GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia

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

Office of Naval Research
Washington, D. C.

TABLE OF CONTENTS

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.

B. Wavelength Control

(i)

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*

By R. A. YOUNG
Engineering Experiment Station and School of Physics
Georgia Institute of Technology
Atlanta, Georgia

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. KIRKPATRICKS 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 subharmonic 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

R. A. YOUNG
Georgia Institute of Technology, Atlanta, Georgia, U.S.A.
MS. received 11*th February* 1966, *in revised form* 13*th 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

Georgia Institute of Technology, Atlanta, Georgia

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 ($T < 300$°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 Θ(x-ray) as a function of temperature for both the monatomic and

diatomic cases. A value for Θ(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 Θ(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 inhomogenity, 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 Θ(x-ray). When first-hand anharmonic effects on the elastic spectrum are also included, the calculated Θ(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 $d(B_{Ag})/dT$ is larger than $d(B_{Cl})/dT$ 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 $d(B_{Cl})/dT$ and to the temperature dependence of Θ(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 Θ(x-ray) could not be entirely accounted for thereby.

For KCl it was found that, between 200 and 300° K, Θ(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, Θ(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. MoKα 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.

Reprinted from THE PHYSICAL REVIEW, Vol. 152, No. 2, 591–596, 9 December 1966
Printed in U. S. A.

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 Kárman 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 Kα 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

$$|F| = |F_o| e^{-M}$$

where $|F_o|$ 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 $10^6/cm^2$ in germanium had no effect on the temperature dependence when Mo Kα radiation was used.

4. Exposure of silicon to fast (>1 mev) neutron damage produced a significant effect on the Mo Kα intensity diffracted when the exposure exceeded $5x10^{19} n/cm^2$.

VI. RESEARCH PERSONNEL AND DEGREES EARNED

Name and Title	Dates Employed	Degree Earned		
		Degree	Field	Date
Dr. R. A. Young Professor of Physics Principal Investigator	1958-1966			
Robert M. Nicklow	1958-1963	M.S. Ph.D.	Physics Physics	1960 1964
William E. Krull	1962-1966	M.S. Ph.D.	Physics Physics	1962 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 and R. M. Nicklow, Annual Report No. 3, 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.

July 1967

BASIC DISTRIBUTION LIST

Technical and Summary Reports

Organization	No. of Copies
Chief of Naval Research Department of the Navy Attn: Code 423 Washington, D. C. 20360	(3)
Director Office of Naval Research Branch Office 495 Summer Street Boston, Massachusetts 02210	(1)
Commanding Officer Office of Naval Research New York Area Office 207 West 24th Street New York, New York 10011	(1)
Director Office of Naval Research Branch Office 219 South Dearborn Street Chicago, Illinois 60604	(1)
Director Office of Naval Research Branch Office 1030 East Green Street Pasadena, California 91101	(1)
Commanding Officer Office of Naval Research San Francisco Area Office 1076 Mission Street San Francisco, California 94103	(1)
Assistant Attache for Research Office of Naval Research Branch Office, London FPO New York 09510	(5)
Director U. S. Naval Research Laboratory Washington, D. C. 20390 Attn: Technical Information Officer, Code 2000 Code 2020 Code 6200 Code 6300 Code 6100	(4) (1) (1) (2) (1)
Commander Naval Air Systems Command, Hqts. Department of the Navy Washington, D. C. 20360 Attn: Code AIR 320A Code AIR 5203	(1) (1)
Commander Naval Ordnance Systems Command, Hqts. Department of the Navy Attention: Code ORD 033 Washington, D. C. 20360	(1)
Commanding Officer Naval Air Development Center Aeronautical Materials Div. Attn: Code MAM Johnsville Warminster, Pa. 18974	(1)
Commanding Officer U. S. Naval Ordnance Laboratory White Oak , Maryland 20910 Attn: Code 210	(1)
Commanding Officer U. S. Naval Weapons Laboratory Dahlgren, Virginia 22448 Attn: Research Division	(1)

BASIC DISTRIBUTION LIST (Cont'd)

Organization	No. of Copies
Commander Naval Ship Systems Command, Hqts. Department of the Navy Attn: Code 0342 Washington, D. C. 20360	(1)
Commander Department of the Navy Naval Ship Engineering Center Attn: Code 6101 Washington, D. C. 20360	(1)
Naval Ships R&D Center Annapolis Division Annapolis, Maryland 21402	(1)
Naval Applied Science Lab. Naval Base Attn: Code 735 Brooklyn, New York 11251	(1)
Commanding Officer Naval Ships R&D Center Attn: Code 735 Washington, D. C. 20007	(1)
U. S. Naval Postgraduate School Monterey, California 93940 Attn: Dept. of Chemistry and Material Science	(1)
Commander Naval Weapons Center Attn: Code 5560 China Lake, California 93555	(1)
Commander Naval Undersea Warfare Center 3202 E. Foothill Boulevard Pasadena, California 91107	(1)
Defense Documentation Center Cameron Station Alexandria, Virginia 22314	(20)

