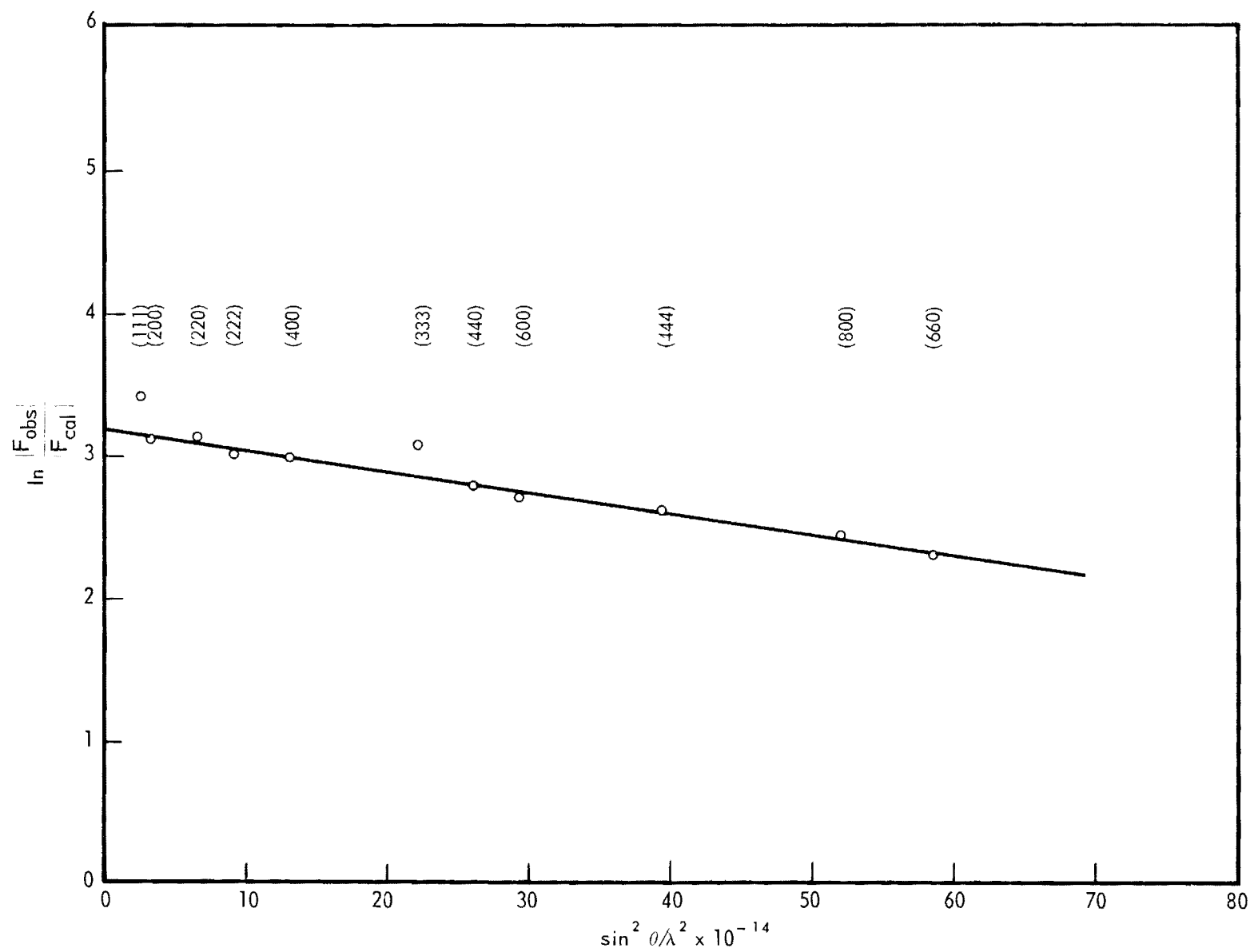


Figure 6. Dependence of $\ln \frac{|F_{obs}|}{|F_{cal}|}$ on $\sin^2 \theta / \lambda^2$, Sample No. 7

seem to be reflection-to-reflection differences similar to those noted in the temperature dependences. (The (111) and (333) deviations are not explained, neither choice of form factors nor absorption errors account for them. Though it does not seem likely at this point, extinction may be responsible.)

The effect of TDS on these isothermal measurements, which is expected to be large¹², is probably responsible for most of the differences between the Debye- Θ result (178° K) determined from these isothermal measurements and those obtained from the TDS, elastic constants, and dI/dT (at 100° K) measurements.

A rough estimate of Θ at 300° K may be obtained from the $\sin \theta = 0$ intercept of the curve through the 300° K data in Figure 4. $\Theta \approx 126^\circ$ K was so obtained. However, the scatter in the 300° K data is rather worse than it is in the 100° K data and, as shown by Equation (3), the one-phonon TDS contribution is not eliminated by this procedure. Hence the value should not be taken seriously except to note that it is smaller than the TDS-free 100° K value, as one would expect (Equation (3)). This value is included in Table I. A value determined by others¹³ from specific heat data is also included.

TABLE I
Debye- Θ Values

<u>Reference</u>	<u>Quantity Measured</u>	<u>Temperature</u>	<u>Θ (°K)</u>
Arenberg ⁸	Elastic Constants	300° K	145.3
Cole ⁹	TDS	300° K	144.3
Present Work	dI/dT	100° K	145
Present Work	dI/dT	300° K	~ 126
Present Work	Isothermal Relative	300° K	178
Blackman ¹³	Specific Heat	~ $\Theta/12$	133

It is felt that the agreement among the first three entries in Table I is significant and demonstrates the underlying validity of our approach to obtaining information from I vs T data.

2. Separate, Pseudo - Θ 's for Ag and for Cl

Several attempts were made to obtain a separate "Debye- Θ " for each atom type by using a computer to fit the intensity data to

$$\sqrt{\frac{I}{G}} = K (f_1 e^{-M_1} \pm f_2 e^{-M_2}) \quad (6)$$

where K is a scaling constant, I is the observed intensity at temperature T, G contains all the geometric factors (which change very little over the temperature range used), f_1 and f_2 are the atomic form factors of Ag and Cl, respectively, the minus applies to reflections with odd indices, and M_i is the Debye-Waller temperature factor for the i^{th} atom type. It contains Θ both explicitly and implicitly (see Annual Report No. 1 or the paper delivered at the January, 1960 ACA meeting for further discussion of M).

In principle, it would seem possible to determine the best Θ_i values by letting them be the adjustable parameters in a least squares procedure. Our computer programmer points out that an ill-conditioned matrix has so far defeated all attempts with a digital computer. The services of an analog computer were tried with equal lack of success. With this computer, the vitiating factor was the 1% internal precision in the instrument. Further attempts at curve fitting with the I vs T data will be made, but not until a different and more promising approach has been chosen. (Fitting to a polynomial, for example, will be tried only as a last resort).

H. Other Information From A vs $\frac{\sin^2 \theta}{\lambda^2}$ Plots.

As can be inferred from Equations (6) and (1), unless $M_1 \approx M_2$, the value of A obtained for a particular reflection would depend on whether its indices were even or odd. Since no systematic dependence of this type is evident in the 100°K data of Figure 4, it is concluded that M_2 is nearly equal to M_1 and hence the vibrational amplitudes of the Ag and Cl atoms are nearly the same. If the vibrational amplitude of the chlorine atom becomes greater than that of the silver atom, as one might expect would occur at higher temperatures, the A values from odd indexed reflections would be the smaller ones. At 300°K, it is possible that the (111) and (333) A -values, Figure 4, are instead larger than the others, but the scatter in the data permit no significant observations.

Evidence of anharmonicity in the thermal vibrations was sought by looking for a directional dependence in A . (In a cubic crystal harmonic vibrations can produce only an isotropic x-ray temperature factor.) The data are plotted separately for each of the three principal directions [100], [110], and [111] at 100°K in Figure 7 and at 300°K in Figure 8. While the data are fewer than are desirable, nonetheless 3 different samples (2 Harshaw and one Eastman) are represented. There does appear to be a directional dependence at 300°K (Figure 8), but not at 100°K (Figure 7). Even if the odd-index reflections are ignored in Figure 8, a slightly larger value of A at $\sin \theta = 0$ seems indicated for the [111] direction.

However, no such directional dependence is apparent in the (normalized) relative intensities at 300°K (Figure 6). In order to reconcile the apparent anisotropy in Figure 8 with the lack of it in Figure 6 on the basis of the TDS contributions, a peculiarly fortuitous circumstance would have to be

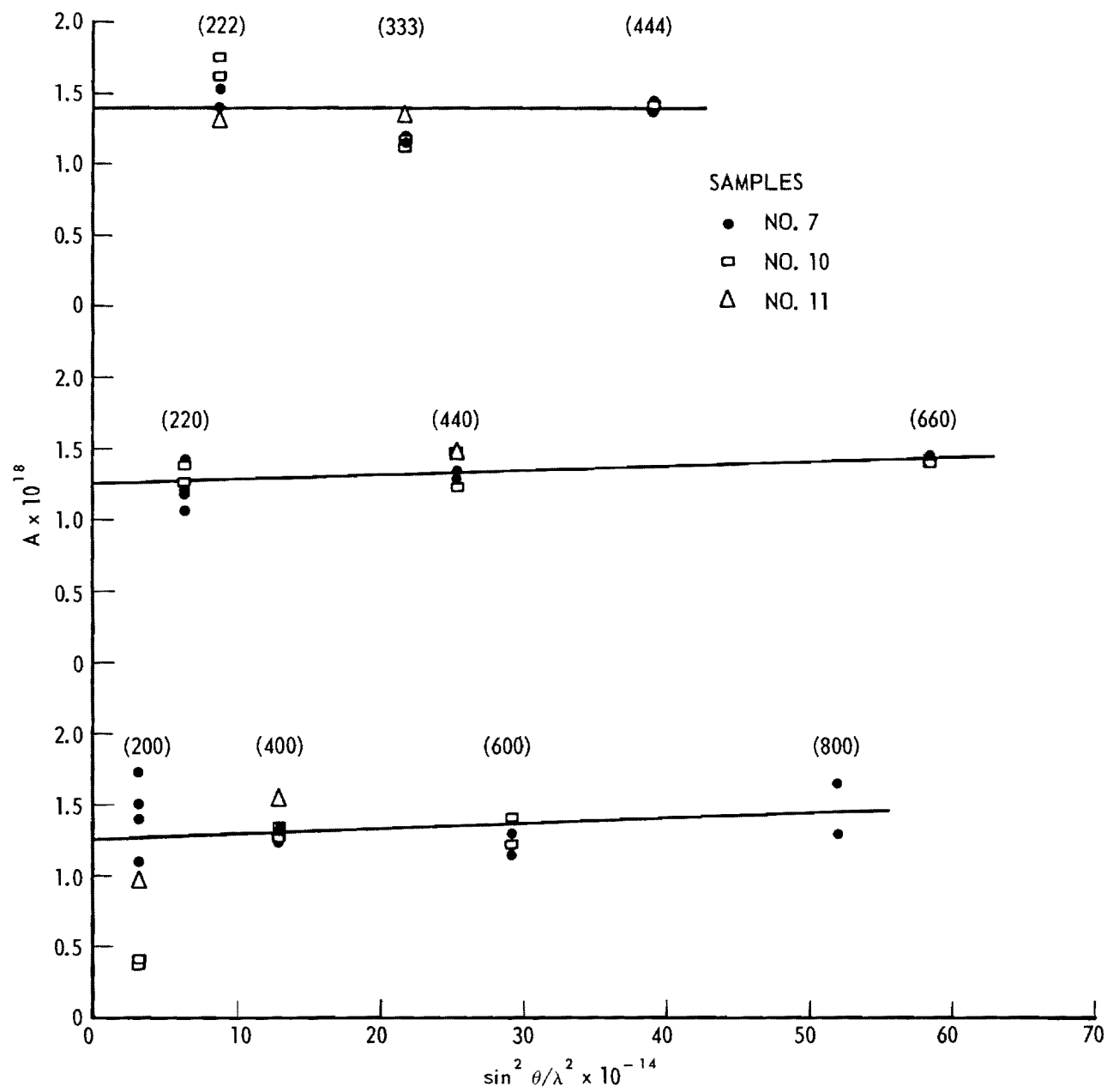
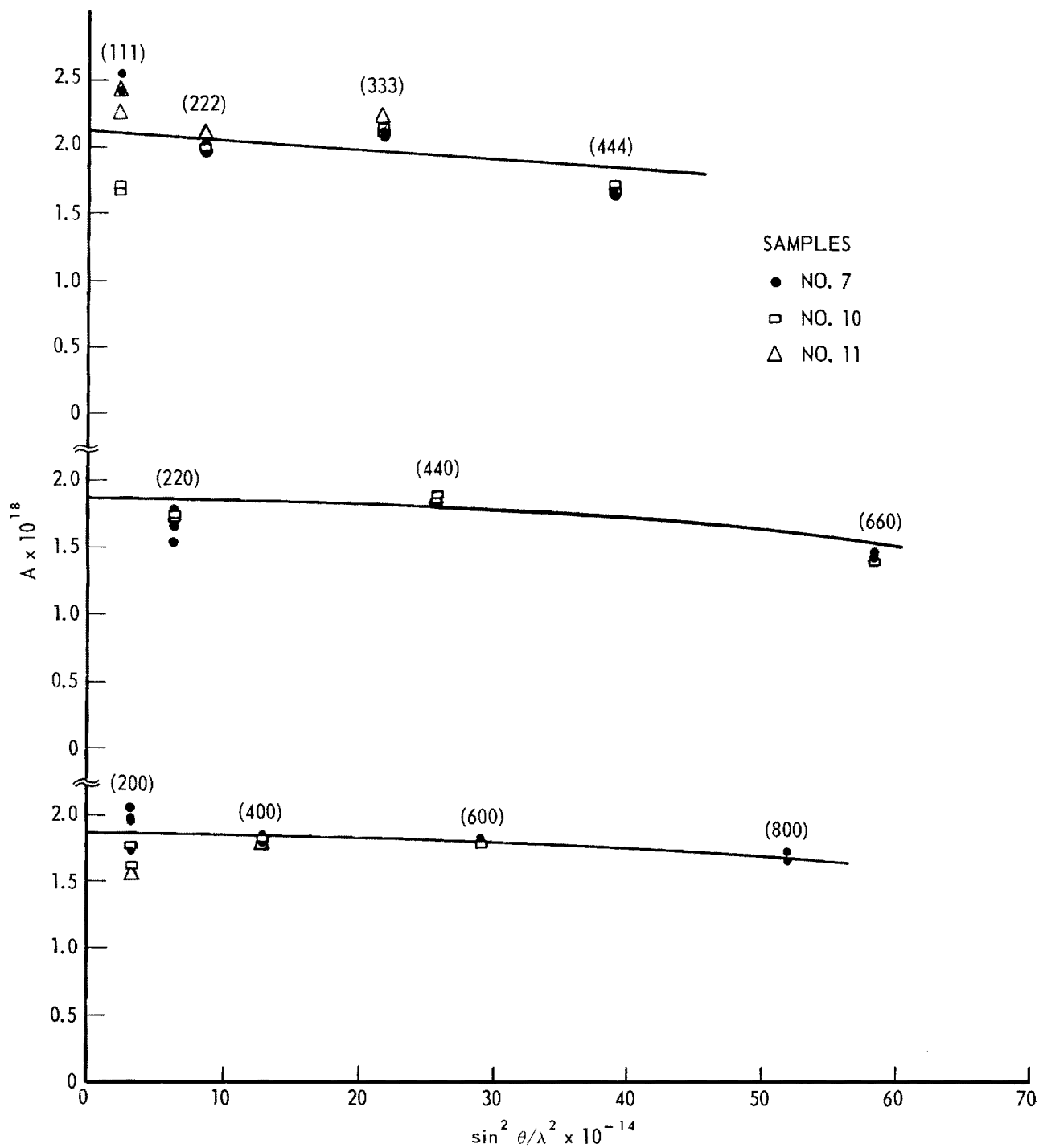


Figure 7. Dependence of A on $\sin^2 \theta / \lambda^2$ at 100° K .



invoked: the fractional TDS contribution to the apparent Bragg intensity would have to be directionally dependent (which in itself seems reasonable), but at the same time the sum of the true Bragg intensity and the TDS contribution would have to be directionally independent. Whether or not this last point is reasonable has not yet been investigated. When further investigation of these differences is made, it will necessarily consider not only the intensity distribution in the reciprocal space of the crystal, but also its relation to the geometry of the sampling method used in each case.

If, in Figure 8, the A-values from the (111) and (333) reflections are ignored, on the basis that they are not directly comparable to A-values from reflections of even index because of differing Ag and Cl vibration amplitudes, the apparent directional dependence of A is based on observations of the (222) reflection alone. The strong agreement among (222) A-values from the 3 samples, however, makes it worthwhile to pursue both the possibility of detecting a real anisotropy and other reasons for differences among reflections which are greater than the differences among samples for a particular reflection. It would seem that there should be considerable information to be gained from demonstrating real reflection-to-reflection differences if they are due to characteristics of the sample material.

I. Miscellaneous Observations

It was noted that the doped AgCl crystal (No. 12), which was never exposed to light other than a red safe-light, visibly fluoresced in the x-ray beam with an intensity which increased with decreasing temperature. The point has not as yet been pursued.

J. Possibilities of the dI/dT Method

Various possibilities of the method were apparent at the outset of

this study, others have become apparent as the work has progressed. Some were stated in Annual Report No. 1. The following are a number of those possibilities which now seem most feasible.

1. The I vs T data, including dI/dT as a function of temperature, are useful parameters to follow as a function of specimen and experimental conditions and may yield the temperature dependence of the condition followed. Examples of such uses are:
 - a. Sample characterization.
 - b. Temperature dependence of bond character.
 - c. Temperature dependence of defect concentration.
 - d. Effect of defects on thermal vibrations.
 - e. Effect of impurities on thermal vibrations.
 - f. Separation of distortion and thermal vibration contributions to the apparent Debye-Waller temperature factor.
 - g. Effect of lattice distortions on thermal vibrations and the temperature dependence of this effect.
2. Debye- Θ values may be determined. For NaCl type structures, at any rate, these points apply:
 - a. A sometimes useful value can be obtained from the temperature dependence (dI/dT) of a single reflection.
 - b. A Debye- Θ value free of errors due to TDS contributions to apparent Bragg intensities can now be obtained from dI/dT measurements on several reflections in some cases. It will probably be possible to obtain such a value in all cases after the present work has progressed further.

- c. Since the Debye- Θ 's determined as in (a) and (b) above correspond to a particular temperature, the temperature dependence of the Debye- Θ may be obtained.
3. Debye-Waller temperature factors at low temperatures, and hence thermal vibration information, may be much more easily determined by the dI/dT method than by the more usual method involving the $\frac{\sin^2 \theta}{\lambda^2}$ dependence of structure amplitudes.
 4. The dI/dT method (actually $\frac{d(\ln I)}{dT}$) shows promise of detecting the breakdown of the Debye assumptions (principally those to the effect that the atomic thermal vibrations are harmonic and that the distribution of normal modes in "k-space" is parabolic) by means of the temperature and directional dependence of the quantity, A , defined by Equation (3).
 5. It seems possible that the constants required for calculations of the separate effects of one-phonon and two-phonon contributions to individual apparent Bragg intensities can be determined from analyses of the A values. Further work on this point is required.
 6. There may be additional details of character in the I vs T data, not so far accounted for, which can yield additional information about the specimens. The dI/dT method is particularly suited to pointing up details of character and to allowing determination of the various quantities studied to be made as continuous functions of temperature.

IV. PLANS FOR FUTURE WORK

A. Introduction

It is now possible to estimate fairly specifically what will be required to bring to some kind of conclusion several of the phases of the work now in progress. These phases provide a convenient framework for detailing the program for future work. The topics are not necessarily arranged in order of priority. The recognition of these problems and the development of these detailed plans for attack on them, constitute a part of the year's work. The program for future work is therefore presented in considerable detail.

B. Balanced Filter Problem

Attempts will be made to find the cause of the difficulties experienced in attempts to balance a Ni-Co filter pair. It is imperative that the cause be identified and its relation, if any, to the large $\frac{dI(111)}{dT}$ values observed with $\text{CuK}\alpha$ radiation be ascertained. A possible connection with the inflection observed in the $I(111)$ vs T data with $\text{MoK}\alpha$ radiation will also be kept in mind.

C. Determination of A

1. Individual Values

A function is needed to which the I vs T data can be fitted by a systematic procedure (e.g. least squares) and which can be differentiated to yield A . The best function would include one-phonon and two-phonon TDS contributions and separate thermal vibration parameters for each atom type. Efforts to obtain or to recognize such a function will be continued. A simple polynomial will be used only as a last resort.

In order to improve the statistics in the determination of A for each reflection, dI/dT data will be collected from two additional pure AgCl specimens. Data on crystals already examined in part will be rounded out so that dI/dT data on all observable (hkl) reflections of 5 "pure" AgCl samples will be on hand.

The effect of extinction and any other factors which prevent our dI/dT measurements from being valid measures of $\frac{d|F|^2}{dT}$ will continue to receive consideration. Some experimental tests for extinction may be performed. Particular attention will be given to the apparent directional dependence of peak "flatness" noted for one sample.

2. Average Value

A systematic, analytic curve fitting procedure is desired for fitting the A vs $\frac{\sin^2 \theta}{\lambda^2}$ data. The functional form to be used should allow valid extrapolations to $\frac{\sin \theta}{\lambda} = 0$ and to $\frac{\sin \theta}{\lambda} = \infty$. It will certainly include the expected behavior of the TDS contributions, which is herein discussed separately. If no acceptable function can be found, a simple polynomial will be used as a last resort. Least squares procedures will probably be employed with the help of a high speed digital computer. The range in $\frac{\sin \theta}{\lambda}$ of the dI/dT data will be extended. Separate A vs $\frac{\sin^2 \theta}{\lambda^2}$ curves for different directions may be required.

Some (hkl) data, $k \neq h$, will be collected in order to improve further the placement of the A vs $\frac{\sin^2 \theta}{\lambda^2}$ curve. Further, (hkl) data corresponding to directions close to the $[111]$ direction may give additional evidence for or against the existence of an anisotropic average A. Other averaging procedures may also be considered.

D. Interpretation of A-Value Results

Plans for further study of the TDS contributions to apparent A-values and of the determination of Debye- θ 's from I vs T data are discussed separately.

The question of reflection-to-reflection differences will be examined further. When the planned full sets of (hhl) dI/dT data for 5 AgCl crystals are available, the question of reality of apparent reflection-to-reflection differences can be better examined. Real differences will be compared with those found in other crystals, e.g. NaCl and AgBr, particularly if they are not accounted for by TDS effects. The significance of any reflection-to-reflection differences (including the temperature dependences of the differences) still remaining after TDS, vibrational anisotropy, and the differences in Ag and Cl vibrational amplitudes (or Na and Cl or Ag and Br) are accounted for will be particularly sought.

The question of possible anisotropy in the A-values will be further examined with the advantage of better statistics, better curve fitting procedures, data on farther out reflections of the (hhh) type, and data on (hkl) reflections corresponding to directions near to [111].

The possible dependence of both the analytic procedures used and the utility of the results on sample material will be considered. Some A-values and possibly Debye- θ 's will probably be obtained for NaCl and AgBr in order to allow comparison in this respect.

The temperature dependence of (1) the individual A's, (2) the average A's, (3) the shape, slope, and placement of the best A vs θ curve, and (4) directional differences (if any) will receive particular attention. Attempts will be made to explain the observations. In addition to TDS, the effects

of such things as the temperature dependence of Θ , anharmonicity in thermal vibrations, differences in the Ag and Cl thermal vibration amplitudes, and the temperature dependence of these differences (particularly if not predicted by a simple parabolic elastic spectrum) are to be considered.

E. TDS Contributions to Apparent Bragg Intensities

1. Elimination of TDS Effect on \bar{A} At Any One Temperature

Attempts will be made further to improve the extrapolation procedure, which now seems capable of yielding an average A value (\bar{A}) free of TDS effects, by considering in more detail the TDS contribution to individual reflections.

The expected dependence of the TDS contribution on $\frac{\sin^2 \theta}{\lambda^2}$ will be critically examined, especially with regard to the relation between the reciprocal spatial distribution of TDS intensity and our detection geometry. A particular question to be settled is whether or not k_1 and k_2 (Equation (2)) do in fact depend on $\frac{\sin \theta}{\lambda}$ for our experimental arrangement. Another particular question is whether there is any directional dependence of the TDS effect on A.

It is expected that the improved knowledge of how the TDS effect should vary from reflection-to-reflection and the more and better data will make possible a fruitful curve fitting procedure. The best procedure and best data obtained will be used to determine the TDS-free A values at 300°K and other temperatures of interest.

2. One-Phonon and Two-Phonon TDS Contributions to Apparent Bragg Intensities

The possibility of determining usable values of k_1 and k_2 (Equation (2)) by extrapolation, first to $\sin \theta = \infty$ and then to $\sin \theta = 0$, will be

further explored. If the dependence of the k 's on choice of reflection is found to be simple or non-existent, improved data and improved knowledge of the expected TDS contribution should make possible the determination of valid k 's. These k 's will be used to correct the individual A values for TDS effects. Better averaging of the A 's and more critical examination for anisotropy and other reflection-to-reflection differences will thereby be made possible.

Efforts will be made to deduce the quantitative relations between the TDS contributions found in the dI/dT method and the TDS contributions to apparent Bragg intensities observed with other experimental geometries, e.g. integrated intensities obtained from rocking curves.

A number of points involving the TDS contributions to the individual A values are of interest. These include (1) the degree of responsibility of TDS for reflection-to-reflection differences, including apparent anisotropy and detailed character of the best A vs $\frac{\sin^2 \theta}{\lambda^2}$ curve (comparisons among crystals with different Debye Θ 's will be of interest here) (2) the question of what thermal vibration information may be obtained from a knowledge of the TDS one-phonon and two-phonon contributions themselves (3) the contribution of TDS effects to the apparent temperature dependence of the individual A 's and the best A vs $\frac{\sin^2 \theta}{\lambda^2}$ curve (4) the nature of and information to be obtained from temperature dependence of the one-phonon and two-phonon contributions themselves, including the temperature dependence of k_1 and k_2 (5) the comparison of the TDS effects on measurements and results of the dI/dT method with those of the isothermal relative intensities method (a convenient check point will be the best Debye Θ obtained with each method) and (6) the possibility of making other applications of the knowledge of k_1 and k_2 .

