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(Electrical Properties-Cellulose)
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THE INSTITUTE OF PAPER CHEMISTRY

QUARTERLY RESEARCH REPORT

DIVISION: Natural Materials and Systems

DATE: Oct. 1, 1974

✓ PROJECT NO.: 2904 - An Investigation of the Electrical Properties of
Cellulose

(FE)

Project Leader - G. A. Baum

OBJECTIVE:

1. To extend the understanding of the electrical conduction phenomena and to elucidate the dependence on time, temperature, moisture content, field strength, etc.
2. To investigate the response of cellulosic materials in static fields, using the thermal depolarization method (TD), to ascertain which polar groups contribute significantly to the electrical response, and
3. To study the effects of mechanical, thermal, or chemical modifications of cellulose using the sensitive TD method.

BUDGET:

\$22,865 over a two-year period.

SCHEDULE: The original time schedule for this program extended from 11/1/69 to 10/31/71, and the majority of work completed was accomplished during this period. Work has continued on an intermittent basis as time allows. During this quarter, this project will be closed, and a new project proposal, with revised emphasis and objectives, will be submitted.

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK: All results are described in detail in the three Project Reports dated February 12, 1970, September 22, 1970, and August 15, 1972.

To date this research has partially fulfilled all of the above objectives. A model has been developed to describe the ionic conductivity in cellulosic systems. This model successfully predicts the observed dependence of conductivity on temperature and field strength, and is in accord with the dependence on moisture content studied by others. The thermal depolarization method has been successfully applied to regenerated cellulose films and the observed depolarization "bands" have been tentatively assigned to various polar groups in the cellulose. For example,

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a band located near -60°C with an activation energy of 0.26 eV, has been attributed to the primary hydroxyl groups on the glucose unit. The -OH groups on C2 and C3 of the pyranose ring are believed to be associated with an observed band near 25°C with an activation energy around 0.56 eV. This work has been published in the Research Bulletin and in the Journal of Applied Polymer Science. The above results imply that the thermal depolarization method will afford information concerning the effects of chemical, thermal, or mechanical modifications of the cellulose, since any of these treatments will alter the local environment of the polar groups, or the type or number of polar groups which can respond to the static electric field. Related student work to date has involved the thermal depolarization response of certain cellulose derivatives, where the hydroxyl groups have been replaced with other groups.

The presence of glycerol as a plasticizer in the cellulose films is evident in the TD spectra as a very strong band around -2°C and an activation energy of 0.51 eV. It is believed that the TD method would be useful in studying the mode of action of plasticizers in cellulose.

The results cited above give rise to a number of interesting areas for study. Many of these are ideally suited for student research and I am working toward that goal. Certain areas, however, are of more immediate concern and provisions should be made for continuation of certain aspects of the existing program. To this end, the present program will be closed and a new proposal will be submitted during the present quarter.

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The results cited above give rise to a number of interesting areas for study. Many of these are ideally suited for student research and I am working toward that goal. Certain areas, however, are of more immediate concern and I feel provisions should be made for continuation of this program so that these areas may be investigated. The proposed future work, which still falls within the original objectives, involves measurements on papers rather than films. It is believed that the effects of different pulps, beating times, strength additives, or other additives should all be manifest in the electrical response. Since the conduction process ultimately depends upon the bonded area between fibers, as well as the fiber properties, investigations of such systems should further our understanding of the consolidation process. It is estimated that the required level of support would be approximately \$9000 per year for two years.

Prepared by G. A. Baum

PROJECT REPORT FORM

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PROJECT NO. 2904
COOPERATOR IPC
REPORT NO. 3
DATE August 15, 1972
NOTEBOOK 2795 PAGE 23 to 48
SIGNED G. A. Baum
G. A. Baum

ELECTRICAL PROPERTIES OF CELLULOSE

INTRODUCTION

This report discusses thermal depolarization, resistivity, and current-voltage measurements on cellulose films, with and without glycerol as a plasticizer. In the case of the thermal depolarization results, experiment is compared with theory¹. All measurements have been performed with vapor deposited aluminum electrodes on the specimens. The temperature range of interest has been from -165 to +50°C. Within this range, prominent thermal depolarization bands occur at approximately -60, -2, and +30°C for the plasticized material. Upon removal of the glycerol plasticizer the band at -2°C disappears. Pending further investigation, no specific assignments as to the dipolar origin of these bands have been attempted. Thus, it is the purpose of this report to only present results.

Recently, an A291 problem was initiated which will investigate the thermal depolarization in some cellulose derivatives, viz. ethyl cellulose, methyl cellulose, hydroxyethyl cellulose, cellulose acetate, and nitrocellulose, at various degrees of substitution. It is anticipated that these results will be valuable in elucidating the overall dielectric characteristics of cellulose and its derivatives.

SAMPLE PREPARATION

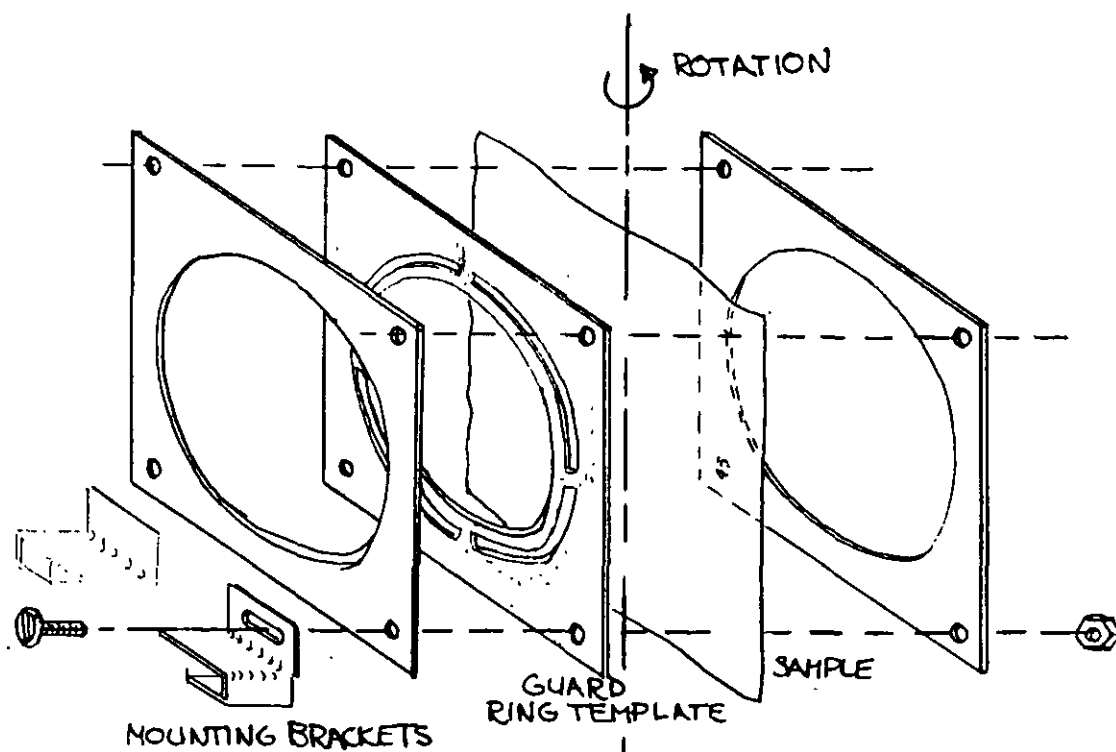
The cellulose film used in this investigation is manufactured by the FMC Corporation, American Viscose Division, their type 124 P-1. As received,² this material contains 12.4% glycerol as a plasticizer, 6.7% water at 45% R.H., and a minute quantity of surface slip agent. These films are prepared by casting a standard viscose into a zinc free bath. Specimen thicknesses are from 1.5 to 1.6 mils, as measured with the Schopper instrument. For studies on unplasticized material, the glycerol was removed from the 124 P-1 via a water treatment. This procedure was similar to that used by Brown³, although slightly more exhaustive. Briefly, a portion of film 3 x 6 inches was washed in 0.5 liters of distilled water for four hours, rinsed, soaked in 0.3 liters of distilled water for one hour followed by a double rinse, and finally soaked again in 0.3 liters for one hour followed by a triple rinse. The wet film was then placed on a flat glass plate, rolled smooth, and the edges taped. The material was allowed to dry at 16% R.H. and 73°F. for 18 hours.

The removal of plasticizer with water and the subsequent drying is believed to cause irreversible changes in the structure of the material. This is evidenced by water regain and dimensional change studies². Film thicknesses, after drying, are in the range 1.3 to 1.4 mils, representing about a 13% decrease in thickness. The plasticizer can also be removed according to the method of Kistler^{4,5} whereby a sequence of solvents of decreasing polarity are used. This technique purportedly yields a film which retains the structural features of the starting film. It is anticipated that future work will include measurements on such specimens.

A special jig has been made for the vapor deposition of the aluminum electrodes. This is depicted in Figure 1. The guard ring-guarded electrode template is made of 10 mil Mylar. As shown in the figure, this template results in a vapor deposited guard ring which is not continuous, but composed of four segments. This is not expected to cause any problem since the thinness of the aluminum film will still allow the brass guard ring of the sample holder to contact the uncoated regions of the specimen.

The aluminum is evaporated from a tungsten "vee" filament at a rate near two to three milligrams/second. This rate corresponds to a power input to the filament of around 500 watts. A typical charge of aluminum is 16 to 24 mg, yielding a deposition time of around 10 seconds. These short times (fast deposition rate) are used to avoid prolonged heating of the specimens. The vacuum is typically --- 1 to 3 X 10^{-5} torr. The deposition jig itself attaches to a turntable within the vacuum system so that both sides of the sample can be coated during a single deposition.

The aluminum, in wire form, readily wets and alloys with tungsten at elevated temperatures, necessitating frequent filament replacement. In addition, the deposited films probably contain small amounts of tungsten but this is not a problem. At the specified charge of aluminum the calculated theoretical film thickness⁶ is around 500Å (either side). Actual film thickness film thicknesses, however, are probably closer to 1500Å, since the system geometry does not approach that called for in the theoretical model.⁷ Point to point measurements on the surface of the film with an ohmmeter verify continuity of the deposited layer.



VAPOR DEPOSITION JIG
FIGURE 1

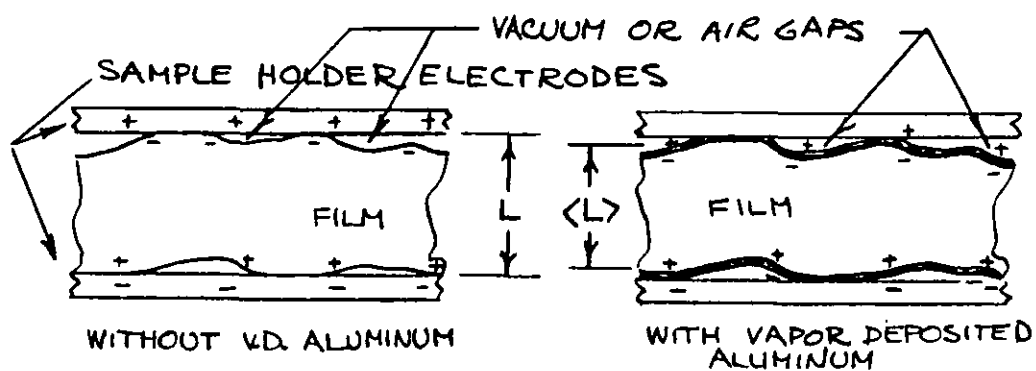


FIGURE 2

The vapor deposited electrodes will increase the effective specimen surface area (by eliminating air gaps) and decrease the effective specimen thickness, as compared to specimens without the deposited layer, and thus increase the overall specimen geometry factor, A/L . This is schematically depicted in Figure 2. The magnitude of this increase is not easily determined, however, and hence the measured geometry factors are still used in all computations. As such, computed values must be considered relative rather than absolute.

CONTROL PARAMETERS

The theoretical bases for the thermal depolarization, current-voltage, and resistivity measurements are recorded elsewhere^{1,8}. In this section the experimental procedures and important variables are discussed in detail.

Clean specimens are removed from storage in the controlled environment and mounted in the sample holder⁸, and the sample chamber evacuated. Care must be exercised in handling the specimens to avoid kinks or fingerprints or scratches in the aluminum electrodes. The lower heater is adjusted to provide a specimen temperature of around 40°C . The chamber pressure is estimated to be around 10^{-3} to 10^{-2} torr. The sample is conditioned in this manner for at least 10 hours, before measurements are started. Since the resistivity of the material is very sensitive to the moisture content, the removal of moisture is monitored during this period by applying a potential across the specimen and observing the current decay with time. After several hours, moisture removal is very slow. In the present system, no measurements of the percent moisture retained after this conditioning period are possible. Stratton, however, has

measured percent water retained for an unplasticized film, at ambient temperatures, as a function of evacuation time⁹. Based on his results, gathered at approximately the same vacuum level as that used in this investigation, the estimated moisture retained is less than 2 per cent. This value may still be large enough to give an observable effect and indeed the effects of changing moisture levels within the material do seem to manifest themselves in some of the data reported later.