Organization	No. of Copies
National Bureau of Standards Washington, D. C. 20234 Attn: Metallurgy Division Inorganic Materials Div.	(1) (1)
Commanding Officer Army Research Office, Durham Attn: Metallurgy & Ceramics Div. Box CM, Duke Station Durham, North Carolina 27706	(1)
U. S. Air Force Office of Scientific Research Attn: Solid State Div. (SRPS) Washington, D. C. 20333	(1)
U. S. Atomic Energy Commission Washington, D. C. 20545 Attn: Technical Library Metals & Materials Branch	(1) (1)
Argonne National Laboratory Metallurgy Division P. O. Box 299 Lemont, Illinois 60439	(1)
Brookhaven National Laboratory Technical Information Division Attn: Research Library Upton, Long Island, New York 11973	(1)
Union Carbide Nuclear Co. Oak Ridge National Laboratory P. O. Box P Oak Ridge, Tennessee 37830 Attn: Metallurgy Division Solid State Physics Div.	 (1) (1)
Los Alamos Scientific Laboratory Attn: Report Librarian P. O. Box 1663 Los Alamos, New Mexico 87544	(1)

BASIC DISTRIBUTION LIST (Cont'd)

Organization	No. of Copies
Commanding Officer Army Materials & Mechanics Research Center Watertown, Massachusetts 02172 Attn: Res. Programs Office(AMXMR-P) Technical Library(AMXMR-ATL)	(1) (1)
University of California Radiation Laboratory Information Division Room 128, Building 50 Berkeley, California 94720 .	(1)
Commanding Officer U.S. Naval Ornance Underwater Station Newport, Rhode Island 02840	(1)
Aerospace Research Laboratories Building 450 Wright Patterson AFB Dayton, Ohio 45433	(1)
Defense Metals Information Center Battelle Memorial Institute 505 King Avenue Columbus, Ohio 43201	(1)
Evans Signal Laboratory Army Electronics Command Solid State Devices Branch c/o Senior Navy Liaison Officer Fort Monmouth, New Jersey 07703	(1)
Commanding General U.S. Army, Frankford Arsenal Attn: Mr. Harold Markus ORDBA-1320, 64-4 Philadelphia, Pennsylvania 19137	(1)
Executive Director Materials Advisory Board NAS-NRC 2101 Constitution Avenue Washington, D. C. 20418	(1)

Organization	No. of Copies
Atomic Energy Commission New York Operations Office Attn: Document Custodian 70 Columbus Avenue New York, New York 10023	(1)
NASA Headquarters Attn: Mr. George C. Deutsch (RRM) Washington, D. C. 20546	(1)
National Academy of Science Attn: Dr. F. J. Weyl 2101 Constitution Avenue Washington, D. C. 20418	(1)
Air Force Materials Lab (MAMC) Wright Patterson AFB Dayton, Ohio 45433	(1)
Deep Submergence Systems Project Attn: DSSP-00111 Washington, D. C. 20360	(1)
Advanced Research Projects Agency Attn: Dr. R. M. Thomson Materials Sciences Washington, D. C. 20301	(1)
Army Research Office Attn: Dr. J. Majowicz 3045 Columbia Pike Arlington, Virginia 22204	(1)
Department of Interior Bureau of Mines Attn: Science & Engineering Advisor Washington, D. C. 20240	(1)

SUPPLEMENTARY DISTRIBUTION LIST

Technical and Summary Reports

Professor H. Brooks
Dean of Graduate School of
Applied Science
Harvard University
Cambridge, Massachusetts 02100

Dr. H. C. Gatos
Massachusetts Institute of Technology
Metallurgy and Electrical Engineering
Cambridge, Massachusetts 02100

Dr. J. C. Grosskreutz
Senior Advisor for Physics
Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

Professor N. Hackerman
University of Texas
Office of the Vice President & Provost
Austin, Texas 78712

Professor J. P. Hirth
Ohio State University
Metallurgical Engineering
Columbus, Ohio 43210

Professor M. B. Ives
McMaster University
Metallurgy Department
Hamilton, Ontario
CANADA

Dr. K. R. Lawless
University of Virginia
Department of Materials Science
Charlottesville, Virginia 22903

Dr. H. W. Paxton
Carnegie Institute of Technology
Metals Research Laboratory
Pittsburgh, Pennsylvania 15213

Professors D. H. Polonis & R. Taggart
University of Washington
Metallurgical Engineering
Seattle, Washington 98105

