THE ELECTRICAL CONDUCTIVITY OF CRYSTALLIZED

LEAD SULPHIDE

by

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I - INTRODUCTION

The metallurgical importance of studies on the intimate structure of minerals is gradually being recognized.

The information and theories deduced from classical crystallography and from the idealized results produced by x-ray investigations are not sufficient to account for the manifold complexities encountered in the chemistry and physics of ore dressing problems. Secondary properties involving perhaps more variables are of fundamental importance in the development of present methods and in the creation of radically new metallurgical processes. It is for this reason that work of the type reported in this paper has been carried on.

Some preliminary work on the applications of the methods of physical metallography to the studies of minerals has already been reported.[1] The present paper presents a continuation of those studies.

In a previous paper[1] measurements of the temperature coefficient of resistance of natural galena specimens were reported and the effect of structural characteristics on the temperature coefficient studied. The conclusions of that work were that specific resistance in itself is of very little significance, but that the temperature coefficient varied over wide limits for different grain sizes. By grain size here is meant either the size of the secondary blocks of Zwicky[2] or Smekal[3] as described for minerals by Head[4] and Buerger[5] and others, or else the term grain size as employed by the metallographists. It was found that the temperature coefficient increased with increasing width of unit blocks for massive crystalline galena and that it became negative for finely

grained steel galena. Hence it seemed that a measure of the extent of
lattice discontinuities in such substances might be obtained from elec-
trical measurements.

II - THE SECONDARY STRUCTURE OF SOLIDS

The concept of lattice discontinuities arose from the theoretical
treatment of x-ray diffraction by Darwin [6] and Ewald [7]. In order to ac-
count for various anomalies in the intensity effects the existence of im-
perfect crystals was postulated. By considering actual crystals to be
made up of a number of smaller units, a new picture of the nature of crys-
tals was superposed on the results of the usual x-ray analysis. Ewald
gave the name Mosaic Crystals to these actual crystals and later work
seems to indicate that Ideal crystals can only be realized on paper and
that all actual crystals no matter how carefully prepared are more or
less imperfect. The theory of Darwin and Ewald permits a small range of
angles for each reflection in place of the single value employed in the
Bragg equation: $n\lambda = 2d \sin\theta$. For ideal crystals the deviation from
the angle, θ, amounts to about 5 seconds.

H. Mark [8] demonstrated that in diamond the deviation was 3 minutes
of arc and that in halite, deviations as high as 15 minutes were obtained.
The orientation of the individual units of the "mosaic" must not corres-
pond exactly to that of the crystal as a whole. This has been recognized
as a serious source of error in precision x-ray spectrometry and rock
salt is not now used for measurements of the highest accuracy. Visible
evidence of a variation in orientation within a given "single crystal"

may be found by close inspection of the cleavage faces. Head [4] has described such variations in galena. The fact that it is generally impossible to obtain perfectly plane cleavage faces lends more support to the conception. A very careful study of cleaved bismuth crystals has been reported by Goetz [9]. This investigator found that systems of fine lines were visible on unetched cleaved faces of single Bi crystals. The distances between the various lines proved to be multiples of the smallest observed distance (about 1.2 microns). Etch figures produced on similar faces were found to be triangular pits with dimensions always some multiple of a minimum size which latter corresponded to the distances between the above-mentioned striae. The blocks of the mosaic very likely possess some fundamental size, generally of the order of a few microns. The theory of Zwicky, to which we shall refer later, permits the sizes of unit blocks to range from 100 $\overset{o}{A}$ to 10,000 $\overset{o}{A}$.

T. H. Johnson [10] obtained pictures of diffraction effects produced by allowing H atoms to be diffracted from a surface of LiF. The pictures so produced were interpreted as diffraction lines from a secondary lattice of dimensions lying between 50 $\overset{o}{A}$ and 100 $\overset{o}{A}$. Such beams of atoms have been shown by Esterman and Stern [11] to behave as waves of wave length $\frac{h}{mv} = \lambda$.

The peculiar reflections observed by stokes from potassium chlorate have been attributed (Lord Rayleigh) to the reflections from a series of equally spaced films within the crystals [12].

Davis and Stempel [13] have investigated the effects produced by the successive reflection of an x-ray beam from the faces of two crystals of the same substance. The two crystals are placed parallel to one another whereby, if they were perfectly constructed, sharp reflection maxima

should be obtained for each wave length. However, it was found that considerable angular deviation occurred which is probably due to the imperfections in the two crystals. The density calculated from the lattice parameter is usually less than that obtained pycnometrically on the same sample. Such discrepancies between the calculated and observed densities can mean nothing more than some sort of discontinuity within the crystal. Kolkmeijer [14] believed that such deviations were due to the physical impurity of the specimens, i.e., that allotropic modifications were present in small amounts. However, allotropy is not known in many of the substances which exhibit this phenomenon and crystal imperfections seem to afford a better explanation.

The work of Born [15], Madelung, Kossel, Ewald, Lennard-Jones, and their collaborators on the electrostatic theory of ionic crystals has given us a certain amount of confirmation of the Ideal crystal as revealed by the x-ray. Born has shown how the potential energy of simple cubic crystals may be calculated entirely from electrostatic considerations. The method is essentially the postulation of a Coulombian law of attraction between ions of opposite signs, as Na and Cl in NaCl, and also a repulsive force which varies as some high power of the distance. Likewise the electrostatic potential energy of the lattice, or the lattice energy as it is called agrees rather well with the "observed" values of lattice energy from thermochemical data. By similar calculations the figure obtained for the tensile strength of rock salt is 350 kg/mm^2. Numerous measurements have been made on the tensile strength of rock salt. Under all ordinary conditions the observed value lies in the neighborhood of 0.5 kg/mm^2. This great discrepancy has been probably the real reason back

of the study of crystal imperfections.

A great many of these observations were brought together in a series of papers by A. Smekal (loc. cit.). According to Smekal it seems that crystals possess two types of properties. One type he calls the structure insensitive properties such as the lattice constant, the energy content, coefficient of expansion, etc. The other group he calls the structure sensitive properties; it includes the elastic limit, ultimate strength, electrical conductivity, thermal conductivity, etc. The latter are supposed to be due to the secondary structure of the crystal. Smekal's conception involves "lokerstellen" or open places within all single crystals. The crystal is thus divided into a number of small blocks. The structure sensitive properties are dependent on these blocks and the ions found between them.

A somewhat different picture of mosaic crystals is offered by Zwicky (loc. cit.), who has presented fundamental reasons for the deviation from ideality. The electrostatic lattice theory demands that a two dimensional crystal, i.e., one consisting of a single plane of atoms should contract to a size about 6% less than that which that same plane would have in the interior of a crystal. Evidence from this contraction is to be seen in the fact that the cross section of a solid diminishes when it is under linear tension. By considerations of the energy involved in this contraction and t e energy necessary on the part of the neighboring planes to prevent the contraction Zwicky arrives at the conclusion that the ideal lattice is thermodynamically unstable. The stable configuration is one where certain planes at uniform distances are pulled together resulting in the separation of those between and giving rise to
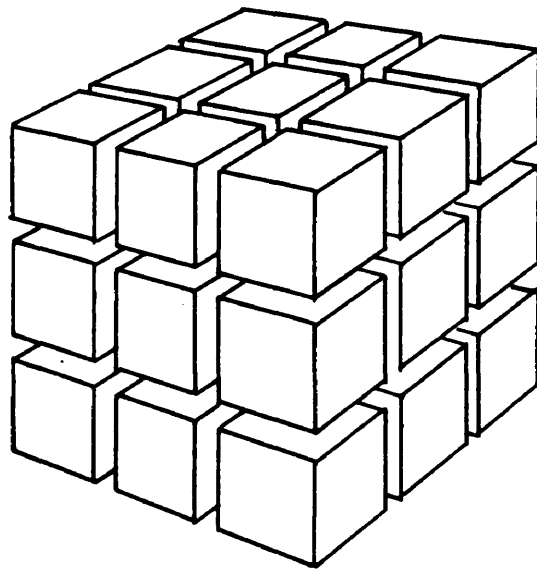
Figure 1

to a periodic variation in density.