After conditioning, the sample is polarized at a predetermined field strength, temperature, and time. Liquid nitrogen is then added to the dewar to cool the specimen to a predetermined temperature. Ideally the cooling process should be as rapid as possible¹⁰, but this is not achieved in the present system. For slower cooling rates the value of T_p loses significance. That is, one must consider an effective polarization temperature which will be less than T_p^{11} . In the present system the cooling rate is around 1 to 2°C. per minute. It is felt however, that as long as the specimen is polarized to saturation this slow cooling rate should not seriously affect results, and in fact, may be beneficial since thermal stresses within the specimen will be kept to a minimum. Sample resistivity can also be monitored during this cooling process. Current-voltage measurements, however, with temperature as a parameter, cannot be made simultaneously with depolarization measurements since this would involve a change in the applied field.

When the specimen has reached the desired low temperature, the sample is open-circuited and the field reduced to zero. Thermal depolarization measurements can be started immediately or further cooling can be accomplished if desired. The latter may be the case when it is desired to separate the effects of two adjacent depolarization bands. Three temperatures are recorded

in this low temperature regime: T_0 , the temperature at which the external field is removed; T_{tsc} , that temperature at which the specimen is connected into the depolarization apparatus; and T_0 , the temperature at which heating begins. The necessity of defining these temperatures will be clarified in the subsequent discussion.

When the specimen is reconnected into the circuitry associated with the depolarization experiment (see Figure 1 of PRL¹), a large current is observed which decays with time. This initial current decays very rapidly at first, but then more slowly at longer times. This initial current decay, not expected, is believed to arise from two sources. First, any free charge on the specimen will rapidly decay once the circuit is completed, that is, once the depolarization mode of the experiment begins. Secondly, any depolarization band with a maximum in the vicinity of T_{tsc} , will simultaneously decay with some time constant. In the former case the time constants would be expected to be small, even at low temperatures. For the spontaneous decay of a polarization band, however, the time constants would be expected to be large, perhaps hundreds or thousands of seconds. A third effect compounds the difficulty in interpreting the observed phenomena. This is that the temperature is also changing, usually very slowly decreasing. More on this later.

During the warmup period the heating rate must be kept constant. This is done by plotting a temperature versus time graph during the experiment, and manually adjusting the heater control whenever deviations from linearity occur. This is a tedious process and not the most desirable scheme, but is satisfactory for the rather slow heating rates employed, viz. about 0.014°K/sec .

An inexpensive, programmable linear heating rate device has recently been described in the literature¹², and some thought has been given to constructing this apparatus.

A total of 26 thermal depolarization measurements have been performed, and 16 of these will be discussed in this report. For convenience these are listed in Table I together with pertinent experimental parameters. In the table, 'Report Name' lists the experiments generally in the order in which they will appear in this report. The letter(s) appearing after the number refer to Glycerol plasticized and Aluminum vapor deposited electrodes. Thus, for example, experiment 10AG involves cellulose film that is plasticized with glycerol and has vapor deposited electrodes, whereas 14A has aluminum electrodes, but the glycerol has been removed by the water treatment. Other columns in the table include: E_p , the applied field strength; T_p , the starting polarization temperature; t_p , the total time of polarization, including polarization time at temperature T_p as well as cooling time; T_o , the temperature at which the applied field was removed; T_{tsc} , the temperature at which the circuit was completed; and, T_o' , the temperature at which specimen heating began. The difference between T_{tsc} and T_o' , of course, is due to the changing temperature during the initial current decay. Specimen heating is starting when the current has decayed to some acceptably small value, typically about 10^{-11} amps.

One specimen included in Table I, 3AG, was used only for current-voltage studies. For all others listed, thermal depolarization and/or resistivity measurements were performed.

TABLE I
EXPERIMENTAL PARAMETERS

Report Name	Data Chart	E_p (kv/cm)	T_D (°C)	t_p (min)	T_0 (°C)	T_{tsc} (°C)	T_0' (°C)
1G	7-29-1-1	50	53	45	25	25	25
2AG	8-12-1-1	74	29	90	-67	-67	-70
3AG	8-30-1-1		I-V Experiment				
4AG	8-13-1-1	74	-29	65	-88	-88	-95
5AG	8-13-1-2	74	-62	21	-96	-96	-106
6AG	8-18-1-1	74	23	57	-75	-75	-92
7AG	8-19-1-1	74	0	53	-41	-56	-72
8AG	8-20-1-1	37	0	48	-43	-50	-65
9AG	8-20-1-2	37	6	15	-10	-10	-36
10AG	8-23-1-1	18	0	60	-40	-51	-61
11AG	8-24-1-1	112	0	60	-41	-60	-70
12A	10-7-1-1	85	22	72	-75	-82	-94
13A	9-8-1-1	85	0	72	-85	-85	-98
14A	9-8-1-2	85	-43	23	-82	-84	-96
15A	9-9-1-2	85	10	16	-10	-23	-40
16A	9-13-1-1	85	22	67	5	-9	-22

RESULTS CURRENT-VOLTAGE MEASUREMENTS

A typical result of a current versus field strength measurement is shown in Figure 3. Also shown on this figure is a best fit of the theoretical expression derived in PRL¹, equation 20, and Ohm's law. Note that this plasticized material is ohmic up to field strengths near 20 kv/cm (about 75 volts for this film), but deviates considerably at higher fields. Generally, the theoretical-experimental fit is quite good, but the data always display the tendency to fall beneath the theoretical curve at the higher fields. Data has not been gathered beyond 120 kv/cm because the cellulose film has been found to breakdown at slightly higher fields, causing irreversible damage. The hyperbolic sine dependence of current against voltage is deduced from a model which involves ion migration under the action of the applied external field, thus the agreement between experiment and theory reconfirms the notion that the conductivity in cellulose is ionic. Interestingly enough, however, a linear relationship is observed if the natural log of the current is plotted against the square root of the applied voltage, as shown in Figure 4. Such a dependence of current on voltage is predicted by Schottky's theory of thermal emission over a barrier. Similar results found for dry capacitor tissue, have led Hanneson, et.al.,¹³ to conclude that the electrodes inject electrons, over the metal-cellulose barrier, and thus that the conductivity is electronic rather than ionic. The adoption of an electronic conduction mechanism requires that we think in terms of a band structure for cellulose, a debatable proposition. This is one area where clarification and definitive experiments are needed. Some preliminary calculations relating to the Schottky theory have been performed from the data presented in Figure 4, but it is felt that they do not warrant reportage at this time.

Figure 3

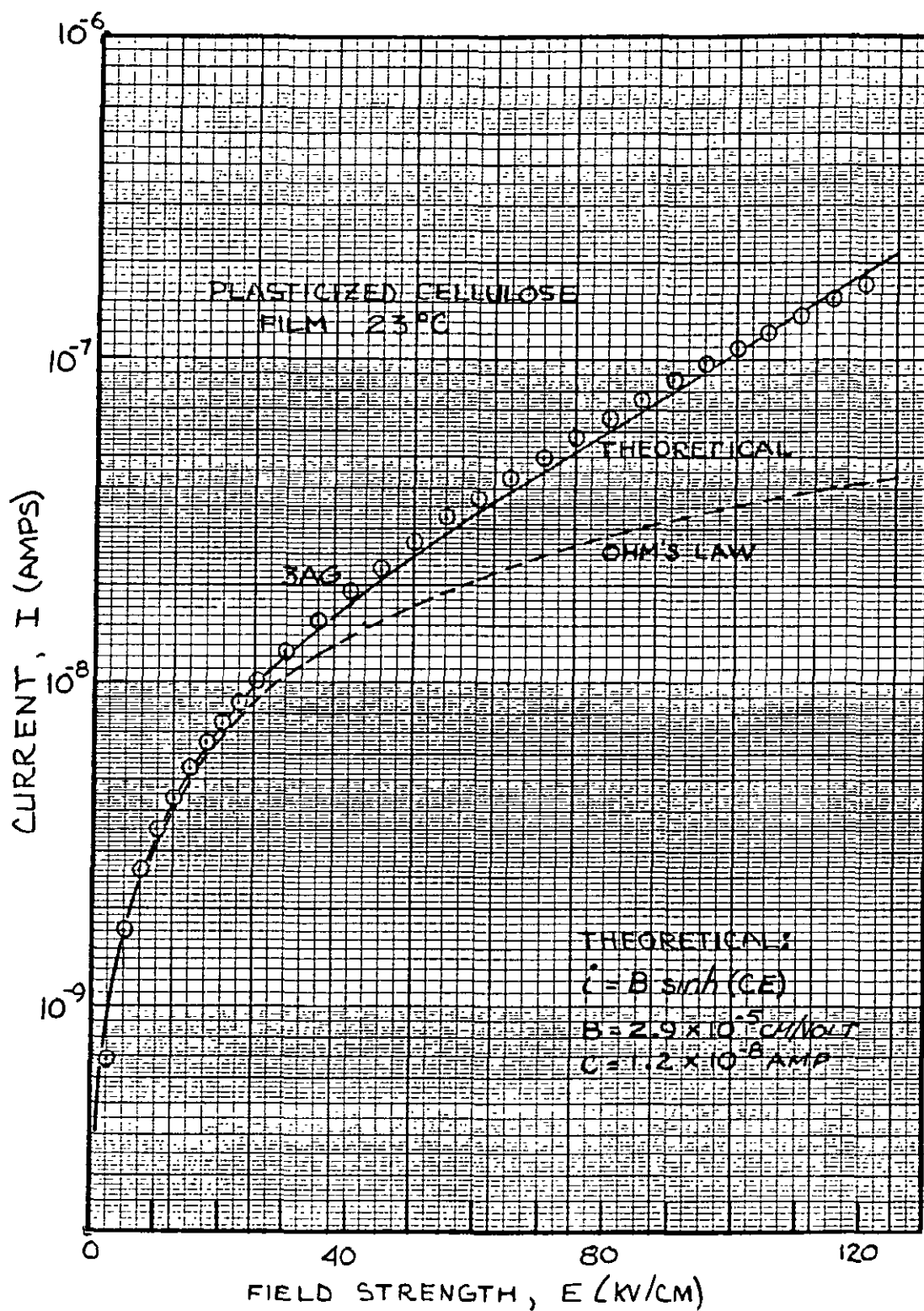
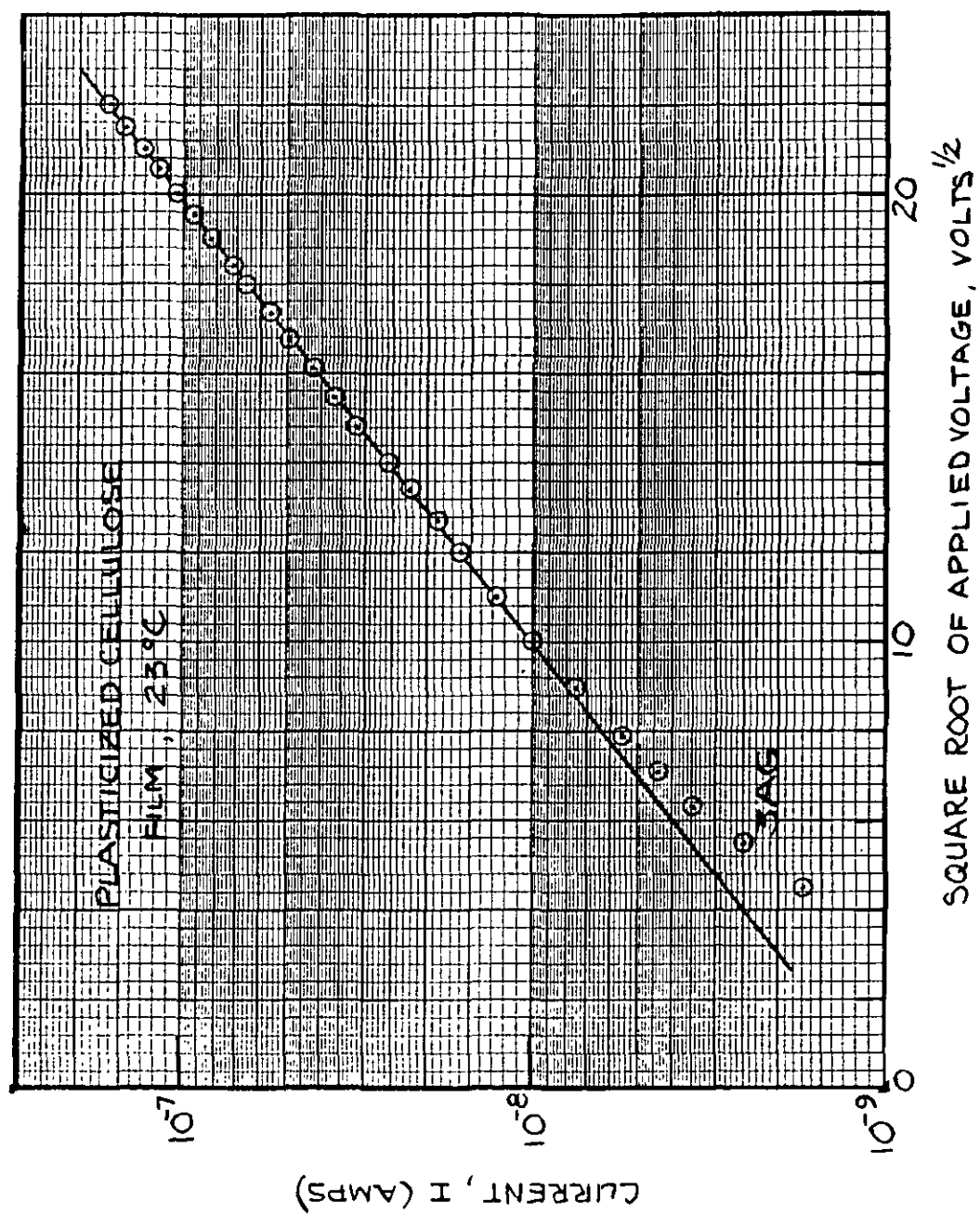