F. Debye Θ

The problems of determining Debye Θ 's from x-ray measurements and of interpreting the results will be given further attention. The best average A-values, presumably free of TDS effects, will be used to determine the best single Θ for AgCl at each of several temperatures. The observed temperature dependence will be compared with that expected from the volume dependence discussed by Paskin¹⁴. Knowledge of the thermal expansion and the Gruneisen constant will be required.

Further attempts will be made to obtain separate " Θ 's" (actually only convenient parameters and not Debye Θ 's at all) in several ways including the following:

- (a) Further attempts will be made systematically to fit the I vs $\sin^2 \theta / \lambda^2$ data of single reflections to Equation (6); separate " Θ 's" for Ag and for Cl will be the adjustable parameters in this procedure. Hopefully, the TDS contribution will be removed from the data used. In any event, the individual results will be plotted against $\frac{\sin^2 \theta}{\lambda^2}$ in an effort to improve the average over several reflections. The calculated volume dependence of Θ , necessarily based on knowledge of the thermal expansion and the Gruneisen constant, will be included.
- (b) The possibility of obtaining separately the Ag and Cl temperature factors by comparison of dI/dT results for even-indexed reflections with those for odd indexed reflections will be further investigated. The additional data on $(hk\ell)$ reflections for which $k \neq h$ will be of value here.

More study is required on several problems concerning the propriety of procedures used or assumptions made in determining Debye Θ 's in our work. These include

- (a) the proper method for averaging individual, pseudo- Θ 's (i.e., the parameters which take the same place in individual x-ray temperature factors, M_i , for individual atom types that the Debye Θ does in the x-ray temperature factor, \bar{M} , for a reflection) to yield the recognized Debye Θ (this will include a detailed consideration of how, for present purposes, \bar{M} , depends on the M_i 's)

- (b) the method to be used for averaging atomic masses.

This will depend on the method of averaging the pseudo Θ 's, the manner in which \bar{M} depends on the M_i 's, and the relative vibrational amplitudes of the different atom types. Clearly the latter may be temperature dependent as the relative occupation of the different branches of the elastic spectrum is expected to be temperature dependent.

G. Thermal Expansion of AgCl

Some additional work on the x-ray measurements of the thermal expansion of AgCl is desired if the results are to be offered for publication even as a note. Measurements will be made on at least two reflections from a doped (5 ppm of Cu) AgCl crystal from 100°K to 300°K to see if the thermal expansion depends significantly on small variations in crystal purity. A number of the data already collected below room temperature will be re-checked. At least two reflections of an undoped crystal will be followed up to about 300°C. The d vs T (d is the interplanar, or Bragg spacing) data will be fitted

to a 4th order polynomial by a least square procedure. The results for the thermal coefficient of expansion as a function of temperature and a critical comparison of our results with those obtained dilatometrically by others^{2,3,4} will be offered for publication as a note or similar short communication. The results will be used in calculation of the expected temperature dependence (due to volume expansion) of the Debye Θ .

H. Possible Effects of Defects.

A number of possible effects of crystal defects on the I vs T data and the results obtainable from observation of these effects will receive consideration. All of the effects may have an apparent temperature dependence because the equilibrium population of defects may be temperature dependent. The following effects are specifically included.

1. Effect on thermal vibrations.

An effect on the force constants and hence the vibration amplitude is expected.

2. Effect of "static" displacements on the temperature factor.

Displacement of the equilibrium positions of the atoms due to the presence of defects is expected to increase the apparent zero-point energy and hence the apparent temperature factor at any temperature. If the defects take up positions that are ordered along certain crystallographic directions, an apparent anisotropy in A-values could result. Data taken from far out in reciprocal space will be most valuable here.

3. Effect on apparent atomic form factors.

If the defect concentration is high enough in the irradiated volume, an observable effect might be produced on the outer electron con-

figuration. A temperature dependence of the magnitude of the effect, due to a temperature dependence of the equilibrium population of defects, will produce an apparent temperature dependence of the atomic scattering factor. This is most likely to be observed with the reflections which occur nearest the origin of reciprocal space.

4. Effect of doping.

The expected observation is that doping will enhance the other effects due to defects.

5. Effect on dependence of results on x-ray wavelength.

It is expected that the more strongly absorbed radiation produces a higher concentration of defects in that volume of the material with which most of the radiation does interact. As long as the incident photons have an adequate energy which is near an absorption edge, it is expected that the various effects of x-ray produced defects will be more noticeable with the longer wavelength x-rays. An apparent angular dependence of the wavelength dependence may be produced if, as seems likely, defects are more easily produced near the surface of the specimen.

I. {111} of AgCl

Further studies will be made relative to the dI/dT behavior of the (111) reflection of AgCl. While it now seems probable that the observed behavior is due to defects, additional information on the temperature dependence of other physical properties will still be sought in order to rule out the possibility of a temperature dependence of the normal bond character. Knowledge of the effect, if any, of the x-ray beam on the temperature dependence of the apparent dielectric constant would be of

considerable interest in interpreting the $dI(111)/dT$ data. However, the experimental difficulty of making the measurements, particularly since the specimen should be of such size and shape that the radiation field remains quite strong throughout its volume, make the task too large to be performed as a part of the present program. One of the questions that will be investigated is whether or not the inflection noted in the I vs T data collected with MoK_{α} radiation is due to the same cause as is the large dI/dT values found with CuK_{α} .

J. Other Points

1. X-Ray Wavelength Dependence of dI/dT

In addition to that caused by defects, there may be a dependence of the dI/dT results on x-ray wavelength for other reasons. Extinction effects and their possible temperature dependence will be kept in mind. Some direct tests for the presence of significant extinction should be performed at some time during the program. This does not appear to be a pressing problem at the moment.

Because of the wavelength dependence of the effective penetration depth, certain surface effects may produce an apparent wavelength dependence of the dI/dT data. The principal surface effect expected is a change in the thermal vibration amplitudes due to distortions near the surface. A possibility which will be considered during the next year is that of making electron diffraction I vs T measurements analogous to those now made with x-ray diffraction. The very small penetration of the electron might make possible observation of surface effects on the thermal vibrations due simply to the proximity of the surface. The angular dependence of the wavelength effect and the dependence of A vs T on wavelength for various

reflections are points particularly to be investigated experimentally.

Comparisons, in respect to the wavelength dependence of the results, among pure AgCl, doped AgCl, and NaCl specimens will also be made.

2. Isothermal Data

Additional data on the best relative intensities (from AgCl) at 300°K will be gathered. The observed deviation of the (111) and (333) intensities from the pattern of the others (Figure 6) will be investigated in respect to reproducibility, occurrence at 100°K, and reason for occurrence. The most nearly spherical crystals will be used to minimize the influence of absorption, the possible existence of significant extinction will be examined, and comparisons will be made with the best set of A-values in an effort to ascertain the reason for the (111) and (333) behavior. Collection of relative intensity data from powdered material will be considered.

K. Time Required and Technical Report

Not all of the above outlined investigations will be brought to a conclusion during the course of the next year. However, it is hoped that enough conclusions can be reached so that a Technical Report can be issued in about 9 months. The report will deal with much the same material discussed in the paper delivered at the January ACA meeting, but will present the material in a more conclusive form. For example, the questions of reality of reflection to reflection differences, of the existence of anisotropy in A, of the Debye Θ at 300°K, and of the reason for the inflection in the {111} I vs T data should be fairly conclusively answered in the report.

V. LONG RANGE PLANS

A. Ph.D. Dissertation

As has been pointed out in the past, Mr. R. M. Nicklow is basing his dissertation for the Ph.D. degree in physics on project work. The dissertation proposal which he submitted for the approval of the Graduate Faculty of the School of Physics is reproduced in Appendix B.

B. Further Studies

Long range plans for future work include continued investigation of the question of what can be learned from the temperature dependence of Bragg intensities, extension of the studies to a variety of other crystals and to temperatures above room temperature, and extension of the method to the study of various crystal physical phenomena for themselves.

Defects, particularly those constituting radiation damage, may provide a fruitful field for investigation with the dI/dT method. A study of surface vibrations, particularly as the melting point is approached and as a function of various specimen treatments and contaminants, may also be an especially fruitful field for investigation through observation of the temperature dependence of Bragg intensities. It would seem that electron, rather than x-ray diffraction, would be most appropriate for such studies. The possibilities for making the necessary quantitative measurements are to be explored during the coming year with just such a long range prospect in mind.

VI. RELEVANT PAPERS THAT APPEARED DURING THE YEAR

The two papers which have come to our attention during the year as being most closely related to our work are those by Chipman¹⁵ and by Roof¹⁶. They are related in that determinations of Debye Θ 's were made from I vs T

data. The approaches used have been quite different from ours, though. Chipman has made use of the temperature dependence of Bragg intensities in a very nice determination of the temperature dependence of the Debye Θ of aluminum, lead, and β -brass. He makes corrections for TDS; he follows only one reflection; his analysis uses incremental differences rather than slopes; and he uses powdered specimens. He finds a temperature dependence of Θ beyond that predicted from its volume dependence.

R. B. Roof has made use of I vs T data to determine the Debye Θ of PuO_2 . A powdered specimen was used. No corrections for TDS were made. The treatment of the data amounts to fitting it to

$$I_{T_2} = I_{T_1} e^{-2(M_{T_1} - M_{T_2})} \quad (7)$$

where I_T is the intensity at temperature T and Θ is the single, adjustable parameter in M_T , the x-ray temperature factor at temperature T . Θ is apparently assumed to be independent of temperature. Observations were made on several reflections at several temperatures and the agreement among the results for the various reflections is good.

VII. OTHER ACTIVITIES OF PROJECT PERSONNEL

Mr. Nicklow, the graduate student associated with the project, attended the Cornell meeting of the American Crystallographic Association (July, 1959), delivered a paper on one aspect of project work (reproduced in Appendix A) at the Georgia Academy of Sciences meeting (April, 1960), and gave a seminar (May, 1960), at a regular, weekly, School of Physics seminar in which he summarized progress to date on the project, and pointed out some of the next steps which would be taken and which would be a part of his dissertation.

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The attendance at a major meeting, the delivery of the paper, and the delivery of the seminar talk were each the first of their kind of activity for him. As such, they conveniently point out some of the contributions of this project to graduate training.

The principal investigator attended one meeting at project expense, The Washington meeting of the ACA in January, 1960, at which he delivered a paper "Temperature Dependence of Bragg Intensities: Debye Θ of AgCl", a report on project work. Copies of the paper were appended to Quarterly Report No. 6, 11 March 1960.

Respectfully submitted,

R. A. Young
Project Director

Approved:

27 September 1960

Vernon Crawford
Head, Physics Branch
Physical Sciences Division

REFERENCES

1. Young, R. A., "X-Ray Diffraction Studies of Thermal Motions in Crystals" Annual Report No. 1, Project A-389 EES, Georgia Institute of Technology, ONR Contract NONr 991(00) and 991(06); NR 017-623 (1959).
2. Sreedhar, A. K., "Thermal Expansion of Crystals at Low Temperatures," J. Indian Inst. Sci. A36, 186 (1954).
3. Sharma, S. S., "Thermal Expansion of Crystals," Proceedings of the Indian Academy of Science 32A, 268-74 (1950).
4. Strelkow, P. G., "Die Wärmekonstanten Bie Hohen Temperaturen," Physik. Zeits. Sowjetunion 12, 77-82 (1937).
5. Gilleo, M. A., "Photoemission from Silver into AgCl, KBr, NaCl, and New Bands of Photosensitivity in AgCl," Physical Review 91, 534-542 (1953).
6. Brown, F. C., "Electron Mobility in AgCl," Physical Review 97, 355 (1955).
7. Ramachandran, G. N., and Wooster, W. A., "Determination of Elastic Constants of Crystals from Diffuse Reflexions of X-rays I Theory of Method," Acta Crystallographica 4, 335-344 (1951).
8. Arenberg, D. L., "Determination of Elastic Constants in Single Crystals with Especial Reference to Silver Chloride," Journal of Applied Physics 21, 941-2 (1950).
9. Cole, H., "Approximate Elastic Spectrum of Acoustic Waves in AgCl from X-ray Scattering," Journal of Applied Physics 24, 482-7 (1953).
10. Quimby, S. L., and Sutton, Paul M., "Computation of Mean Debye Temperature of Cubic Crystals from Elastic Constants," Physical Review 91, 1122-26 (1953).
11. Sutton, Paul M., "Computation of Mean Debye Temperature of Cubic Crystals from Elastic Constants," Physical Review 99, 1826-30 (1955).
12. Nilsson, Nanny, "On the Corrections of the Measured Integrated Bragg Reflections due to Thermal Diffuse Scattering," Arkin för Fysik XII, 247-257 (1957).
13. Blackman, M., "The Theory of Specific Heat of Solids," Reports on Progress in Physics 8, 11-40 (1941).

14. Paskin, Arthur, "A Reformulation of the Temperature Dependence of the Debye Characteristic Temperature and its Effects on Debye-Waller Theory," Acta Crystallographica 10, 667-669 (1957).
15. Chipman, D. R., "Temperature Dependence of the Debye Temperature of Aluminum, Lead, and Beta Brass by an X-ray Method," preprint, portions presented in paper No. 42, Pittsburgh Diffraction Conference, Pittsburgh, Pennsylvania, November, 1958.
16. Roof, R. B., "An Experimental Determination of the Characteristic Temperature for PuO_2 ," paper No. 3, Pittsburgh Diffraction Conference, Pittsburgh, Pennsylvania, November, 1959.

APPENDIX A

THE THERMAL COEFFICIENT OF
EXPANSION OF AgCl BETWEEN
 100°K and 300°K

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Presented at the April, 1960 Meeting
of the Georgia Academy of Sciences
in Athens, Georgia

Research Performed on Project A-389 Under
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With the Office of Naval Research

THE THERMAL COEFFICIENT OF EXPANSION
OF AgCl BETWEEN 100°K and 300°K

by R. M. Nicklow and R. A. Young

INTRODUCTION

The thermal coefficient of expansion, α , of AgCl was required in connection with the interpretation of data collected in a current x-ray diffraction study of thermal motions in crystals. The value of the coefficient was required as a function of temperature over the range 100° to 300°K.

A search of the literature revealed no measurement of α for AgCl below room temperature. Measurements have been made, however, on polycrystalline AgCl by S. S. Sharma^{A1}, and on single crystal AgCl by P. G. Strelkow^{A2} at temperatures above room temperature. The measurements of Sharma and Strelkow agree very well.

The x-ray diffraction study of thermal motions in crystals is being made on small single crystal AgCl samples. It was therefore desirable to measure α for small single crystals of AgCl, making it convenient to use an x-ray diffraction method for the measurement of α as a function of temperature between 100°K and 300°K and as a function of crystallographic direction. It was thought that if the x-ray beam produced defects at preferred locations in the crystal, the α might have an apparent dirrectional dependence.

THEORY

The definition of the thermal coefficient of expansion in terms of the distance, d , between a set of Bragg planes is

$$(1) \quad \alpha = \frac{1}{d} \frac{dd}{dT} \quad \text{where} \quad T = \text{temperature.}$$

If (1) is substituted into

$$(2) \quad \frac{d\lambda}{dT} = 0 = 2 \frac{dd}{dT} \sin\theta + 2d \cos\theta \frac{d\theta}{dT}$$

where

λ = wave length

θ = Bragg angle

the temperature derivative of Bragg's law, the following is obtained for α ,

$$(3) \quad \alpha = - \cot \theta \frac{d\theta}{dT}$$

here θ = Bragg angle at temperature T.

EXPERIMENTAL PART

The measurements were made on a rod shaped AgCl single crystal (sample # 13), approximately 1 mm long and 0.5 mm in diameter, using either Cu or Cr radiation and a General Electric XRD5 x-ray unit equipped with a single crystal orienter (Goniostat).

Cu radiation was used for reflections of high Miller indices, and Cr radiation was used for those of low Miller indices so that θ and hence $\Delta \theta$, would be maximized.

The sample was cooled by a cold stream which consisted of a variable mixture of dry nitrogen gas at liquid nitrogen temperature and dry air at room temperature. The stream temperature was monitored by a thermocouple to within $\pm \frac{1}{2}^\circ \text{K}$.

The maximum intensity of a reflection at each temperature was determined after optimization of the crystal orientation. The Bragg angle of the reflection was determined by arithmetically averaging the angles, on either side of the maximum, at which 90% maximum

intensity was observed. The method is illustrated by Figure A 1. While cooling the sample, 2θ was determined at temperatures separated by 20° intervals and while warming, 2θ was determined at 20° intervals interspaced with the cooling set. Thus, values of 2θ were obtained at 10° temperature intervals between 100°K and 300°K .

RESULTS AND DISCUSSION

Data Collected

Figure A 2 is a plot of the data collected for the (444) reflection of AgCl sample #13. The maximum deviation of the data points about the smooth curve shown is less than .1%.

2θ versus temperature data were collected from the (400), (600), (220), (440), (222), and (444) reflections of AgCl sample #13 making possible the determination of $\alpha(T)$ in each of the three principal crystallographic directions. Differences in $\alpha(T)$ determined from reflections in the same direction provide a measure of experimental error.

Data Reduction

$\Delta\theta/\Delta T$ was determined graphically by measuring the slope of the best curve fitted to a plot of the data at temperatures differing by 10° intervals between 100°K and 300°K . α was then calculated at each of these temperatures by multiplying $\Delta\theta/\Delta T$ by $\cot \theta_0$, where θ_0 was evaluated at 0°C . Since $\cot \theta$ changed less than 1% over the entire temperature interval, the use of $\cot \theta_0$ seemed justified.

Figure A 3 is a plot of $\alpha(T)_{\text{ave}}$ versus temperature where $\alpha(T)_{\text{ave}}$ is the average of the individual $\alpha(T)$'s obtained from the above six reflections. The average was taken because there appeared to be no consistent variation of α with crystallographic direction. The vertical lines represent the rms deviation of the individual α 's from α_{ave} and amounts to approximately 1% at 300°K and 10% at the lower temperatures.

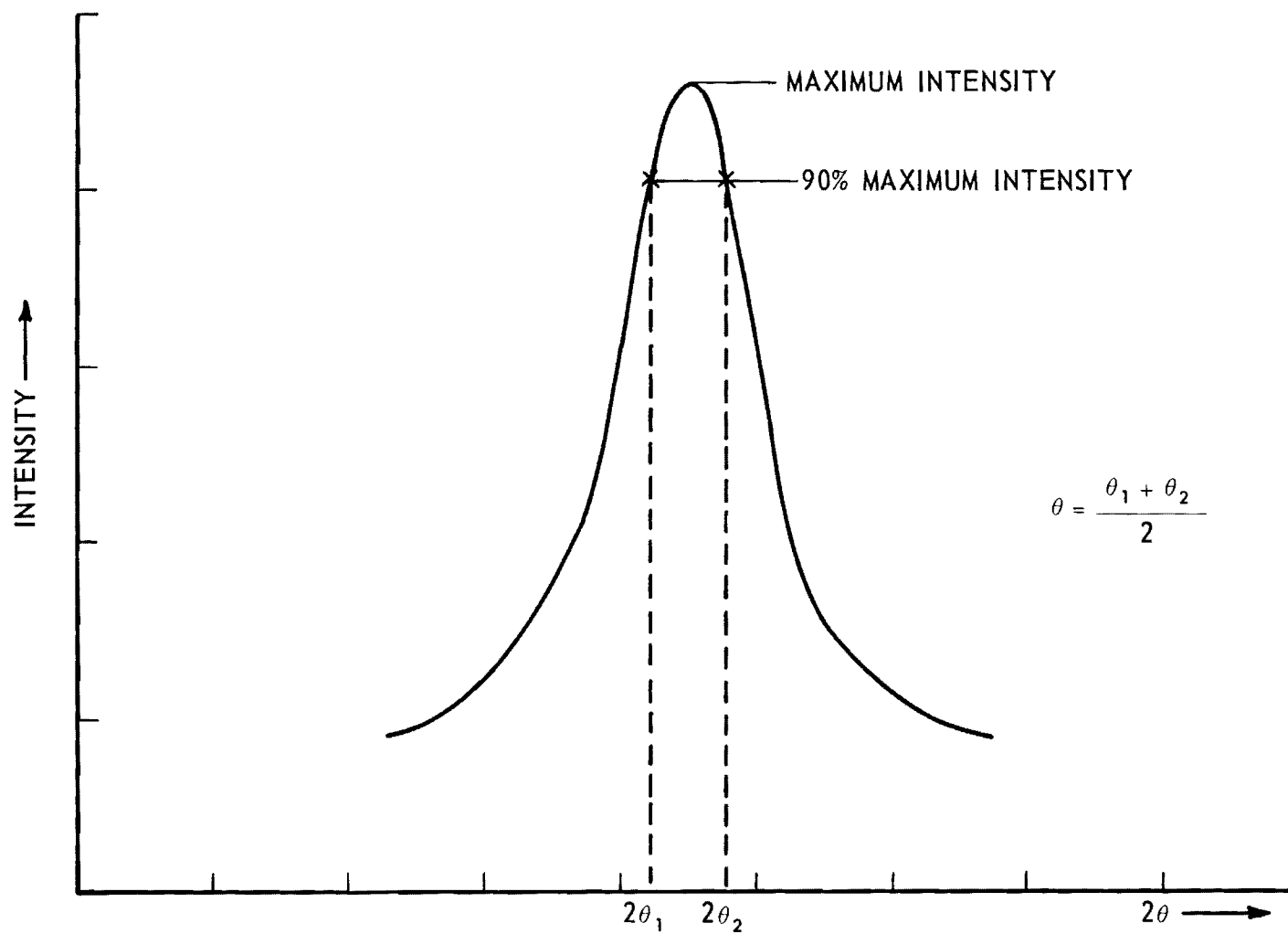


Figure A1. Determination of Diffraction Angle, θ .

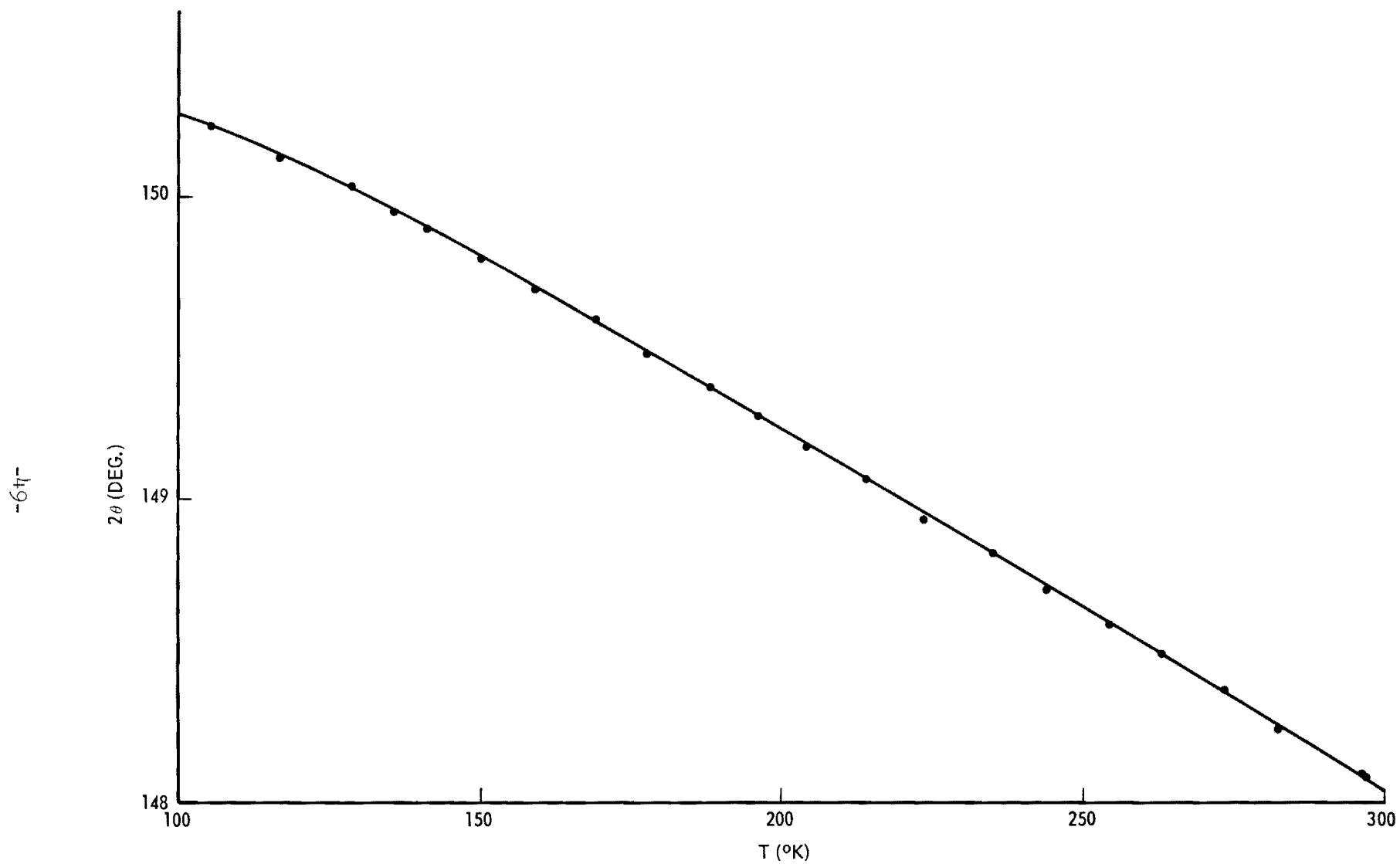


Figure A2. Temperature Dependence of 2θ for the (444) Reflection of AgCl.