III - PRELIMINARY WORK ON SECONDARY STRUCTURE

(a) Theory of the Capacitance Method

It seems logical that if lattice discontinuities of any type are present that they should function as small capacitances and hence that a measurement of the capacitance of a mineral specimen should give some measure of the secondary structure. A prism of galena might be visualized in an ideal state as shown in figure 1, where the space between unit blocks is greatly exaggerated. If electrodes are placed at each end of the prism, all of the blocks in contact with any one electrode would be at the same potential and such an arrangement would function as a series connection of small condensers. If c_1 be the capacitance between the first layer of blocks and the second, c_2 between the second and third, and so on,

$$\frac{1}{c} = \frac{1}{c_1} + \frac{1}{c_2} + \ldots = \frac{l \, n - 1}{c_1}$$

where n = number of blocks per unit length, and l = length of the prism. If a = cross section of the prism, then any one of the capacitances c_1, c_2, ... etc., will be given by

$$c_1 = \frac{ka}{4\pi\tau}$$

where k = dielectric constant of interstitial material and τ = thickness of interstitial layers.

Let d = dimension (linear) of one block.

Then $$n = \frac{1 + \tau}{d + \tau} = \frac{1}{d} \text{ approximately}$$
since is very small.

Hence $$\frac{1}{c} = \frac{l \, n - 1}{c_1} = \frac{l \, n}{c_1} \text{ since } n \text{ is very large.}$$

or $\qquad \dfrac{1}{c} = \dfrac{l\, 4\, \pi\, \Upsilon}{d\; ka}$

or $\qquad c = \dfrac{kd}{4\, \pi\, \Upsilon}\; \dfrac{a}{l}$

The quantity $\dfrac{kd}{4\pi\Upsilon}$ might be called the specific capacitance by analogy to specific resistance. It is seen that this capacitance should vary with the size of the unit blocks and inversely as the thickness of interstitial material between them. A true single crystal then should have a maximum capacitance.

(b) Discussion of Methods of Measurement

1 - Ballistic galvanometer

Attempts to measure the capacitance of galena prisms by means of the ordinary ballistic method showed that an electric charge could be stored in galena, the amount of charge being a function of the applied potential and the time of charging in a manner exactly like an ordinary condenser. However the time constants derived from the ballistic measurements were all of the order of tens of seconds and did not correspond to the product of the known direct current resistance and the deduced capacity. Crude experiments on the thermoelectric effect in galena were made and thermo E.M.F.'s of the order of 2 millivolts per degree were found. This is extremely high and probably accounts for much of the stored charge in the ballistic experiments.

2 - Alternating current methods

Alternating current methods should eliminate the trouble caused by the Peltier effect. Accordingly attempts were made to measure the capacitance by means of wave meter circuits and bridge circuits using frequencies ranging from 400 cycles to 18,000,000 cycles. It was found from the

wave meter measurements that the effective resistance of the specimen
dropped rapidly with the frequency and that the resistance decrease was
irreversible at first, and that only by standing for two weeks or more
would the resistance return to its original value. Bridge methods were
very difficult due to the high value of standards required. Further-
more the accurate determination of the null point on A. C. bridges
requires that a considerable amount of energy be put into the bridge and
it was found that the specimens became quite warm. This heating effect
produced great changes in the resistance of the specimens due to their
high temperature coefficients of resistance. It was found that the
direct current resistance varied as the square of a simultaneously super-
posed alternating current and was independent of the frequency.

This is reasonable and can be explained on the following basis.
Consider a specimen of material connected to one arm of a bridge and sus-
pended in a constant temperature bath. Let current I flow through the
specimen when the bridge is balanced. The heat supplied will be

$$J I^2 R t = H$$

where t = seconds, R = resistance, J = mechanical equivalent of heat.
Hence the rate of supplying heat will be

$$\frac{dH}{dt} = J I^2 R$$

Now, assume Newtons law of cooling which is

$$\frac{dT}{dt} = K (T - T')$$

Where T = temperature of body

T' = temperature of surroundings

t = time

K = a constant for a given set up.

We know

$$dH = C_p dT \qquad \text{where } C_p = \text{specific heat}$$

or the rate of losing heat will be:

$$\frac{dH}{dt}_{lost} = C_p \frac{dT}{dt} = C_p K(T - T')$$

At thermal equilibrium

$$\left(\frac{dH}{dt}\right)_{gained} = \left(\frac{dH}{dt}\right)_{lost}$$

or,

$$C_p K(T - T') = J I^2 R$$

Hence,

$$R = \frac{C_p K(T - T')}{J I^2}$$

Therefore in any bridge measurement the values obtained are not only going to be functions of the temperature of the specimen but also of the temperature of the bath and will likewise be inversely proportional to the square of the current. In measurements on good metallic conductors the effect will probably be very alight due to their low temperature co-efficient of resistance. However, with substances like galena the effect becomes preponderating and is sufficient to mask the other more interesting effects. It was for this reason that alternating current measurements of the type described were abandoned.

IV - THE CONDUCTIVITY OF GALENA BY DIRECT CURRENT MEASUREMENTS OF CURRENT AND VOLTAGE

It became of importance to know whether galena strictly obeyed Ohms Law at low current densities. Obviously from the foregoing equation in

To vacuum pump

Thermocouple leads

Leads to potentiometer

Figure 2.