Dr. M. E. Straumanis
University of Missouri
School of Mines and Metallurgy
Department of Metallurgical Engineering
Rolla, Missouri 65401

Dr. A. R. C. Westwood
RIAS, Inc.
Materials Department
1450 S. Rolling Road
Baltimore, Maryland 21227

Professor H. G. F. Wilsdorf
University of Virginia
Department of Materials Science
Charlottesville, Virginia 22903

Professors R. A. Young & R. Gerdes
Georgia Institute of Technology
Physics Department
Atlanta, Georgia 30313

Drs. P. Gordon and D. Rausch
Illinois Institute of Technology
Metallurgical Engineering Department
10 West 35th Street
Chicago, Illinois 60616

Professor W. D. Robertson
Yale University
Hammond Laboratory
14 Mansfield Street
New Haven, Connecticut 06520

Dr. H. Leidheiser, Jr.
Virginia Institute of Scientific Research
P. O. Box 835
6300 River Road
Richmond, Virginia 23226

SUPPLEMENTARY DISTRIBUTION LIST (Cont'd)

Professor J. R. Bartlett
University of Alabama
Department of Physics
University, Alabama 35486

Dr. Philip Goodman
Parametrics, Inc.
221 Crescent Street
Waltham, Massachusetts 02154

C

July 1967

SUPPLEMENTARY DISTRIBUTION LIST

Technical and Summary Reports

Professor H. Brooks
Dean of Graduate School of
Applied Science
Harvard University
Cambridge, Massachusetts 02100

Professor P. Delahay
New York University
Chemistry Department
Washington Square
New York, New York 10522

Dr. H. C. Gatos
Massachusetts Institute of Technology
Metallurgy and Electrical Engineering
Cambridge, Massachusetts 02100

~~Dr. R. J. Gerdes~~
Georgia Institute of Technology
Engineering Experiment Station
Atlanta, Georgia 30332

Professor N. Hackerman
Office of the Vice President & Provost
University of Texas
Austin, Texas 78712

Professor G. J. Janz
Rensselaer Polytechnic Institute
Department of Chemistry
Troy, New York 12181

Professor H. W. Paxton
Carnegie Institute of Technology
Dept. of Metallurgical Engineering
Pittsburgh, Pennsylvania 15213

Dr. M. E. Straumanis
University of Missouri at Rolla
Dept. of Metallurgical Engineering
Rolla, Missouri 65401

Professor E. A. Yeager
Western Researve University
Department of Chemistry
Cleveland, Ohio 44106

Professor R. T. Foley
American University
Chemistry Department
Washington, D. C. 20016

Dr. M. C. Bloom
Naval Research Laboratory
Code 6107
Washington, D. C. 20390

Mr. Paul Schatzberg
Naval Ships R&D Center
Annapolis Division
Code M851
Annapolis, Maryland 21402

Professor W. D. Robertson
Yale University
Hammond Laboratory
14 Mansfield Street
New Haven, Connecticut 06520

Dr. Henry Leidheiser, Jr.
Virginia Institute for
Scientific Research
P. O. Box 8315
6300 River Road
Richmond, Virginia 23226

Professor J. R. Bartlett
University of Alabama
Departmentof Physics
University, Alabama 35486

Dr. Philip Goodman
Parametrics, Inc.
221 Crescent Street
Waltham, Massachusetts 02154

SUPPLEMENTARY DISTRIBUTION LIST (Cont'd)

Dr. Warren P. Iverson
National Bureau of Standards
Metallurgy Division
Corrosion Section, IMR
Washington, D. C. 20234

Naval Civil Engineering Laboratory
Code L70
Port Hueneme, California 93041

Dr. Morris Cohen
National Research Council
Ottawa, Ontario
CANADA

Naval Applied Science Laboratory
Code 943
Naval Base
Brooklyn, New York 11251

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Georgia Institute of Technology Engineering Experiment Station Atlanta, Georgia	2b. GROUP

3. REPORT TITLE

"X-Ray Diffraction Studies of Thermal Motions in Crystals"

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final Report of Research, 1 June 1958 - 31 May 1966

5. AUTHOR(S) (Last name, first name, initial)

R. A. Young

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
30 June 1969	33	

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
Nonr 991(06) 991(00) b. PROJECT NO. A-389 c. d.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. AVAILABILITY/LIMITATION NOTICES

Reproduction in all or in part is permitted for any purpose of the United States Government.
Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
None	Office of Naval Research Physics Branch Washington, D. C.

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.

DD FORM 1 JAN 64 1473

Unclassified
Security Classification

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						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2*a*. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2*b*. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7*a*. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7*b*. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8*a*. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8*b*, 8*c*, & 8*d*. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9*a*. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9*b*. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.