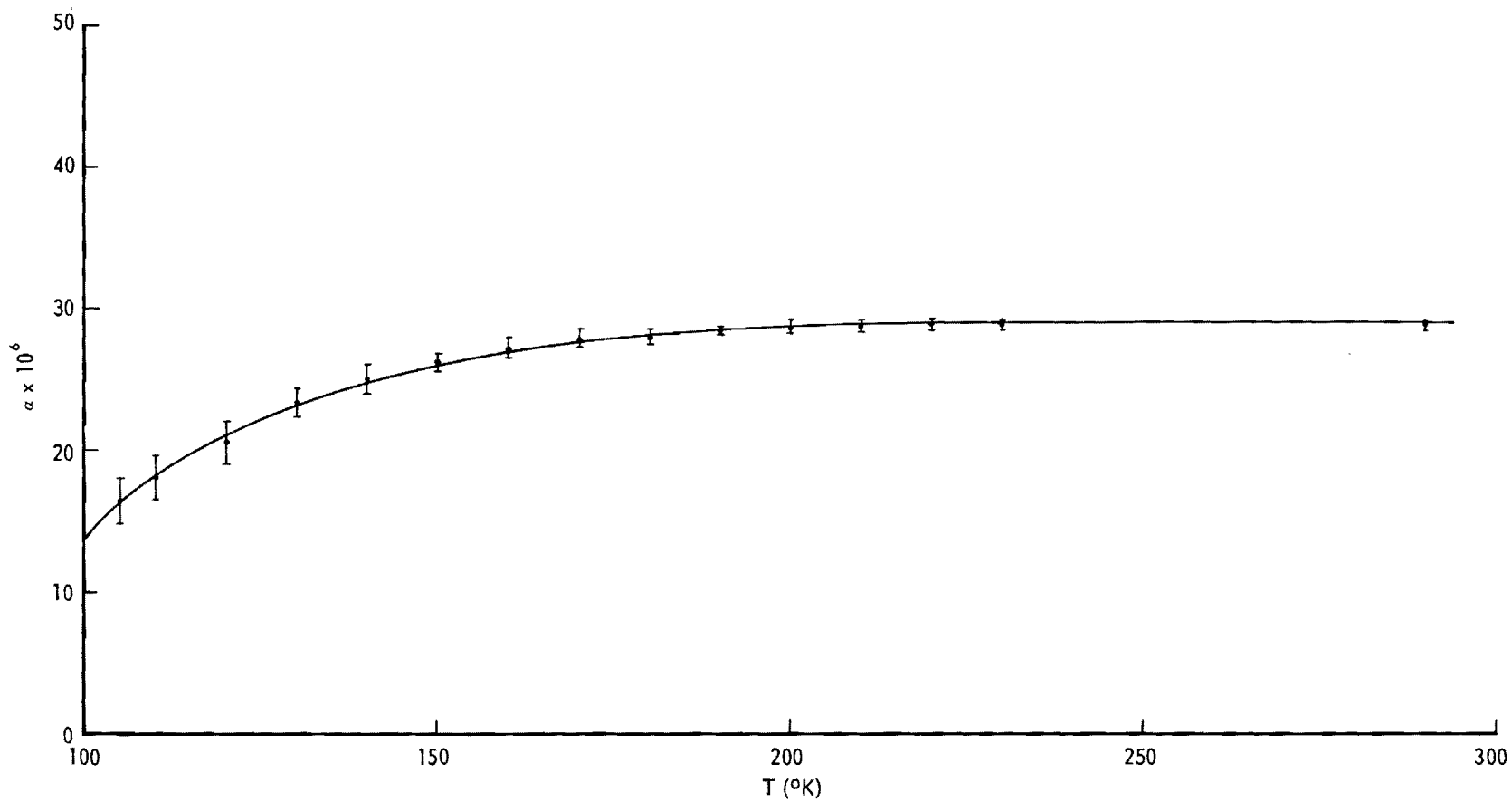


Figure A3. Thermal Coefficient of Expansion of AgCl Between 100°K and 300°K .

Discussion

We were unable to find an equation relating the thermal coefficient of expansion to temperature which was valid over a temperature range which included the Debye temperature; the Debye temperature of AgCl is approximately 145°K. However, we feel relatively certain that α should decrease with decreasing temperature since it results from anharmonic thermal vibrations and the anharmonicity is expected to decrease with decreasing temperature.

Even though the exact temperature dependence of α has not been found, the Grüneisen relation

$$(5) \quad \gamma = \frac{3\alpha V}{K C_v} \quad \text{where}$$

γ = Grüneisen constant (temperature independent)

V = volume

K = compressibility

C_v = specific heat at constant volume

indicates that the temperature dependence of α should be similar to that of the specific heat of a solid. Figure A⁴ shows the $\alpha(T)$ we measured for AgCl and the specific heat, C_v , of a solid. Both are plotted against the "reduced" temperature T/Θ , where Θ is the Debye temperature (according to the Debye theory, C_v is the same function of T/Θ for all solids and C_v vs. T for AgCl was not available at the time).

Both curves drop sharply below a temperature corresponding roughly to Θ . Although the drop in the $\alpha(T/\Theta)$ curve occurs nearer to Θ , there is at least qualitative agreement between our measurement of $\alpha(T)$ and theory.

Any directional dependence which α might have in AgCl due to a preferred location of x-ray produced defects was obscured by the experimental error.

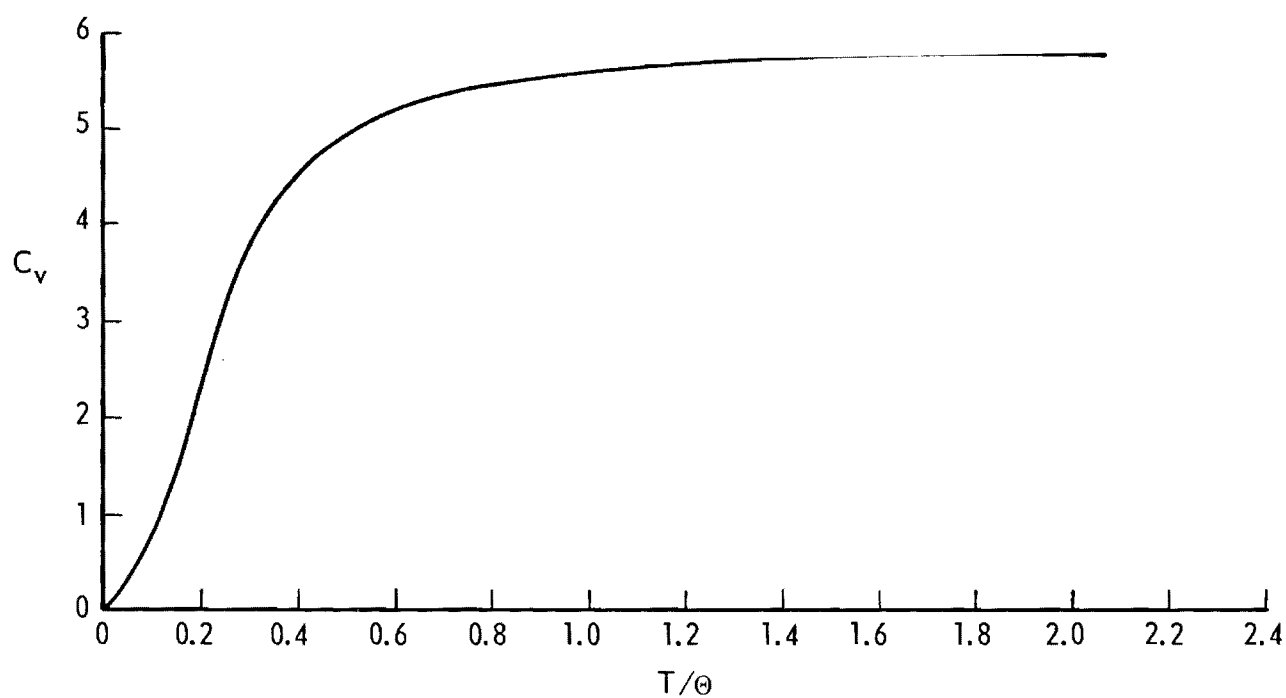
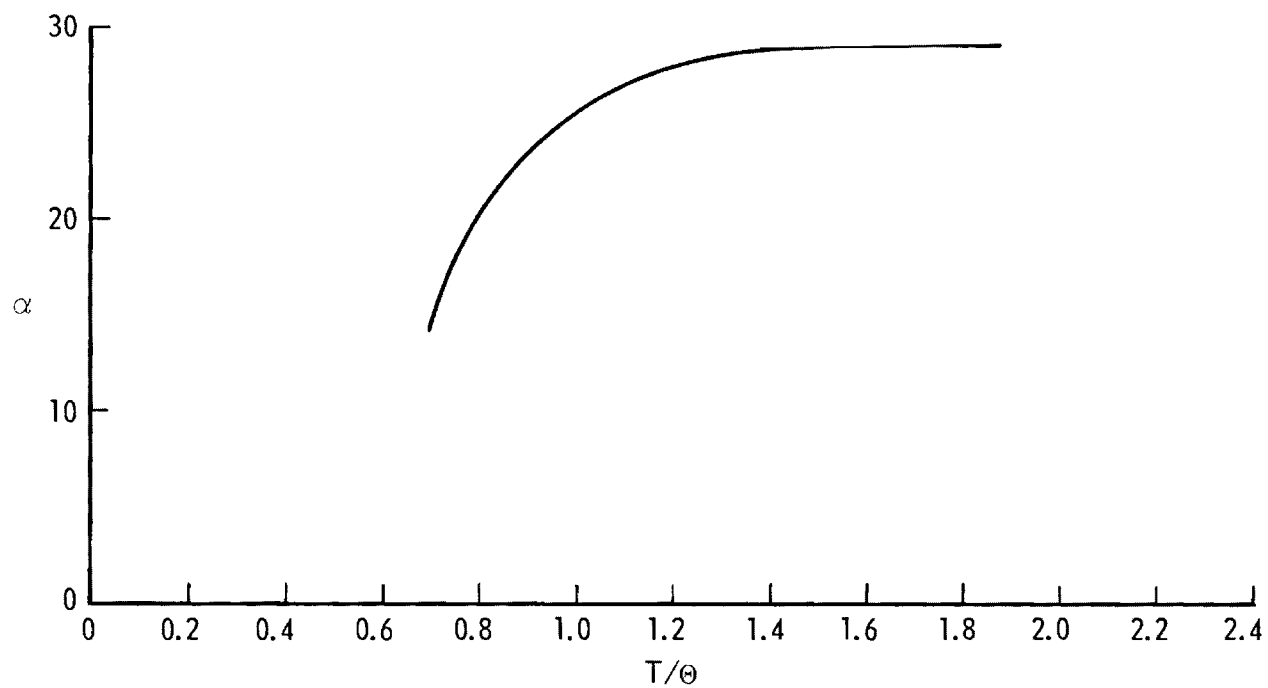


Figure A4. Comparison of the Specific Heat, C_v , of a Solid with the Thermal Coefficient of Expansion, α , of AgCl.

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Figure A5 shows our measurement of $\alpha(T)$ below room temperature and those of Sharma above room temperature. The difference between the two curves extrapolated to room temperature appears to amount to approximately 5%.

We intend to measure $\alpha(T)$ above room temperature so that a more complete comparison can be made with the measurements of Sharma^{A1} and Strelkow^{A2}.

Conclusion

In conclusion,

1. We have measured the thermal coefficient of expansion of AgCl between 100°K and 300°K to a precision ranging from 1% near 300°K to 10% near 100°K.
2. We have found that the temperature dependence of $\alpha(T)$ agrees qualitatively with what is predicted by the Grüneisen theory and that our measurements at 300°K agree with the measurements of Sharma to within 5%.
3. We do not find any dependence of α on crystallographic direction greater than experimental error.

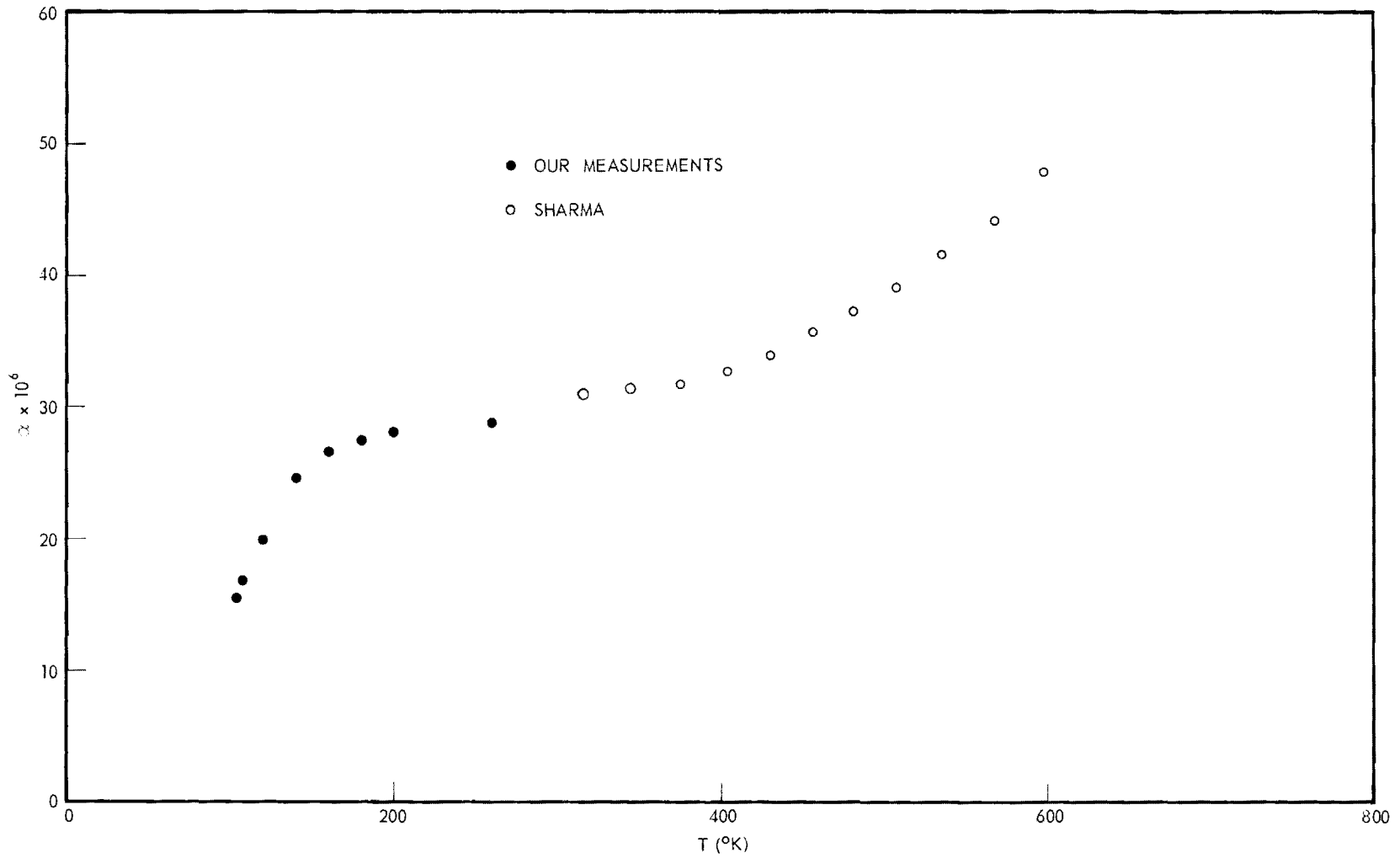


Figure A5. Temperature Dependence of α for AgCl.

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REFERENCES FOR APPENDIX A

- A1. S. S. Sharma, Proceedings of the Indian Academy of Science 32A,
268-74 (1950).
- A2. P. G. Strelkow, Physik. Zeits. Sowjetunion 12, 77-82 (1937).

APPENDIX B

"THESIS PROPOSAL"

A study of Thermal Vibrations in Crystals

by means of

the Temperature Dependences of Bragg Intensities

Proposed Content of Ph.D. Dissertation of R. M. Nicklow

Advisor - Dr. R. A. Young

In principle, the entire vibrational spectrum of a solid can be deduced from observations of diffusely scattered x-rays or inelastically scattered cold neutrons. The measurements are difficult to make because of the low intensities involved and are usually subject to large and relatively poorly determined corrections, e.g. Compton scattering in the x-ray case.

It is therefore intended to make an experimental and theoretical study of what knowledge about thermal vibrations can be obtained from measurements of the temperature dependences of Bragg (x-ray diffraction maxima) intensities. The bulk of the intensity measurements will be obtained from single crystal samples at temperatures differing by increments which will be small enough to allow the determination of the slope, dI/dT , of the intensity vs. temperature data.

The most closely related works of which we are aware are those of R. B. Roof, Jr.^{B1} and D. R. Chipman^{B2}. Both investigators measured Bragg intensities of polycrystalline samples at a few different temperatures. They then used ratios of the intensities measured at these various temperatures to determine, respectively, the Debye Θ of PuO_2 and the temperature dependence of the Debye Θ of several metallic specimens. Chipman computed corrections for the TDS* contributions to the apparent Bragg intensities at a given temperature. His computations were based on measurements of the TDS intensity near the Bragg reflections. Roof made no TDS corrections to his intensity measurements. Neither

*Thermal diffuse scattering

"Thesis Proposal" (continued)

R. M. Nicklow

investigator has made any attempt to base his analyses on slope (dI/dT) information nor to use the intensity versus temperature measurements for the investigation of any crystal properties other than the Debye Θ . Both of these papers appeared after the present Georgia Tech program on "X-ray Studies of Thermal Motions in Crystals" had been started.

The intensity vs. temperature measurements will be carried out principally over the range of 100°K to 300°K . Preliminary intensity vs. temperature data (collected here) have been remarkably reproducible ($\pm 1/2\%$) for x-ray data, and have yielded a value for the Debye Θ of AgCl which is in good agreement with that derived from elastic constant measurements reported in the literature^{B3}.

The principal treatment of these data which has been used so far^{B4, B5} takes some advantage of the experimentally obtainable precision, but does not completely take account of the details of the contribution of thermal diffuse scattering (T.D.S.) to the apparent dI/dT 's, nor of the effect of thermal expansion on the Debye Θ . It is expected that improved treatments of the data can be developed and will be employed.

The following points are particularly to be emphasized in the proposed work.

1. The relationship of the lattice vibration information obtained from the intensity vs. temperature method to that obtained from T.D.S., inelastic scattering of neutrons, specific heat measurements, resistivity measurements, Raman spectra, etc. will be investigated.
2. The determination of the thermal diffuse scattering contribution to the apparent Bragg intensities from the effects on the dI/dT measurements, including the possible separation of the one-phonon and two-phonon

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"Thesis Proposal" (continued)

R. M. Nicklow

contributions, will be undertaken. This will be followed by an investigation of the significance of the separate contributions so determined.

3. A determination of the extent of the breakdown of the Debye assumptions, e.g. the degree of anharmonicity in thermal vibrations, etc. will be attempted. Determinations of the extent to which such breakdowns affect interpretation of the data for other purposes will be a minimum requirement in this connection.

4. A variety of ancillary problems, e.g. a determination of the thermal coefficient of expansion of AgCl over the range 100°K to 300°K, and a brief study of the various factors (other than thermal vibrations) which contribute to dI/dT , will necessarily be undertaken.

AgCl will continue to be one of the principal specimen materials. Other materials which have the NaCl type crystal structure will also be used.

REFERENCES FOR APPENDIX B

- B1. R. B. Roof, Jr., "An Experimental Determination of the Characteristic Temperature for PuO_2 ", paper no. 3, Pittsburgh Diffraction Conference, Pittsburgh, Pennsylvania, November, 1959.
- B2. D. R. Chipman, "Temperature Dependence of the Debye Temperature of Aluminum, Lead, and Beta Brass by an X-Ray Method", preprint, portions presented in paper no. 42, Pittsburgh Diffraction Conference, Pittsburgh, Pennsylvania, November, 1958.
- B3. D. L. Arenberg, "Determination of Elastic Constants in Single Crystals with Especial Reference to Silver Chloride", Journal of Applied Physics 21, 941-2 (1950).
- B4. R. A. Young, "X-Ray Diffraction Studies of Thermal Motions in Crystals", Annual Report No. 1, Project A-389, Engineering Experiment Station, Georgia Institute of Technology.
- B5. R. A. Young and R. M. Nicklow, "Temperature Dependence of Bragg Intensities: Debye Θ of AgCl ", paper no. B-7, American Crystallographic Association meeting, Washington D.C., January, 1960.

ENGINEERING EXPERIMENT STATION
OF THE GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

ANNUAL REPORT NO. 3

Project No. A-389

X-RAY DIFFRACTION STUDIES OF THERMAL MOTIONS IN CRYSTALS

by

R. A. Young and R. M. Nicklow

June 1, 1960 to May 31, 1961

Contract No. NONr 991(00) and 991(06); NR 016-623

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ABSTRACT

Research has been continued on the general study, primarily by x-ray intensity-vs-temperature (I vs T) measurements, of thermal motions in crystals and their interaction with other phenomena of interest in crystal physics.

Critical re-examination of experimental techniques has led to a better understanding of background intensities and subsequently to the solution of several persistent problems including (1) difficulties with balancing filters, (2) abnormally high relative intensities of the (111) and (333) reflections of AgCl, (3) the "anomalous" behavior of the (111) intensity of AgCl as a function of temperature and of wavelength, and (4) the peaking, large size, and angular dependence of the under-peak background observed with balanced filters.

A graphical method ("curvature method") has been developed for comparing the temperature dependence of the normalized temperature slope of $\log I$ vs T, $A(T)$, with the theoretical prediction, $f(x)$, by means of log-log plots. Results indicate that the "curvature method" is very sensitive to discrepancies between experimental observations and theory, and that the Debye-Waller theory does not adequately describe the temperature dependence of Bragg intensities for AgCl.

Further analytic investigation of the dependence of A on $\frac{\sin^2 \theta}{\lambda^2}$ for an NaCl type crystal, including a certain simple thermal diffuse scattering contribution, has resulted in a graphical method which can be used to separate the contributions of the individual atom types to the slope of $\log I$ vs T. No data as yet have been analyzed by this method.

Thermal expansion data for AgCl, NaCl, and Al in the 100° K to 300° K temperature range were obtained. The AgCl data were used to determine the Debye Θ

through comparison of the experimental results with the Mie-Grüneisen theory. The discrepancies found between theory and experiment indicate a breakdown in the simplified Mie-Grüneisen thermal expansion theory used, or the Debye lattice vibration theory, or both, for AgCl.

X-RAY DIFFRACTION STUDIES OF THERMAL MOTIONS IN CRYSTALS

I. INTRODUCTION

A. Review

The general problem continues to be the study, primarily by x-ray means, of thermal motions in crystals and their interaction with other phenomena of interest in crystal physics. Particular attention continues to be directed to the temperature dependences of Bragg intensities. Among the more specific areas of interest are:

- (1) Techniques for making precision measurements of Bragg intensities both at a single temperature and as a function of temperature.
- (2) The determination both of various types of information that may be extracted from the experimental results and of the analysis methods for doing so, (which methods make particular use of the available precision and continuity of the data by dealing particularly with dI/dT , the temperature slope of the apparent Bragg intensity, I).
- (3) The influence of a wide variety of factors on the results (e.g., crystal perfection in a dynamic theory sense, lattice defects, thermal diffuse scattering, etc.), including the possible study of the factors themselves.
- (4) The comparison of various results obtained from temperature-dependence-of-intensity studies with those obtained by ourselves and by others by other means.

In past years much of the technique has been worked out, some promising analytic methods were established and some encouraging results were obtained from temperature slope data (such as those for the Debye Θ). Attention was given

to a variety of factors which might influence the apparent dI/dT and its temperature and $\frac{\sin \theta}{\lambda}$ dependence. The general promise of the method (i.e., that of study of thermal motions through their effect on dI/dT and the study of other phenomena in turn) was demonstrated, and a number of specific problems and observations of particular interest were pointed out.

B. Summary of Third Year Results

During the period of this report, the third year of the project, substantial progress toward the general goals was made in several specific ways which will be discussed at greater length in later sections.

The major accomplishments of this third year are:

- (1) Solutions were obtained to several outstanding and persistent problems (see enumeration below).
- (2) Material was gathered for two technical reports: "Balanced Filters for X-ray Diffractometry" and "Background Intensities in Single Crystal Diffractometry," and a paper was planned on the latter to be presented in August, 1961 at the annual meeting of the American Crystallographic Association.

The technical reports were actually issued and the paper was given after the end of the present annual report period but before the present writing. The contents of these technical reports, which bear on matters of technique and previously (generally incorrectly) made determinations of background, are of general interest in the field of x-ray diffraction and crystallography. They are particularly pertinent to precision measures of Bragg intensities.

- (3) A promising new analytic technique for application to continuous Bragg-intensity-versus-temperature data was evolved and tried briefly. We refer to this new technique as the "curvature method."

The several outstanding problems that were solved include:

- (1) Previously mentioned difficulties with balancing filters (see, for example, p. 28 Annual Report No. 2),
- (2) the previously much discussed but unexplained "anomalous" behavior of the (111) intensity of AgCl as a function of temperature and of wavelength, (e.g., Figure 10, Annual Report No. 2),
- (3) the abnormally high relative intensities of the (111) and (333) reflections of AgCl (Figure 6, Annual Report No. 2),
- (4) the peaking, large size, and angular dependence of the under-peak background observed with balanced filters, pointed out in Figure 1 of Annual Report No. 2.

Among the other accomplishments of the report period are the following:

- (1) Further analytic investigation of the character of A (the normalized temperature slope of the Bragg intensity) as a function of φ ($\varphi = \frac{\sin^2 \theta}{\lambda}$) was carried out for an NaCl type crystal with several results:
 - a) A simple graphical method was thereby discovered for separating the contributions of the two atom types to the overall temperature slope.
 - b) A much clearer picture of the character of A vs φ expected from simple theory, even with a certain simple TDS (Thermal Diffuse Scattering) contribution and as a function of temperature, was obtained.
 - c) As a result of (b) it has been made clear that the A vs φ curves presented in Annual Report No. 2 could be substantially improved on, though the Debye Θ results would not be greatly affected as a consequence.
- (2) Use was made of the thermal expansion data on hand for AgCl, NaCl, and Al (much of which was collected during the report period) to attempt a determination of the Debye Θ through comparison of the observed temperature

dependence of thermal expansion with the prediction of the Mie-Grüneisen theory. The frequently poor results obtained are informative in regard to the limitations of the theory, and, by inference, the applicability of the Debye assumptions to AgCl.

Progress was also made along several other specific lines. Some further refinements of experimental technique were made, many more I vs T data were collected for AgCl, some I vs T data were collected for other specimen materials, and additional thermal expansion data for AgCl, NaCl, and Al were collected and analyzed. It was found necessary to improve the accuracy of our temperature measurements and efforts to do so were initiated. Attention was given to the problem of determining suitable analytic methods for fitting curves to the intensity vs temperature data and to the thermal expansion data.

Our interest in the thermal behavior of the diffracted intensity from perfect crystals was considerably heightened during the year, partially through visits from B. W. Batterman (Bell Labs) and H. Cole (IBM Research Center), both of whom are actively investigating dynamic theory effects. First steps (consisting primarily of arranging to obtain from Dr. Cole a crystal suitable for use as a "Cole Monochromator" and information on a suitable holder for the crystal) were taken toward making possible the direct experimental study of the effect of extinction as a function of temperature. The temperature dependence of dynamic theory effects may in fact become a major subject for our investigations.

Many of the topics just treated in summary form are, along with other topics, treated individually in the following pages.