Figure 4

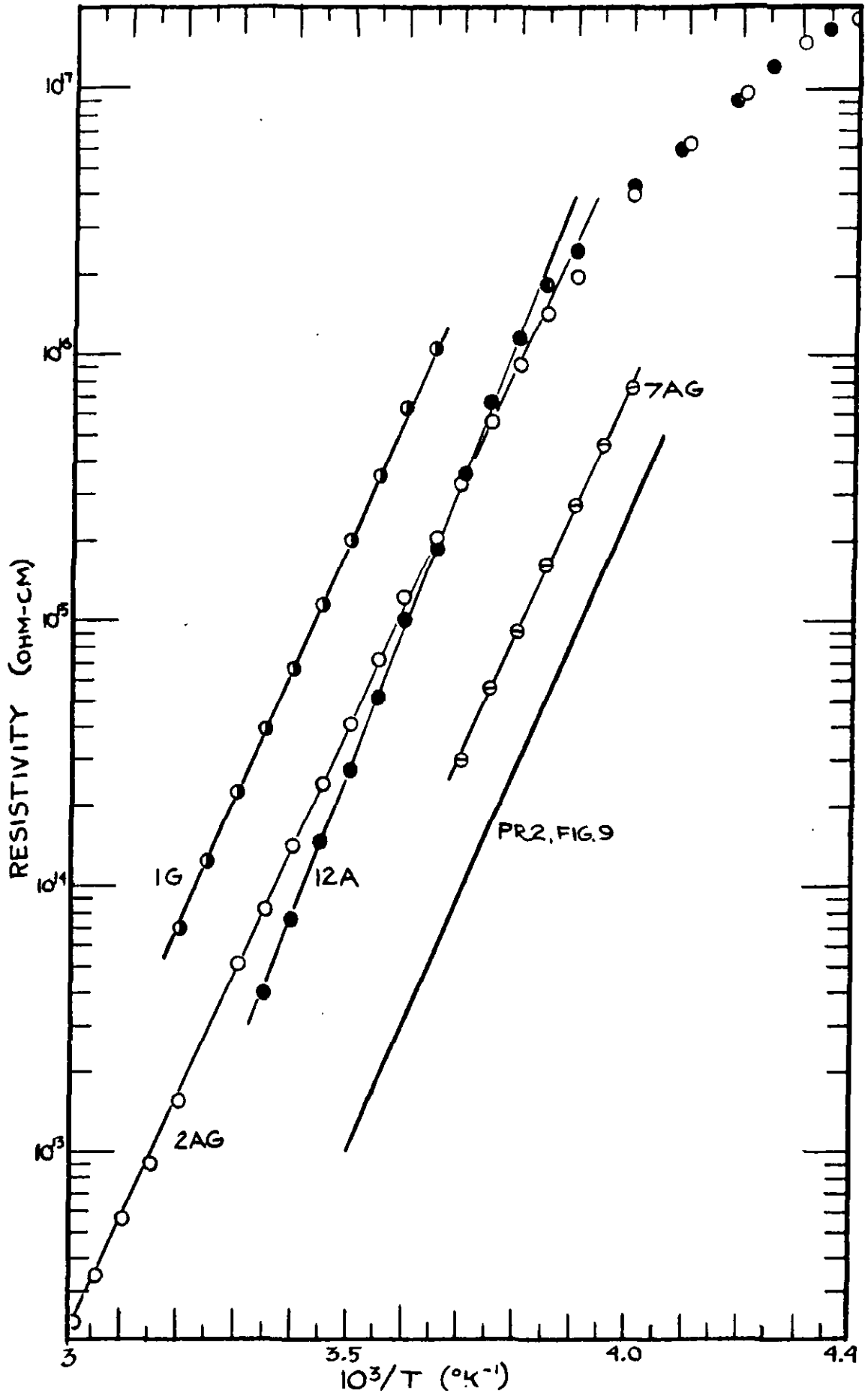


RESISTIVITY

Measurements of resistivity versus inverse temperature are shown in Figure 5 for several specimens with and without the plasticizer. Also included for comparison is the data reported in PR2, Figure 9⁸. The differences in magnitude reflect differing moisture contents, since the resistivity is very sensitive to water content. In the case of 1G, which had an applied field strength of 50 kv/cm, as compared to 74 kv/cm for the others, part of the increased resistivity is due to the nonlinearity between the current and applied voltage as reported in Figure 3, that is, the material is not ohmic. The differing moisture contents do not seem to affect the slopes of the curves. The activation energies for the plasticized material, as computed from the slopes, range from 0.90 eV to 0.93 eV. The data is log-linear over the entire temperature range from +70 to -20°C. At lower temperatures, past $10^3/T = 3.8$ in Figure 5, a pronounced decrease in slope is observed. This is believed to arise because of leakage currents in the sample holder or adjacent circuitry. The leakage resistance, in parallel with the specimen, can be computed if it is assumed that the log-linear behavior would continue to lower temperatures. This has been done for both 12A and 2AG, and in both cases the leakage resistance is computed as 4×10^{13} ohms, a reasonable value. Measurements have been performed down to -75°C ($10^3/T = 5.0$) with the resistivity reaching a plateau, the value of which also agrees with the calculated value for the leakage resistance.

The leakage resistance, although it affects the resistivity data, should not cause any problem in the thermal depolarization measurements, since

Figure 5



the load resistor in this case is around 10^8 or 10^9 ohms. This means that essentially all of the discharge current flows through the load resistor and is detected.

The activation energy computed for the unplasticized material, 12A, is 1.08 eV, compared with 0.92 eV for the plasticized specimens. The magnitudes of 12A and 2AG are comparable, both specimens being 'dry'. One cannot be sure that these two have similar levels of moisture, however, so the similarity in magnitudes may simply be fortuitous. The excellent agreement beyond $10^3/T = 4$, of course, is due to the leakage current.

Table II lists the experiments cited in Table I, except 3AG, and presents the results of the resistivity measurements and thermal depolarization measurements. In this table the activation energies computed for the conduction process are labelled as E' . The other quantities are defined in later sections.

THERMAL DEPOLARIZATION - INITIAL DECAY

As mentioned earlier, when the thermal depolarization experiment begins at the temperature T_{tsc} , a rather large current is observed which decays with time. This behavior is shown on Figure 6 for the unplasticized material, 12A. Several possible explanations have been suggested but this phenomena requires further investigation. Consider what may happen during the initial time period following the completion of the circuit.

Prior to circuit completion the capacitor containing the specimen may have a total charge composed of both free and bound charges. The bound charges are those which are neutralized by the internal polarization of the dielectric

TABLE II

SUMMARY OF RESULTS

Report Name	E_p (kv/cm)	E' (eV)	n	[Low T Band] ⁺			[Midrange Band] ⁺			[High T Band] ⁺		
				E	T_m	i_m	E	T_m	i_m	E	T_m	i_m
1G	50	0.93	1.12				(0.4)	6	10.0			
2AG	74	0.90	1.11	0.25	-55	(0.85)	*	-3	4.9			
4AG	74											
5AG	74		1.16	0.25	-56	1.3	*	-1	10.0	*	*	*
6AG	74		1.21	0.27	(-54)	(0.7)	0.53	-2	9.3	*	(25)	*
7AG	74	0.90	1.10									
8AG	37		0.96				0.54	-2	4.4	*	(27)	*
9AG	37		1.09							0.61	16	(1.2)
10AG	18		0.82				0.51	-3	2.2	*	(27)	*
11AG	112		1.15				0.47	-5	13.4	*	*	*
12A	85	1.08	1.22	0.26	-60	0.56				*	22	2.4
13A	85		1.16	0.29	-58	0.57				*	21	1.3
14A	85		1.15	0.25	-60	0.56						
15A	85		0.88							0.56	25	1.9
16A	85		0.74							0.65	(36)	(3.0)

⁺ E' from $p = P_0 e^{E'/KT}$

n is the exponent in $i_{tsc}(\text{decay}) = A(t)^n$

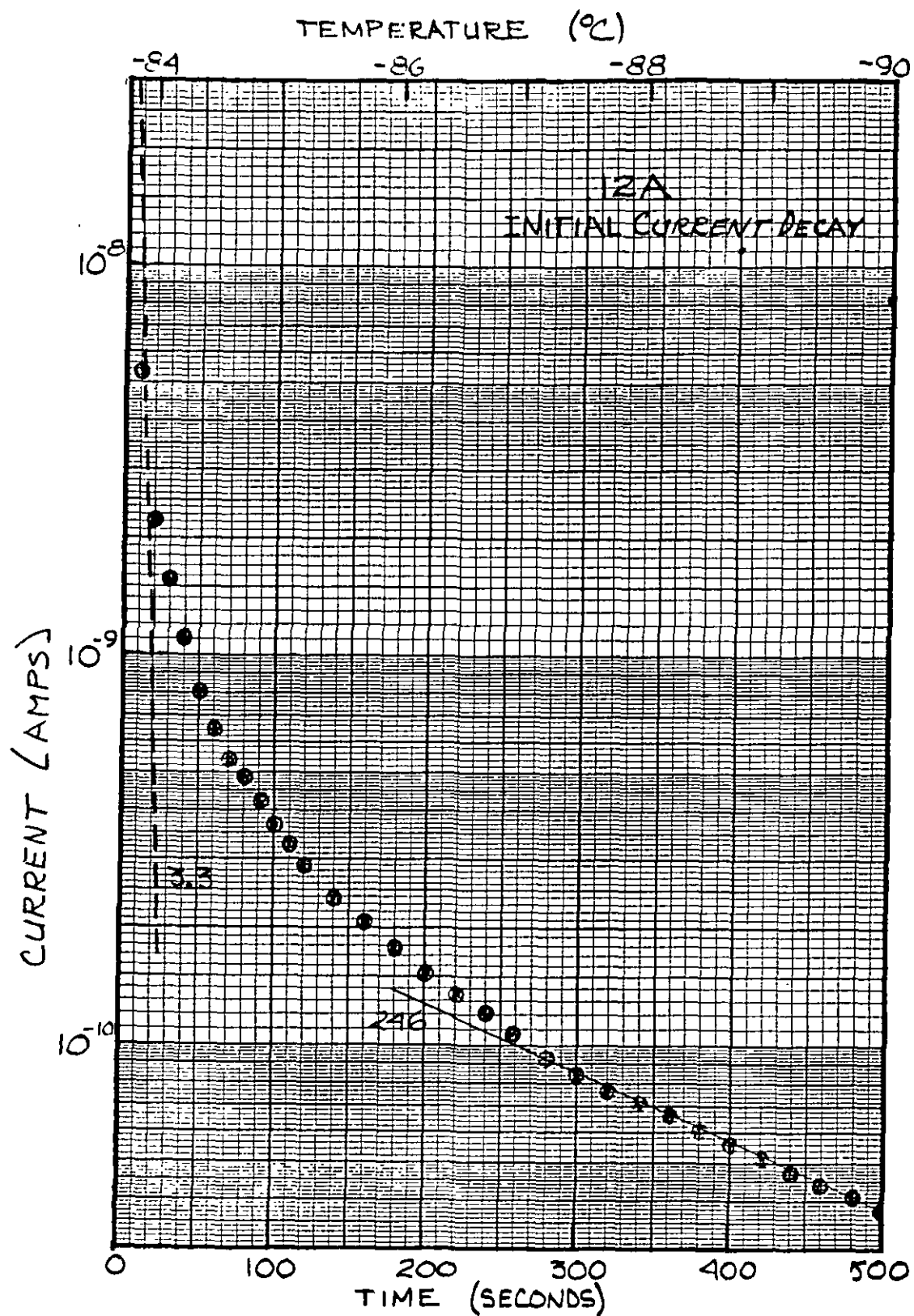
E is the activation energy for the stated band, in eV.

T_m is the temperature of the maximum for the stated band, in °C.

i_m is the maximum value of the depolarization current for the stated band $\times 10^{10}$, in amps.

Symbols * and () are explained in text.

Figure 6



(the sample). The surface charges within the dielectric, which have the opposite polarity of the electrode bound charges, are called heterocharges. It is the release of the bound charge that is measured during the depolarization experiment. The initial current decay with time then, at the temperature T_{tsc} , must be due to (1) the free charges or atomic polarizations and/or (2) the decay of a depolarization band with its current maximum occurring near the temperature T_{tsc} . This latter case then results in the decay of a portion of the bound charge, and in this event, a long relaxation time is expected, since dipolar relaxations are strongly temperature dependent. In the first case, however, small relaxation times are anticipated because these phenomena (atomic or electronic) are not temperature dependent.