Thermocouple

Specimen holder

Electric furnace

Leads to potentiometer

Bakelite

Isolantite

Lead sulphide

Silver

Brass

Figure 3.
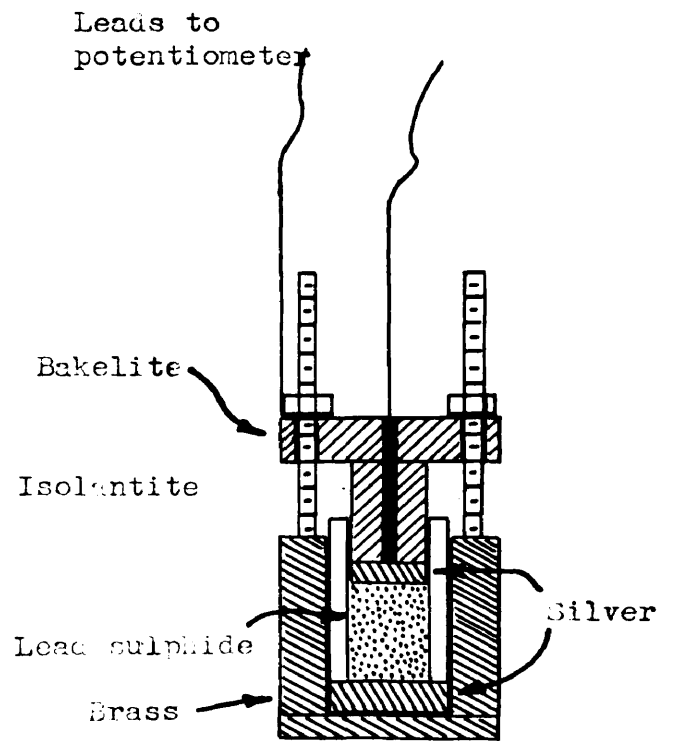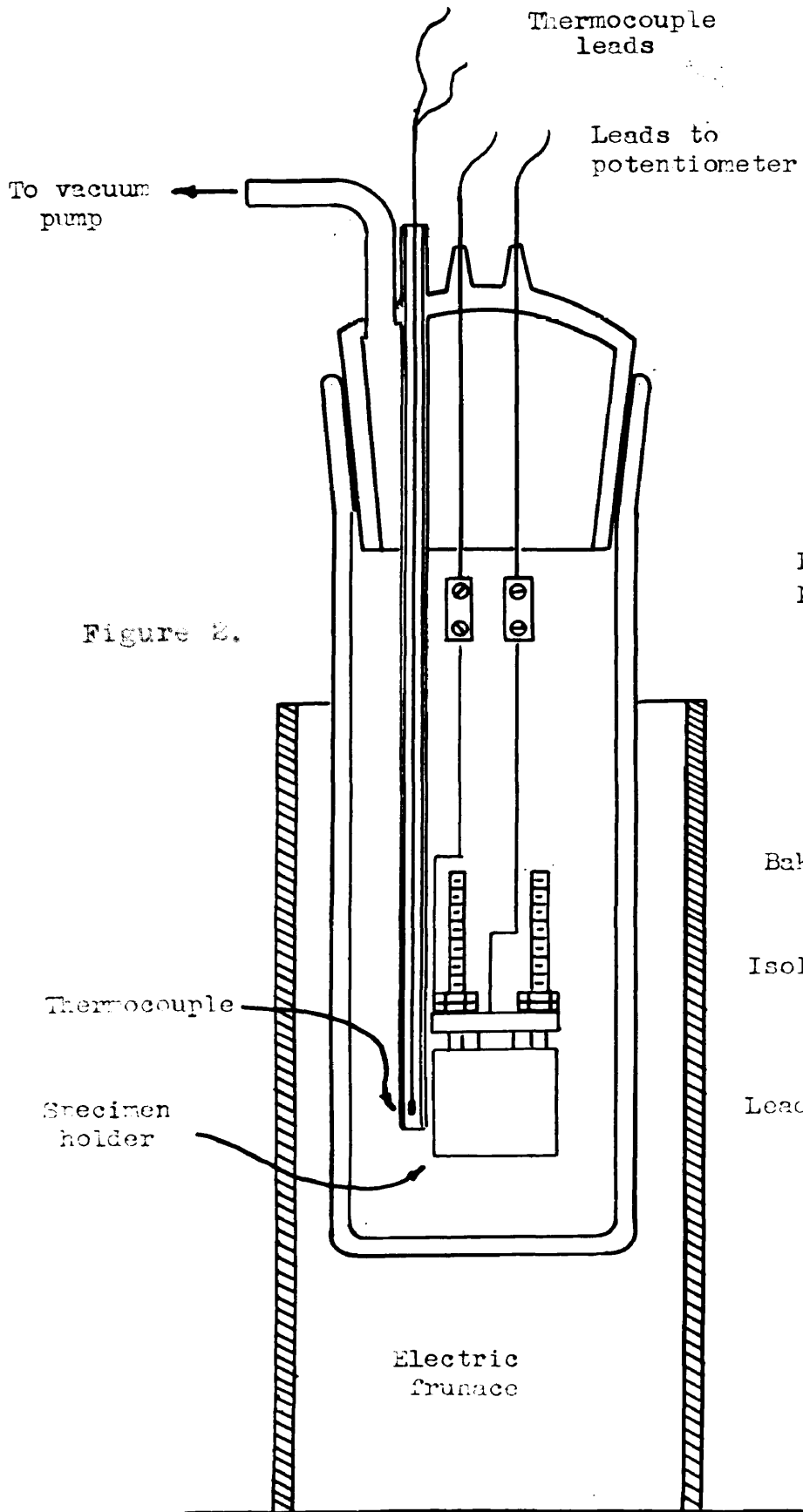
which

$$R = \frac{C_p K(T - T')}{J I^2} = \frac{const.}{I^2}$$

it would not do so at current densities high enough to produce appreciable Joule Heat. Any attempts to eliminate the heating effect by determination of the constant K in the above equation, at each temperature would involve rather complicated experimental technique and be subject to considerable error. Hence it was decided to eliminate heat effects as much as possible and work at as low current densities as feasible with the equipment at hand.

Experiments on many types of PbS specimens, natural, and synthetic and in massive or granular condition were made. The granular material was pressed into pastilles and mounted in a clamp between platinum electrodes. Practically all of the tests showed that the slopes of the voltage versus current curves were constant but that the curves intercepted the axis. It was decided to investigate this thoroughly and with the same material at different grain sizes since extrapolation to the effect of secondary blocks might thus be possible.

(a) Choice and Preparation of Material

Natural galena was subject to too much variation even from point to point within any one good sized piece. Hence, synthetic crystals were prepared by fusing precipitated lead sulphide in the presence of a great excess of sulfur. The material was cast into crucibles. The product so formed was nicely crystalline and appeared like natural galena in every way. Microscopic inspection of cleavage surfaces showed all of the characteristics of natural galena cleavage faces as described by Buerger [5], Head [4], and
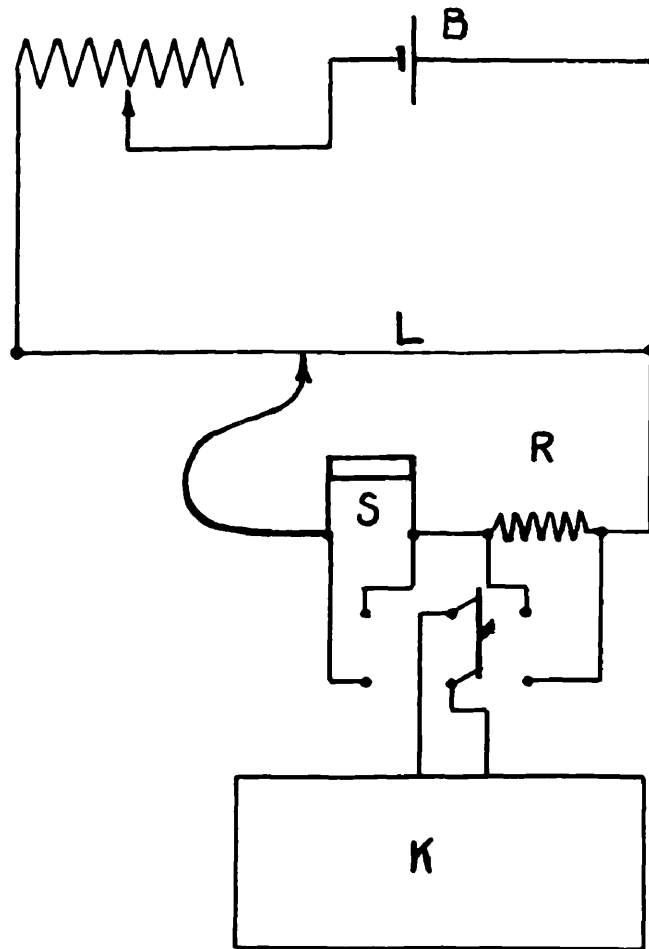
Figure 4.

Dean and Koster [1]. The material was then crushed through 20 mesh and the excess sulphur removed by prolonged extraction with CS_2. It was then dried and screened through a set of ordinary laboratory screens and the various fractions separately bottled for future use. No analysis was made of the material because only the one specimen was to be used throughout the subsequent measurements.

(b) Apparatus

Preliminary experiments had indicated that pastilles which were mechanically strong enough to be self-supporting required pressures which caused considerable deformation and secondary crushing of the grains. Since it was desired to study the effect of grain size obviously self-supporting pastilles could not be used.

The device finally adopted to hold the specimen and apply the electrodes is shown in figure 3. The sketch is self-explanatory. This was suspended in an evacuated system as shown in figure 2.

The electrical circuit was as shown in figure 4. K is a Leeds and Northrup Type K Potentiometer. L is a Leeds and Northrup Kohlrausch slide wire. The battery, B, supplied current to the Kohlrausch slide wire and leads were taken from one end and the movable contact and connected in series with the specimen, S, and a standard resistance, N. In this way very delicate control of the current through the specimen could be obtained. The potential across the specimen was measured across the leads to the silver electrodes on the specimen holder. The total resistance of these leads and electrodes without a specimen in the holder was of the order of 10^{-4} ohms and hence was entirely negligible. Measurements were made with current flowing in both directions, reversal of the current being accom-

plished by merely interchanging the leads to the specimen.

Temperatures from 125° C. to room temperature were obtained by means of the electric furnace surrounding the evacuated jacket as shown in figure 2. The temperature was measured by a calibrated copper-advance thermocouple as shown. Vacuum was obtained by a Megavac pump connected to the evacuated jacket. The pump was kept running continuously night and day until a set of readings were finished.