II. EXPERIMENTAL TECHNIQUES FOR INTENSITY MEASUREMENTS

A. Introduction

Substantial progress made in matters of technique has solved several outstanding problems not previously recognized as being connected with technique. The progress mentioned has to do principally with a recognition and study of the components of background intensity in single crystal (counter) diffractometry. This work has also pointed out an intensity measurement error, sometimes of major proportions, which has been generally overlooked in single crystal diffractometry and has provided some additional valuable criteria for selection of scanning techniques.

B. Balanced Filters

The difficulties with balancing filters, pointed out in Annual Report No. 1, have now been eliminated. It had been mentioned that filters balanced on the Norelco diffractometer (and later on the G. E. goniostat) appeared to be unbalanced when used on the counter-adapted Weissenberg. There were also differences in the character of the background under the Bragg peak. These apparent discrepancies have been shown to be not errors at all but just what should be expected as a result of the different background composition and sampling in the 2θ scan technique (used with the Norelco diffractometer and the G. E. goniostat) and the ω -scan technique. The apparent unbalance was due primarily to a large off-peak background component of non Bragg-scattered radiation of the characteristic wavelength. The filters were in fact well balanced, and improved collimation of the incident beam markedly reduced this particular "miscellaneous" background component.

Certain additional troubles in balancing filters, even with the goniostat, had been mentioned in previous reports. These troubles, which had for some time effectively prevented us from balancing a Ni-Co filter pair, (see, for example, p. 28 of Annual Report No. 2), were found to be due to (1) harmonic (including sub-harmonic) content in the crystal-monochromatized beam used to select wavelengths and (2) lack of a systematic procedure for going about the balance process.

Proper selection of monochromatizing crystal planes and x-ray tube voltage eliminated the background problems. For example, the (111) of Si is a good choice because neither sub-harmonic wavelengths nor $\lambda/2$ are then possible. Since the (111) is a very strong reflection a favorable ratio of Bragg-scattered to non Bragg-scattered radiation at the detector is maintained. With this choice of Bragg planes $\lambda/3$ is the first harmonic wavelength that can be diffracted. When the x-ray tube voltage is then set at just under 3 times the excitation potential of the desired wavelength the diffracted beam will be truly monochromatic.

The systematic balancing procedure devised assumes such a monochromatic beam, makes use of a third filter material which has no absorption edges near the filter pass-band, and involves the specification of a particular pre-balance condition to be obtained before the third material is added. A thorough discussion of the systematic procedure, the theoretical basis for it, results obtained with it, and other experimental points to be controlled in the process of balancing filters constitute Technical Report No. 1, "Balanced Filters for X-ray Diffractometry," issued 15 June 1961. (i.e., 15 days after the end of the present report period). The abstract of that report is here included as Appendix A.

C. Background Intensities

A re-examination of the question of background intensities in single crystal diffractometry led to the recognition of several separate components and to some investigation of the dependence of the individual component on several parameters such as temperature, angle, scanning technique, instrument geometry, etc.

A principal result is that, in the ω -scan (moving-crystal, stationary-counter) and peak-height (stationary-crystal, stationary-counter) methods in particular, there is often* a substantial harmonic contribution to the apparent Bragg peak which is itself peaked at the Bragg position. The harmonics involved may have wavelengths both longer and shorter than the principal wavelength being used and the ratio of harmonic wavelength to principal wavelength need not be an integer but only a rational fraction. Since pulse height analysis is not sufficiently selective of wavelengths in general, a balanced filter technique appears to be required adequately to assess these harmonic contributions. The balanced filter method is also particularly suited (and perhaps necessary if crystal monochromatized radiation is not used) to the elimination of errors due to the strongly angle dependent relative amounts of Bremsstrahlung included under the main peak at low angles in both ω -scan and 2θ -scan techniques. (As the diffraction angle is decreased the entire Bremsstrahlung (white radiation) "hump" tends to become compressed under the main Bragg peak. At low angles in particular the peak breadth is due almost entirely to instrumental geometric factors and not to wavelength dispersion, and therefore changes very little with angle.)

* Unless truly monochromatic incident radiation is used.

When balanced filters are employed however, in contrast to generally used procedure, it is in general necessary to make 3 measurements of background in order properly to determine the actual background under the apparent Bragg peak.* Thus 4 measures are required correctly to determine the Bragg intensity: with each member of the filter pair one off-peak measure and one measure of either the peak maximum or of the integrated area under the peak are required.

In addition to solving some outstanding problems (to be discussed shortly) and indicating how one may improve the accuracy of precision intensity measurements, the new understanding of background provides new criteria for the selection of equipment parameters and use modes. Some of the results are:

- (1) An ω -scan technique should never be used without balanced filters or other suitably wavelength-selective technique unless the absence of harmonic and other Bremsstrahlung peaking at the Bragg position has been specifically demonstrated.
- (2) Similarly, in the absence of such demonstration, the balanced filter technique must always employ at least 4 different measures for each reflection, 3 of which are required for determination of background.
- (3) The 2θ -scan technique may be used without balanced filters except at low angles.
- (4) The balanced filter ω -scan technique is a relatively easily carried out procedure capable of yielding high precision results and quite suitable for general use.
- (5) The peak height method is an inherently poor method, even if the background is properly determined (which is not the case in current general practice)

* The procedure still neglects much of the thermal diffuse scattering contributions at the peak position.

particularly because of probable anisotropy of the mosaic spread in most crystals.

- (6) The minimum detector aperture in the ω -scan increases with angle because of wavelength dispersion but is independent of mosaic spread; the minimum detector aperture in the 2θ -scan is essentially independent of angle but is dependent on the mosaic spread. Thus, for a given crystal, if the mosaic spread is not too large there will be some angle above which the 2θ -scan will be preferable to the ω -scan. If the mosaic spread is large, the ω -scan may be preferable all the way up to the angle at which the required aperture becomes too large adequately to resolve the various reflections.
- (7) For truly monochromatic incident radiation the ω -scan would generally be preferred for mosaic crystals. If the crystals had essentially zero mosaic spread the choice would be dictated by other considerations, such as the region of reciprocal space around the reip for which sampling was desired.
- (8) It is advantageous to "collimate", in a sense, both the incident beam and the detected beam even with the broad beam technique usually used in single crystal diffractometry. The purpose of this collimation may be stated as being to limit the view which the target, on the one hand, and the detector, on the other, have of the region around the specimen, without limiting in either case the view of the specimen itself.

This re-examination of background in x-ray diffraction experiments also contains implications for single crystal film techniques. The present work on background intensities has, as of this writing, been discussed fairly extensively

in Technical Report No. 2 "Background Intensities in Single Crystal Diffractometry" dated 27 July 1961, and finally released about 1 September 1961. Some of the principal results were presented at the 31 July - 4 August 1961 American Crystallographic Association meeting in Boulder, Colorado. The abstract of that paper, which was submitted during the present report period, is here reproduced as Appendix B. The abstract of Technical Report No. 2 is here reproduced as Appendix C, even though the actual writing of the report was done after the end of the present report period.

D. Outstanding Problems Solved Through Improved Understanding of Background Composition

The resolution of previous difficulties with the balancing of filters has been discussed. We select 3 other persistent problems for discussion here, all of which turned out to be background intensity effects.

In figure 6 of Annual Report No. 2 it was shown that the apparent relative values of $|F_{111}|$ and $|F_{333}|$ for AgCl were inexplicably large by about 10%. When the background was properly measured to take account of the harmonic components the apparent values for $|F_{111}|$ and $|F_{333}|$ fell into line with the others. The (111) and (333) reflections were particularly affected because, in this NaCl type structure, they are relatively weak reflections.

In figure 1 of Annual Report No. 2 there was shown the diffracted intensity profiles from the (200), (220), and (400) reflections of NaCl. In each case the profile was determined twice, once with each member of the filter pair. It was shown in that figure that the intensity profile obtained with the α -filter (i.e. the member which strongly absorbs K_{α} radiation) was peaked at the Bragg setting and varied in relative size from about 2/3 of the β -filter profile

for the (200) to nearly zero for the (400). It has now been established that the filters used for those profiles were not properly balanced so that the relative size of the α -filter profile for the (200) should have been nearer $1/3$ than $2/3$. However, the α -filter profile, which in its peaking represents the harmonic and certain other Bremsstrahlung* contributions to background, is a very substantial portion of the β -filter profile even when correctly balanced filters are used. Further, the dependence on (hkl) shown by figure 1 of Annual Report No. 2 persists. It is now recognized that the peaking of the α -filter profile is due to harmonic as well as the previously mentioned other Bragg-diffracted Bremsstrahlung contributions. A quantitative expression has been found to describe the dependence of the relative magnitudes of these contributions on angle, (hkl) , aperture, and a variety of other factors. The expression is given in detail in Technical Report No. 2 and provides at least a plausible qualitative explanation for the just mentioned features of figure 1, Annual Report No. 2. Even the asymmetric character of the α -profile has been explained — the profile of the "other Bragg diffracted Bremsstrahlung" contributions is asymmetric about the Bragg position for K_{α} .

Finally we turn to the temperature behavior of the (111) of AgCl, which has been mentioned at some length in Annual Report No. 2, Annual Report No. 1, and the paper given at the January 1960 meeting of the American Crystallographic Association. We are concerned with the intensity, I , plotted as a function of temperature, T , over the range 100° K to 300° K for the (111) of AgCl. A highly reproducible** inflection had been found in the curve when MoK_{α} radiation was

* i.e., that due to wavelengths outside the filter pass-band but yet diffracted in the same order as the pass-band wavelengths.

** even among specimens from different sources and including one doped specimen.

used. Further, the average slope seemed to be too large to be commensurate with the slopes found for other reflections. Since the measurement statistics were not as good when AgK_{α} was used, it was not possible to be sure whether or not the inflection was present. It did seem, though (as may be seen from figure 3 of Annual Report No. 2) that the average slope with AgK_{α} was somewhat smaller, approximately commensurate with the results from other reflections. The slope obtained with CuK_{α} radiation, as is also shown in the same figure, was impossibly large. Further, two sets of measurements made some months apart, and for one of which (the one shown in the figure) pulse height analysis was used, gave substantially different results. Considerable thought had been given to the possibility that radiation induced defects might somehow be responsible for the observed features of the (111) dI/dT behavior. However, it now appears conclusive that these "anomalies" in the slope are due to the effects of harmonic contributions to the background. It appears likely that the inflection is also due to the same effects. The explanation is that each individual harmonic contribution has the temperature dependence associated with the Bragg planes from which it is diffracted. All harmonic contributions to the (111) intensity are diffracted from higher order planes, i.e., (222), (333), etc. for which larger temperature factors apply. (No sub-harmonics are possible in this particular case). Thus the intensity as measured with a β -filter alone (or no filter) reflects in part the temperature dependence of reflections from higher order planes. The x-ray tube was normally operated at 40 KV for Ag, 45 KV for Cu, and 45 to 50 KV for Mo. Many harmonic wavelengths were excited when CuK_{α} was used; the use of pulse height analysis diminished the effectiveness of the higher harmonics in particular. Thus the composite (uncorrected for harmonics)

(111) temperature slope was greatest when CuK_α was used and was diminished by the use of pulse height analysis. When MoK_α was used only one harmonic, $\lambda/2$, was excited, hence the measured average slope was greater than that due to diffraction from (111) alone but was not nearly as large as it was with CuK_α radiation (plus harmonics). When AgK_α radiation was used, no possible harmonic was excited, hence the measured (111) slope was free of harmonic contributions. When the CuK_α data were re-taken with the benefit of properly balanced filters, correctly used to determine the harmonic contributions, the slope was very much smaller and was, within experimental error, equal to that obtained with AgK_α and expected on the basis of results with other reflections. Technical Report No. 2 discusses the harmonic contribution to apparent temperature slope more thoroughly.

The inflection in the (111) I vs T curve obtained with MoK_α is not as easily explained as is the large slope. It happens that to date no direct experimental test of the presence or absence of the inflection when the harmonic contributions are removed from the MoK_α data has been made. (It is thought that a similar inflection could be present in the AgK_α and CuK_α data but not noticed because of the poorer measurement statistics.) If the inflection is in fact due simply to harmonic contributions it would appear that either the non-linear temperature dependence of the temperature factor or some temperature dependence of form factors is required to explain it.

Another effect of the harmonic contributions which is of particular interest in I vs T measurements is that on B_0 , the ratio of integrated area to peak height. Since the harmonic contributions have generally much larger B_0 's than does the pure K_α peak, it is clear that the apparent B_0 of the composite peak may thereby have a temperature dependence of which the sign depends on whether

sub- or super-harmonics contribute more. The temperature dependence of B_0 shown in figure 22 of Annual Report No. 1 may possibly be due to the effect of sub-harmonic contributions. The effect of harmonic contributions on composite profile is discussed and demonstrated in Technical Report No. 2.

E. Temperature Control and Measurement

Temperature control of the specimen is obtained through blowing a gas, usually either dried air or dry nitrogen, over it. The specimens are (to date) always small crystals, usually approximately spherical, with a maximum dimension of about 0.3 mm or less. It has occurred to us, and we feel it is worth writing down, that in addition to being convenient this temperature control method is in fact a particularly good one, in a thermodynamics or heat-transfer sense, in comparison to other possible heating or cooling methods. The moving gas amounts to a nearly perfectly agitated, fluid bath of the correct temperature and effectively infinite heat capacity. The movement of the gas also facilitates heat transfer between the specimen and the fluid bath and hence enhances the dynamic temperature response of the specimen. With the surface held quite rigidly at gas-stream temperature then either poor infrared transmissivity or fairly good thermal conductivity will assure that the body of the specimen is also very near to gas-stream temperature even if the temperature difference between the specimen and its surroundings outside the gas stream is large (assuming, of course, that heat conduction along the mounting fiber is not significant).*

* That the argument given here does in fact apply has been indicated experimentally at about 100° K. A chromel-alumel thermocouple made of 3 mil wire was found to give the same temperature indication whether the junction was placed 1 cm outside the Dewar nozzle with the leads perpendicular to the flow direction or several centimeters inside the nozzle where it was essentially surrounded by surfaces of the gas stream temperature and several cm of the leads were also in the stream.

If the temperature difference is small then there is no question of radiation heat transfer anyway.

One may find in standard works on heat transfer, such as those used by mechanical engineering or chemical engineering students, discussions of heat transfer between flowing fluids and objects of various shapes as a function of flow velocity and position on the object. The treatments for spheres and low Reynolds numbers (approximately the case of interest here) indicate that generally excellent heat transfer may be expected all over the surface, and that the heat transfer at the back surface is as good or nearly as good as it is on the front surface. ("Front" and "back" are based on the flow direction). The position on the sphere where the heat transfer is least is where the flow velocity is greatest, i.e., at the "sides" of the sphere as viewed along the flow direction. The foregoing heat transfer considerations have encouraged us to direct the gas stream along the axis of the mounting fiber rather than perpendicular to it as we had been doing. It is to be expected that much of the mounting fiber adjacent to the specimen will also be held at temperature through direct contact with the gas stream. We now take advantage of a particular construction feature of our counter-adaptor (for the Weissenberg) to direct the gas-stream along the spindle axis. This new geometry allows us to bring the end of the "Dewar nozzle" to within 0.5 cm from the specimen during x-ray examination and also offers some other experimental conveniences. We have no direct indication of the possible magnitude of thermal gradient in the specimen used here. However, work done on another project with similar gas-stream geometry and with quartz specimens indicates that the gradients in that case are less than 10°C/mm at 600°C and are probably less than 4°C/mm , i.e. the specimen temperature is probably uniform to within 1°C or less.

A problem has been encountered in regard to the absolute accuracy of our temperature measurement, however. It was not initially anticipated that anything more than precision would be required. However, it turns out that in connection with the thermal expansion analyses, in particular, accuracy is also required. Accuracy of temperature measurement, and particularly of temperature difference measurements, is also desirable for the temperature slope of intensities analyses and particularly for the new "curvature method" of analysis.

The thermocouple calibration attempts made during the present report period have been shown to be inadequate,* so no more will be said of them here. The things that were established during the report period were (1) that good calibration was required and (2) that the thermocouple used apparently did in fact measure the gas-stream temperature to within better than 0.5° C (see footnote, p. 14).

F. Need for Written Expositions of Single Crystal Diffractometry Techniques

The general level of interest in single crystal diffractometry is rising rapidly. Perhaps surprisingly, much of the needed exposition of techniques can not be found in the literature. Dr. Furnas' manual for the goniostat, "Single Crystal Orienter Instruction Manual" is almost the only place where one may find substantial discussion of techniques for intensity measurements with single crystal diffractometers. It is known to the writer that a number of persons are presently, of necessity, independently working out or temporizing with many of the same aspects of technique because they can not be found in the

* Primarily because of initially unsuspected uncertainties about certain "fixed" points used and because too few fixed points between dry ice temperature and room temperature were used.

literature. (We are using the term "technique" in a broad sense here to include not only procedures but also instrument design and the theoretical bases for the choices made.) The rapidly developing interest in automatic single crystal diffractometry makes acute the need for having the basic considerations and many of the special considerations of greatest interest adequately treated in the literature. We believe that our work on background intensities represents a contribution along this line, particularly since it points out significant errors in certain approaches which are fairly widely used, but we feel surprised that it had not already been done. Apparently this is the reaction of most people who find it necessary to work out some aspect of single crystal diffractometry technique, i.e. they are surprised it has not been done already, feel they must have overlooked it in the literature or it is of very limited interest, and hence neglect to publish their results. The result is that soon two or three other groups work out the same things and also do not publish. However, it is clear from conversations, from the papers now being presented at ACA meetings, and from the requests for our results on techniques that interest in these matters is no longer limited to the very few and is rapidly becoming even less limited. All of our spare copies of Annual Report No. 1, which dealt in part with these matters of technique, are now gone and several more requests are on hand. We also hope and expect that the general interest in precision intensity measurements as a function of temperature will increase substantially in the next few years. Thus it would appear worthwhile for us to update the portion of Annual Report No. 1 which deals with single crystal diffractometry technique, to extend it somewhat (to include additional topics since treated and our current best practice, particularly in regard to temperature-dependence-of-intensity measurements), and to issue the result

as a technical report. It may be that, because of their allowable length and detail, Technical Reports or their equivalent, rather than the regular literature, may be the most appropriate medium for communicating these matters of technique. One would hope, of course, that each author would place a brief resumé or other indication of the content of the report in the regular literature as well, so that the existence of the report may be made more widely known.

III. NEW ANALYTIC PROCEDURES FOR I VS T DATA AND OTHER RESULTS

A. A vs ϕ Character and Separation of Contributions to A

1. Introductory Comments

An analytic method has been found which makes possible the separate determination, from temperature slope of intensity data alone, of the contribution of the two temperature factors in an NaCl type structure. It is convenient to discuss the method in conjunction with other aspects of the dependence of A on ϕ .

The thermal motions of the two atom types in an NaCl type structure are, in general, not identical.* Even in the simple theory this difference will make A, the normalized temperature slope, dependent on ϕ . ($\phi \equiv \frac{\sin^2 \theta}{\lambda^2}$).

We investigate the first and second derivatives of A with respect to ϕ . With the help of particular choices of the form of the various expressions we find (1) we can separate the effects of the two temperature factors by a suitable extrapolation technique, (2) there are simply located points of inflection and discontinuity in A vs ϕ , and (3) several observations about the expected character of A vs ϕ may be made which can facilitate curve-fitting with experimental data.

* Although at room temperature the two kinds of motion are very similar in both AgCl and NaCl.

We start from $I \propto |F|^2$ and ignore thermal expansion effects on $\frac{\sin \theta}{\lambda}$.

$$\frac{d(\ln I)}{dT} = 2 \frac{d}{dT} (\ln F) = 2 \frac{d}{dT} \left[\ln (f_1 e^{-M_1}) + \ln (1 \pm \mathcal{F} e^{-\Delta M}) \right] \quad (1)$$

where $\mathcal{F} = \frac{f_2}{f_1}$, $\Delta M = M_2 - M_1$, and the plus sign is used for reflections with even Miller indices.

$$\frac{d(\ln I)}{dT} = -2 \frac{\sin^2 \theta}{\lambda^2} \left[\frac{dB_1}{dT} \pm \frac{\mathcal{F} e^{-\Delta M}}{1 \pm \mathcal{F} e^{-\Delta M}} \frac{d(\Delta B)}{dT} \right] \quad (2)$$

where $B = \frac{M}{(\sin^2 \theta)/\lambda^2} = M/\varphi$. I , $|F|^2$, f_1 , f_2 and M have their usual definitions which can be found in previous annual reports. Recalling the definition of the normalized temperature slope, A , $A = -\frac{1}{2\varphi} \frac{d(\ln I)}{dT}$, rearranging and using primes to denote temperature derivatives:

$$A = B'_1 \pm \frac{\Delta B'}{\frac{\mathcal{F} e^{-\Delta M}}{\pm 1}} \quad (3)$$

Recalling that $M = B\varphi$ and taking $\frac{dB}{d\varphi} = \frac{dB}{d\varphi} = 0$ one obtains:

$$\frac{dA}{d\varphi} = \mp \frac{\Delta B \Delta B' \frac{\mathcal{F} e^{-\Delta M}}{\pm 1}}{\left(\frac{\mathcal{F} e^{-\Delta M}}{\pm 1} \pm 1 \right)^2} \quad (4)$$

then

$$\frac{d^2 A}{d\varphi^2} = \pm (\Delta B)^2 \Delta B' \frac{\left(\frac{\mathcal{F} e^{-\Delta M}}{\pm 1} \mp 1 \right)}{\left(\frac{\mathcal{F} e^{-\Delta M}}{\pm 1} \pm 1 \right)^3} \frac{\mathcal{F} e^{-\Delta M}}{\pm 1} = - \Delta B \frac{\frac{\mathcal{F} e^{-\Delta M}}{\pm 1} \mp 1}{\frac{\mathcal{F} e^{-\Delta M}}{\pm 1} \pm 1} \frac{dA}{d\varphi} \quad (5)$$

We are now in a position to make several observations.

2. Separation of Contributions to A

$$A \xrightarrow{\varphi \rightarrow \infty} \text{smaller of } B_1' \text{ and } B_2' \quad (6)$$

$$A \xrightarrow{\varphi \rightarrow 0} \frac{B_1' + \phi B_2'}{1 \pm \phi} \quad (7)$$

Since ϕ will generally be known fairly well, both B_1' and B_2' may be separately determined by extrapolation first to $\varphi = \infty$ and then to $\varphi = 0$.

3. Character of A vs φ Curve

- a. If either ΔB or $\Delta B'$ is zero then A vs φ is a horizontal straight line.
- b. The slope of A vs φ is never negative for the case of odd parity of the Miller indices and is never positive for the even parity case (ΔB and $\Delta B'$ always have the same sign on the basis of the simple theory used here).
- c. The curve asymptotically approaches a horizontal straight line as φ tends to infinity. The approach is from the bottom for the odd parity case and from the top for the even parity case.
- d. For the usual situation in which ΔB (and $\Delta B'$) are positive if $\phi < 1$ there are no singularities or points of inflection throughout the entire positive range of φ .
- e. (1) A singularity (odd parity case) or an inflection point (even parity case) occurs at

$$\varphi = \frac{\ln \phi}{\Delta B}. \quad (8)$$

- (2) Since in the usual case a positive ΔB is associated with an $f < 1$, the singularity or inflection will not usually occur in the observable positive region of ϕ .
- (3) In those cases in which the heavier atom has the larger vibrational amplitude, so that a positive ΔB is associated with an $f > 1$, the singularity and inflection will occur in the positive and possibly observable range of ϕ . The experimental observation of these effects may be used for two things:
- (1) to demonstrate that the heavier atom has the larger amplitude and (2) to determine the magnitude of ΔB , by use of equation (8) to approximately the accuracy with which the ϕ location of the singularity or inflection can be established.
- (It is presumed that $\ln f$ will be rather well known in advance.)

If ΔB were to be established by, for example, the extrapolation technique described earlier, equation (8) could be used experimentally to determine $\ln f$, i.e., the log of the ratio of atomic form factors. The interaction of anomalous dispersion effects with this analysis, particularly if the effects were chosen to change the sign of $(f - 1)$, might also be of particular interest.

4. Further Observation with the Help of a Sketch

A qualitative sketch of A vs ϕ may now be constructed and will aid further observations. Figures 1 and 2 are such sketches. From an analytic point of view the distinguishing features of the A vs ϕ curves are the singularities and points of inflection; the sketches are therefore made with reference to these points as fixed points. The point where $\phi = 0$ is then treated as a dependent variable in the sketches. Because the designations 1 and 2 for the atoms is

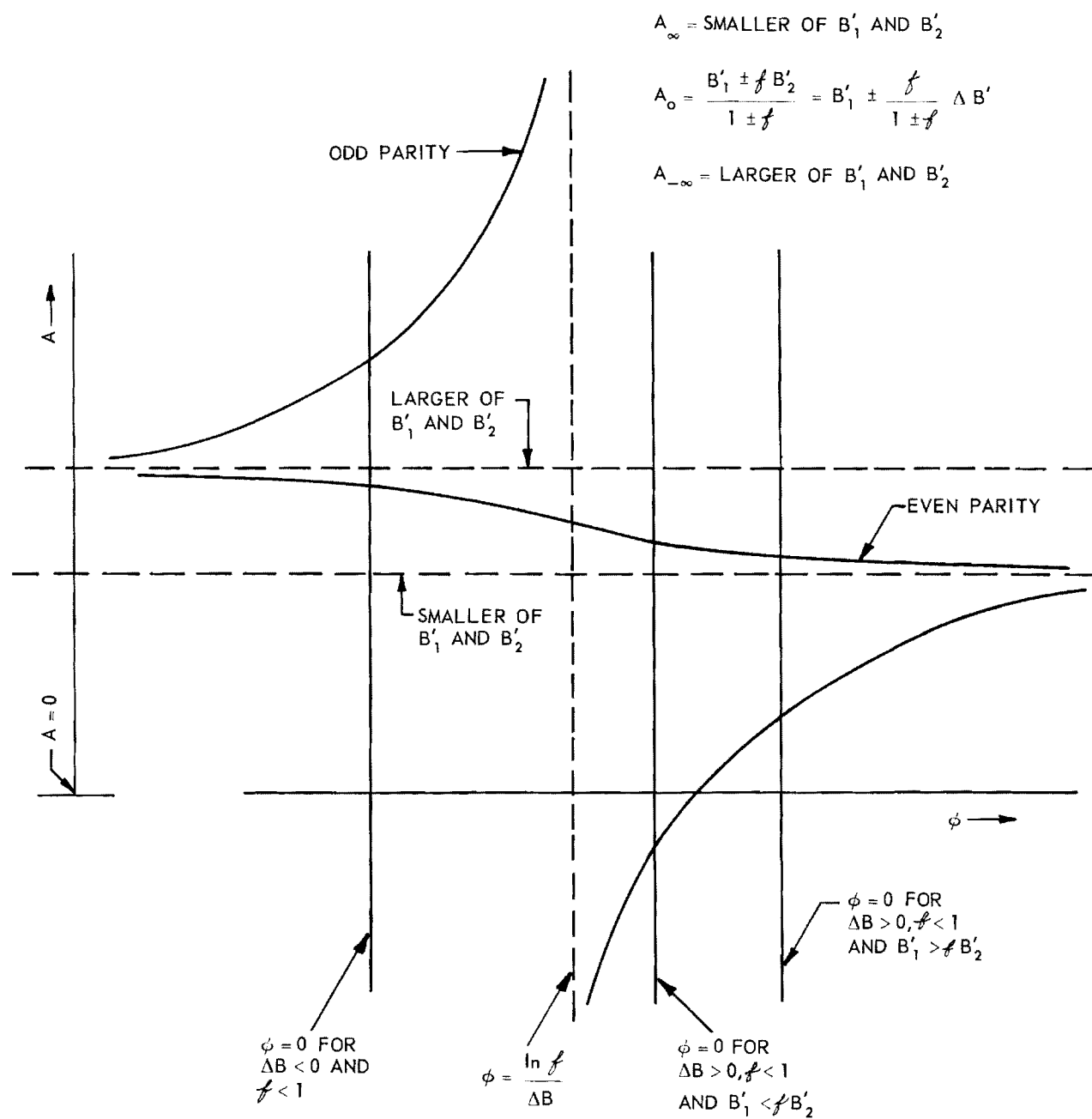


Figure 1. Dependence of A on ϕ .