It is possible to estimate these relaxation times in the following manner. Either process (1) or (2) can be described quantitatively by an expression:

$$i(t) = i_0 \exp(-t/\gamma),$$

where γ is the relaxation time in question. (A derivation of this expression for a dipolar relaxation is given in Appendix I of PR2⁸.) The usual relaxation time for a capacitor is given as the product of the capacitance and the external resistance, RC . This is the time required for the current to decay to $1/e$ of its original value, i_0 .

For the unplasticized material, a later calculation yields an effective static dielectric constant, at temperature T_p , of 6. Using this value the capacitance of the sample capacitor is about 3000 pF. Neglecting cable and electrometer capacitances (about 30 pF total) and using a value for the load

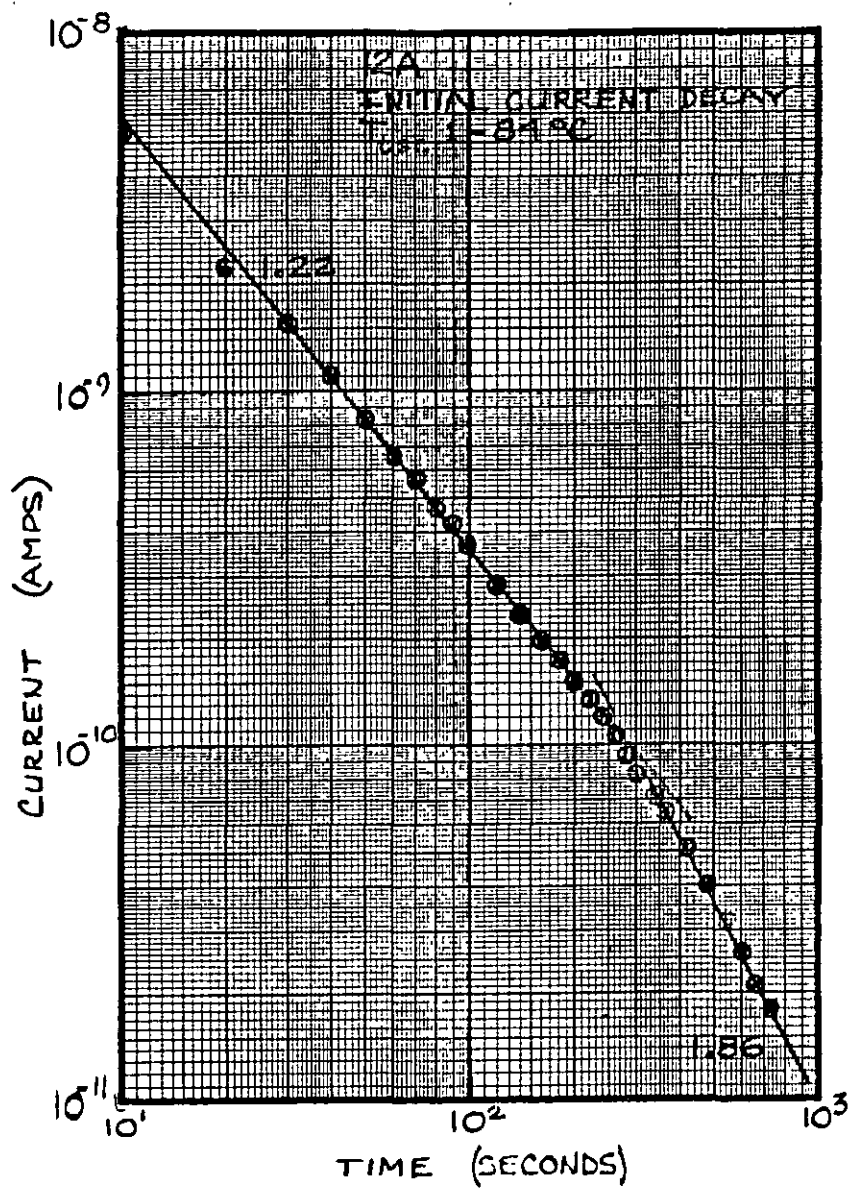
resistor of 10^9 ohms (typical) a relaxation time of 3 seconds ($= RC$) is computed. Thus for 99% of the charge to decay would require 14.6 seconds.** That the initial decay is very rapid can be seen on Figure 6. If we let V be the original applied voltage of 300 volts for this specimen (remembering that the bound charges do not contribute to the voltage since they are neutralized by the dielectric polarization) then $i_0 = V/R = 3 \times 10^{-7}$ amps. This value would be consistent with the data of Figure 6 and the expected current decay is shown as the dotted line. The slope of this line yields a time constant of 3.3 seconds. At longer times, around 7 or 8 minutes, the curve is once again nearly linear with a measured time constant of 246 seconds. This long relaxation time is typical of a dipolar relaxation. Thus it appears that the initial current decay phenomena can be interpreted as a sum of at least two separate mechanisms. Such data would be useful to elucidate the characteristics of the dipolar relaxation process, except however, for the fact that the temperature is also slowly decreasing with time. Elimination of this complicating factor would require a more sophisticated temperature control. As shown on Figure 6, for the particular experiment 12A, the starting temperature was -84°C while after an elapsed time of about 7 minutes the temperature was -89°C .

As a means of comparing this initial current decay between samples, it has been useful to plot the decay data as log current versus log time, as shown for 12A on Figure 7. In this typical plot two linear regions are observed, and both are representable by an equation of the form

$$i = A t^{-n}.$$

** Actually one should probably use the vacuum capacitance for the specimen holder in this calculation, since the dielectric constant of the material at T_D involves the polar groups. If this is done the relaxation time is 0.53 seconds, and the time for a 99% decay is 2.4 seconds.

Figure 7

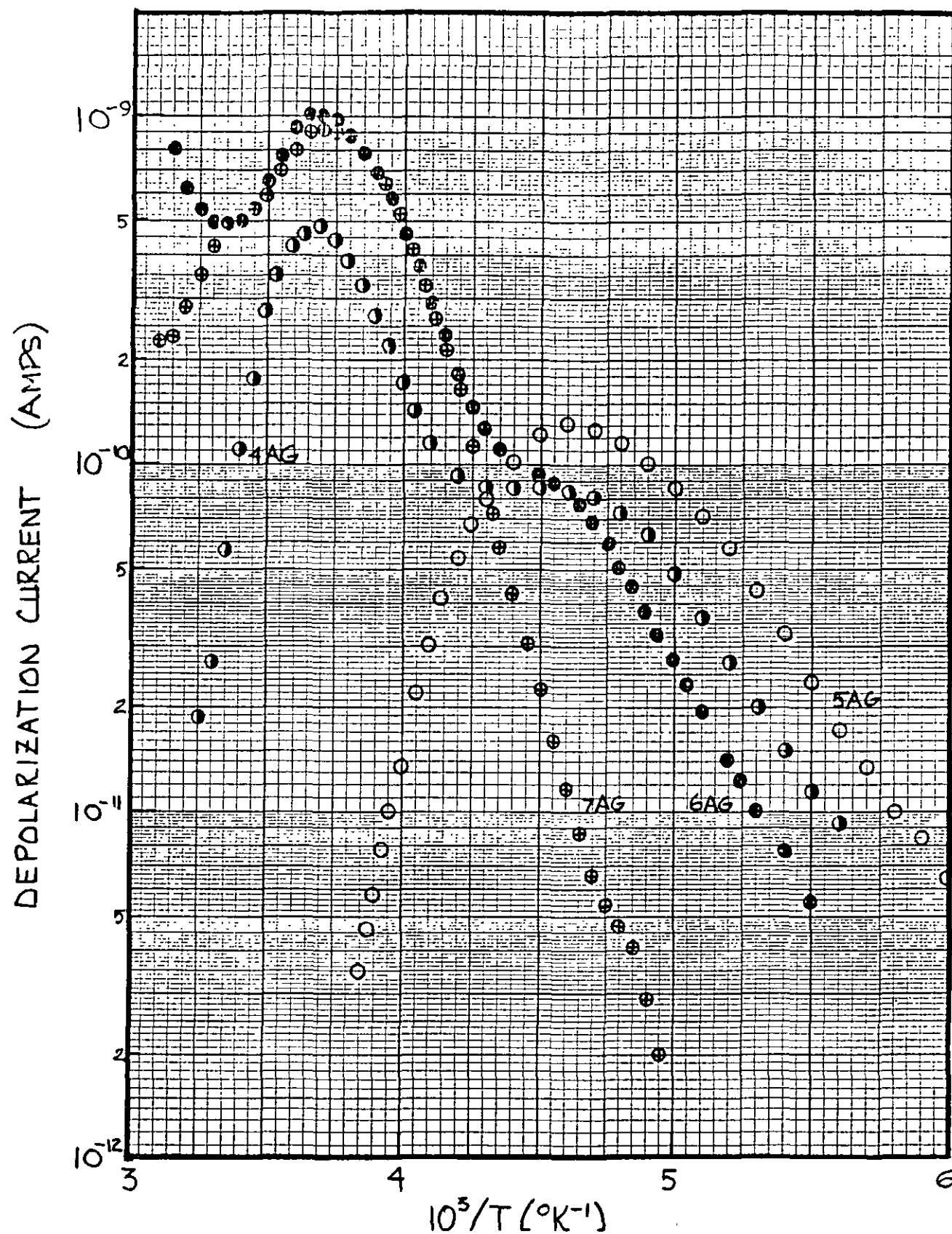


The value of n may be determined from the slope of the linear region. For 12A the values of n are 1.22 and 1.86 for short times (≤ 300 seconds) and long times, respectively. All experimental trials have been characterized in this manner, using the value of n deduced for short times, and these values are included in Table II. If n is plotted against T_{tsc} , the temperature at the start of the depolarization experiment, the data is 'bunched' according to which dipolar band is discharging. For example, in the next section it will be shown that a depolarization band occurs around -60°C . At values of T_{tsc} near or less than this temperature, all values of n are between 1.1 and 1.2, and the average value of the constant A is determined to be 6.7×10^{-8} . A has a range from 4.6 to 10.0×10^{-8} . At higher values of T_{tsc} , say around -20°C , the values of n are less than 0.9 and A has a value near 5.5×10^{-9} , implying the discharge of another, different depolarization band. At present there is no quantitative basis for representing the data as in Figure 7, but such plots have been useful in comparisons between the different experimental trials.

THERMAL DEPOLARIZATION RESULTS
PLASTICIZED CELLULOSE

Typical results for specimens plasticized with glycerol are shown in Figure 8. Consider first the curve labelled 4AG. This data appears to be a composite of at least two separate depolarization bands. To confirm this, that is to separate the two bands, a second experiment was performed by polarizing the specimen at much lower temperatures, $T_p = -62^{\circ}\text{C}$. These results are labelled 5AG, and indeed, a single polarization band is observed, with a maximum near $10^3/T = 4.6$ or -56°C . To clarify the nature of the band at higher temperatures another experiment polarized the specimen at $T_p = 0^{\circ}\text{C}$, and the field subsequently removed at -41°C . When the open circuited specimen had cooled to -56°C , the temperature of the maximum of the low temperature band, the specimen was connected into the depolarization mode, and this band was allowed to discharge before heating the sample. This technique resulted in only the high temperature band, with a maximum near 0°C , as shown in curve 7AG. The small shoulder on the high temperature side of this latter band suggests the presence of another (third) band around room temperature. The curve 6AG was an attempt to verify this, but it can be seen that by polarizing at higher temperatures, $T_p = 23^{\circ}\text{C}$, the current shows a marked increase above room temperature ($10^3/T = 3.2$). This rapid rise in current is presumably the start of the band(s) shown in Figure 4 of PRL¹, and unfortunately masks the presence of the suspected band near room temperature. As noted earlier, the bands shown in PRL have not been investigated with the present apparatus because of the unsatisfactory heater performance at temperatures above room temperature. In addition, specimen heating beyond about 50°C is not desirable, since irreversible structural changes can occur at higher temperatures. The suspected band near room temperature is observed in later data, however.

Figure 8



The depolarization band centered around 0°C is apparently the same one depicted in Figure 10 of PR2.

To verify that these bands are truly dipolar in origin, a series of experiments were performed to determine if the maximum depolarization current was linear with the applied field strength. Recall that if space charges are giving rise to the observed bands that a linear relationship is not expected (PRL). Measurements were performed with polarizing field strengths of 18, 37, 74, and 112 kv/cm, with all other parameters held constant, and these results are reported on Figure 9 as 10AG, 8AG, 7AG, and 11AG respectively. The temperature of the current maximum in all cases occurs at the same temperature (nearly) of -2°C or 271°K , and furthermore, the existence of a band around room temperature is also evident, especially for specimens 8AG and 10AG. Figure 10 is a plot of maximum current versus polarization field strength. At the temperature of 271°K the relationship is linear. The error bars on this upper curve are $\pm 5\%$, an estimated value for the upper bound of experimental error. The data was also examined for linearity at 298°K , the approximate temperature of the high temperature band. As shown, the single point at the highest field strength deviates from a linear relationship.