(c) Experimental Procedure

The actual manipulations were as follows: Three grams of a given sized specimen of the synthetic galena were weighed into the specimen holder. The holder was tapped 80 times to pack the powder. It was found that tapping 50 times on the table packed any of the grain sizes to a minimum volume. Then a brass plunger was placed on top of the specimen in the cylinder and the specimen subjected to a pressure of 175 Kg/cm² for 3 hours. The pressure was applied by means of a lever arm and weights operating on the brass plunger. At the end of this time the brass plunger was removed and the top silver electrode screwed firmly into place by driving the Bakelite block into the cylinder by means of the nuts shown in figure 3. It was attempted to always draw those nuts up to the same tightness for each specimen which was done by tightening as far as possible with the fingers and then giving a definite number of turns with a small wrench.

The holder was then suspended in the jacket by means of its leads, the pump started and the furnace brought up to 100° to 125° C. Each specimen was pumped for 24 to 36 hours or until repeat readings could be made at 2-hour intervals. After a set of check readings were obtained the

temperature was lowered to another value by means of a lamp board and
rheostat in the furnace circuit. After the first equilibrium conditions
had been obtained it took from 6 to 12 hours to arrive at a steady state
at the next lower temperature.

Readings were made by adjusting the current through the specimen to
10, 20, 30, 40, 50, microamperes in successive steps and obtaining the
corresponding IR drops across the specimen. The E-I curves were perfectly
reversible at any temperature, and the temperature-resistance curves were
likewise reversible for a given specimen.

(d) Determination of Grain Size

Since standard screens were not available the figures of Gross [16] or
others on surface or diameter of galena particles could not be used and
the grain size had to be determined by some other method. This was done
by randomly selecting from 50 to 150 grains from each size range and
sketching their images at known magnification by means of an Abbe Drawing
Camera mounted on a microscope. The projected area of each grain was then
determined by using a planimeter on the sketches obtained. This method
yielded the figures shown in table 1. They are not claimed to be anything
more than approximations and the mean area is the straight arithmetic mean
of the individual readings.

Table 1

Screen size	Mean Projected Area sq. mm.
-100-200	0.0129
-80-100	.0369
-60-80	.0587
-40-60	.177
-20-40	.617
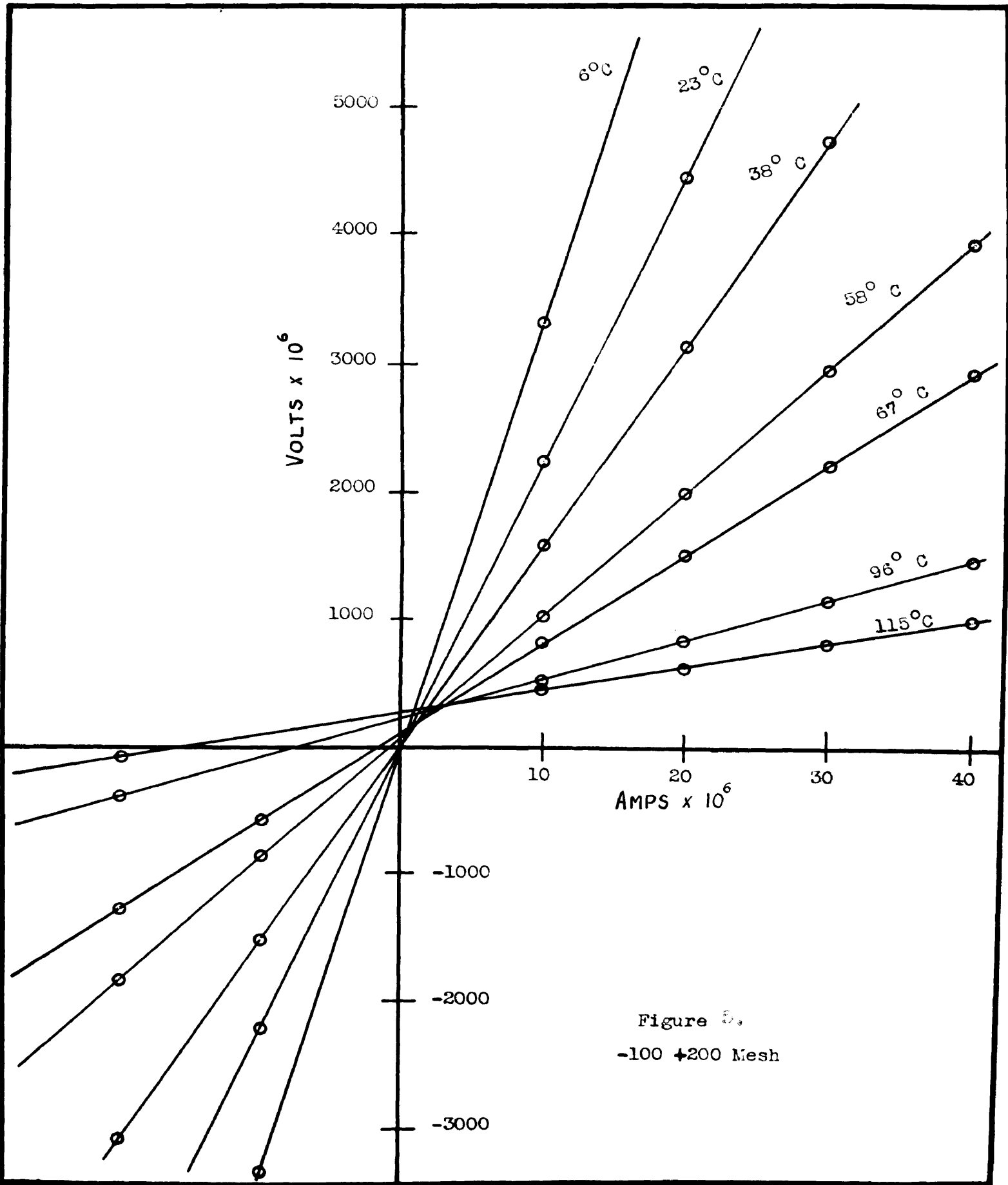
Figure 5.
-100 +200 Mesh

(e) The Experimental Results

Since a great number of values of current and voltages were required, their tabulation would be too bulky. Consequently a sample set of readings for one specimen and temperature is given in table 2, and they are plotted for an entire set at all temperatures in figure 5. The linearity and the intercept are readily seen. All the rest of the data are reported as the

Table 2

Screen size -100-200
Temperature 310.9° K

Current amps x 10^6	Volts x 10^6
10	1,600
20	3,157
30	4,714
40	6,271
50	7,826
-10	-1,516
-20	-3,072
-30	-4,626
-40	-6,180
-50	-7,735

constants for the straight line equation deduced from each set of voltage-current values. This equation is

$$E = IR + A$$

where,

R = slope of curve expressed as ohms

A = intercept expressed in volts

I = current in amperes

E = volts

The results are shown in tables 3 to 8, inclusive.