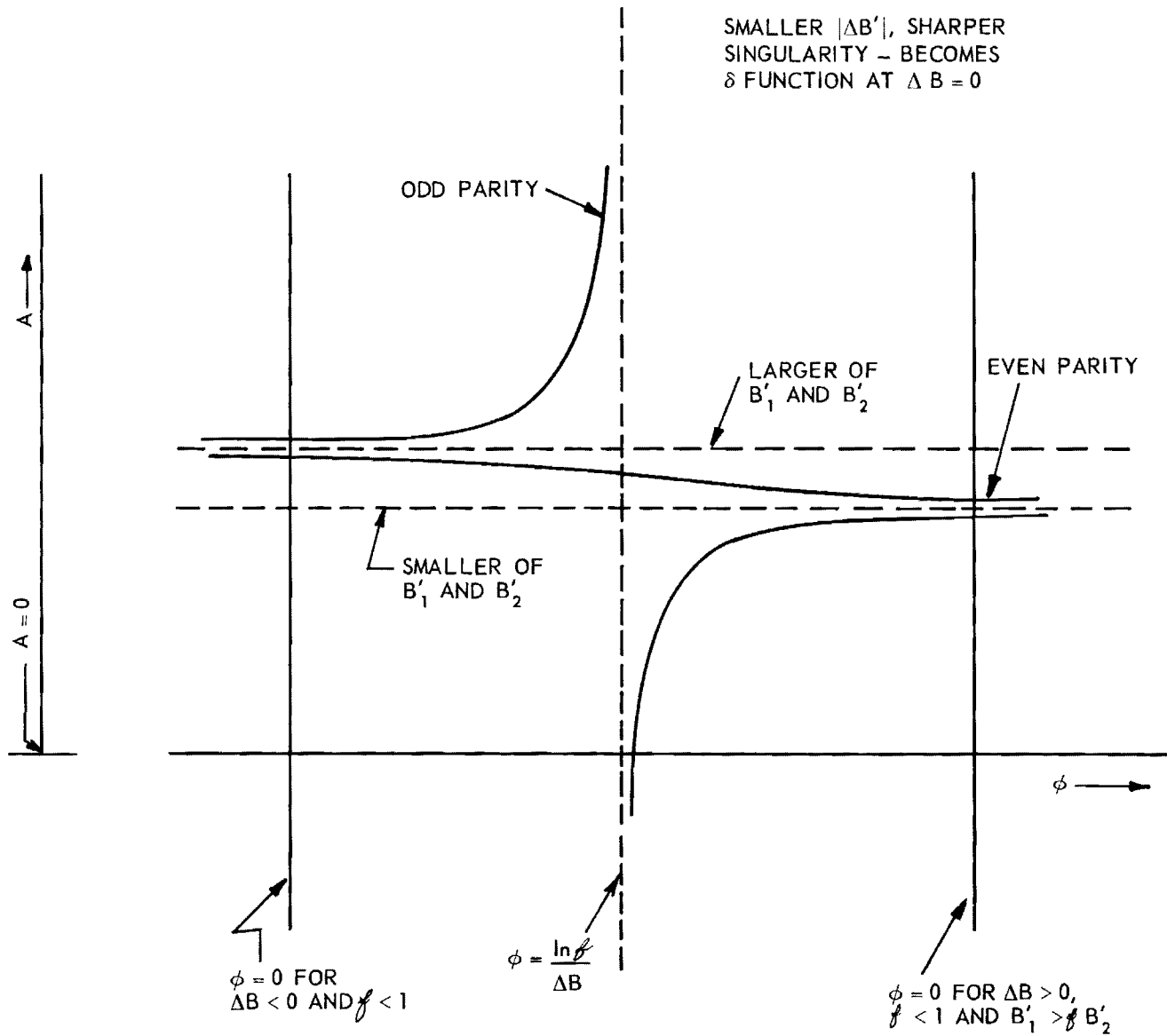


Figure 2. Dependence of A on ϕ for Small $|\Delta B'|$.

arbitrary the case of $\Delta B > 0$ and $f > 1$ is redundant with $\Delta B < 0$ and $f < 1$, as an example.

Further observations follow.

- (1) For the even parity case the value of A always lies between B_1' and B_2' .
- (2) For the odd parity case it is possible for A to be negative for some positive ϕ value even when the lighter atom has the larger vibrational amplitude ($\Delta B > 0$ for $f < 1$), the requirement being that $B_1' < f B_2'$. (i.e. $B_1'/B_2' < f_2/f_1$).
- (3) As $\Delta B \rightarrow 0$ (see figure 2)
 - (a) the singularity becomes sharper and moves toward either $+\infty$ or $-\infty$ depending on the sign of ΔB , and
 - (b) the curve for the even case approaches its asymptotes more slowly.
- (4) The difference between A (odd) and A (even) at various ϕ 's might be used as an experimental check on the sign of ΔB , the proximity of the singularity to the observable range of ϕ , and the proximity to the asymptotes which lie between the two types of A values. It is given by

$$A_{(\text{even})} - A_{(\text{odd})} = \frac{2\Delta B'}{\frac{e^{\Delta M}}{f} - \left(\frac{e^{\Delta M}}{f}\right)^{-1}} \quad (9)$$

At $\phi = 0$ (9) becomes

$$A_{(\text{even})} - A_{(\text{odd})} = \frac{2\Delta B'}{\frac{1}{f} - f} \quad (10)$$

In the particular case for which $\beta = 2/5$ (roughly true for AgCl) at $\phi = 0$,

$$A_{(\text{even})} - A_{(\text{odd})} = \frac{20}{21} \Delta B' \approx \Delta B' . \quad (11)$$

The expected dependence of A on parity is hereby shown as a function of $\Delta B'$, the difference in the temperature dependences of the two temperature factors. A lack of significant difference of A (even) and A (odd) at $\phi = 0$ is therefore a good indication that $\Delta B'$ is small and that the observation range is far enough from the singularity and/or point of inflection so that a straight line is a good approximation to the A vs ϕ curve. A better approximation, of course, is an exponential as is shown by letting $e^{\Delta M}$ in (9) become $\gg \beta$ with the result

$$A \approx B_1' \pm \beta \Delta B' e^{-\Delta M} . \quad (12)$$

From the preceding discussion it appears that for the even parity case A vs ϕ may never have a positive slope such as is shown in figures 4 and 5 of Annual Report No. 2.

Perhaps contributions of TDS could change this situation. We consider the effect of the particular TDS contribution discussed in Annual Report No. 2 and included in I_A (apparent intensity) as*

$$I_A = I_B (1 + K_1 T \phi + K_2 T^2 \phi^2) \quad (13)$$

where I_B is the true Bragg intensity, the temperature dependence of which we have just been discussing. K_1 and K_2 are slowly varying functions of temperature, may be treated as constants here, and refer respectively to one phonon and two phonon contributions.

* Equation (2), p. 12, Annual Report No. 2.

With the notation used and results obtained on the preceding pages:

$$A = \frac{-1/2 \frac{d}{d\varphi} (\ln I_A)}{\varphi} = - \frac{1}{2\varphi} \left\{ \frac{d}{d\varphi} (\ln I_B) + \frac{d}{dT} \ln (1 + K_1 T\varphi + K_2 T^2 \varphi^2) \right\}$$

$$A = B_1' \pm \frac{\frac{\Delta B'}{\varphi} e^{\frac{\Delta M}{\varphi}}}{e^{\frac{\Delta M}{\varphi}} \pm 1} - \frac{1/2 K_1 + K_2 T\varphi}{1 + K_1 T\varphi + K_2 T^2 \varphi^2} \quad (14)$$

Then

$$\frac{dA}{d\varphi} = \mp \frac{\Delta B \Delta B' \frac{e^{\frac{\Delta M}{\varphi}}}{\varphi}}{(e^{\frac{\Delta M}{\varphi}} \pm 1)^2} - \frac{T [4K_2 - K_1^2 - 2K_2(1 + K_1 T\varphi + K_2 T^2 \varphi^2)]}{2(1 + K_1 T\varphi + K_2 T^2 \varphi^2)^2} \quad (15)$$

As φ approaches infinity the last term in (15) vanishes and thus contributes nothing to the slope at infinity. At $\varphi = 0$ the TDS contribution to $dA/d\varphi$ is $-T(K_2 - \frac{K_1^2}{2})$ and thus for the even parity case the slope of A vs φ at $\varphi = 0$ must always be negative. Hence the curves in Figures 4 and 5 of Annual Report No. 2 are probably incorrectly drawn, at least for the 100° K cases.

Even though the TDS contribution to A is limited to $1/2 K_1$ at $\varphi = 0$ and to 0 at $\varphi = \infty$ we have not established whether the contribution might not be substantially larger at intermediate values. Let A_B be the A value arising from the true Bragg peak. Then

$$A - A_B = - \frac{1/2 K_1 + K_2 T\varphi}{1 + K_1 T\varphi + K_2 T^2 \varphi^2}, \quad (16)$$

the latter part of (14).

From (15) it may be shown that

$$\frac{d(A-A_B)}{d\phi} = 0 \quad (17)$$

when

$$\phi = \frac{-K_1 \pm \sqrt{4K_2 - K_1^2}}{2K_2T} \quad (18)$$

The extremum values of $(A - A_B)$ are then

$$(A-A_B)_{\text{Extremum}} = \frac{+K_2}{\sqrt{4K_2 - K_1^2}} \quad (19)$$

The one possible singularity, which obtains only for the special case of $4K_2 = K_1^2$, occurs at

$$\phi = \frac{-K_1}{2K_2T} = \frac{-2}{K_1T}, \quad (20)$$

which is safely in the unobservable (negative) region of ϕ .

For
$$4K_2 \leq K_1^2 \quad (21)$$

there will be no extremum in the positive range of ϕ (for $4K_2 < K_1^2$ the roots given in equation (18) will be imaginary). It is expected that (21) will generally apply for the AgCl and other specimens studied here. Hence in our plots of A vs ϕ we may expect the TDS contribution to be monotonic in ϕ , provided that the experimentally effective K_1 and K_2 values are in fact independent of ϕ .

The TDS contribution to A will vary from $-K_1/2$ at $\phi = 0$ to 0 at $\phi = \infty$. The TDS contribution to $dA/d\phi$ will vary from

$$T \left(\frac{K_1^2}{2} - K_2 \right) \text{ at } \varphi = 0 \quad (22)$$

to

$$0 \text{ at } \varphi = \infty . \quad (23)$$

It would appear then that the slope of the overall A vs φ at $\varphi = 0$ (even parity case) could be positive at sufficiently high temperatures. However if the slope were positive due to TDS it would be markedly temperature dependent.

The situation shown in figure 4 of Annual Report No. 1, in which the higher temperature shows the more negative slope at $\varphi = 0$, is therefore impossible on the basis of the simple theory treated here. Another way in which the data in that figure may be in disagreement with the theory is that A(333) at room temperature appears to be larger than the A(even) values. According to our theory this could only be possible if the vibrational amplitude of the Ag atom were greater than that of the Cl atom — as, of course, is a possibility. If that is the case, however, then, since $|\Delta B|$ is undoubtedly small, the singularity in the A(odd) curve and point of inflection in the A(even) curve occur at such large values of φ that the limited φ range covered by our data will not support a valid extrapolation to $\varphi = \infty$. Thus perhaps it should only be said that the A(even) curves in figure 4 lie somewhere between B_1^i and $(B_1^i + \frac{\Delta B}{1+\varphi} - K_1/2)$.

B. Curvature Method for Analyzing I vs T Data

It was first hinted in Annual Report No. 1 (p. 40) that the temperature dependence of the function $\{\varphi(x) + x/4\}$, which appears in the Debye-Waller Temperature factor, might be used to determine a Debye Temperature at low temperatures. During the present year we made a direct attack on this idea with interesting results.

From Annual Report No. 1 we have

$$A = \frac{6h^2}{mk\Theta^2} f(x) \quad (24)$$

from Debye-Waller theory for the monatomic case neglecting thermal expansion and thermal diffuse scattering, where A is the normalized temperature slope of intensity ($= -\frac{1}{2\phi} \frac{d \ln I}{dT}$), h is Planck's constant, k is Boltzmann's constant, m is the atomic mass, and f(x), which comes from the temperature dependence of $\{\phi(x) + x/4\}$, is given by

$$f(x) = 2\phi(x) - \frac{x}{e^x - 1} \quad (25)$$

x is Θ/T , and the Debye function, $\phi(x)$ is given by

$$\phi(x) = \frac{1}{x} \int_0^x \frac{\xi d\xi}{e^\xi - 1} \quad (26)$$

A plot of f(x) was given in Annual Report No. 1 (figure 2, p. 38). It is a non-linear monotonic function of x which is unity at $x = 0$ ($T = \infty$), about 0.97 at $x = 1$ ($T = \Theta$), and about 0.5 at $x = 7$. Equation (24) shows that, neglecting the possible temperature dependence* of Θ and m, the normalized temperature slope A will have the same temperature dependence as does f(x) and will become observable at temperatures below Θ ;

$$\frac{dA}{dT} \approx (\text{constant}) \frac{d}{dT} f(x) \quad (27)$$

* m could be temperature dependent if it referred to the effective average atomic mass in a diatomic substance.

Carrying out the indicated operations we find

$$\frac{dA}{dT} = \frac{6h^2}{mk\Theta^2} \frac{df(x)}{dx} \frac{dx}{dT} = \frac{6h^2}{mk\Theta^2} \frac{df(x)}{dx} \left(-\frac{x}{T}\right), \quad (28)$$

$$\frac{df(x)}{dx} = \frac{d}{dx} \left[\frac{2}{x} \int_0^x \frac{\xi d\xi}{e^{\xi}-1} - \frac{x}{e^x-1} \right] = -\frac{1}{x} \left[f(x) - \frac{x^2 e^x}{(e^x-1)^2} \right], \quad (29)$$

and

$$\frac{dA}{dT} = \frac{6h^2}{mk\Theta^2 T} \left[f(x) - \frac{x^2 e^x}{(e^x-1)^2} \right]. \quad (30)$$

Then

$$\frac{d(\ln A)}{d(\ln \frac{1}{T})} = -\frac{d(\ln A)}{d(\ln T)} = -\frac{T}{A} \frac{dA}{dT}, \text{ or} \quad (31)$$

$$\frac{d(\ln A)}{d(\ln \frac{1}{T})} = -\left[1 - \frac{x^2 e^x}{f(x)(e^x-1)^2} \right] \xrightarrow{x \rightarrow \infty} -1. \quad (32)$$

We note with approval that the unknown quantity m has disappeared from the temperature "curvature" of intensity as written in equation (32) and we are left only with a calculable function of x .

The more interesting form at the moment is equation (24), however. The graphical approach based on it will further clarify the significance of equation (32), and vice versa. Equation (24) says in effect that except for a scale factor A is the same function of x that $f(x)$ is. Now we can plot $f(x)$ as a function of x , that is Θ/T . We know from experiment the value of A as a function of T and hence of $1/T$ or any constant times $1/T$, including the unknown Θ . If we plot $\log A$ as a function of $\log 1/T$ and, to the same scale, plot

$\log f(x)$ as a function of $\log x$, the two curves should be exactly superimposable by translation. The amount by which the A curve must be translated along the $\log x$ axis to produce superposition will represent the log of the constant by which the argument of A, $1/T$, must be multiplied to make it equal to x , i.e. the translation will be $\log \Theta$.

Similarly the required translation along the $f(x)$ axis will represent the log of the scale factor, which also contains Θ . However, the scale factor contains m as well, a quantity which may not be known due to lack of knowledge of the proper averaging procedure to be used in case more than one kind of atom is present. However, in principle, one could determine Θ from the x axis translation and then use this Θ and the $f(x)$ axis translation to determine m . We have not yet tried this type of determination. In those cases in which m is known the two translations may be used to check on each other.

There are several particularly attractive aspects to this "curvature method."*

- (1) It does not depend on a knowledge of the average atomic mass, only on the assumption that the average mass is a constant.
- (2) It is precisely at low temperature where the Debye temperature is most nearly constant (provided the temperature is not too low, say $T < \Theta/10$), thermal expansion may be neglected, the harmonic assumptions are best satisfied, TDS contributions are minimized, and the isothermal x-ray method fails (because of insufficiently accurate data) that this method is at its best.
- (3) As for the slope method itself, this method in principal requires the measurement of only one reflection, which may be chosen far out in reciprocal space to give high sensitivity, and is free of many of the experimental errors which beset isothermal relative intensity measurements.

* so-called because it involves $\frac{d^2 I}{dT^2}$ in fact even if not explicitly.

- (4) Even a certain kind of extinction effect will cancel itself out in this method. This extinction effect is the one which Parthasarathy (1961) suggests on the basis of a quasi-dynamic theory approach. He argues that for a perfect crystal the factor e^{-2M} becomes replaced by e^{-M} for intensities and suggests that for intermediate cases

$$I_T = I_{T=0} e^{-PM} \quad (33)$$

where P is a constant independent of temperature. If so then equation (24) becomes

$$A = \frac{P6h^2}{2mk\Theta^2} f(x) \quad (34)$$

where we retain the operational definition of A

$$A = - \frac{1}{2\phi} \frac{d(\ln I)}{dT} . \quad (35)$$

and the only effect on the curvature method is the insertion of the additional scale factor of $P/2$. The x -axis translation required to superimpose $A(1/T)$ and $f(x)$ curves is in no way affected. Possibly, if Parthasarathy's suggested behavior should turn out to be right, one might use the curvature method and a knowledge of m to determine P , a kind of measure of crystal perfection. At the moment however this particular edifice of argument is rather too full of "if's" to be taken very seriously.

Unfortunately all of the results obtained with the curvature method during the report period were based on intensity data which are now suspect because, as was shown by our work on background intensities, inadequate measures of background were made. Thus the results on hand are not suitable for critical

interpretation. However, they still hold some general interest. The A values required for making the $\log A$ vs $\log 1/T$ plots were obtained from graphical determinations of the slopes of I vs T curves. Figure 3 shows a result which is fairly typical of those obtained so far for AgCl . The solid curve is $\log f(x)$, the points are $A(1/T)$ values. The typical (for present AgCl data uncorrected for harmonic contributions) features are

- (1) The $\log A$ curve appears to have too much curvature - i.e. it is not possible to get both high- and low-temperature ends to fit the $\log f(x)$ curve simultaneously.
- (2) The x -axis translation required to produce the best fit at the low temperature end yields an x in the neighborhood of 2 for $T = 300^\circ \text{K}$. This x would give a Θ value too large by nearly a factor of four (it is known from other work that $\Theta(\text{AgCl})$ is probably in the range 130 to 160°K).
- (3) If the fitting is done at the high-temperature end a Θ is obtained which is substantially smaller but is still too large by about a factor of two. Figures 4 through 6 show additional AgCl results and 7 shows results for a few reflections from a single crystal aluminum specimen. In each case the format of the figures is similar to that of figure 3, except that in many cases the $f(x)$ curve is shown in the two positions corresponding to the best fits in the low and high temperature regions separately.

The positioning accuracy along the x -axis for a given set of data is surprisingly good, particularly at the low temperature end of the curve where the repositioning uncertainties in this graphical method appear to be about 1%.

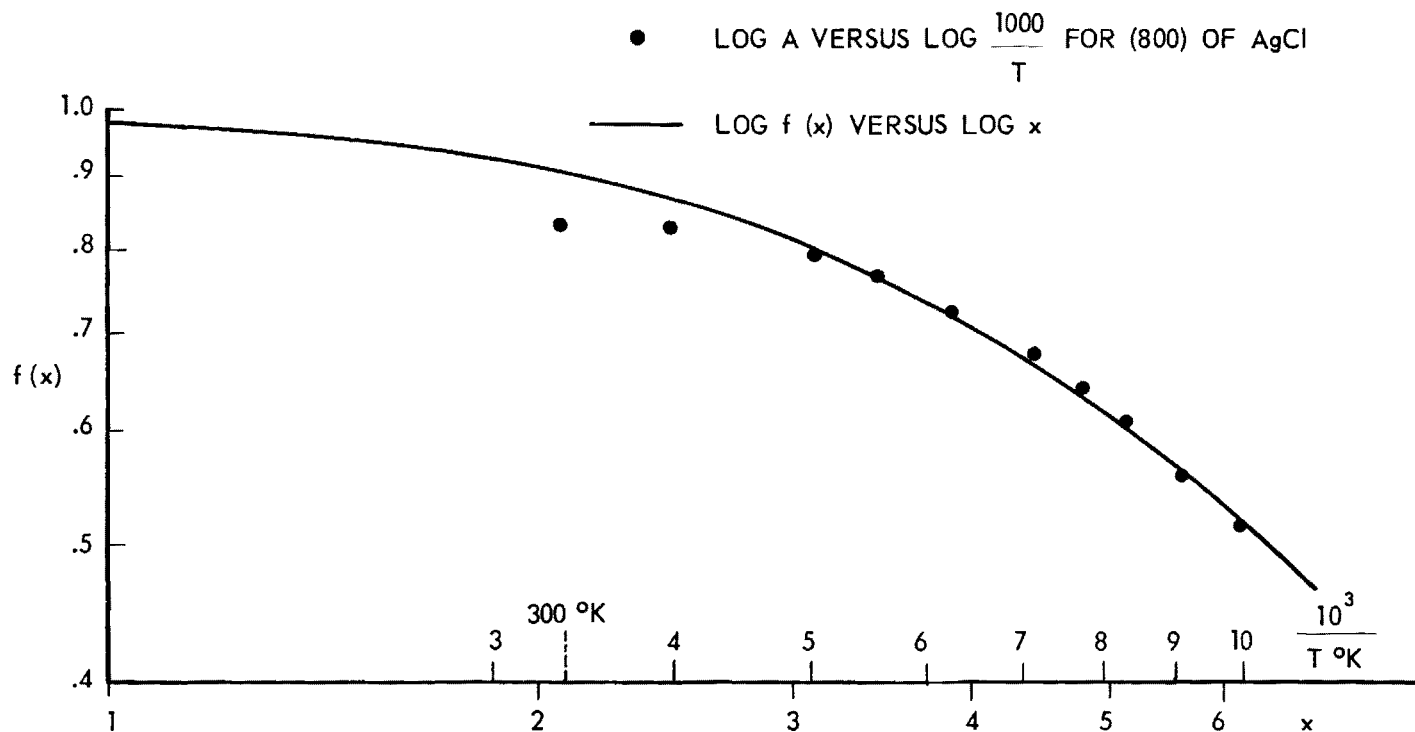


Figure 3. Fitting A (T) to f (x) by Use of Log-Log Plots.

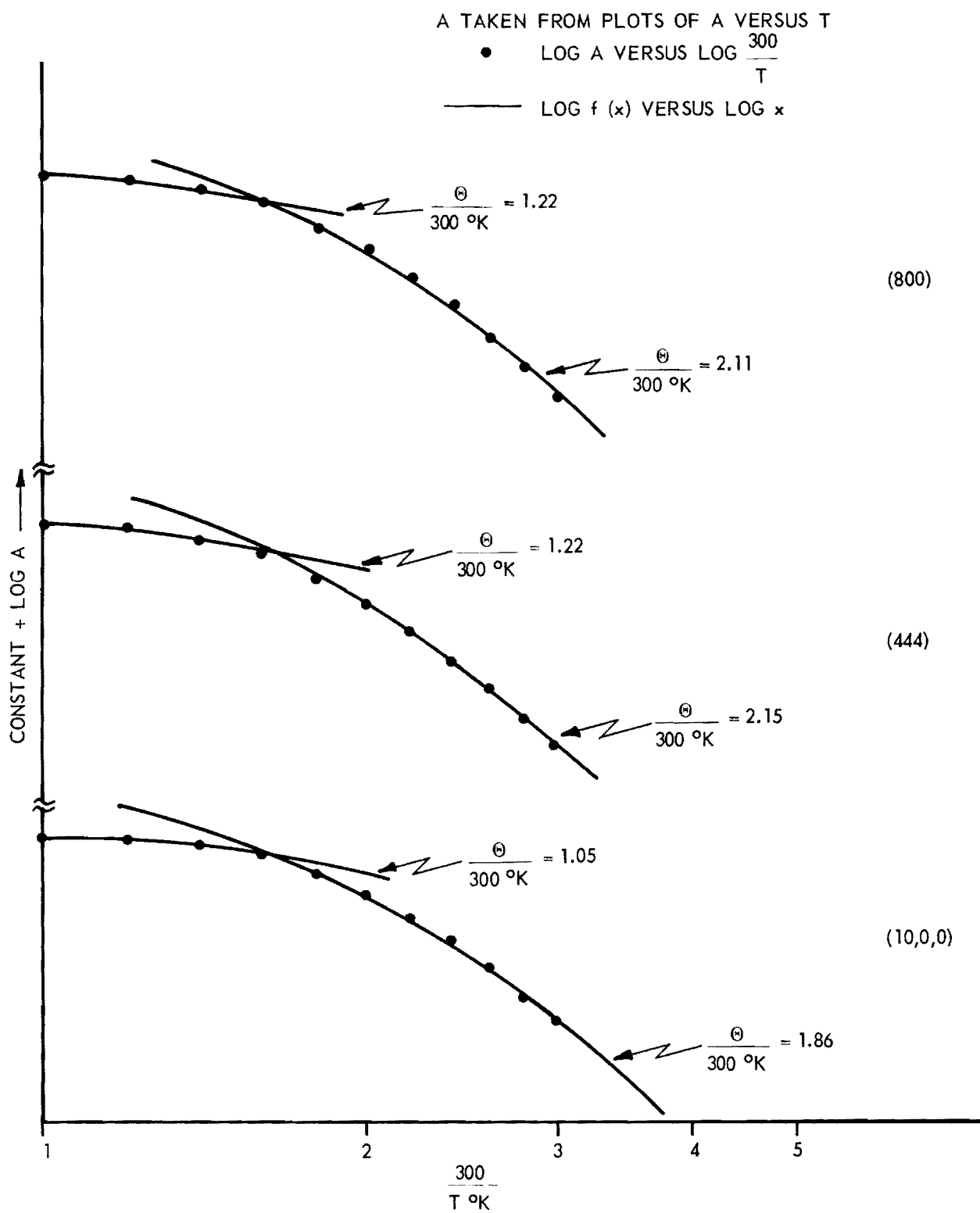


Figure 4. Log A Versus Log $\frac{300}{T}$ for AgCl Sample No. 16.