Activation energies have been determined from the data of Figure 9, according to the method described in PRL. This is done by representing the data as log current versus inverse temperature, as shown in Figure 11, and computing the slopes on the low temperature side of the maximum. Computed values are shown on Figure 11. Also shown on this figure is another attempt to isolate the suspected band around room temperature. This trial, labelled

Figure 9

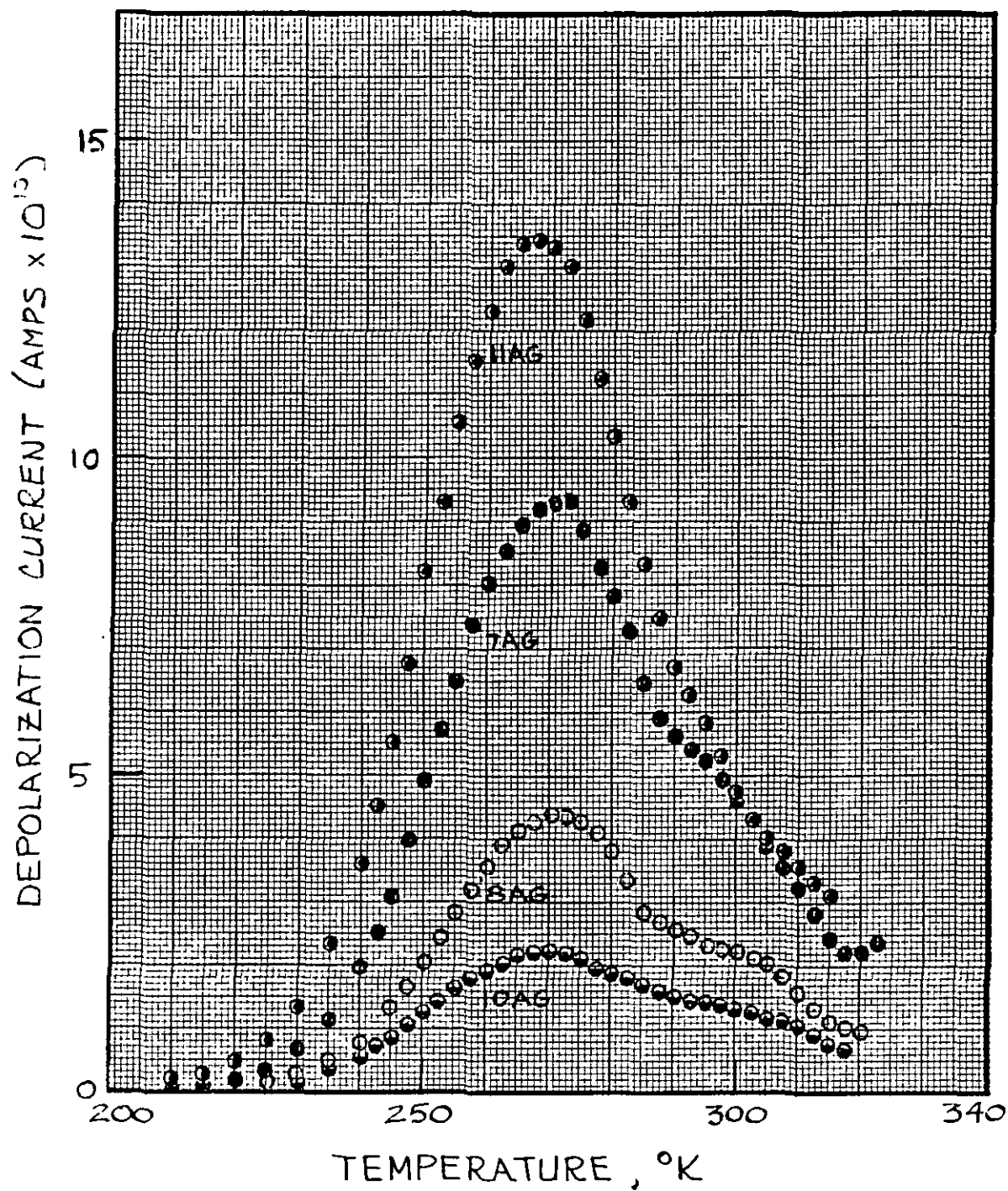


Figure 10

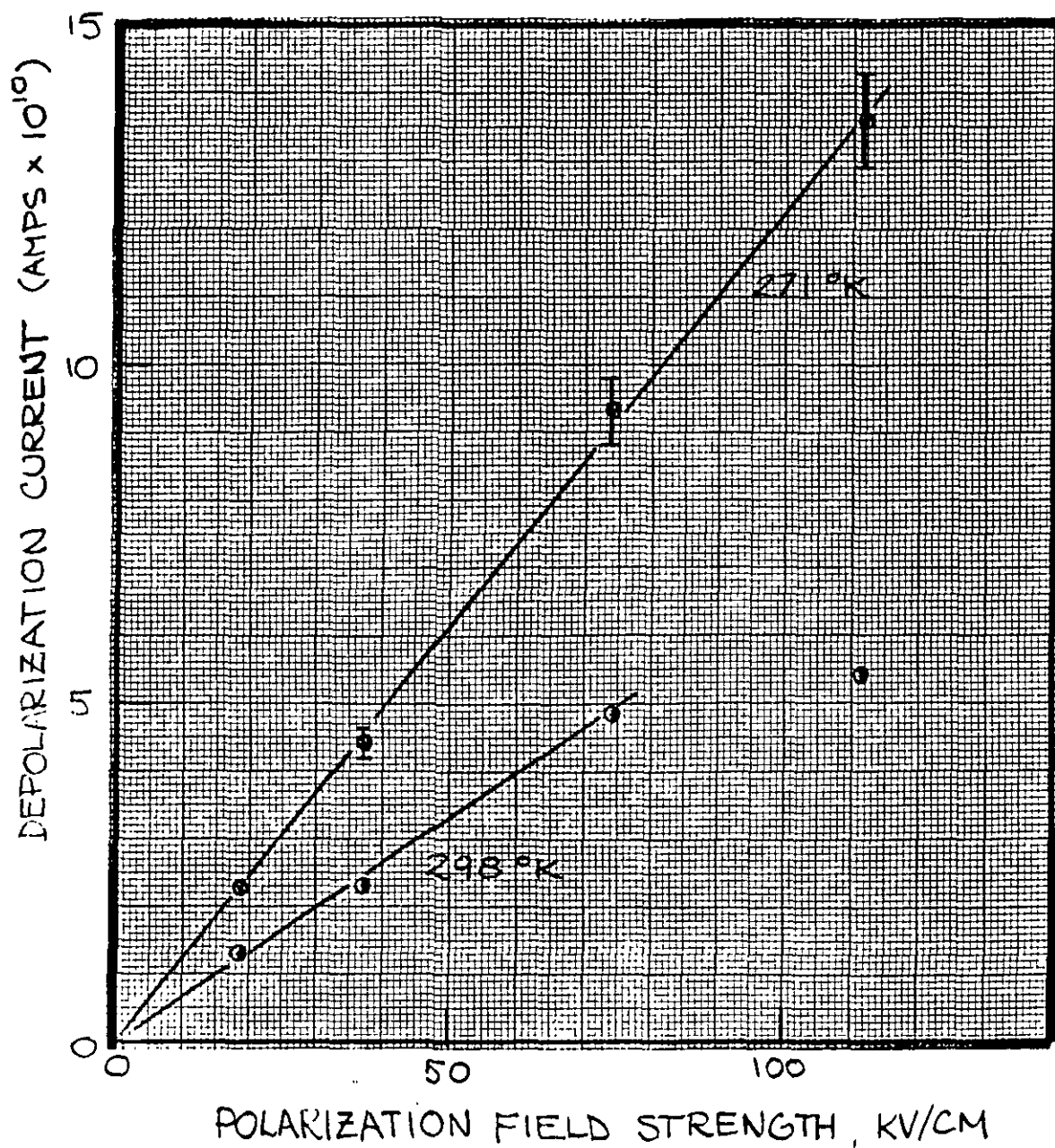
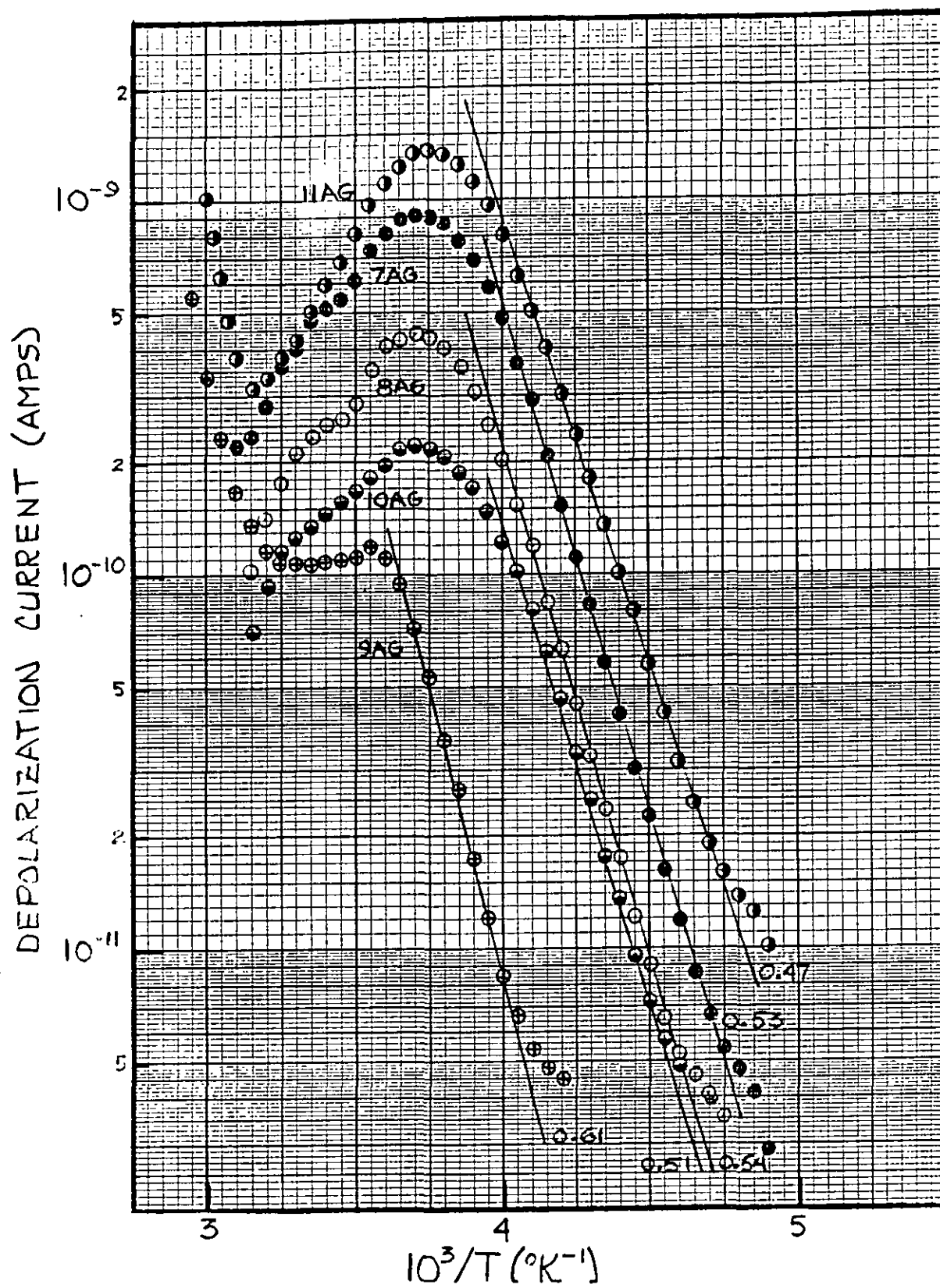


Figure 11



9AG, should be compared to 8AG. The differences in magnitude between these two probably reflects the fact that part of the room temperature band was depolarized during the depolarization of the -2°C band. The measured slope, however, of 0.61 eV, does suggest that a unique band does exist around room temperature.