Table 3

Screen size -200 mesh

T $^{\circ}K$	R ohms	A volts $x10^6$	$\frac{1}{T}$ $x10^3$	$Log_{10}R$
380.5	76.0	479	2.628	1.881
369.4	89.2	402	2.707	1.950
358.1	105.0	337	2.793	2.021
353.1	122.7	330	2.832	2.089
346.4	139.2	283	2.887	2.144
333.9	172.9	225	2.995	2.238
317.3	262.8	144	3.152	2.420
294.9	491.1	18	3.391	2.691

Table 4

Screen size -100-200 mesh

T $^{\circ}K$	R ohms	A volts $x10^6$	$\frac{1}{T}$ $x10^3$	$Log_{10}R$
388.6	18.3	287	2.573	1.262
386.1	20.6	252	2.590	1.314
369.5	31.4	223	2.706	1.497
340.4	70.3	159	2.938	1.847
330.9	96.4	105	3.022	1.984
310.9	155.7	42	3.217	2.192
295.4	222.6	-14	3.385	2.348
279.6	330.5	-21	3.577	2.519

Table 5

Screen size -80-100 mesh

T $^{\circ}K$	R ohms	A volts $x10^6$	$\frac{1}{T}$ $x10^3$	$Log_{10}R$
389.6	9.26	71	2.567	0.967
360.1	15.8	41	2.777	1.199
329.6	31.3	26	3.034	1.496
307.4	56.6	0	3.253	1.753
273.1	145.6	-1	3.662	2.163
248.3	317.1	-4	4.027	2.501

Table 6

Screen size -60-80 mesh

T $^{\circ}K$	R ohms	A volts $x10^6$	$\frac{1}{T}$ $x10^3$	$Log_{10}R$
393.9	4.76	56	2.539	0.678
378.7	6.04	51	2.641	.781
365.6	7.57	43	2.735	.879
354.6	9.19	39	2.820	.963
345.9	11.0	34	2.891	1.041
318.4	21.3	8	3.141	1.328
299.6	31.5	0.4	3.338	1.498
298.1	33.2	0	3.355	1.521
293.1	39.4	2	3.412	1.596
286.6	45.2	3	3.489	1.655
282.1	49.3	1	3.545	1.693

Table 7

Screen size -40-60 mesh

T $^\circ$K	R ohms	A volts $\times 10^6$	$\frac{1}{T}$ $\times 10^3$	$Log_{10}R$
392.9	3.68	35	2.545	0.566
380.6	4.19	28	2.627	.622
363.6	5.29	23	2.750	.723
341.6	7.18	19	2.927	.856
327.6	9.17	16	3.053	.962
316.4	11.2	6	3.161	1.049
298.1	16.0	-1	3.355	1.204

Table 8

Screen size -20-40 mesh

T $^\circ$K	R ohms	A volts $\times 10^6$	$\frac{1}{T}$ $\times 10^3$	$Log_{10}R$
391.1	1.71	17.9	2.557	0.233
350.1	2.14	10.4	2.856	.330
308.7	2.67	0	3.239	.427
293.6	2.96		3.460	.471

Figure 6.

FIGURE 7.

FIGURE 8.