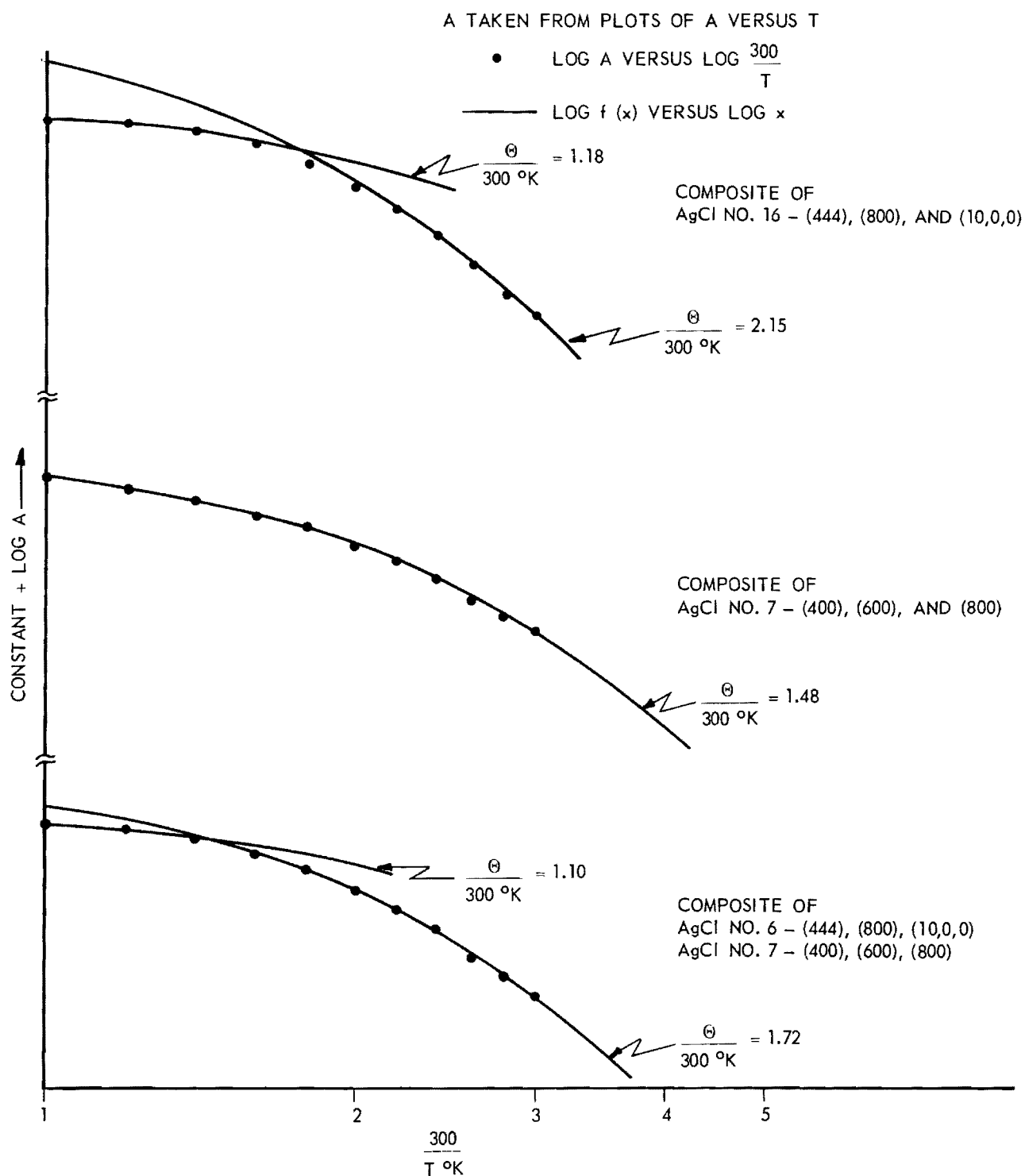


Figure 5. Composite Log A Versus Log $\frac{300}{T}$ Plots for AgCl Samples No. 7 and No. 16.

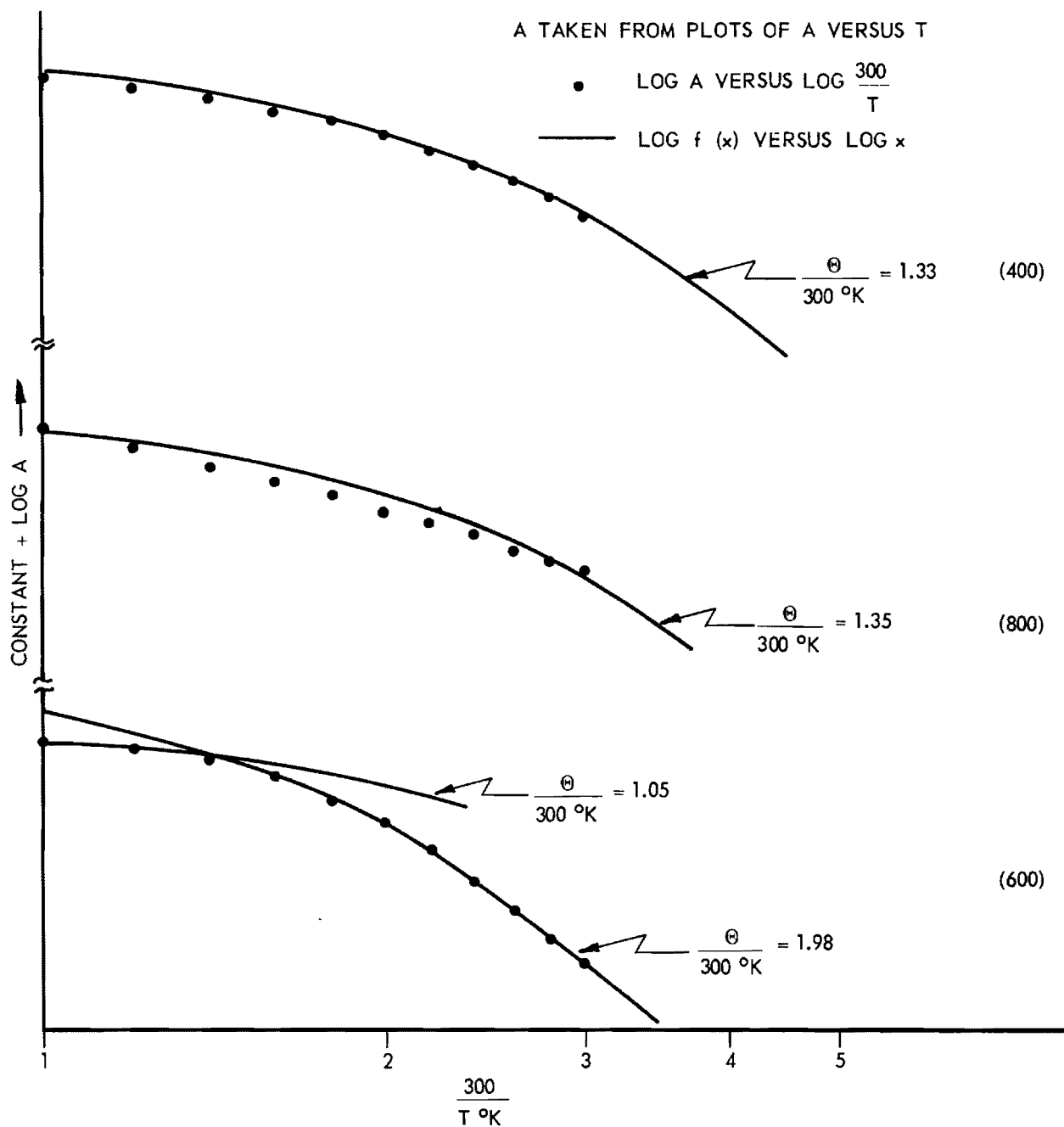


Figure 6. Log A Versus Log $\frac{300}{T}$ for AgCl Sample No. 7.

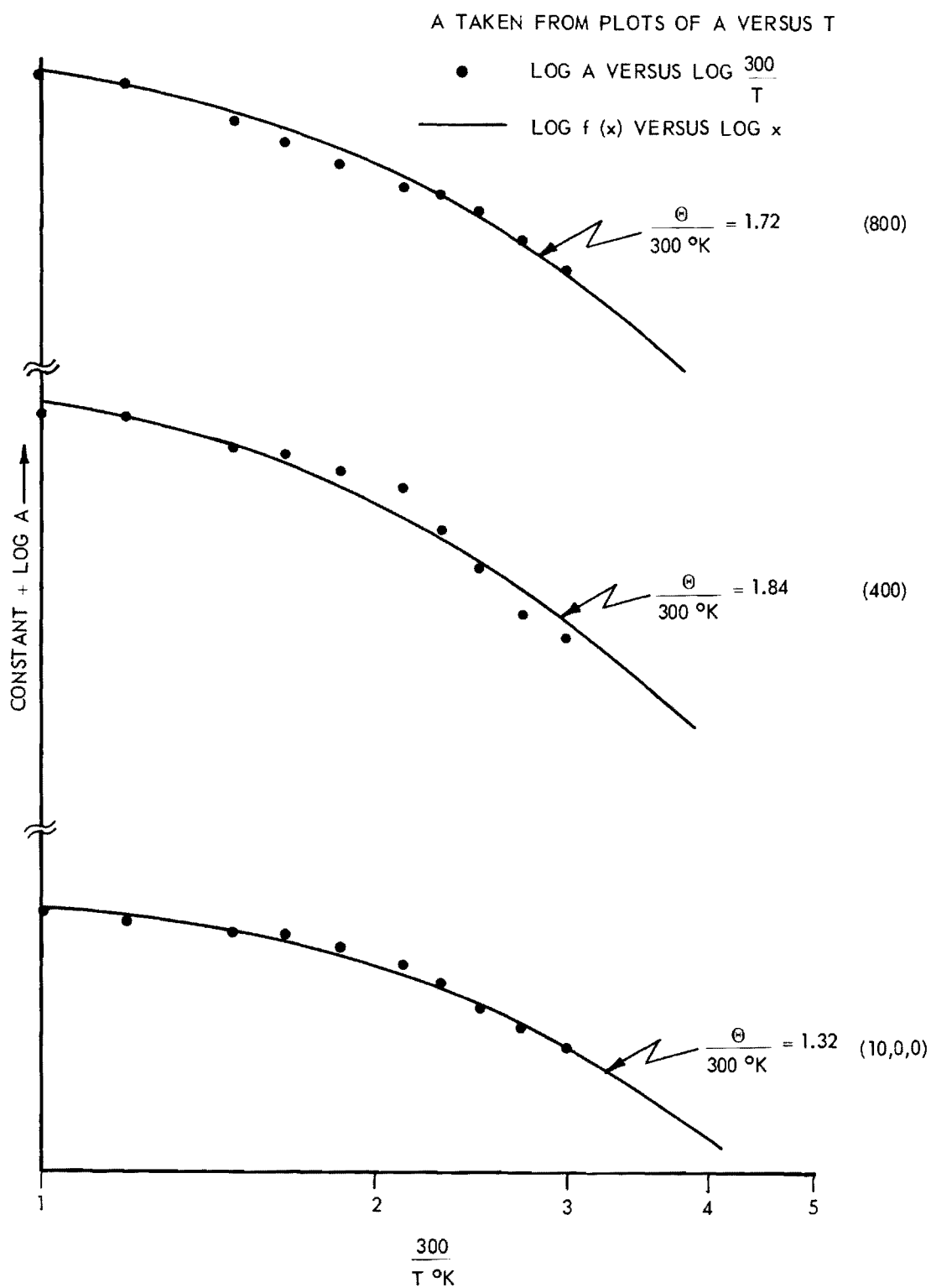


Figure 7. Log A Versus Log $\frac{300}{T}$ for Al Sample No. 1.

It is interesting to note in figure 5 that the composite data for the three AgCl No. 7 reflections appears to fit $f(x)$ well over the whole temperature range. The indicated Θ , however, is far too large even so.

That the method is capable of yielding "correct" results is indicated by the result for the (10, 0, 0) of Al (figure 7). For the set of data collected for this particular reflection the Debye Θ values obtained from the curvature method and from the temperature slope method (i.e. directly from the A values) agree both with each other and with the literature values (based on specific heat and other methods). Here there is no question of either the value or constancy of m , as there may be with AgCl. Figure 8 shows the Θ value indicated by the temperature slope method for several Al reflections.

Since these intensity data for Al have since been shown to be unreliable (for reasons beyond those having to do with background), particularly for the stronger (lower order) reflections, no inference is intended here that the data tell us anything about aluminum.* They do show that the data which gave the "right" result with the curvature method, the (10, 0, 0) data, also indicated by the temperature slope method no change in the Debye Θ between 300° K and 100° K. Hence it appears that the curvature method is capable of yielding good results, given good data and no temperature dependence of $m\Theta^2$.

Why then are the Θ results so "bad" for AgCl? If the discrepancies were due to the uncorrected-for harmonic contributions they would be expected to vary considerably from reflection to reflection and, probably, generally to be

*Valid data for these same reflections are to be collected during the coming year.

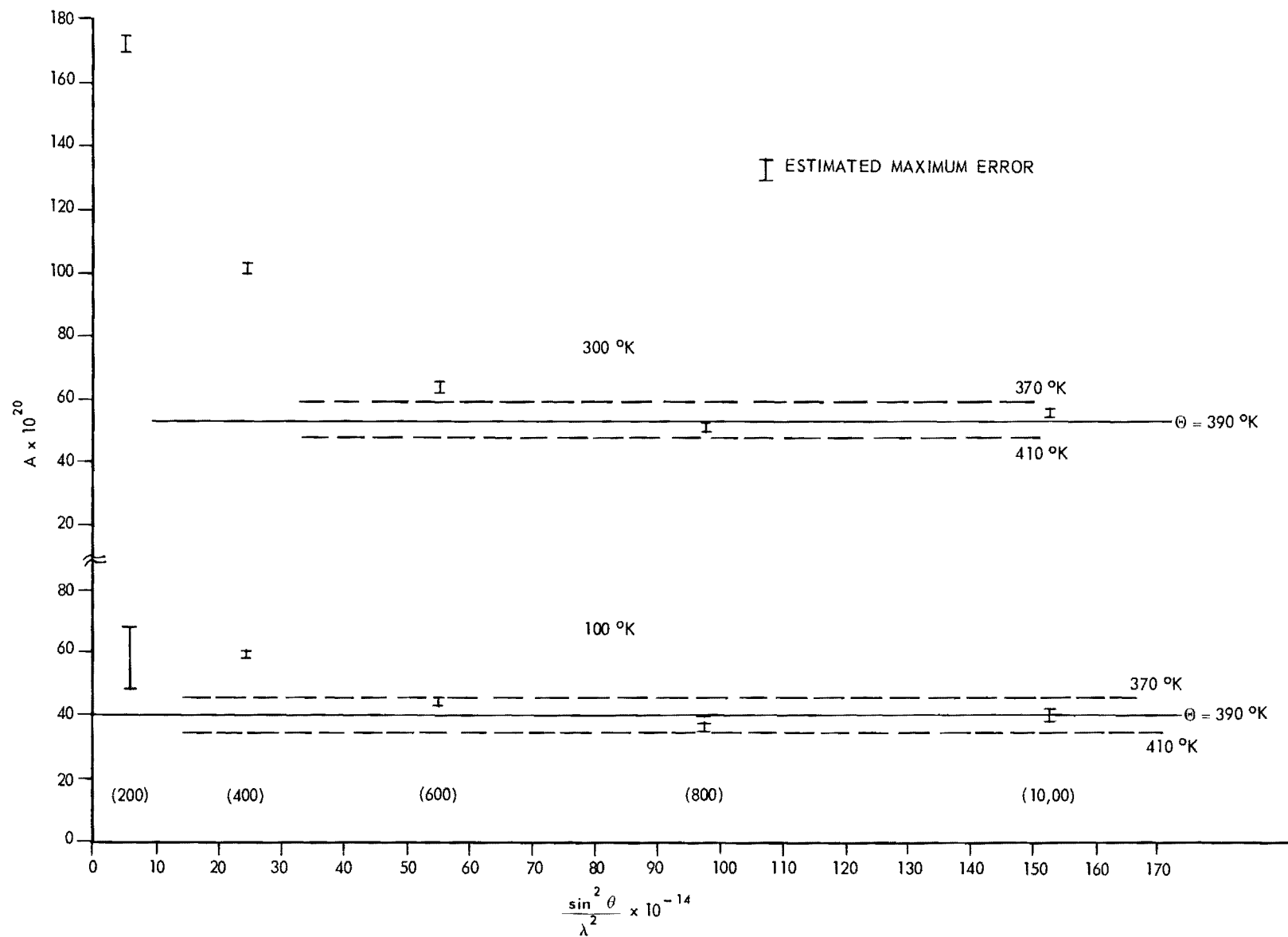


Figure 8. The Dependence of A on $(\sin^2 \theta)/\lambda^2$ for Al, Sample No. 1.

less or of opposite sign for the higher order reflections. During the coming year new I vs T data for which proper account is taken of harmonic background contributions will be collected for these same AgCl reflections.*

In the meantime, however, it appears that harmonic background contributions can not account for any major portion of the "errors" in the Θ 's obtained by the curvature method.

It also seems unlikely that the actual Debye Θ changes enough with temperature to cause the $A(x)$ curvature so to exceed the $f(x)$ curvature.

Extinction effects are a possibility, but they, too, seem unlikely to explain the fairly consistently (from reflection to reflection) very large Θ values indicated by the curvature at, for example, low temperatures. The fact that the results are "worse" at the lower temperature would also seem to rule out anharmonic vibration effects as a cause.

In AgCl, however, there are optic lattice vibrational modes present, there are two different atomic masses, and the effective average mass, m , in equation (24) may change with temperature as the relative excitation of the various optical and acoustic modes changes with temperature. However, we do not see large temperature-dependent differences between the A values for odd parity reflections and those for even parity reflections such as one would expect (see discussion A vs ϕ character for more detail) if the relative vibrational amplitudes of the two atom types were markedly temperature dependent.

It appears quite possible, then, that the curvature method may afford a particularly sensitive test of the breakdown of some of the assumptions in the

* In fact, as of this writing, the data have been collected though the analyses have not yet been done.

simple theory used here. The kind of data being collected in this work does have sufficient precision to permit the use of the curvature method with the attendant advantages pointed out at the outset of this discussion. When new data corrected for harmonic background components are available, and particularly if extinction may be shown experimentally to be either absent or independent of temperature, one may hope to try to use the curvature method not only to indicate the presence of a breakdown in the assumptions but the extent of the breakdown and what modifications to the theory are required.

IV. THERMAL EXPANSION STUDIES

A. Introduction

Work has continued on X-ray measurements of the thermal expansion of AgCl in the 100° - 300° K temperature range.

The measurement of thermal expansion has become of interest in itself for

- (1) evaluating some experimental techniques, e.g. temperature measurement,
- (2) the results themselves and their implications to lattice vibration theory, and
- (3) the determination of the Debye Θ for comparison with the results obtained from intensity vs temperature measurements.

We now have available a program for the Burroughs 220 computer which fits experimental d_{hkl} vs T data with a polynomial of order one to five, takes the derivative of the computed polynomial at selected temperatures, and then divides the derivatives by the d computed at 0° C to give directly the coefficient of thermal expansion at the selected temperatures.

Originally the purpose for our measurements of the thermal expansion of AgCl in the 100° to 300° K temperature range was to permit the calculation of the

volume dependence of the Debye Θ ; no AgCl thermal expansion data in this temperature range could be located in the literature at first. However, when Sreedhar's (1954) data became known to us it was found that our data did not agree favorably with his. Additional thermal expansion data were then collected from a total of three AgCl crystals, one of which was doped with Cu impurities in an effort to determine the effect of X-ray induced defects (if any) on our measurements and to permit a critical comparison of our results with those of Sreedhar. These data were also needed before a note could be published in a journal. Additional thermal expansion data were also obtained from AgCl in the 300° to 600° K temperature range and from NaCl and Al in the 100° to 300° K temperature range for the purpose of evaluating our experimental techniques. Similar measurements had been reported in the literature by several investigators (Sharma (1950), Strelkow (1937), Buffington and Lattimer (1926)) and are apparently on firm ground.

Although our thermal expansion data for NaCl and Al agree much better with those reported in the literature than do our AgCl data,^{*} there are still slight differences. To explain the discrepancy in the NaCl data would require an error in our temperature measurement of several degrees Kelvin at 100° K or a shift in sample position of about 0.004 in. between room temperature and 100° K. After taking into consideration various aspects of our experiment it is felt that the most likely source of error on our part is the calibration of our thermocouple (see footnote page 16). The recalibration of our thermocouple will employ a platinum resistance thermometer recently calibrated by N.B.S. as a standard.

* Our high temperature AgCl data agree within experimental error with those found in the literature.

B. Theory

A brief search of the literature for a theory of thermal expansion with which to compare our data revealed that the Mie-Grüneisen theory is probably best suited and is frequently used by other investigators. In this theory it is assumed that (1) when the atoms are at rest at their equilibrium positions the internal energy of a solid depends only on the volume, (2) the atoms are at rest at their equilibrium positions at $T = 0^\circ \text{K}$, and (3) the temperature derivative at constant volume of γ (the Grüneisen constant) is zero. The Mie-Grüneisen theory then yields

$$3\alpha = \frac{\gamma K_T C_V}{V}, \quad (36)$$

which is a low temperature approximation derived from the more general relation,

$$\frac{V - V_0}{V_0} = \frac{E/Q_0}{1 - k(E/Q_0)}, \quad (37)$$

where

- α = linear coefficient of thermal expansion
- K_T = compressibility
- C_V = specific heat
- V = volume
- $Q_0 = V_0/\gamma K_0$
- E = vibration energy of the atoms
- k = constant

and subscript "0" refers to $T = 0^\circ \text{K}$. In the Mie-Grüneisen theory γ is given by

$$\gamma = - \frac{V}{E} \left(\frac{\partial \tau}{\partial V} \right)_T \quad (38)$$

where τ is the vibrational free energy of a solid.

The above assumptions are probably not met by any real solid. They do not take into account temperature-induced changes at constant volume in the binding energy or force constants, which changes would be expected as a result of the dependence of the electron distribution in the bonds on temperature and the thermal vibrations of the atoms. It is also well known that atoms are not motionless at $T = 0^\circ \text{K}$ and that γ is usually a function of temperature. In spite of the obvious shortcomings of the theory, equations (36) and (37) often describe thermal expansion in an adequate and simple form so that they are often used for evaluating thermal expansion data. Discrepancies between theory and experiment should not be alarming however.

An interesting method, due to A. Taylor (1960), for comparing thermal expansion data with theory involves the use of equation (36) in a manner similar to that used in our "curvature method." Assuming that the major temperature dependence of the right side of equation (36) is due to C_V then,

$$\alpha \approx (\text{constant}) C_V \quad (39)$$

The Debye theory of specific heats has been quite successful in describing the temperature dependence of C_V of most solids in terms of the "reduced" temperature $T/\Theta (=1/x)$; thus a plot of $\log \alpha$ vs $\log T$ should be superimposable upon a plot of $\log C_V$ vs $\log (1/x)$. The amount by which one plot has to be moved along the abscissa to superimpose upon the other will permit a determination of Θ .

It is interesting to note that thermal expansion occurs as a result of the anharmonic lattice vibrations so that the Debye Θ obtained by the above method is actually based on this anharmonicity. However, the concept of the Debye Θ originated in a lattice vibration theory which is only valid for harmonic vibrations.

It will also be of interest to compare the Θ obtained by the above method with that obtained from the slope and curvature analyses of our intensity vs temperature measurements.

Figure 9 is a plot of $\log \alpha$ vs $\log T$ for AgCl (circles) superimposed on a plot of $\log C_V$ vs $\log (T/\Theta)$. The Debye Θ obtained is 300° K , approximately a factor of two larger than expected. Even though the data are suspect due to possible temperature measurement errors, it is felt that the possible magnitude of such errors is much less than could possibly explain such a large discrepancy in Θ .^{*} It is felt rather that the discrepancy is primarily due to a breakdown in the assumptions of either the simplified Mie-Grüneisen or Debye theories, or both, for AgCl. It is interesting to note that A. Taylor finds no discrepancies for SiC, which has a $\Theta \approx 1430^\circ \text{ K}$. It is our opinion that for AgCl the discrepancy in Θ obtained from a curvature method analysis of both the thermal expansion and intensity vs temperature data provide an interesting demonstration that a breakdown in the assumptions of the Debye theory of lattice vibrations exists.

V. OTHER PROGRESS

A. Data Collection

Work has continued on collecting I vs T data on several AgCl samples. In addition some similar data were collected on single-crystal Al. Al should provide a convenient check on the validity of some of our analytic procedures since in it there is no question of average atomic mass. Further the specific

^{*}The recalibration of our thermocouple, which was performed after the end of this report period, reveals that this is indeed the case.