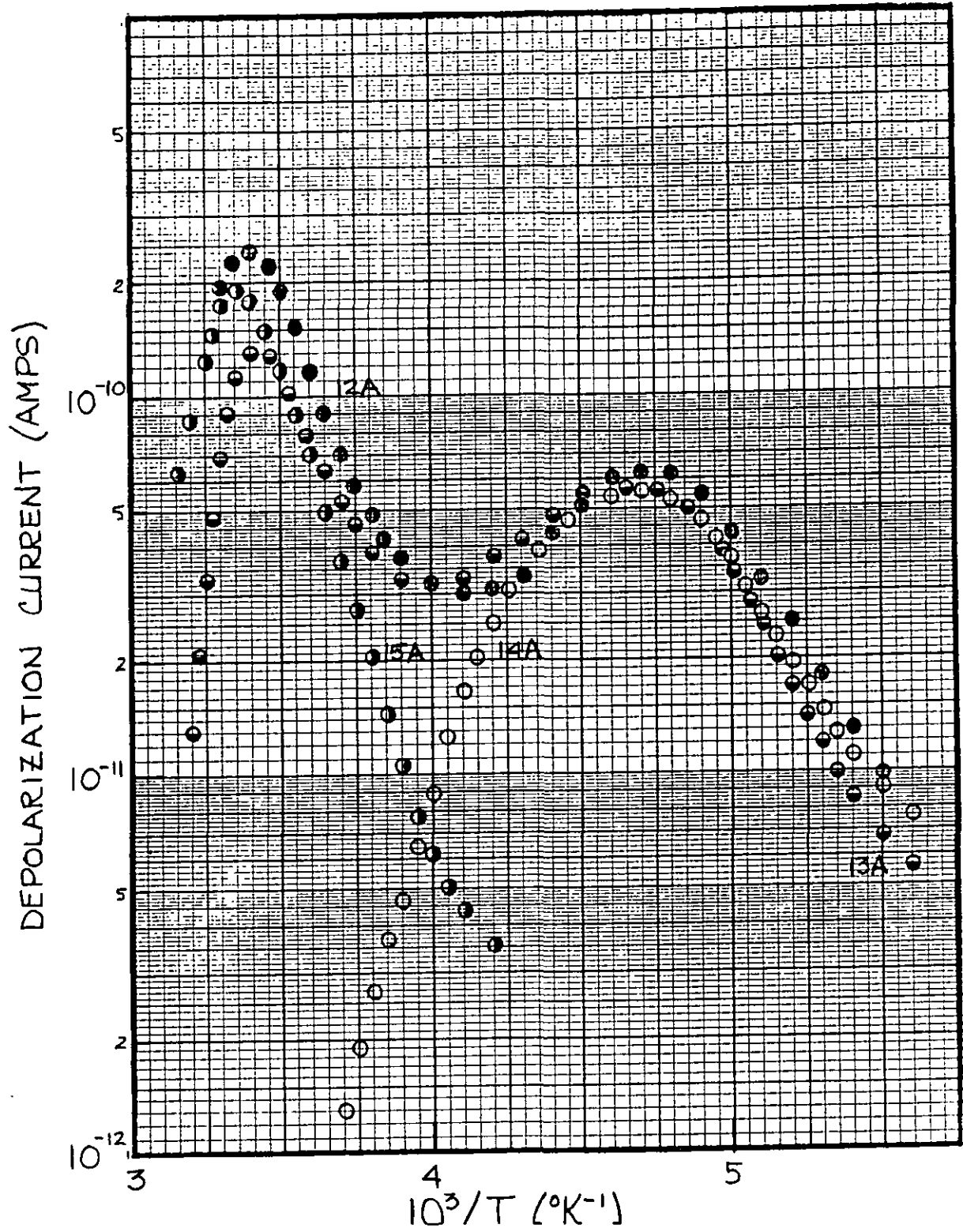
To recapitulate, the measurements on the plasticized material reveal at least three depolarization bands, with maxima near -56 , -2 , and $+25^{\circ}\text{C}$. The measured parameters for these three bands are included in Table II, where E is the measured activation energy for each band, and T_m and i_m are the temperature at maximum current, and the maximum value of the depolarization current, respectively. In Table II the lack of an entry in the respective columns means the band in question was not observed, the symbol * denotes that the band in question was too close to a stronger band to allow measurements or was ill-defined, and () are used to indicate that the value must only be considered an estimate. All other entries are assumed accurate to within experimental error, estimated to be $\pm 5\%$. These bands will be discussed again in a later section.

THERMAL DEPOLARIZATION RESULTS
UNPLASTICIZED CELLULOSE

Typical results for the unplasticized material are depicted in Figure 12. It can be seen that the band at $10^3/T = 3.7$ (-2°C) is no longer present. Instead the data reveals only two obvious bands, one at -58°C and the other at approximately $+23^{\circ}\text{C}$. The single depolarization bands, 14A and 15A, were obtained by techniques similar to those discussed in the last section, and roughly add to give 13A or 12A. The difference in magnitude between 12A and 13A, in the high temperature region, is presumably due to the different polarization temperatures of $+22$ and 0°C , respectively.

The low temperature band is apparently the same one observed in the plasticized material. The room temperature band, however, may not be the same one observed in the plasticized material at the same temperature, since a plasticizer would be expected to shift the maxima of the bands. The effect of a plasticizer would be to shift the band maxima to lower temperatures, and thus the room temperature band observed in the unplasticized material could very well be the same band that occurs at -2°C in the plasticized material. The shift in maxima through 25 degrees, from -2 to $+23^{\circ}\text{C}$, would not be an unusual value upon removal of the plasticizer. In addition, since water acts as a plasticizer, varying moisture levels from experiment to experiment may result in shifting maxima. For example, this might explain the variations in in the temperatures of the 25°C band maxima for experiments 12A, 13A, and 15A. From Figure 12 these temperatures are 29.5, 20.5, and 25°C , respectively. The heating rate might also be expected to cause small shifts in the temperatures of maxima, but for all data presented in this report, the heating rate was constant

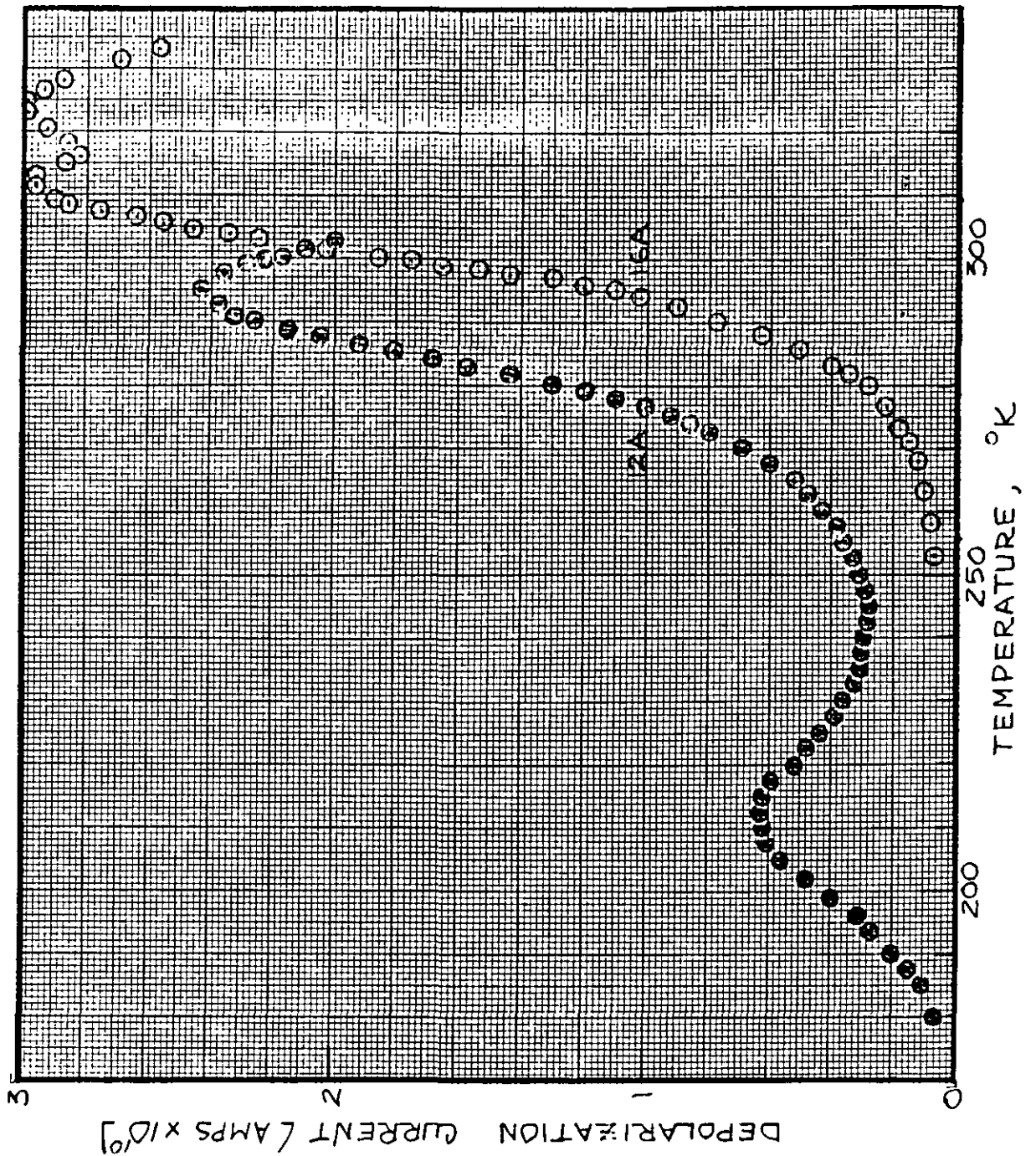
Figure 12



at $0.0137^{\circ}\text{K}/\text{second}$.

The activation energy determined from the slope of experiment 15A might be a clue as to whether the room temperature band of Figure 12, is the -2°C band for the plasticized material. If both of these bands arise from the same source, we would expect similar activation energies. The energy computed for 15A is 0.56 eV whereas the average activation energy for the -2°C band, from Figure 11, is 0.52 eV. To resolve these inconclusive results, a second experiment was performed and this data is shown on Figure 13 as curve 16A. Curve 12A is also shown for comparison. 16A was polarized at a higher temperature and for a longer time than 15A, (see Table I) and the temperature of the (first) maximum for this experiment was about 35°C , and the computed energy is 0.65 eV. This last result would imply that this band is not the one observed in the plasticized specimens at -2°C . As before, pertinent results are recorded in Table II.

Figure 13



DISCUSSION THE LOW TEMPERATURE BAND

The low temperature band is observed in both plasticized and unplasticized material at approximately the same temperature of -58°C . Figure 14 depicts data of two measurements, 14A and 5AG, which represent the two extreme cases, nearly, as far as the magnitudes are concerned. All other measurements on this band fall in the vicinity of 14A, whether the material was plasticized or not. With respect to the section titled "Thermal Depolarization-Initial Decay", it is believed that in all measurements of this band, the band has been partially discharged, or, has not been polarized to saturation. These could account for the differences in magnitude observed. Recalling that all initial current decays, at the lower temperatures, have a value of n between 1.1 and 1.2, it is likely that this band has partially discharged before the linear heating began. To confirm this, one experiment was performed in which the polarizing field was maintained from 0 to -150°C , and heating started immediately upon field removal. In this case the maximum again occurred near -58°C with a maximum current of 1.9×10^{-10} amps, compared with 1.35×10^{-10} amps for 5AG. This supports the notion of a partial discharge. Experimental difficulties in working at the very low temperatures, viz. very long cooling times and vacuum leaks, preclude a more thorough description of this band.

Even if the band has been partially discharged, however, one can still expect consistency in the value of the computed activation energy from curve to curve. This is illustrated in Figure 15 for five measurements, including both plasticized and unplasticized material. The computed energies are shown on the figure, and the average of these values is 0.27 eV. This value has been used to generate a theoretical curve for comparison with the data and this is shown on