Temperature in $^{\circ}$K

$+ A \times 10^6$
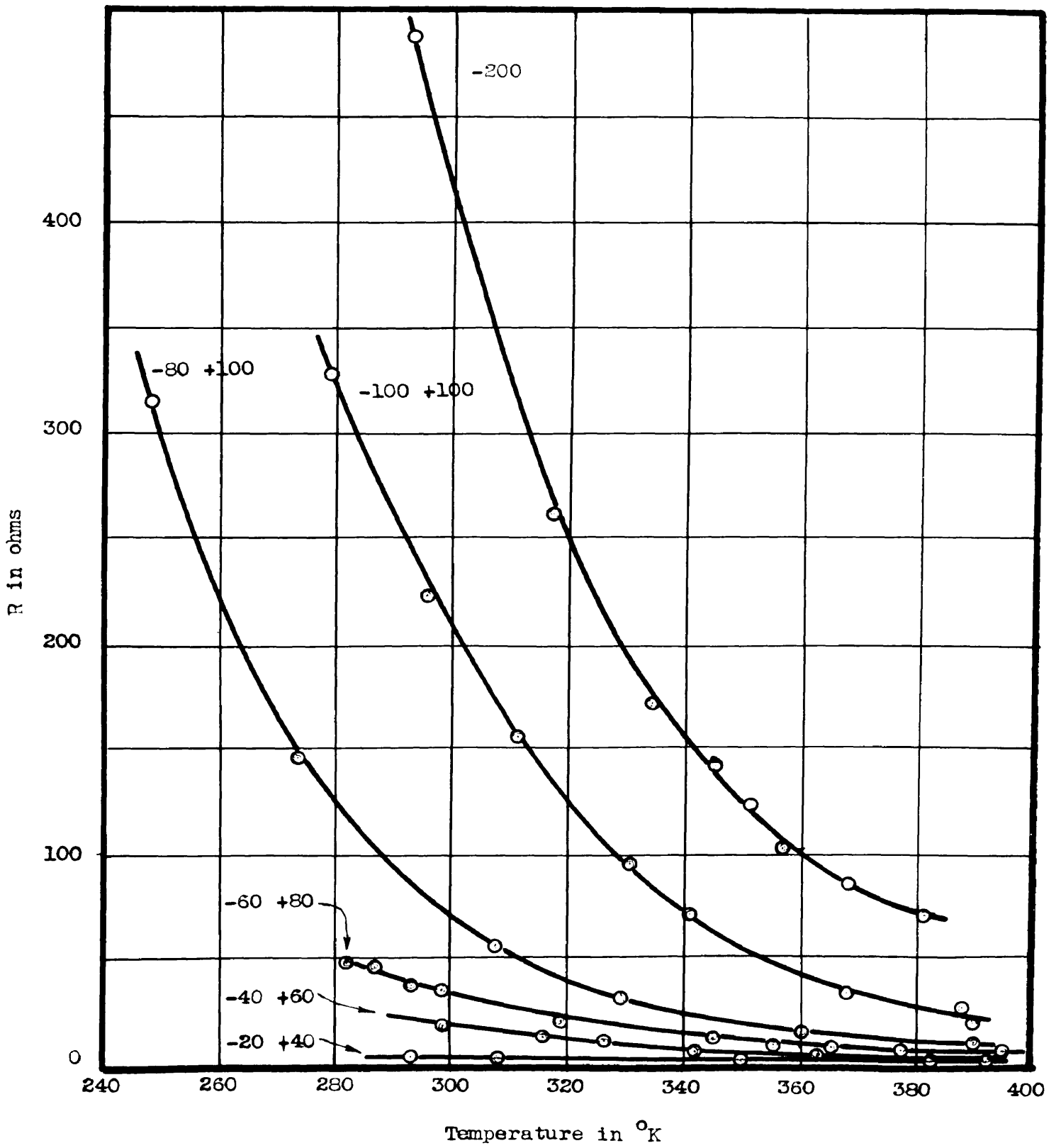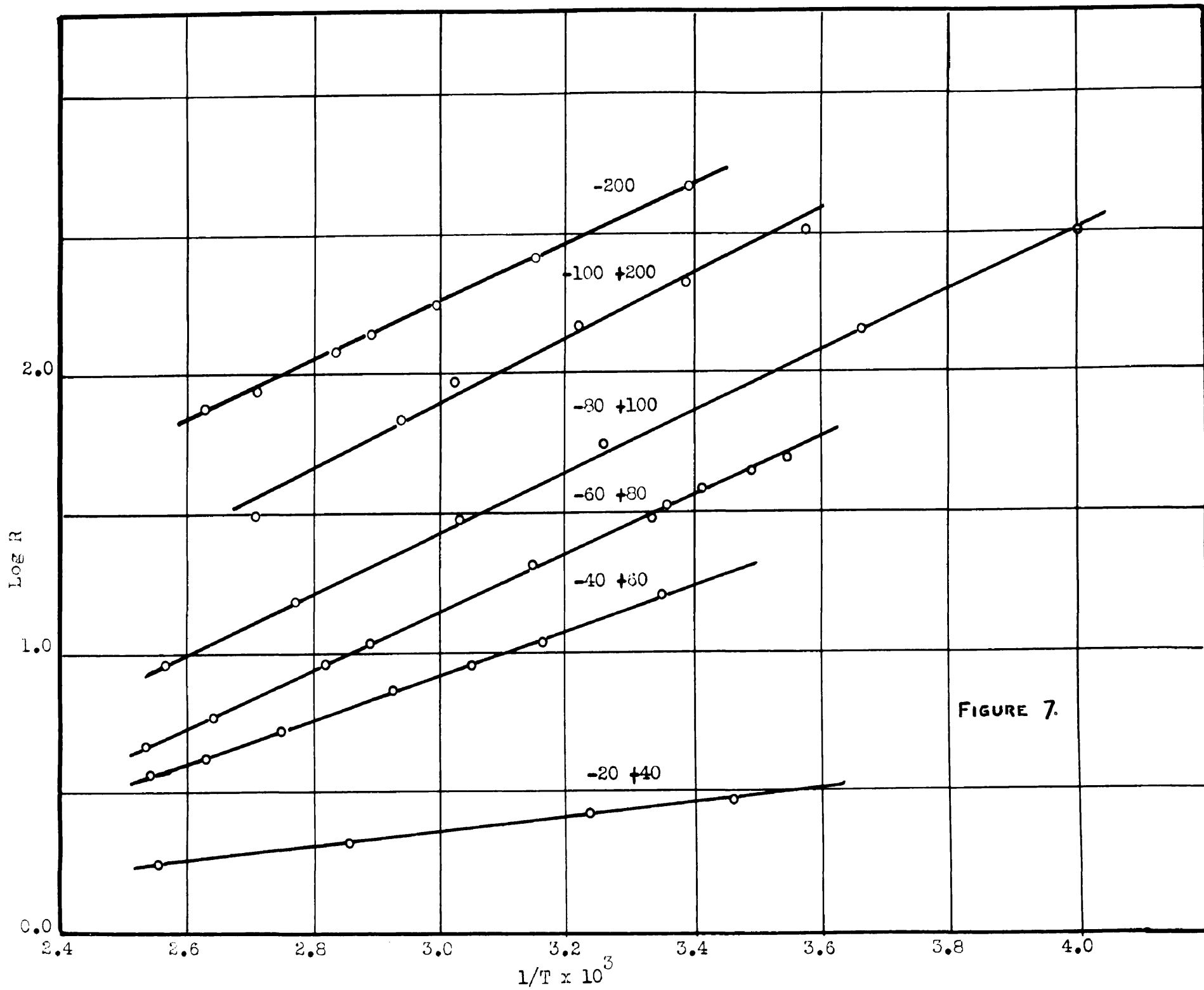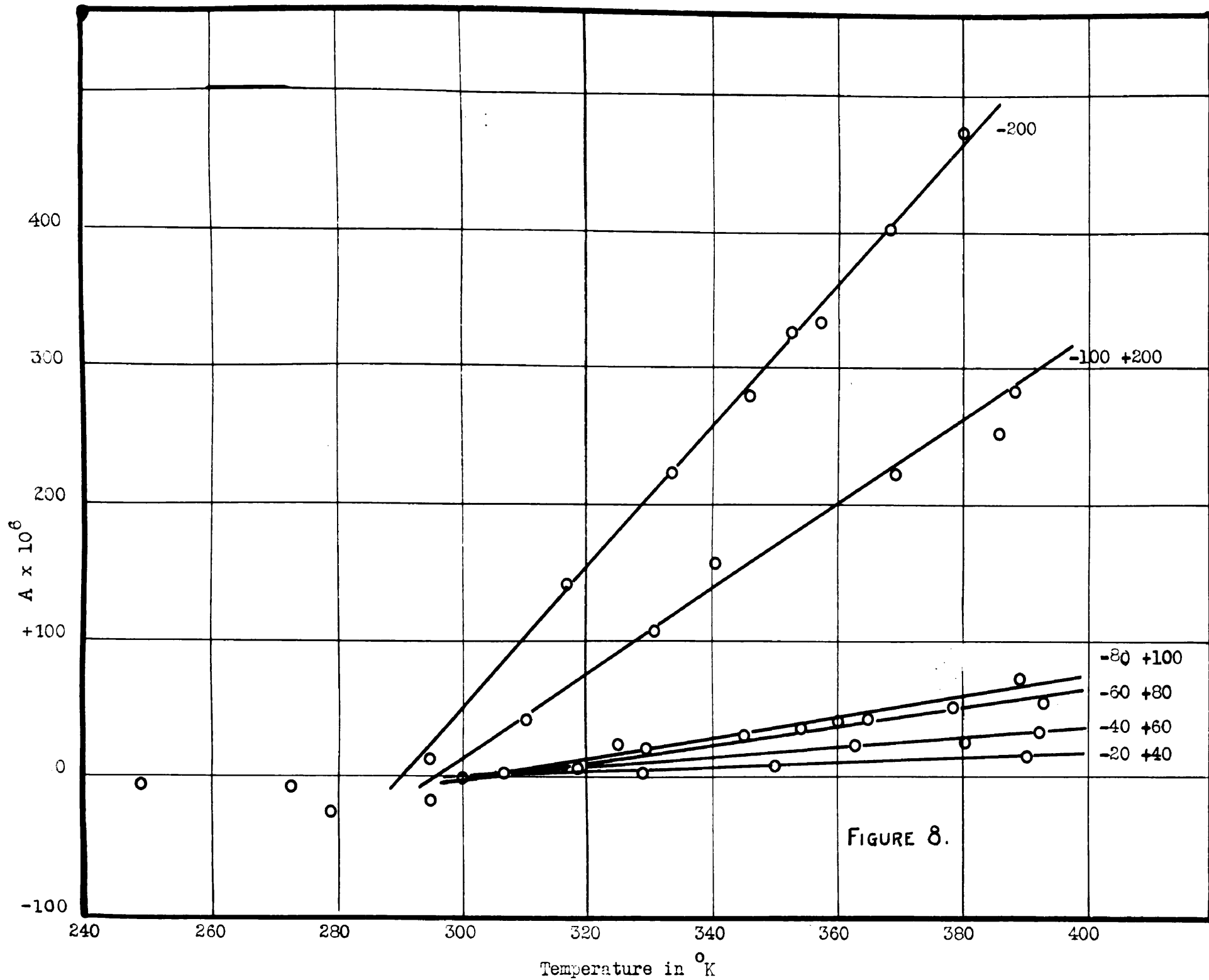
If, now, R is plotted against the temperature the curves shown in figure 6 are obtained. Figure 7 shows the relation between log R and the reciprocal of the temperature. The linearity is readily apparent and hence the relation between R and T is expressed by

$$R = M \epsilon^{Q/T}$$

where M and Q are constants. The numerical values for M and Q are shown in the third and fourth columns of table 9.

Table 9

Screen size	Mean Projected Area per Grain mm^2	M	Q	B volts $\times 10^6$	C volts $\times 10^6$
-200	-----	0.122	2436	5.195	-1511
-100-200	0.0129	.0294	2638	3.10	- 913
-80-100	.0369	.0164	2477	.76	- 229
-60-80	.0587	.0110	2390	.73	- 221
-40-60	.177	.0334	1839	.35	- 101
-20-40	.617	.375	601	.20	- 60

(f) The E-I-T Equation for Galena

The intercept, A, from the equation

$$E = IR + A$$

is readily seen to be a function of the temperature and the grain size. A vs. T is plotted in figure 8. Here also a linear relation obtains and hence

$$A = BT + C.$$

Values of B and C are shown in the fifth and sixth columns of table 9.

In view of all of this, the final equation of the current and voltage relations for the present set of data is of the form

$$E = IM \epsilon^{Q/T} + BT + C.$$

No mathematical expression has been found to take care of the influence

of grain size. The trends are evident from the tables but considerations based on number, size, or surface of the grains and either gross E-I relations or those based on a unit volume of pressed powder give no definite numerical results. Table 9 summarizes the values of M, ,, B, and C together with the corresponding screen sizes and the mean projected area of the grains.

The interpretation of such data has been approached from many angles. Some of them shall be reviewed in the following.

V - THE ELECTRICAL CONDUCTIVITY OF SOLID COMPOUNDS

The electrical conductivity of matter probably varies between wider numerical limits than does any other common property. Thus: the specific resistance of silver is approximately 0.6×10^{-6} ohms while that of fused quartz is approximately 10^{18} ohms. The mechanism by which electricity is transferred is generally conceded to belong to one or both of two distinct processes called electronic and ionic.