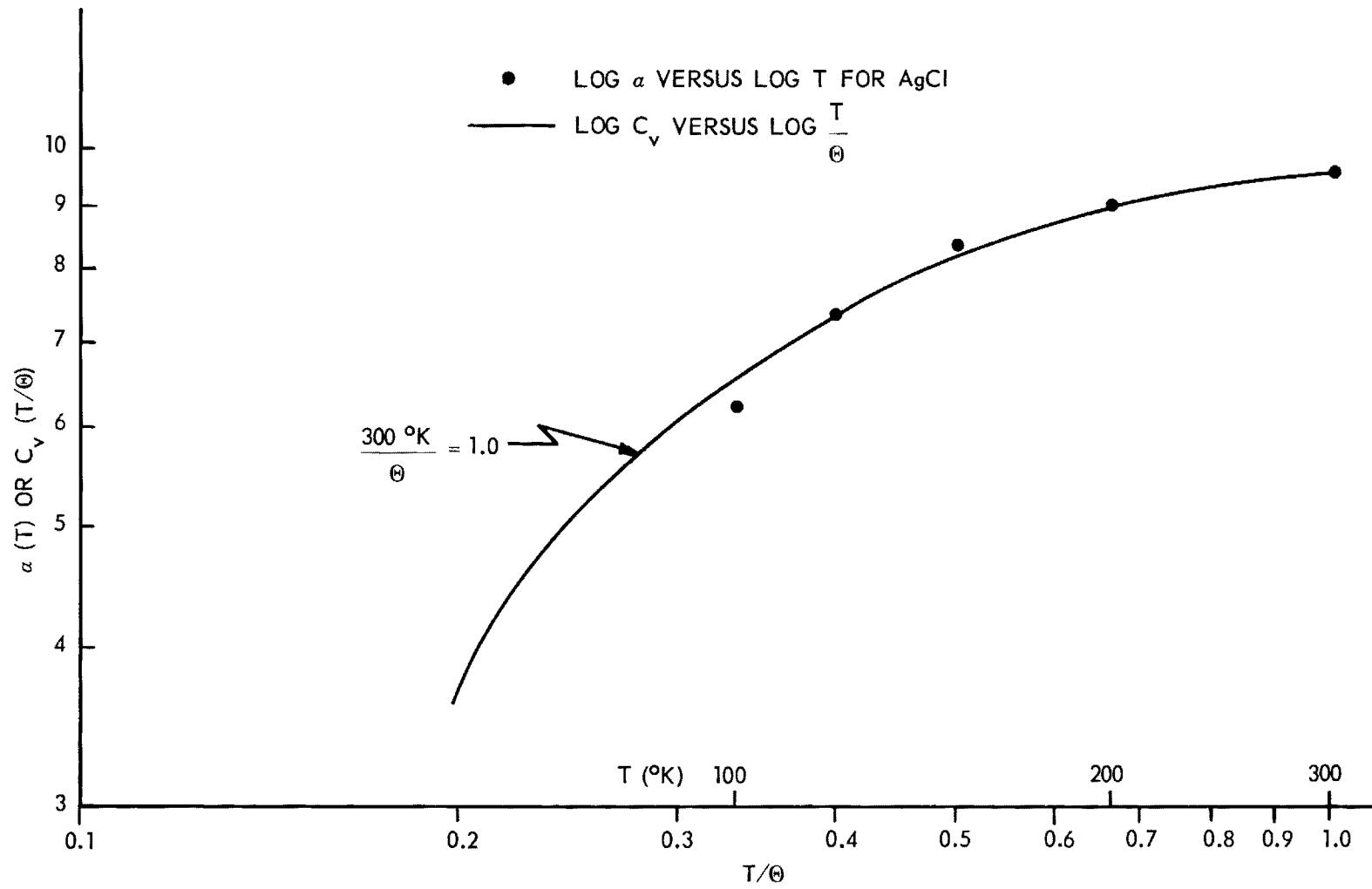


Figure 9. Log a Versus Log T for AgCl.

heat (Griffiths, 1914), elastic constants (Jones, 1949), and lattice vibrational spectrum as determined both by X-ray IDS methods (Walker, 1956) and inelastic scattering of cold neutrons (Carter, 1957) are well known.

As was implied earlier, however, most of the data collected have since been found to be unreliable; it is now recognized that the background problems discussed in Technical Report No. 2 largely invalidate most of the precision data collected prior to February 1961. In addition to that, all of the data collected with one particular instrument over a period of several months (December 1960 to May 1961) have had to be largely discounted because of intermittent malfunctions and non-linearity in the detection circuitry. Since the aluminum data were taken with that instrument no significance can be attached to the discrepancies, where they occur, between results obtained and those expected. Results shown in figure 8 are useful only to show that the "right" answer can be obtained at least sometimes with our slope method and that, for this simple material, when the "right" result is obtained from the slope method the curvature method yields the same result (see discussion of curvature method for further details).

The "loss" of so much of our "best" I vs T data collected over the last three years made acutely felt the need for faster ways to take such data. At the end of the report period plans were being formulated to partially automate, in simple fashion, some of the data-taking procedures. As of this writing (October 1961) some relatively simple additions and modifications to the equipment have been made with the result that the actual data-taking process has been speeded up by more than a factor of 3. Nearly all of the I vs T data on AgCl that were previously (before the re-examination of the background question) considered valid have now been recollected with proper (see Technical Report No. 2) background assessments.

B. Curve Fitting Considerations

In past reports, particularly Annual Report No. 2, the desire for analytic curve fitting procedures for I vs T data, A vs ϕ , and thermal expansion data has been emphasized. In the case of the I vs T data and thermal expansion data, in particular, the points of interest are the first and sometimes the second derivative of the "best-fit" curve. It appears that in general the problem of analytically fitting a curve to experimental points in such a way as to yield reliable derivatives is quite difficult. While we have not made any real search of the literature on this point ourselves, the experience of our applied mathematicians (Dr.'s J. Walker and J. McKay, Private Communications) and other groups (Blanks, et. al., 1958), is that even a well damped fitting function such as, for example, Tschebyscheff polynomials do not yield generally valid results.

If the correct functional form were known, of course, there would be no such problem about unreliable derivatives; the known functional form provides the rule for interpolation between the experimental points and hence properly controls the derivatives both at and between points.

In the case of the I vs T data for AgCl it is now clear, from the comparisons of $A(T)$ and $f(x)$ made in connection with the curvature method, that the functional form we provided for I vs T was probably not correct. It is therefore not surprising that we had little success in trying to make a least-squares fitting of our data to the (incorrect) function (see p. 21, Annual Report No. 2).

In conclusion then, it appears that, until the actual functional form of the variables is better known, there is little point in trying to use analytic curve fitting procedures on either our I vs T data or our thermal expansion

data with the hope of getting usable derivatives. The better approach seems to be a straightforward graphical approach such as we have been using.* If an analytic approach is to be used for the determination of slopes it probably should be applied directly to first differences rather than to the experimental values themselves. It can be argued that whatever experimental information is available about the slope is contained in these first differences anyway, so no loss of accuracy in slope determination will be encountered by fitting them directly.

C. Crystal Perfection (Dynamic Theory) Considerations

The question of both the existence of extinction and its possible temperature dependence has been of interest throughout the work of this project.

We are of course interested in extinction because of its possible effect on our I vs T data and their subsequent analysis by slope or curvature methods. We are also interested in extinction as one of a number of "dynamic theory effects," i.e., effects which can be explained only by the dynamic and not by the kinematic theory of diffraction. We are particularly interested in the role of thermal vibrations in the dynamic theory and look forward to experimental work, no doubt involving the temperature dependence of various dynamic theory effects, along that line.

Parthasarathy's (1960) result for the temperature factor of a perfect crystal has been mentioned. He makes an interesting suggestion to the effect

* An interesting point of technique for graphically obtaining slopes was provided us by Mr. Bruce Warren of the Georgia Institute of Technology. Consider a plane mirror such as a silvered microscope slide placed across the curve and perpendicular to the paper. The mirror surface will be perpendicular to the curve at the point of contact when the curve and its mirror image appear to form one unbroken smooth curve.

that for a real crystal the temperature factor might be given by

$$I_T = I_0 e^{-PM} \quad (40)$$

where P is a constant independent of temperature and

$$1 \leq P \leq 2 \quad (41)$$

For the ideally mosaic crystal $P = 2$; for the perfect crystal $P = 1$. As was pointed out in connection with the discussion of curvature studies, such an extinction effect would not affect the curvature analysis. On the other hand, it would affect the slope analysis and presumably one could find P for the particular reflection by comparison of the two results.

If it turns out that such a P exists, or if it exists even as a slowly varying function of temperature, and can be found or approximated from the temperature dependence of a single reflection this comparison of slope and curvature results could possibly be a valuable means for (1) determining extinction corrections for relative intensity data in special cases, (2) following extinction, (and hence crystal perfection), as a function of various treatment parameters in the presence of changing temperature factors. In any event it seems likely that our present slope and curvature analysis methods will provide the means for showing whether P is or is not independent of temperature, a point which is of some interest in itself.

As a first step toward making a direct attack on dynamic theory effects we started collecting a few I vs T data on single crystal Si which is expected to exhibit considerable extinction. No results are available yet. Si and Ge are particularly good choices not only because they are available in highly

perfect form but because Dr. Batterman of Bell Labs has recently undertaken a study of the temperature dependence of some dynamic theory effects in these materials. He is particularly working on the effect of temperature on line profiles (as determined by high resolution double crystal spectrometry); it will be of interest to compare our results with his and perhaps to share specimens.

There does exist one way of making experimental determination of the extinction for single reflections. This is Chandrasekhar's (1960) method, which makes use of the fact that in the dynamic theory there is a reflection intensity dependence on incident beam polarization which is additional to that found in the kinematic theory. One therefore wishes to use a plane polarized incident beam and to be able to rotate the plane of polarization. The use of a diffracted beam as a source of polarized X-rays is a possibility, but rotation of the plane of polarization entails rotation of either the specimen or the X-ray tube and monochromator about the diffracted beam as axis.

A much preferred arrangement is made possible by use of the Borrmann effect. Cole (1961) has described the use of the Borrmann effect to provide crystal monochromatization. One of the attractive features is that the anomalously transmitted beam is parallel to and offset very little from the incident beam. Furthermore, this anomalously transmitted beam is completely plane polarized and the plane of polarization may be changed simply by rotating the crystal about the incident beam. Since the anomalously transmitted beam is essentially coaxial with the incident beam, then neither the specimen nor the X-ray tube need be moved when the plane of polarization is rotated. The rotation of the plane of polarization in the beam incident on the sample is then as simple as is the rotation of the plane of polarization in a polarizing microscope. We were favored

with a visit from Dr. Cole in March 1961. It turned out he had been using just such a rotatable polarizing monochromator for about one year. He has kindly sent us a suitable crystal along with plans for his rotatable holder and, as of this writing, we now have such a monochromator in operation. We have been referring to the device as a Borrmann monochromator because it employs the Borrmann effect, however, it is more appropriate to call it a Cole monochromator as it seems to have been Dr. Cole's development from the beginning. We therefore recommend the use of the term "Cole monochromator".

There are of course no results to be reported here on the use of the Cole monochromator and Chandrasekhar's method to assess extinction as a function of temperature. We hope to apply this method and our slope and curvature methods to some of our samples during the coming year.

VI. FUTURE WORK

A. Temperature Measurement

A first task in the following report period will be the recalibration of our thermocouples. The recalibration will make use of a platinum resistance thermometer in order to eliminate possible uncertainties in "fixed" melting and freezing points.

B. Data Collection and Analysis

Now that our experimental techniques are fairly well established it is expected that during the coming year relatively more attention will be given to data interpretation. The procedures discussed in this report pertaining to slope and curvature analysis will be used to study TDS effects and to separate the individual contributions of each atom type to the AgCl data.

Where obvious discrepancies between theory and experimental results occur (such as is expected with the curvature analysis of AgCl data), attempts will be made to determine the nature and extent of the discrepancies so that the simple theory can be modified. Such modifications may involve taking into account anharmonic vibrations and the difference between the real vibration spectrum and the Debye spectrum. Some other, more specific points of interest which will be pursued are:

- (1) a separation of the one-phonon and two-phonon TDS contribution and an investigation of the lattice vibration information obtainable from a knowledge of K_1 and K_2 , (equation (13)),
- (2) the dependence of the recognized Debye Θ on the individual pseudo Θ 's pertaining to the two atom types in AgCl,
- (3) the temperature dependence of Θ and the comparison of this dependence with (a) that predicted by Paskin and (b) that obtained with other experimental techniques,
- (4) possible dependence of A on crystallographic direction.

All of the AgCl and Al intensity-vs-temperature data that are on hand will be recollected with improved background determinations. With the use of the anticipated partially automatic data collection procedure, the recollection of these data should not be very time consuming. Some data will be collected with the use of a Cole monochromator in order to assess the possible change in extinction with temperature. Data obtained from an especially pure Si sample may also be of interest in this last case.

Our work on AgCl seems to indicate that the simple lattice vibration theory of Debye breaks down for this substance. To investigate this point further,

it is desirable to compare results obtained for AgCl with those obtained from solids, such as Al, for which the Debye theory should be a good approximation. KCl may also be of interest here. Even though it is diatomic, both the scattering powers for x-rays and the atomic masses are nearly equal for the two atoms. The simple theory assumptions of a simple cubic structure with one atom per unit cell are therefore well approximated by KCl. The breakdown (if any) of the Debye theory in diatomic solids having mass ratios different than AgCl (e.g. AgBr and NaCl) also deserves investigation.

C. New Directions

Relatively little has been done in the way of treating the dynamic theory with temperature motion as a function of temperature, either experimentally or theoretically. Our interest in this area continues to grow and has been further enhanced by our contacts with Dr. Cole and Dr. Batterman. As the work on the slope and curvature methods applied to ideally imperfect crystals reaches conclusions, we will probably shift the project emphasis more and more to the role of temperature motion in dynamic theory effects.

D. Probable Publications

Soon after recalibration of our thermocouple and possible reanalysis of the AgCl, Al, and NaCl thermal expansion data, we intend to submit for publication our results for the coefficient of thermal expansion of AgCl in the 100° to 300° K temperature range. The publication probably will be a short note and will include a comparison of our results with those obtained by Sreedhar (1954).

The need for written expositions of single crystal diffractometry techniques has already been mentioned. It is hoped that a technical report pertaining to this subject can be published during the next year.

VII. OTHER ACTIVITIES

During this report period the principal investigator addressed the Polytechnic Institute of Brooklyn "Point Group" seminar on February 9 in New York City and the Washington Crystal Colloquium meeting at the National Bureau of Standards on February 10. The topics chosen for discussion were almost entirely based on the work of this project. The measurement of background was discussed at both meetings. In addition, our work on thermal expansion and on the slope and curvature methods of analysis of intensity-vs-temperature data were discussed at "Poly" while our work on the systematic procedure for balancing filters was presented at the Washington meeting.

Mr. Nicklow, the graduate student associated with the project, delivered a paper at the 1961 Southern Metals Conference which was held in Atlanta on April 24, 25, and 26, 1961. The talk pertained to possible metallurgical applications of intensity-vs-temperature measurements.

During this past year we were favored with visits from Dr. H. Cole of IBM, Dr. B. W. Batterman of Bell Labs, Dr. George Vineyard of Brookhaven National Labs, and Ephraim Segerman of the Lever Brothers Company in New Jersey. The informal discussions which we had with these gentlemen concerning our work and theirs were very informative and encouraging. We thank them for the discussions.

Annual Report No. 3, Project No. A-389

In particular our interest in dynamic theory effects was further enhanced by our discussions with Dr. Cole and Dr. Batterman.

Respectfully submitted,

R. A. Young ✓
Project Director

REFERENCES

- Blanks, B. L., Free, W. R., McKinley, H. L., Meek, R. E., Dropp, R. R., and Robinette, S. L., (1958), "Investigation and Study of Communication Interference Reduction Techniques," Final Report, Project A-312 EES, Georgia Institute of Technology, RADC Contract AF-30(602)-1638.
- Buffington, Ralph M., and Latimer, Wendell M., (1926), "The Measurement of Coefficients of Expansion at Low Temperatures- Some Thermodynamic Applications of Expansion Data," J. Amer. Chem. Soc. 48, 2305.
- Carter, R. S., Palevsky, H., and Hughes, D. J., (1957), "Inelastic Scattering of Slow Neutrons by Lattice Vibrations in Aluminum," Phys. Rev. 106, 1168.
- Chandrasekhar, S., (1960), "An Experimental Method of Correcting for Extinction in Crystals," Acta. Cryst. 13, 588.
- Cole, H., Chambers, F. W., and Wood, C. G., (1961), "An X-Ray Polarizer," J. Appl. Phys. 32, 1942.
- Griffiths, E. H., and Griffiths, Ezer, (1914), "The Capacity for Heat of Metals at Low Temperatures," Proc. Roy. Soc. 90, 557.
- Jones H., (1949), "Structural and Elastic Properties of Metals," Physica 15, 13-22.
- Parthasarathy, R., (1960), "The Temperature Factor in the Dynamical Theory of X-ray Interference for a Perfect Crystal with Heat Motion," Acta. Cryst. 13, 802.
- Sharma, S. S., (1950), "Thermal Expansion of Crystals," Proceedings of the Indian Academy of Science, 32A, 268-74.
- Sreedhar, A. K., (1954), "Thermal Expansion of Crystals at Low Temperatures," J. Indian Inst. Sci. A36, 186.
- Strelkow, P. G. (1937), "Die Wärmekonstanten Bie Hohen Temperatures," Physik. Zeits. Sowjetunion 12, 77-82.
- Taylor, A., and Jones, R. M., (1960), "The Crystal Structure and Thermal Expansion of Cubic and Hexagonal Silicon Carbide," Silicon Carbide, Pergamon Press.
- Walker, C. B., (1956), "X-ray Study of Lattice Vibrations in Aluminum," Phys. Rev. 103, 547.
- Young, R. A., (1959), "X-ray Diffraction Studies of Thermal Motions in Crystals," Annual Report No. 1, Project A-389 EES, Georgia Institute of Technology, ONR Contract NONr 991(00) and 991(06); NR 017-623.
- Young, R. A., (1960), "X-ray Diffraction Studies of Thermal Motions in Crystals," Annual Report No. 2, Project A-389 EES, Georgia Institute of Technology, ONR Contract NONr 991(00) and 991(06); NR 017-623.

APPENDIX A

Balanced Filters for X-ray Diffractometry^{*}

R. A. Young

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Atlanta 13, Georgia

Abstract

The theoretical basis and the experimental specifics are presented for a generally valid, systematic procedure which achieves simultaneous balance of x-ray filter pairs over a wide range of wavelengths. Kirkpatrick's¹ third material is necessarily employed. Corollary topics discussed include the preparation of filters and holders, criteria for balance, methods of testing for balance, and the role of pulse height analysis in the balanced filter technique. It is shown how a number of points of possible experimental difficulty may be recognized and overcome. Results obtained by following the described procedure are presented.

¹Kirkpatrick, Paul, Rev. Sci. Instrum. 15, 223 (1944).

^{*}Technical Report No. 1.

APPENDIX B

Background Intensities^{*}

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Abstract

The contribution to apparent Bragg intensities of harmonic and even sub-harmonic wavelengths in crystal - monochromatized incident radiation is generally recognized (Batterman¹). However, in current practice at least, the fact appears usually to be overlooked that harmonic wavelengths contribute to the observed intensity at the Bragg setting even in the ordinary, filtered-radiation techniques. In certain popular methods this harmonic contribution will be peaked at the Bragg position. Neglect of this contribution would have produced an intensity error larger than a factor of two in one example on hand. The ω -scan and peak-height methods of single crystal diffractometry are particularly affected. Pulse height discrimination alone is inadequate to correct the problem; it appears necessary to use balanced filters and to make measurements both on and off the Bragg setting.

An expression is presented for the dependence of the harmonic contribution on counter aperture, structure factors, Bragg angle, and other parameters. The qualitative correctness of the expression is demonstrated by experimental results.

While the present discussion is concerned principally with single crystal diffractometry, there exist obvious implications to film methods as well.

¹B. W. Batterman, Rev. Sci. Instru., **32**, 393 (April 1961).

^{*}Paper presented at the August, 1961 ACA meeting.

APPENDIX C

Background Intensities in Single Crystal Diffractometry*

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Abstract

The question of the component parts and character of the background in x-ray diffraction has been re-examined in some detail. The components are divided into two classes: those which may be peaked at the Bragg position, principally the harmonic components; and those which do not peak at the Bragg position, here called the miscellaneous components.

The contribution to apparent Bragg intensities of harmonic and even sub-harmonic wavelengths in crystal - monochromatized incident radiation is generally recognized (Batterman¹). However, in current practice at least, the fact appears usually to be overlooked that harmonic wavelengths contribute to the observed intensity at the Bragg setting even in the ordinary, filtered-radiation techniques. Neglect of this contribution would have produced an intensity error larger than a factor of two in one example on hand. The ω -scan and peak-height methods of single crystal diffractometry are particularly affected. Pulse height discrimination alone is inadequate to correct the problem; it appears necessary to use balanced filters and to make measurements both on and off the Bragg setting. The common method of taking as the whole background the intensity obtained by off-setting the crystal alone completely misses these harmonic contributions.

¹B. W. Batterman, Rev. Sci. Instru. 32, 393 (April 1961).

* Technical Report No. 2.

An expression is presented for the dependence of the harmonic contributions on counter aperture, structure factors, Bragg angle, temperature, and other parameters. The qualitative correctness of the expression is demonstrated by experimental results. The consequences of neglecting this component are discussed in several connections and are demonstrated in some.

The control and measurement of the miscellaneous component is also considered. Particular attention should be given to the counter aperture size and to both incident and receiving collimators even with the large beam used in single crystal diffractometry.

The circumstances under which each scanning method may be used are examined. It is concluded that the peak height method is inherently a poor method. It is strongly recommended that a balanced filter technique be used with the ω -scan at all times and in some cases with the 2θ -scan. The ω -scan is then slightly preferable for other reasons.

Detailed procedures for correct background determination with balanced filters are presented.

While the present discussion is concerned principally with single crystal diffractometry, implications to film methods and to powder diffractometry are also pointed out. It is concluded that background measurements are best made on the Laue streaks and that all strong reflections should be made to appear on zero layer photographs where the full extent of these Laue streaks may be seen.

X-RAY DIFFRACTION STUDIES OF THERMAL MOTIONS IN CRYSTALS

R. A. Young

Final Report

30 June 1969



Contract Nonr 991(00) 991(06); NR 017-623 (Project A-389)
Physics Branch, Office of Naval Research
Washington, D. C.



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X-RAY DIFFRACTION STUDIES OF THERMAL MOTIONS IN CRYSTALS

by

R. A. Young

Final Report, Contract Nonr 991(00) 991(06); NR 017-623

Project A-389

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ABSTRACT

Primarily through abstracts of reports and published papers, this final report recounts project work done from 1958 through 1966 on x-ray studies of thermal motions in crystals. Principal use was made of the temperature dependence of x-ray Bragg-reflection intensities. Precision was emphasized. Both new experimental procedures and new analytical procedures were developed to produce and to exploit the precision inherently available. Instrumental design and use strategy, X-specimen temperature control, understanding and control of the background, and wavelength control received extended attention. Analytic techniques were developed to yield, from "continuous" intensity-vs-temperature data, absolute Debye temperatures and separate measures of Na and Cl (or Ag and Cl) atomic thermal motions in crystals with the NaCl structure. The resulting information was surprisingly detailed. For example, comparison with calculations based on the elastic spectrum of Al showed the experimentally observable quantities to be sensitive to a 5% scaling error in one branch of that spectrum.

In an ancillary effort, the thermal coefficient of expansion of AgCl was determined over the range 120-710°K and the activation energy for Frenkel defects was determined.

Extension of the studies to perfect crystals and slightly distorted perfect crystals was initiated and is the subject of an unfinished Ph.D. thesis.

I. INTRODUCTION

The dominant theme throughout the life of the project has been the exploitation of the precision with which changes in x-ray diffraction intensities can be measured for the purpose of studying thermal motions in crystals both as (i) time averages of the vibrations of individual atoms and (ii) lattice vibrations. Comparison of the intensity of a reflection at one temperature to its intensity at another temperature (or under some other condition of environmental change) avoids many corrections that otherwise would have to be applied to the measured relative intensities. In this manner the change of intensity can be determined with far greater precision and accuracy than the intensity itself is known. The technique has proved to be almost surprisingly successful, especially when a single reflection intensity was monitored continuously while the temperature was changed. For example, in the case of aluminum it was shown that the second derivative of intensity-with-respect-to-temperature was sensitive to a 5% error in the scale factor of one branch of the elastic spectrum.

To a very large extent the work has been, necessarily, devoted to the development of both experimental and analytical techniques for acquiring suitable data and for extracting the desired information from them. Even the development of the experimental techniques required a certain amount of analysis. The most interesting of such processes and results have been described in the papers and reports produced on this project, a complete list of which is given in Section VII. In Section II we have collected the abstracts of those papers and reports which dealt primarily with experimental techniques. There are two general aspects, (i) matters of instrumental and

diffraction geometry, of wavelength control, and of proper background measurement in which some advances were required in order that intensities could be measured with the required precision and (ii) methods of controlling the specimen temperature with suitable precision and sufficiently small thermal gradients.

Not finding suitable measures of the thermal expansion coefficient of AgCl below room temperature in the literature, we recognized that our experimental apparatus lent itself to such measurements. Initially thinking to spend only a few days, at most, on this subject, we found that each technique improvement and each result showed more promise and more interest. The eventual result was that we acquired what appeared to be the best data available for the thermal expansion of silver chloride over the entire range from 120°K to 710°K (18° below the melting point). We then were able to compare the results to theory with a view towards anharmonicity in the thermal vibrations and towards the thermal generation of defects near the melting point. The abstract of the resulting paper constitutes Section III of this report.

Both AgCl and Al were studied as examples of the ideally imperfect crystal and the results are reported in the Ph.D. thesis of Robert M. Nicklow, issued as Techinal Report No. 3. More importantly, this report describes the derivation and application of most of the analytic techniques developed (for extracting the desired information from the data). In fact, except for the experimental techniques developed, this rather large report presents all of the scientific results up to the time of its issue. Several papers should result from this report, one dealing with lattice vibrations and the temperature dependence of Bragg intensities in aluminum, a somewhat similar one on silver chloride, and one dealing with correction of Bragg

intensities for thermal diffuse scattering contributions. The first paper has been published and its abstract is included in Section IV along with the abstract of the Technical Report No. 3. The second paper is presently in draft but is being delayed pending the possibility of including some additional calculations better relating the results to the probable elastic spectrum. The third proposed paper is probably no longer timely and publication plans have been dropped.