Figure 14

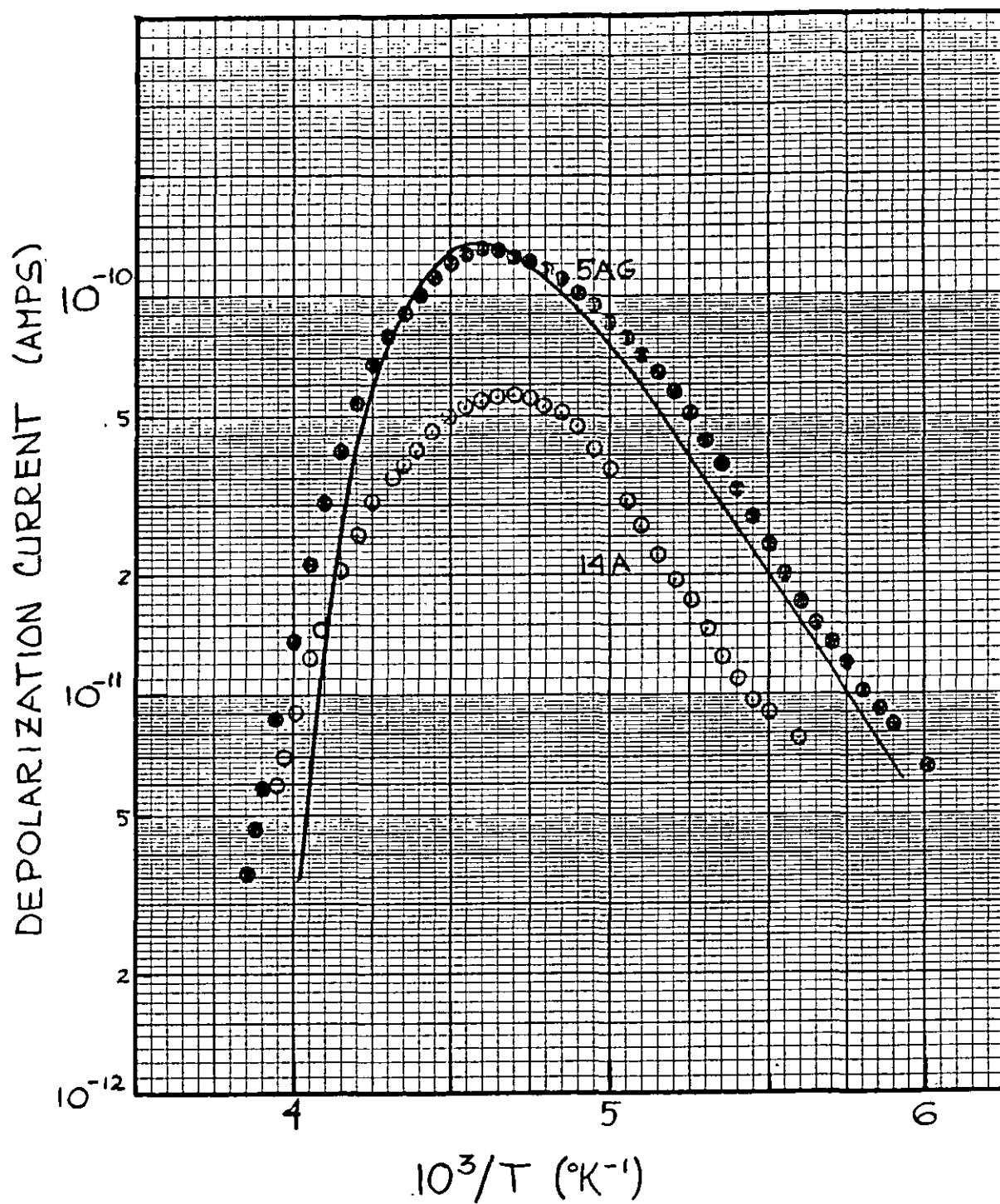


Figure 15

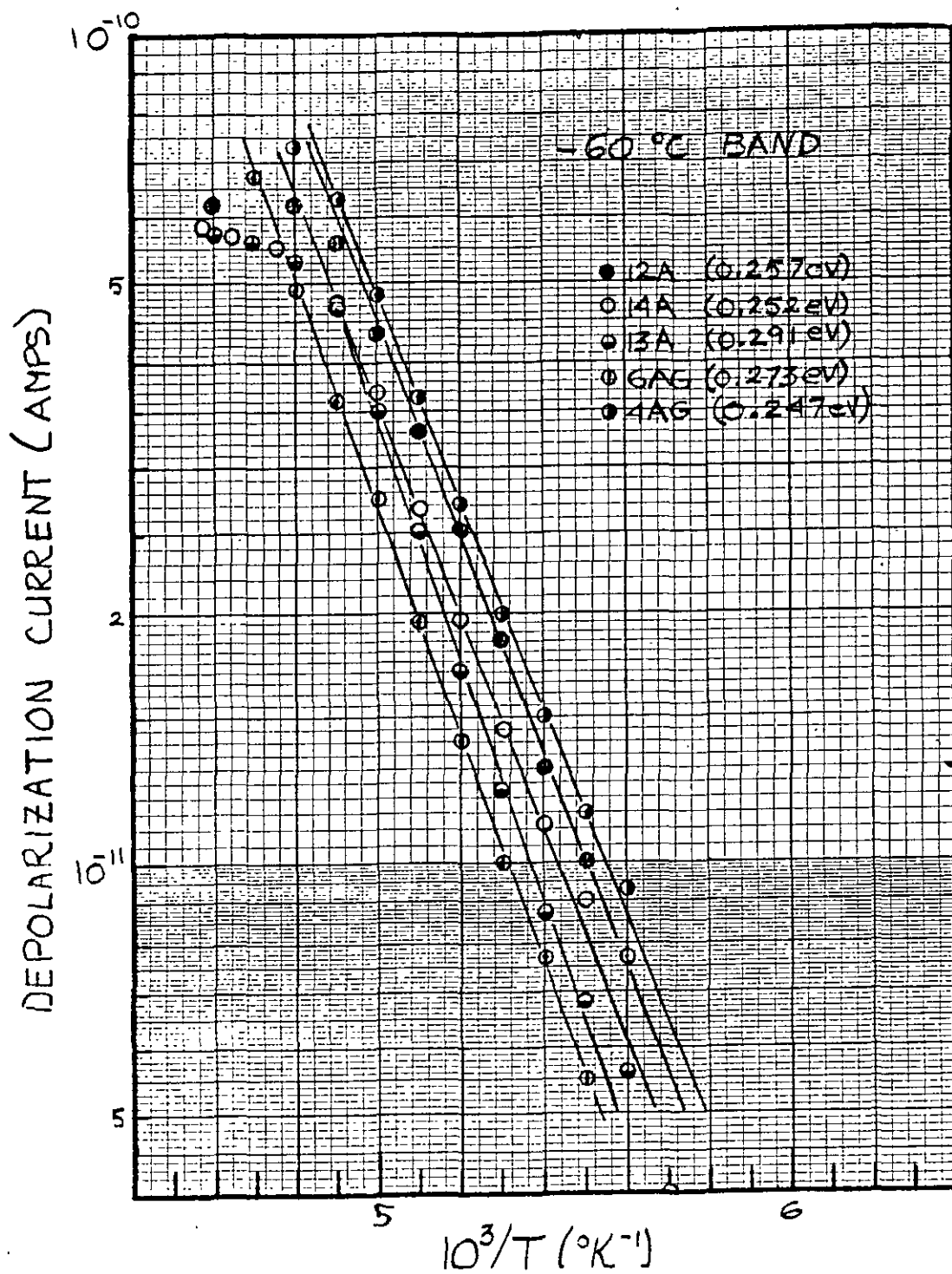


Figure 14 as the solid line. The agreement is generally rather good. Although only the theoretical curve for 5AG is shown, similar curves have been computed for the other measurements on this low temperature band. A computer program has been written which computes the theoretical curves, as well as other significant parameters, as outlined in PRL¹, when E , T_m , and i_m are given. This program is discussed briefly in the Appendix.

Although partial band discharges do not effect the calculation of activation energies, errors will arise if the value of $\beta N p^2$ is computed from the data. (N is the concentration of dipoles, p is the effective dipole moment of the molecule or molecular segment, and β is a geometry factor, equal to $1/3$ for freely rotating dipoles.) Nevertheless, such calculations should provide order of magnitude estimates. To illustrate for example, in experiment 14A, the product $\beta N p^2$ is computed to be $4.0 \times 10^{-34} \text{ coul}^2/\text{cm}$. If p is arbitrarily chosen as 1.5 Debyes ($1 \text{ Debye} = 3.3 \times 10^{-28} \text{ coul-cm}$), then $\beta N = 1.6 \times 10^{21} \text{ cm}^{-3}$. Since $\beta \leq 1/3$, the minimum value of N , when $p = 1.5$ Debyes, is $4.8 \times 10^{21} \text{ cm}^{-3}$. The calculation of $\beta N p^2$, however, involves the polarization temperature T_p . If the effective value of T_p is lower than that stated in Table I, because of the slow cooling rate, then the computed value of N will correspondingly be less by the same ratio.

It is of interest to compare this estimated dipole concentration, N , with the number of glucose residues per cm^3 . Using the density value for crystalline cellulose this latter value is $5.6 \times 10^{21} \text{ cm}^{-3}$, or, approximately one polar group for every glucose unit is important in this low temperature band.

These calculations, of course, suppose an effective moment of 1.5 Debyes. A larger moment will decrease the computed N , whereas a decrease in β , indicating hindered rotation, would increase the value of N .

The absence of a temperature shift in the current maximum upon plasticizer removal suggests that this band originates within the crystalline regions of the material, since these regions should be inaccessible to the plasticizer. The computed value of γ_0 for experiment 14A is about 8.9×10^{-4} seconds. According to the arguments given in PR2⁸ a value of this magnitude suggests that the effect of the polarizing field was to create disorder at the molecular level. Frolich¹⁴ suggests this would probably be the normal course of events in a dipolar solid.

DISCUSSION

The Mid-Temperature Range Band

The disappearance of the band at -2°C in the unplasticized material suggests that this band must arise from the glycerol plasticizer or/and its interaction with water. The possibility that the -2°C band in the plasticized material and the band near room temperature in the unplasticized material have the same origin, is dismissed on the bases of the different activation energies found, as well as the marked differences in magnitude. If one assumes the uniqueness of these two bands, it is very tempting to subtract the data for the unplasticized material from that of the plasticized material. The separate curves are shown in Figure 16. In this figure the upper curve is 7AG while the lower curve is 12A, except, in the lower curve in the high temperature region, the band has been replaced by a composite or average of the separate bands measured in this region. This figure does not include any shifts in peak maxima due to plasticizer removal, although this effect is most probably present.

Figure 17 depicts the results of subtracting the unplasticized data from the plasticized. In this figure the difference is assumed attributable to only the plasticizer and is so labelled as the 'glycerol' band. Using theory for a single depolarization band, with $E = 0.52 \text{ eV}$, it is not possible to obtain a reasonable fit to the solid curve of Figure 17. It is possible, however, to fit the 'data' reasonably well if at least two subbands are assumed. Two such theoretical subbands, as well as their sum (dotted line) are shown on Figure 17. These bands were computed using activation energies and maxima

Figure 16

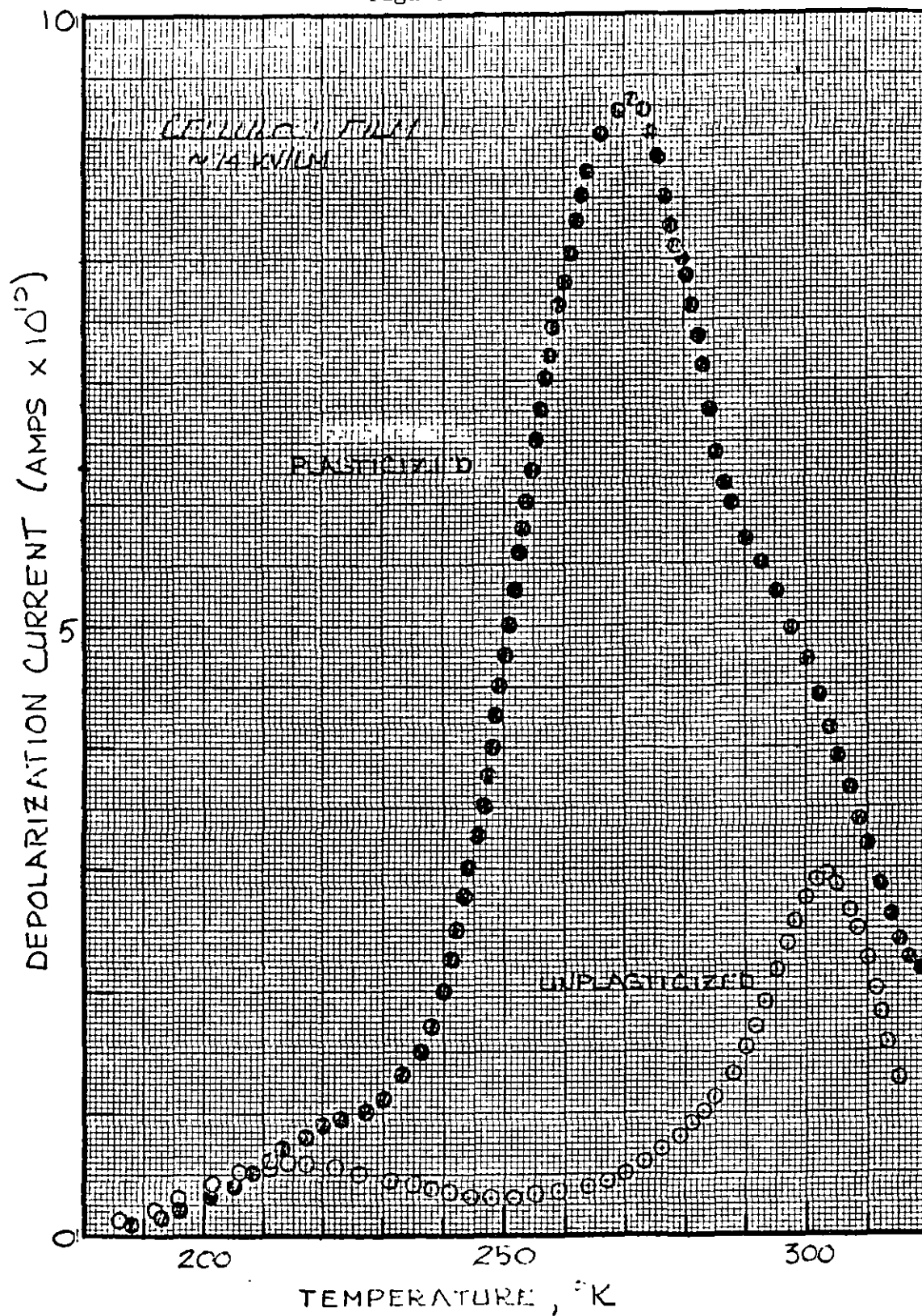
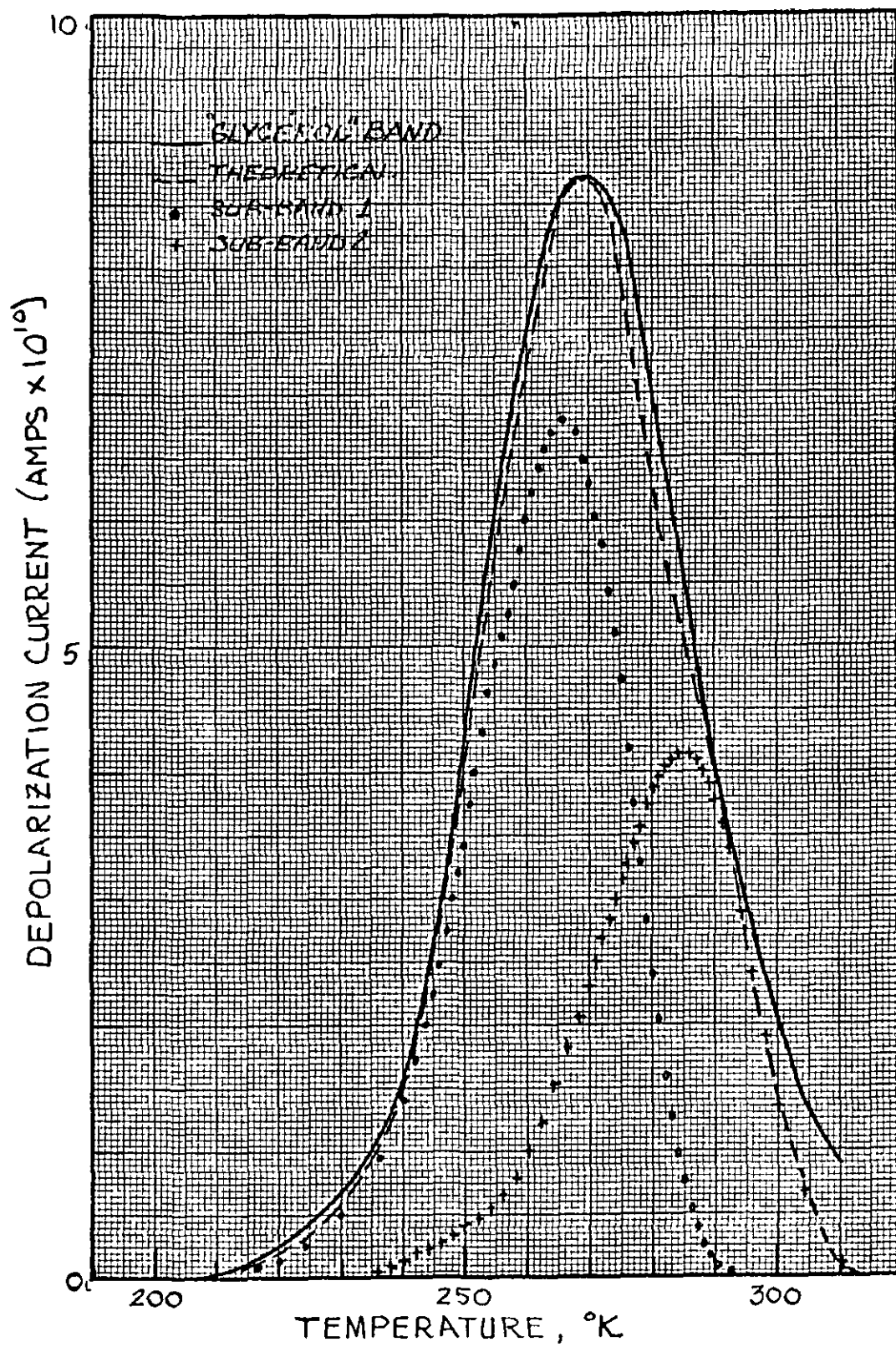
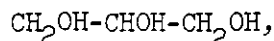