Electronic conduction is that kind found in all good metallic conductors and which involves only the transfer of electrons, no appreciable mass taking place in the movement. It seems to be closely related to thermal conductivity since the law of Wiedemann and Franz states as an empirical fact that the ratio between the specific electric and thermal conductivities is a constant for good metallic conductors. Drude developed a theoretical treatment from the electronic theory and succeeded in calculating the Wiedemann-Franz constant from fundamental constants. Lorentz amplified the electronic theory and it has given rise to numerous treatments of metallic conduction none of which are yet thoroughly satisfactory. However, the existence of mobile electrons in metallic substances has been

thoroughly substantiated by our knowledge of thermionic emission, the Peltier effect, the Hall effect, photoelectric emission, metallic reflection of light, and other properties. A review of electronic conduction theories has been given by T. J. Webb [17].

Ionic conduction is that kind observed in electrolytes and in which the transfer of charge is accompanied likewise by a transfer of matter. It is sufficiently familiar in conductivity experiments on aqueous solutions and occurs likewise in solid electrolytes such as the alkali halides.

Both ionic and electronic conduction can occur together and such is believed to be the case in the so-called variable or semi-conductors such as many sulphides and oxides of the metals.

However, the actual specific conductivity of a substance is governed by so many variables that little reliable information can be gained from that figure alone. In metals and alloys the conductivity varies with the degree of cold work, the grain size, composition, etc. In alloys forming two distinct phases and no solid solutions the conductivity is directly proportional to the percentage by volume of the components. However, alloys which give rise to solid solutions always have conductivities much lower than either of the components individually. Intermetallic compounds generally have lower conductivities than their components.

The temperature coefficient of resistance or conductance is a much more critical index of the nature of the conduction process in solid bodies.

The temperature resistance relations in metals and metallic substances generally follow an equation of the form -

$$R_T = R_0 \left[1 + a(T - T_0) \pm b(T^2 - T_0^2) \right]$$

where, $\qquad$ R = resistance at temperature T

R_o = resistance at temperature T_o, usually 0° C.

a and b are constants

Differentiation yields

$$\frac{1}{R_o}\frac{dR}{dt} = a \pm 2bT = \alpha$$

α is generally called the temperature coefficient and is itself a function of the temperature. Near room temperature α for metals such as Ag, Cu, Al, Fe, Mg, etc., has a value of about 0.004, varying from 0.003 to 0.005 for different metals. Mathiesen [18] noted an empirical relation between temperature coefficient of alloys and their composition which is that their temperature coefficients are proportional to their conductivities as calculated by the rule of mixtures mentioned previously. The temperature coefficient likewise is a function of the physical state of the metal. However, the important fact is that the resistivity of good electronic conductors is directly proportional to the temperature.

Now numerous measurements on solid electrolytes have shown the resistance decreases with increasing temperature and that the conductance generally follows an exponential curve of the form -

$$K = A \varepsilon^{-Q/T} = \text{conductance at temp. T.}$$

A and Q are constants.

If the temperature range is great enough the equation takes the form:

$$K = A_1 \varepsilon^{-Q_1/T} + A_2 \varepsilon^{-Q_2/T}$$

Tubandt [19] has divided solid electrolytes into 3 classes. The first class obeys the temperature conductivity relations expressed by

$$K = A \epsilon^{-Q/T}$$

and includes $PbCl_2$, αAgI, αCuI, $\beta CuBr$, $TlCl$, $TlBr$, glasses and the systems $AgI-CuI-$, $AgBr-CuBr$. The second class follows the two membered equation

$$K = A_1 \epsilon^{-Q_1/T} + A_2 \epsilon^{-Q_2/T}$$

and is characterized by such substances as the alkali halides. The third class are compounds whose temperature resistance variations are not mathematically expressible.

Smekal (loc. cit.) attributed the two membered equation to conductivity of two types of ions, the first member supposedly taking care of conduction at low temperatures due to the greater mobility of ions within his "lockerstellen." The second member only becomes effective at higher temperature and is due to ion migration within the unit secondary blocks. However, Phipps [20] and his coworkers have shown that at low temperatures only one ion moves in alkali halides and that at high temperatures both ions migrate.

However in the case of $AgCl$, a two membered equation is likewise obtained. Tubandt and Rheinhold [21] showed by transference experiments that only pure cation conduction takes place. Hence Smekal [22] points out that two kinds of Ag ions must be present, one is structure sensitive, and the other structure insensitive. Also Smekal goes on to show that for the true conductivity of alkali halides at least a three membered expression, as -

$$K = A_1 \epsilon^{-Q_1/T} + A_2 \epsilon^{-Q_2/T} + A_3 \epsilon^{-Q_3/T}$$

holds and that M. Kassel has followed the change of A_1 and Q_1 under systematically controlled grain growth in $NaCl$. They increase up to the

pure undeformed crystal and are then to be traced back to diffusion and reaction processes within the crystal.

W. Jost [23] has always been strongly opposed to Smekal's ideas of conduction on internal surfaces and showed that the electrolytic conductance of good conducting silver iodide crystals is not influenced by surfaces and does not depend on internal boundaries. The same author in a recent paper has developed the theory for bi-polar conductants based upon Frenkel's [24] treatment of diffusion within ionic solids. A sort of chemical reaction is postulated wherein an atom in a regular lattice position dissociates into an atom in an irregular position and a vacant place. Jost is able, by his mathematics, to calculate from fundamental data numerical values of the constants A_1 and A_2 in the aforementioned equations to within at least the same order of magnitude as those obtained experimentally.

The most obvious interpretation of the exponential equations for ionic conductivity is that the quantity Q relates to the energy required to free an ion from its constraints in the lattice and that A depends on the diffusion coefficient or the mobility of that ion, the ion concentration and the charge.

Von Hevesey [25] considers that conduction in ionic solids is nothing other than the chemical reaction in which the same kind of atoms or ions react with one another in which case the conductivity itself is a measure of the velocity constant of the reaction. Those ions move first in conductivity experiments which are also emitted first upon heating. Such a conception likewise permits of an explanation of the exponential shape of the curve. Fick's law of diffusion does not necessarily apply to ions

moving under the influence of a potential in conducting solids since the process is a sort of irreversible diffusion between two different phases. Using a concept of diffusion in solids developed by Langmuir and Dushman [26] von Hevesey has computed the work of dissociation of ions in various metals and metallic salts and has obtained fairly good agreement with the observed values. Such an energy of dissociation is related, according to von Hevesey, with two values, (1) the melting point of the solid and the other, (2) a quantity which depends on the charge, polarization properties, etc., of the lattice ions.

However, other phenomena have been observed which cannot be explained on the basis of internal migration of ions. For example, [27] the resistance of copper oxides has been shown to depend in a specific fashion on the pressure of the surrounding gases. With decreasing air and hydrogen pressures the resistance decreases, but increasing oxygen pressures causes the resistance to decrease and nitrogen and neon give no definitely determinable effects. Resistance changes of as much as hundreds of percent are observed under various gas pressures.

Obviously another type of conduction must be postulated in order to account for this pressure effect. For some time it was believed that substances lying on the border line between metals and nonmetals such as silicon, zirconium, titanium, and graphite, were examples of the so-called semiconductors but it has been shown by Seeman [28] and Schulze [29] for silicon; Clausing and Moubis [30] for zirconium and titanium, and Ryschke-witch [31] and Nishiyama [32] for graphite, that the temperature coefficient of resistivity of massive single crystals is positive and characteristic of the usual metallic conductors. However, when these materials are

studied in the form of pressed powders the negative temperature coefficient and exponential temperature resistance relationships characteristic of ionic conductors are obtained. Kaptiza [33] has shown that the temperature coefficient of sputtered metals is negative and Nishiyama (loc. cit.) and Koenigsberger and Reichenheim [34] have shown that pressed powdered metals exhibit a negative temperature coefficient. Dean and Koster [1] found that finely grained steel galena follows an exponential equation in its temperature resistance relations whereas massive crystalline galena has a distinctly metallic type of temperature coefficient.