The success of the experimental and analytical approaches with the imperfect crystals, and certain features of the theory used in the analyses, suggested that a study of thermal motions in perfect and nearly perfect crystals, for which the dynamical theory of diffraction must be employed, would be fruitful. Of particular interest were (i) the form of the temperature factor for the ideally perfect crystal and (ii) the dependence of certain of its coefficients on the degree and type of imperfection introduced into the crystal. This work has formed the basis for the Ph.D. dissertation in physics for William E. Krull. Though the experimental work was essentially complete some time ago, the thesis is not yet fully written. However, an abstract of it is provided in Section V.

In Section VI of this report there are listed the research personnel involved and the degrees earned by students associated with the project. Section VII is a complete list of the publications and reports issued on the project.

II. TECHNIQUES

A. X-Ray Diffraction and Instrumental Geometry

- (i) "X-Ray Diffraction Studies of Thermal Motions in Crystals," R. A. Young, Annual Report No. 1, Contract Nonr 991 (00) and 991 (06), Office of Naval Research (Physics Branch) 31 May 1959.

Abstract

The general problem is the study, by x-ray means, of thermal vibrations of the atoms in crystals and their interactions with other phenomena of interest in crystal physics. The first experimental studies deal with the temperature dependences of the motions in AgCl as revealed by their effect on the Bragg intensities. Extended consideration has been given to the background of the problem as found in the theory of and the literature on thermal motions of atoms, or lattice vibrations, as related to x-ray measurements of Bragg intensities.

A method for determining temperature factors (and hence Debye- Θ 's) from temperature dependences of x-ray intensities is derived and experimentally illustrated. A second method is suggested.

Possible effects on the data of such things as (1) thermal diffuse scattering (TDS), (2) temperature dependence of primary extinction, and (3) defect concentration are considered in some detail. Possibilities for assessing or studying the same factors through their effects on the apparent Bragg peaks are noted.

Equipment design and performance, design of experiments, experimental techniques, and characteristics of the specimen, etc. are discussed in de-

tail, especially in connection with accuracy and reproducibility.

Particular attention has been given to means for shaping the specimens without distorting them. Economical use of personnel time and materials has been considered.

A conceptual device referred to as the "acceptance region" model has been developed and utilized to determine the requirements on and the factors affecting the x-ray beam geometries.

Intensity data were collected for (hhh), (hh0), and (h00) reflections of AgCl at 10-degree intervals over the temperature range 90°K to 300°K.

Variations in diffraction peak breadths with temperatures were observed and are discussed.

Reproducibility in the intensity vs. temperature measurements was of the order of 1/2 to 3/4%.

The amplitudes of thermal motions of the silver and chlorine atoms were found to be quite similar, in agreement with observations by others. This result is interpreted to mean that the acoustic (rather than optical) modes of lattice vibrations have dominant importance to x-ray observations of the present type in AgCl.

An inflection in the semi-log plot of intensity vs. temperature was found in the case of the (111) reflection. The possibility that the inflection may indicate a temperature induced change in bond character will be investigated.

The errors introduced by TDS and α -doublet separation (both of which are temperature dependent) in the measures of Bragg intensities vs. tempera-

ture were partially overcome by a technique involving extrapolation to $\sin \Theta = 0$.

Evidence for anisotropy in the thermal motions of the atoms in AgCl was not conclusive; further effort will be expended definitely to support or to reject present indications of anisotropy. Existence of anisotropy would probably indicate anharmonic thermal vibrations.

Approximate Debye- Θ 's have been determined from the intensity vs. temperature data which are in reasonable agreement with literature values obtained by other means.

The general technique of extracting crystal-physics information from careful measurements of the temperature dependence of the Bragg intensities continues to show promise. Contemplated applications of the results includes preparation of detailed electron density maps (for which the temperature factors will be determined from their temperature dependences), first of AgCl and then of other materials. The study of various kinds of lattice defects and crystal imperfections will follow.

Sonderdruck aus: „Zeitschrift für Kristallographie“, 118, 3/4, 1963

Herausgegeben von G. E. Bacon, M. J. Buerger, F. Laves, G. Menzer, I. N. Stranski
Akademische Verlagsgesellschaft, Frankfurt am Main

Balanced filters for x-ray diffractometry*

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With 6 figures

(Received August 27, 1962)

Auszug

Es werden die theoretischen Grundlagen und die experimentellen Bedingungen für ein allgemein gültiges systematisches Verfahren zur Auswahl von Kompensations-Filterpaaren (balanced filters), die für einen weiten Wellenlängen-Bereich verwendbar sind, dargelegt. KIRKPATRICK'S Kunstgriff, einem der Filter eine dritte Substanz beizufügen, wird notwendigerweise angewandt. Die Diskussion schließt die Herstellung der Filter und der Filterhalter, die Ausgleichskriterien, die Methoden der Ausgleichsprüfung und die Rolle der Pulshöhenanalyse bei der Anwendung von Kompensationsfiltern ein. Es wird gezeigt, wie manche experimentelle Schwierigkeit erkannt und behoben werden kann. Über Ergebnisse, die auf Grund des angegebenen Verfahrens erhalten wurden, wird berichtet.

Abstract

The theoretical basis and the experimental specifics are presented for a generally valid, systematic procedure which effectively achieves simultaneous balance of x-ray filter pairs over a wide range of wavelengths. KIRKPATRICK's technique of adding a third material to one of the filters is necessarily employed. Corollary topics discussed include the preparation of filters and holders, criteria for balance, methods of testing for balance, and the role of pulse-height analysis in the balanced-filter technique. It is shown how a number of points of possible experimental difficulty may be recognized and overcome. Results obtained by following the described procedure are presented.

- (ii) "Balanced Filters for X-Ray Diffractometry," R. A. Young,
Technical Report No. 1, Contract Nonr 991(00) and 991(06),
Office of Naval Research (Physics) 15 June 1961.

Abstract

The theoretical basis and the experimental specifics are presented for a generally valid, systematic procedure which achieves simultaneous balance of x-ray filter pairs over a wide range of wavelengths. Kirkpatrick's (1944) third material is necessarily employed. Corollary topics discussed include the preparation of filters and holders, criteria for balance, methods of testing for balance, and the role of pulse height analysis in the balanced filter technique. It is shown how a number of points of possible experimental difficulty may be recognized and overcome. Results obtained by following the described procedure are presented.

C. Background Measurement

- (i) "Background Factors and Technique Design," R. A. Young,
Transactions of the American Crystallographic Association, Vol. 1,
42-66 (1965).

Abstract

The importance, effect, and control of random errors in background measurements, plus geometric requirements for proper measurement, are considered in terms of the signal-to-noise ratio and the various experimental variables affecting it. By appropriate choice of instrumental conditions the signal-to-noise ratio can be substantially improved in many cases without any loss in net intensity or increase in time required. The use of a crystal monochromator always increases the signal-to-noise ratio but it does so at some cost in net intensity. A chart showing the relationship of gain to loss in use of a crystal monochromator is provided for guidance of the experimenter. This loss makes the use of a monochromator disadvantageous for reflections which have a good signal-to-noise ratio, e.g. >1 , without it. The monochromator offers significant advantages for the study of weak reflections.

Three sources of systematic error are considered, extraneous wavelengths (e.g. m/n harmonics), structure in the background and thermal diffuse scattering. All can be sources of major error. The first two can be eliminated or obviated experimentally. The latter can be minimized and calculations of its effect can be checked by properly chosen experimental procedures, here described, which involve temperature dependence. However, TDS can not be so eliminated and it remains a potential source of serious error in precision determination of Bragg intensities.

C. Background Measurement (continued)

- (ii) "Background Intensities in Single Crystal Diffractometry," R. A. Young, Technical Report No. 2, Contract No. Nonr 991(00) and 991(06), Office of Naval Research (Physics Branch), 27 July 1961.

Abstract

The question of the component parts and character of the background in X-ray diffraction has been re-examined in some detail. The components are divided into two classes: those which may be peaked at the Bragg position, principally the harmonic components; and those which do not peak at the Bragg position, here called the miscellaneous components.

The contribution to apparent Bragg intensities of harmonic and even sub-harmonic wavelengths in crystal - monochromatized incident radiation is generally recognized (Batterman, 1961). However, in current practice at least, the fact appears usually to be overlooked that harmonic wavelengths contribute to the observed intensity at the Bragg setting even in the ordinary, filtered-radiation techniques. Neglect of this contribution would have produced an intensity error larger than a factor of two in one example on hand. The ω -scan and peak-height methods of single crystal diffractometry are particularly affected. Pulse height discrimination alone is inadequate to correct the problem; it appears necessary to use balanced filters and to make measurements both on and off the Bragg setting. The common method of taking as the whole background the intensity obtained by off-setting the crystal alone completely misses these harmonic contributions.

An expression is presented for the dependence of the harmonic contributions on counter aperture, structure factors, Bragg angle, temperature, and other parameters. The qualitative correctness of the expression is demonstrated by experimental results. The consequences of neglecting this component are discussed in several connections and are demonstrated in some.

The control and measurement of the miscellaneous component is also considered. Particular attention should be given to the counter aperture size

C. Background Measurement (continued)

and to both incident and receiving collimators even with the large beam used in single crystal diffractometry.

The circumstances under which each scanning method may be used are examined. It is concluded that the peak height method is inherently a poor method. It is strongly recommended that a balanced filter technique be used with the ω -scan at all times and in some cases with the 2θ -scan. The ω -scan is then slightly preferable for other reasons.

Detailed procedures for correct background determination with balanced filters are presented.

While the present discussion is concerned principally with single crystal diffractometry, implications to film methods and to powder diffractometry are also pointed out. It is concluded that background measurements are best made on the Laue streaks and that all strong reflections should be made to appear on zero layer photographs where the full extent of these Laue streaks may be seen.

D. Specimen Temperature Control

(i)

Reprinted from the *Journal of Scientific Instruments*, Vol. 43, pp. 449-453, JULY 1966

X-ray specimen temperature control with gas streams

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MS. received 11th February 1966, in revised form 13th April 1966

Abstract. The convenient gas-stream method can be thermodynamically desirable, minimizing thermal gradient problems, providing stable temperatures for isothermal experiments and providing rapid yet well-controlled dynamic response to programmed temperature changes. Inert atmospheres can be employed with some additional advantages concerning protection. Equipment design and use considerations are presented. Experimental configurations effectively used and specimen temperature-control results obtained in the range 90–1000°K are described.

D. Specimen Temperature Control (continued)

- (ii) "Counter Adaptor and Furnace for Weissenberg Camera," R. A. Young, "Advances in X-Ray Analysis," Vol. 4, Proceedings of the Ninth Annual Conference on Application of X-Ray Analysis held August 10-12, 1960, p. 219.

**COUNTER ADAPTOR AND FURNACE FOR
WEISSENBERG CAMERA***

R. A. Young

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ABSTRACT

A rugged and versatile counter adaptor for a Weissenberg camera is described. It has performed well in two years of daily use which has included collection of intensity vs. temperature data with conventional cold-stream techniques.

Advantage has recently been taken of the adaptor design to mount, directly on the Weissenberg base, a furnace device which blows hot air along the crystal mounting axis. Crystal temperature may be held constant or easily varied over the range up to about 700°C, with no obstruction of the X-ray beams and no readjustment of the furnace position, while the entire zero layer and close-in upper layers are explored.

(Note: Though the furnace was developed and used on another project, the counter-adaptor was initially developed for use on this project.)

III. THERMAL EXPANSION - MEASUREMENT TECHNIQUE, RESULTS, INTERPRETATION

(i)

Reprinted from THE PHYSICAL REVIEW, Vol. 129, No. 5, 1936-1943, 1 March 1963
Printed in U. S. A.

Thermal Expansion of AgCl†

ROBERT M. NICKLOW AND R. A. YOUNG
Georgia Institute of Technology, Atlanta, Georgia
(Received 17 August 1962)

The thermal coefficient of expansion of AgCl has been measured as a function of temperature from 120 to 710°K (melting point = 728°K) by means of x-ray diffraction from small single crystals. Above 300°K the results agree well with the dilatometric measurements reported by Strelkow. Such agreement indicates that the concentration of Schottky defects in AgCl is not large enough to influence significantly the thermal expansion below 710°K. The thermal expansion for the entire temperature range is described rather well by Grüneisen's theory, (1) if it is assumed that thermally generated Frenkel defects contribute significantly to the high-temperature thermal expansion, and (2) if two parameters in the theory are chosen to give a good fit to the low-temperature ($T < 300^\circ\text{K}$) x-ray data. Attempts to determine the activation energy of the Frenkel defects from comparison of the thermal expansion data with theory indicate that certain constants of the theory are probably temperature dependent. Below 300°K the x-ray results differ significantly from the dilatometric results reported by Sreedhar. Low-temperature x-ray measurements of the thermal expansion of Al are, therefore, included and compared with existing data in the literature to demonstrate the validity of our experimental technique. The especially convenient experimental technique used is described.

IV. THERMAL MOTIONS IN THE IDEALLY IMPERFECT CRYSTAL

- (i) "A Study of Lattice Vibrations Through the Temperature Dependences of X-Ray Bragg Intensities," R. M. Nicklow and R. A. Young, Technical Report No. 3, Contract Nonr 991(00) and 991(06), 257 pp. (1964).

Abstract

New experimental and analytical techniques have been developed for the study of thermal vibrations through measurements of the temperature dependences of Bragg intensities. These techniques have been applied to the study of thermal vibrations in Al, KCl, and AgCl in the 100 to 300° K temperature range. These techniques involve the collection of precision intensity data at temperature intervals which are small enough to allow useful determination of the slope and curvature of the intensity versus temperature data. From these slopes it is possible to obtain meaningful values for the temperature derivatives, dB/dT , of the Debye-Waller factors for both a monatomic (copper type) structure and for each type of atom, individually in an NaCl type structure. The temperature dependences of these temperature derivatives were also experimentally observed and were particularly significant.

These intensity-vs-temperature results have been related in a straightforward way to the elastic frequency spectrum, and detailed comparisons have been made with predictions based on the actual spectra in two cases. To facilitate comparisons with other methods, we specifically discuss the indicated Debye temperature, Θ . Our results provide determination of $\Theta(\text{x-ray})$ as a function of temperature for both the monatomic and

diatomic cases. A value for $\Theta(\text{x-ray})$ so obtained at a given temperature is absolute in the sense that it does not depend on the values which are appropriate to other temperatures.

Our own review treatment of the theory relating thermal vibrations to Bragg intensities is presented and some extensions of the theory are made in the process. Specifically treated are the cases of primitive and non-primitive (e.g. face-centered) cubic Bravais lattices containing both one and two atoms per lattice point. Expressions which relate the temperature slope of intensity to the temperature derivatives of the Debye-Waller factors for these crystal structures, and which relate these temperature derivatives to the frequency spectrum and $\Theta(\text{x-ray})$, are presented and discussed. Anharmonic contributions to the Debye-Waller factor are treated. An analytical method developed for separating the contributions of the two atom types in an NaCl type structure to the observed slopes of intensity versus temperature curves is described.

Attempts to fit the x-ray data with an expansion in terms of the moments of the frequency spectrum failed. Possible reasons for this failure are pointed out.

A rather extensive investigation of the thermal diffuse scattering (TDS) contributions to the Bragg intensities measured in this study was made, as corrections for the TDS contributions were necessary. Particularly examined were the possible effects of all experimental parameters, e.g., sample size and shape, beam divergence and inhomogeneity, counter window size, etc., on the TDS contributions. Expressions have been derived which can be used to determine both the one and two phonon contributions to

the Bragg peak intensity. The results of specially devised experimental tests indicate that TDS contributions in this study were determined to within 5 to 15%.

Detailed studies were made on three separate materials: (1) Al, a simple monatomic structure, for which the elastic spectrum was well-known; (2) AgCl, a simple diatomic structure, for which an elastic spectrum was also fairly well-known; and, (3) KCl, a simple structure closely approaching the idealized simple cubic, one atom per lattice point, model initially used in the derivation of the Debye-Waller factor.

As expected, for all three materials $\Theta(\text{elastic}) > \Theta(\text{x-ray})$ at the temperatures where they could be compared. The discrepancy (according to Blackman) between theory and experiment which once existed for KCl, viz., $\Theta(\text{x-ray}) > \Theta(\text{elastic})$, has been removed by our data. At room temperature $\Theta(C_V)$ is approximately 25% larger than $\Theta(\text{x-ray})$ for AgCl. This large difference is presumably due to the existence of optic branches in AgCl which constitute a high frequency peak in the vibrational spectrum and which contribute more to $\Theta(C_V)$ than to $\Theta(\text{x-ray})$.

Comparison of the intensity versus temperature results obtained for Al in this study with calculations based on Walker's vibration spectrum for Al indicate that dB/dT is sensitive both to anharmonicity and to some detail in the character of the low and, possibly, intermediate frequency portion of the vibrational spectrum. For example, a five percent increase in the frequencies in the transverse branch of Walker's spectrum, suggested by the neutron inelastic scattering results of Brockhouse and Stewart, makes a significant improvement in the

agreement between our calculated and observed results for $\Theta(\text{x-ray})$. When first-hand anharmonic effects on the elastic spectrum are also included, the calculated $\Theta(\text{x-ray})$ versus temperature curve is in excellent agreement with our experimental curve. Anharmonic effects of higher than first order were not found to be significant in Al in the 100 to 300° K temperature range.

The experimental results obtained for AgCl show that $d(B_{\text{Ag}})/dT$ is larger than $d(B_{\text{Cl}})/dT$ by approximately 20 - 30% in the 100 to 300° K temperature range. This result is in substantial agreement with our calculations which are based on Cole's dispersion curves for AgCl and on Brillouin's expression for the wave vector dependence of the atomic vibrational amplitude ratio in a one-dimensional diatomic lattice. According to these calculations the optic modes contribute significantly to $d(B_{\text{Cl}})/dT$ and to the temperature dependence of $\Theta(\text{x-ray})$. However, these contributions were not well determined. Therefore, no attempt was made to estimate the size of anharmonic effects beyond first order in the AgCl, even though the temperature dependence of $\Theta(\text{x-ray})$ could not be entirely accounted for thereby.

For KCl it was found that, between 200 and 300° K, $\Theta(\text{x-ray})$ agrees well with the high temperature value calculated by Blackman and has a temperature dependence which is fully accounted for by first order anharmonic effects on a Debye spectrum. As the temperature decreases below 200° K, $\Theta(\text{x-ray})$ increases more than can be accounted for by first order effects alone. This increase is presumably due to differences between the real vibration spectrum of KCl and the Debye spectrum.

The intensity versus temperature data were obtained from small (maximum diameter ~ 0.5 mm) approximately spherical single crystal samples with a counter adapted Weissenberg camera and a Philip's x-ray unit. MoK α radiation, balanced filters, and a scintillation counter were used throughout the work. The geometry used was such that all parts of the sample could "see" all parts of the x-ray target and the counter intercepted all of the diffracted beam. The bulk of the data consisted of measurements of peak heights versus temperature. The desired integrated intensity versus temperature information was obtained from these data and measurements of the temperature dependence of the ratio of integrated intensity to peak height. The integrated intensities used for the determination of this ratio were obtained by the ω -scan technique. All the data were obtained from zero layer reflections. Control of the sample temperature was achieved by means of a gas stream directed onto the sample.

(ii)

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Lattice Vibrations in Aluminum and the Temperature Dependence of X-Ray Bragg Intensities*

R. M. NICKLOW† AND R. A. YOUNG

Georgia Institute of Technology, Atlanta, Georgia

(Received 24 June 1966)

x-ray intensity data have been obtained from aluminum single crystals at temperature intervals that were small enough to allow determination of $d(\ln I)/dT$ in the 100-300°K temperature range. From these measurements the temperature dependence of dM/dT (or M'), the temperature derivative of the Debye-Waller factor M was determined. These derivatives are related in a straightforward way to the frequency distribution $g(\nu)$ and hence to an equivalent characteristic temperature $\Theta_{M'}$. Comparisons of experimental results with calculations based on actual approximate frequency distributions for aluminum indicate that the sensitivity of $\Theta_{M'}$ to the shape of the frequency distribution can be experimentally significant. These experimental results for $\Theta_{M'}$ are in very good agreement with calculations based on a frequency distribution derived by means of an 8-neighbor Born-von Kármán force model from a previously reported analysis of neutron inelastic scattering data. Calculations using a simple one-neighbor force model based only on elastic constants were inadequate. In the 100-300°K range the entire temperature dependence of the experimental $\Theta_{M'}$ can be accounted for by anharmonicity associated with thermal expansion. The experimental and analytical techniques used make possible the determination, at a given temperature, of a relatively accurate and unambiguous value for $\Theta_{M'}$. The determination does not depend on $\Theta_{M'}$ values at other temperatures.

V. THERMAL MOTIONS IN PERFECT AND NEARLY PERFECT CRYSTALS

- (i) "Role of Atomic Thermal Motions in Diffraction from Nearly Perfect Crystals" (Ph.D. Thesis of William E. Krull, writing-up in progress).

Abstract

An investigation has been made into the effect of thermal motions on the x-ray intensity diffracted from near-perfect crystals (dynamical diffraction). The major effort of the experiment was directed to the symmetric Bragg case (reflection geometry) using germanium crystals and Mo K α radiation. Additional facets of the investigation included the substitution of silicon for germanium, alterations to the geometry, the effect of edge dislocations and fast neutron irradiation and the effects of altering the wavelength of the radiation.

Two methods were used in the investigations. The first of these consisted of measuring the integrated intensity from a set of Bragg planes as a function of the temperature (I vs T method) in the range 100 to 400°K. This method provided a direct determination of the temperature dependence. As employed in this experiment the method was unique in that the temperature interval extended both below and above room temperature. The second method consisted of measuring the integrated intensity for a series of planes in a single crystal at a fixed temperature (isothermal method) and then relating these measurements. This method had not been previously used for dynamical diffraction analysis.

The conclusions of this experiment are as follows:

1. The I vs T results for germanium confirm that one can account for the thermal motions in the theoretical expression for diffracted intensity by writing the structure amplitude F as

$$|F| = |F_0| e^{-M}$$

where $|F_0|$ is the value of the structure amplitude at zero temperature and M is the Debye factor.

2. Similar measurements on silicon were inconclusive because of a lack of reliability in the data but did not disagree with the above result.

3. Edge dislocations up to $10^6/\text{cm}^2$ in germanium had no effect on the temperature dependence when Mo $K\alpha$ radiation was used.

4. Exposure of silicon to fast (>1 mev) neutron damage produced a significant effect on the Mo $K\alpha$ intensity diffracted when the exposure exceeded $5 \times 10^{19} \text{ n/cm}^2$.

VI. RESEARCH PERSONNEL AND DEGREES EARNED

<u>Name and Title</u>	<u>Dates Employed</u>	<u>Degree Earned</u>		
		<u>Degree</u>	<u>Field</u>	<u>Date</u>
Dr. R. A. Young Professor of Physics Principal Investigator	1958-1966			
Robert M. Nicklow	1958-1963	M.S.	Physics	1960
		Ph.D.	Physics	1964
William E. Krull	1962-1966	M.S.	Physics	1962
		Ph.D.	Physics	1970 ?
Charles E. Wagner [*]	1962-1966	M.S.	Physics	1966
W. A. Stephens [*]	1960-1964	B.S.	Physics	1964
Alan Friedman [*]	1960-1964	B.S.	Physics	1964
R. M. Sarper [*]	1964-1966	B.S.	Physics	1967

* Only partial support supplied by this project.

VII. PUBLICATIONS LIST

Papers

"Thermal Expansion of AgCl," Robert M. Nicklow and R. A. Young, Phys. Rev.

129, 1936-1943 (1963).

"Balanced Filters for X-Ray Diffractometry," R. A. Young, Z. Krist. 118,

233-247 (1963).

"Background Factors and Technique Design," Transactions American Crystallographic Association I, 42-66 (1965).

"X-Ray Specimen Temperature Control with Gas Streams," R. A. Young, J. Sci.

Instr. 43, 449-453 (1966).

"Lattice Vibrations in Aluminum and the Temperature Dependence of X-Ray

Bragg Intensities," R. M. Nicklow and R. A. Young, Phys. Rev. 152,

No. 2, 591-596 (1966).

Reports

- "X-Ray Diffraction Studies of Thermal Motions in Crystals," R. A. Young, Annual Report No. 1, Contract No. Nonr 991(00) and 991(06), Office of Naval Research, Physics Branch, May 31, 1959.
- "X-Ray Diffraction Studies of Thermal Motions in Crystals," R. A. Young, Annual Report No. 2, Contract No. Nonr 991(00) and 001(06), Office of Naval Research, Physics Branch, May 31, 1960.
- "X-Ray Diffraction Studies of Thermal Motions in Crystals," R. A. Young Annual Report No. 3, and R. M. Nicklow, Contract No. Nonr 991(00) and 991(06), Office of Naval Research, Physics Branch, May 31, 1961.
- "Balanced Filters for X-Ray Diffractometry," R. A. Young, Technical Report No. 1, Contract No. Nonr 991(00) and 991(06), Office of Naval Research, Physics Branch, 15 June 1961.
- "Background Intensities in Single Crystal Diffractometry," R. A. Young, Technical Report No. 2, Contract No. Nonr 991(00) and 991(06), Office of Naval Research, Physics Branch, 27 July 1961.
- "A Study of Lattice Vibrations through the Temperature Dependences of X-Ray Bragg Intensities," R. M. Nicklow and R. A. Young, Technical Report No. 3, Contract No. Nonr 991(00) and 991(06), Office of Naval Research, Physics Branch, 20 July 1964.

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13. ABSTRACT Primarily through abstracts of reports and published papers, this final report recounts project work done from 1958 through 1966 on x-ray studies of thermal motions in crystals. Principal use was made of the temperature dependence of x-ray Bragg-reflection intensities. Precision was emphasized. Both new experimental procedures and new analytical procedures were developed to produce and to exploit the precision inherently available. Instrumental design and use strategy, X-specimen temperature control, understanding and control of the background, and wavelength control received extended attention. Analytic techniques were developed to yield from "continuous" intensity-vs-temperature data, absolute Debye temperatures and separate measures of Na and Cl (or Ag and Cl) atomic thermal motions in crystals with NaCl structure. The resulting information was surprisingly detailed. For example, comparison with calculations based on the elastic spectrum of Al showed the experimentally observable quantities to be sensitive to a 5% scaling error in one branch of that spectrum. In an ancillary effort, the thermal coefficient of expansion of AgCl was determined over the range 120-710°K and the activation energy for Frenkel defects was determined. Extension of the studies to perfect crystals and slightly distorted perfect crystals was initiated and is the subject of an unfinished Ph.D. thesis.		

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
X-ray diffraction Thermal motions Lattice vibrations Elastic spectrum Temperature variation X-ray intensity measurement Debye temperature XRD instrument design X-ray diffraction technique Thermal expansion						

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