Figure 17



temperatures of 0.51 eV and 366°K , and 0.56 eV and 285°K , respectively.

The glycerol molecule,



is symmetrical so that the $-\text{CH}_2\text{OH}$ groups are identical. Thus glycerol possesses multiple hydroxyl groups and, generally, the two primary hydroxyl groups are more reactive than the secondary group. This distinction between hydroxyl groups may offer a logical explanation for the necessity of involving two subbands in the 'experimental' glycerol band. Alternatively, the hygroscopic character of glycerol might also lead to a band in some way associated to the water present. Apparently the mode of action of glycerol as a plasticizer for cellulose film is not completely understood.

One purpose in obtaining a theoretical fit to the data is to obtain curve areas and volume polarizations. For example, for the 'glycerol' band shown in Figure 17, the total measured charge is found to be 2.4×10^{-6} coulombs, yielding a total volume polarization $P_0 = 1.2 \times 10^{-7}$ coulombs/cm². This is assumed to be the volume polarization of the specimen at temperature T_p ($= 0^{\circ}\text{C}$ here) and subsequently 'frozen into' the material upon cooling. That is, this measured charge is assumed to be the bound charge. (Actually, as Gross points out¹⁰, this measured charge is probably too large because of the slow cooling rates employed here.) The volume polarization may be expressed in terms of the dielectric coefficient and the applied field, according to the usual expression:

$$P = (k-1)\epsilon_0 E,$$

where ϵ_0 is the permittivity of free space. The static dielectric coefficient, k , at temperature $T_p = 0^{\circ}\text{C}$, is thus 19.5.

It is informative to compare this value with that estimated by an independent method. Venkateswaran¹⁵ has derived an expression for the effective dielectric constant of a composite material as $k_{\text{eff}} = a_1 k_1 + a_2 k_2$, where the a 's are the volume fractions of the components and the k 's are the dielectric coefficients. Morgan¹⁶ has measured the dielectric constant for glycerol as a function of temperature and frequency. At 30 Hz the dielectric constant varied from 60 at -50°C to 50 at 0°C . This latter value was taken as the dielectric constant for glycerol and the value for cellulose film, computed in the next section, was chosen as 6. From the percent weight glycerol, using handbook values for densities, and neglecting any water present, the volume fractions may be estimated. The resulting dielectric constant for the composite is computed as 12.6 and this figure should be compared with the value of 19.5 computed from the depolarization data. Any water present in the system greatly affect the dielectric constant. If, for example, the specimen contains 2% by weight water, the estimated dielectric constant increases to 15.0.

The data presented in Figure 10 are a strong argument in favor of the dipolar origin of this -2°C band. Estimated values of N or p (assuming p or N , respectively), however, do not seem reasonable. For example, the density of glycerol molecules within the material may be computed as $1.2 \times 10^{21} \text{ cm}^{-3}$. If this value is used in the values of $\beta N p^2$ found for the two subbands, with $\beta = 1/3$, then $p_1 \doteq 9$ Debyes and $p_2 \doteq 7$ Debyes. These are not realistic values. By way of comparison, the substituents $-\text{OH}$ and $-\text{CH}_2\text{OH}$, in a benzene solution, have experimental values of 1.6 and 1.68 Debyes respectively. The source of this problem may result from an inadequate knowledge of T_p and the effect of the extremely slow cooling rate, or it may be that the glycerol band cannot be

described by a simple sum of single relaxation processes.

The High Temperature Band

Theoretical curves have also been computed for the high temperature band in the unplasticized material. At temperatures above the maximum, where data is not available, these theoretical curves offer estimates for the volume polarization and net bound charge. For example, in experiment 12A, with $E = 0.61$ eV and $T_m = 298^\circ\text{K}$, the computed volume polarization is about 3.0×10^{-8} coul/cm², yielding a bound charge of 6.0×10^{-7} coulombs. This is the high temperature band only. If the polarization of the low (-58°C) band is included, the total volume polarization (computed) is 3.6×10^{-8} coul/cm². By estimating the missing high temperature side of the band, and then graphically integrating the data, the measured value of the volume polarization is about 4.0×10^{-8} coul/cm².

For the unplasticized material the thickness of the film decreased to about 1.35 mils resulting in an applied field strength of about 85 kv/cm for these experiments. Using this value and the total computed volume polarization, the static dielectric coefficient is found to be 5.8. This compares favorably with other reported values for the dielectric constant of unplasticized cellulose film, viz. 2.2^{17} and 8.0^{18} .

The capacitance of the empty sample holder, at a plate separation of 1.35 mils, is 520 pf. With an applied potential of 300 volts, the free charge would be 1.56×10^{-7} coulombs. If the explanation of the initial decay process presented earlier is accurate, then a quantity of charge comparable to the above value should be observed. Graphical integration of the initial decay data yields

a value of 1.8×10^{-7} coulombs, and, as mentioned earlier, this measured value is assumed to receive a contribution from the partial decay of the low temperature band.

FUTURE WORK

The results presented in this report do indicate that the depolarization technique can be useful for looking at the effects of additives, or mechanical, thermal, or chemical treatments. From the previous discussion it appears probable that the hydroxyl groups in the glucose unit are involved on one or more of the observed depolarization bands. Since the hydrogen atom in the -OH group forms the hydrogen bond in the crystal lattice, any alteration in the state of the hydrogen bond should influence the thermal depolarization effect. It is likely that the state or degree of hydrogen bondage differs for the various crystalline forms of cellulose. That is, with changes in the crystal lattice, the number of hydrogen bonds, as well as their directions and distances, may also be expected to vary. Such an argument has been advanced to explain the differences in behavior of the piezoelectric effect in cellulose, which also involves the -OH group, for crystalline cellulose structures I, II, and III¹⁹. The thermal depolarization technique, performed on the various crystalline forms of cellulose, should thus provide a method for investigating the nature of the hydrogen bondage in these forms. The transition possibilities between the various crystalline forms of cellulose have been reported by Ellefsen, et.al²⁰, and are shown in Figure 18.

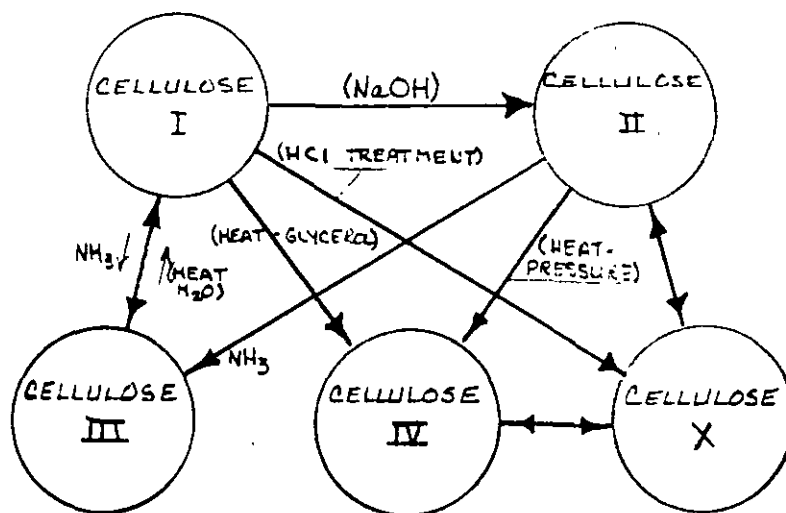


FIGURE 18: CELLULOSE STRUCTURES (REF. 20)

It is anticipated that chemical modification of the present cellulose II structure, and subsequent depolarization measurements, will be the next phase of this investigation. Initial efforts will involve the II to III transition via the liquid ammonia treatment. If these results appear significant, later studies may involve the IV, X, or I structures.

The Special Studies program, mentioned earlier, will provide additional insight into the role played by these groups.

Another possibility for future study would involve measurements on material where the plasticizer has been removed via the Kistler technique. Since plasticizer removal by the water method is reported to result in structural damage, whereas the Kistler method does not, such structural changes should be manifest in the thermal depolarization data.

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APPENDIX

COMPUTER PROGRAM

The theoretical depolarization current expression is given in PR2, equation 2, as:

$$i(T) = C \exp(-E/kT) \exp(-u(T)), \quad \text{where}$$

$$C = ABNp^2 E_p / [\gamma_o k T_p], \quad \text{and}$$

$$u(T) = (b\gamma_o)^{-1} \int_0^T \exp(-E/kT) dT.$$

In practice, the activation energy E is computed from the slope of the log current versus inverse temperature plot on the low temperature side of the maximum. On the low temperature side of the maximum, the function $u(T) \doteq 0$, and thus the pre-exponential constant, C , can also be found. Evaluation of C in this manner, however, sometimes leads to mismatches at the current maximum and the high temperature side of the band. One alternative procedure is to evaluate the pre-exponential constant at the current maximum. This is the procedure used in computer program TOTAL, and is the technique used on a routine basis. The calculations are carried out in the following manner.

Input consists of the measured quantities: E ; T_m , the temperature of the current maximum; and i_m , the magnitude of the current at the maximum; as well

as the control parameters, b , E_p , and T_p . The value of γ_0 may be found from

$$\gamma_0 = [kT_m^2/bE] \exp(-E/kT_m),$$

which is equation 11 of PR1. Once this value is known, the function $u(T)$ is evaluated by numerically integrating from 0 to T_m . This is, at the current maximum, the above expression for u may be written:

$$u[T_m] = (b\gamma_0)^{-1} \int_0^{T_m} \exp(-E/kT) dT,$$

and once this has been evaluated, the pre-exponential factor is deduced from

$$C = i_m(T_m) \exp(E/kT_m) \exp(u[T_m]).$$

The actual computation of depolarization current as a function of temperature, when C is known, is performed using the series expansion for $u(T)$ given in PR2 as equation 4:

$$u(T) = (b\gamma_0)^{-1} T \exp(-E/kT) \sum_{n=1}^{\infty} (-1)^{n-1} n! (E/kT)^{-n},$$

and truncating after the first 10 terms in the series. As $i(T)$ is computed, the relaxation time $\gamma(T)$, and the area under the curve, are also simultaneously computed. Finally, the total volume polarization and the product $\beta N p^2$ are computed. Program TOTAL will compute up to four bands and add the results for $i(T)$ to produce a composite depolarization band. Output consists of E , T_m , i_m , γ_0 , C , band area, volume polarization, and $\beta N p^2$ for each band, and $i(T)$ and $\gamma(T)$ for each band as well as $i(T)$ for the composite.