All of the electrostatic theories of ionic lattices have as one their conclusions that on the surface layer of crystal grains the lattice dimensions will be larger than they are within the lattice proper and consequently a certain number of the free electrons are more firmly bound on the surface than they are in the interior. Nishiyama (loc. cit.) concludes from this, that the resistance of powdered metals and granular graphite will increase as the size of the grains decreases; that is, as the extent of the surface increases. As the temperature is raised the thermal agitation increases and the electrons are gradually set free giving rise to a negative temperature coefficient which would probably obey an exponential law. This is nothing more than the conception closely allied to our ideas concerning electronic emission from hot bodies, which also follows an exponential law as expressed by Richardson's equation. It is obvious that the mere exponential relation between temperature and resistance is no indication of the type of conduction occurring in a conductor since it can be explained equally well on the basis of ion diffusion or electronic emission. The influence of gases in the case of copper oxides previously

cited may just as well be due to a diminiution in electronic emission caused by the increased gas pressure itself as to any other cause.

In the present experiments crystallized lead sulphide was used throughout and was shown to follow in all cases the same type of exponential law. The experiments were carried out in vacua which though not of an extremely high order (approximately one micron) should be sufficient to prevent considerable influence on electronic emission between grains if such emission actually occurred. The influence of pressure on the conductivity of lead sulphide was observed in a qualitative manner on a few of the last readings made in the present series of experiments. Dry air was allowed to flow into the vacuum chamber and the resistance measured. In all cases the resistance increased about one-hundred fold.

The experiments of Volmer [35] have shown that adsorbed molecules are capable of migration over the surface of solid adsorbants. It might also be postulated that the conduction of pressed powders of substances which are known to conduct electronically in the massive condition is due to a surface migration of adsorbed gases. The amount of such migration would naturally be an exponential function of the temperature in spite of the little understood kinetics of two-dimensional gas systems.

However, the fact that the resistance increases with increasing gas pressure would not aid in interpreting the conduction as due to migration of adsorbed gases. Baumbach and Wagner [36] noted that the conductivity of NiO varied with the pressure of O_2 in accordance with an equation of the form

$$\kappa = Kp^{\frac{1}{n}}$$

where κ = conductivity; p = pressure; and K and n are constants. But

they maintained that the conduction was nearly all electronic.
Trzebiatowski [37] reports that the conductivity of pressed powders of
gold and silver has a positive temperature coefficient up to 100° C.
which, however, is negative between 100° C. and 300° C. Contact resis-
tance unquestionably enters into any consideration of the electrical
resistance but reported work on the so-called sieve contacts of R. Holm [38]
does not lend itself toward elucidating the general phenomena observed
in pressed powders.

The chief conclusion to be drawn from the data on electrical con-
ductivity of solids is that the actual processes are in most cases but
very little understood and that extreme care must be exercised in their
interpretation. Furthermore the conductivity of pressed powders seems
to have but little to do with the actual conductivity of the material
forming the grains.

VI - INTERPRETATION OF THE RESULTS OF THIS RESEARCH

The present data show peculiarities which must be mentioned. The
intercept of the E-I curves on the E axis shows that the specimens used
in the present work have a self E.M.F. of their own. This E.M.F. was
observed before any current was allowed to pass through the specimen and
hence cannot be attributed to chemical polarization of the ordinary kind.
Also the E intercept was found to be a function of the temperature and the
grain size. However, within the limits of error of such low values, the
self E.M.F. steadily decreases to what seems to be a common threshold
value for all grain sizes as the temperature decreases, but does not re-
verse below this threshold temperature. That is, A is always positive

or zero and never negative -- within the limits of error. Actually this threshold might be the intercept of some curves having an abrupt bend and a might fall gradually by very small steps to zero. It seems that the common intercept is a property characteristic of the PbS itself and independent of the grain size.

Just what causes the self E.M.F. is not readily explained. It cannot be thermal E.M.F. because that would reverse at lower temperatures. The only explanation which can be offered tentatively at the present time is based upon the observed facts that the polarity of this self E.M.F. was always the same, i. e., the top electrode was always positive; and also the top end of the cylinder of pressed powder was more firmly packed than the bottom. This packing at the top was due to the motion of the brass plunger during the three hour pressing period. Furthermore, preliminary experiments on pastilles made in a separate mold and which were clamped between electrodes in such a way that the more firmly packed material was along one edge and ran from one electrode to the other did not show a self E.M.F. Hence, the initial electromotive force is believed to be due to a concentration effect of some sort. The grains at one end of the cylinder were probably subjected to more cold work during the pressing period than were those at the other. This might account for the potential difference between the ends of the cylinder since cold work or deformation is known to change the electron pressure within metals. It is to be expected that plastically deformed grains should liberate their electrons much more sluggishly than unworked or annealed grains, and if a thermionic process is assumed, electrons will be more abundantly emitted by the less severely worked particles at the lower end of the cylinder and hence would

give rise to a higher negative space charge between grains. In this
manner a potential difference between the ends of the specimen would be
developed. This idea receives further confirmation from the fact that
the lower end of the cylinder was negative in all cases and furthermore
the temperature threshold observed could only arise from some such irrever-
sible process as thermionic emission.

It is highly probable that the entire conductivity of the various
specimens is due to a sort of electronic emission by the grains. Such a
concept permits an interpretation of the decrease of resistance with in-
creasing temperature in accordance with an exponential law as expressed,
perhaps, by Richardson's equation, which is

$$i = A T^2 \epsilon^{-\frac{\phi}{KT}}$$

where i = the saturation current from a hot filament; T is the absolute
temperature; ϕ is the work necessary to liberate an electron; K is Boltz-
man's constant; and A is another constant.

The increase in resistance with decreasing grain size can be attri-
buted to the fact that an electron must jump from one grain to the other
and hence makes many more jumps in the case of the fine grained material
with a consequent decrease in its gross rate of migration through the
cylinder.

The effect of particle size on the conductivity in the present case
cannot be expressed mathematically as yet. The various curves for R vs.
T were reproducible within about 8 to 10 percent for a given grain size.

Reference to table 9 will reveal a similar trend for values of ζ, D,
and C and the grain size. B varies differently. Smekal[22] has pointed

out that Q and M vary with the grain size but has offered no data nor hypothesis to account for such variation.

Data at higher temperatures are needed to thoroughly confirm the emission hypothesis advanced here. Perhaps higher vacua should be employed for this purpose.

However, it is conclusively demonstrated that the electric conductivity of solids is some function of their state of aggregation although the type of function has not yet been elucidated. So far it is not possible to determine the size of unit secondary blocks by extrapolation of the electrical measurements.

Some practical applications may arise from the present studies. The fact that a good conductor like galena can be made to store an electric charge no matter by what mechanism, indicates that processes for the electric separation of metallic minerals are not beyond possibility. The high thermoelectric force of lead sulphide may lend itself readily to pyrometry. Its great change of resistance with temperature, particularly when in a finely divided condition, may likewise prove of service in resistance thermometers. The self E.M.F. generated by nonuniformly pressed rods indicate a possibility of producing artificial crystal rectifiers for alternating currents. Furthermore the variation of the resistance of pressed powders with the pressure of the surrounding gas may be applied to pressure measurements in gas systems.

VII - SUMMARY

1 - The current ideas on the secondary structure of solids have been briefly reviewed.

2 - The possibility of using electrical capacity as a measure of the secondary structure is advanced and some of the difficulties in its measurement are discussed.

3 - The electrical resistance of fused crystallized lead sulphide has been measured for various grain sizes at various temperatures.

4 - Ohm's Law has been investigated for the same material over a range of low current values at different temperatures and for different grain sizes.

5 - Pressed powders of crystallized lead sulphide show a linear relation between the current flowing and the applied potential difference for a given temperature, but the current-voltage curves show also an intercept on the voltage axis which intercept is a function of the temperature.

6 - The slope of the current vs. voltage curves is an exponential function of the reciprocal of the temperature in all cases.

7 - The influence of grain size on the current voltage relations is readily seen although no mathematical interpretation can be suggested.

8 - The electric conductivity of solids in general has been briefly reviewed.

9 - A tentative explanation of the observed results is offered.

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