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# DAVID SARNOFF RESEARCH CENTER

ELEVENTH

INTERIM REPORT

**CONFIDENTIAL**

INFRARED PHOTOCONDUCTORS

N6onr-23603

July 15, 1952 - October 15, 1952

**RADIO CORPORATION OF AMERICA  
RCA LABORATORIES DIVISION**

PRINCETON, N. J. Jan. 5, 1953

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## I. Laboratory Equipment

### A. External Cryostat

The final design of the external cryostat for measurements of the spectral response using the monochromator and absolute response using a standard black body source of a sample at liquid helium temperatures has been developed. Detailed drawings for its construction will now be made by the Drafting Department. The units will then be constructed.

The particular features incorporated in the design are as follows:

1. The cryostat is all metal except for the windows. All vacuum surfaces are polished silver plate. Non-magnetic and non-superconducting materials are used at the low temperature end to allow measurements with a magnetic field to be made.
2. Positioning of the cryostat after installation is accomplished by leveling screws for vertical motion and sliding tables for horizontal motion.
3. There are five separate systems in the cryostat:
  - a. A liquid helium chamber having a filling tube and an exhaust tube. Provision is made for closing off both of these tubes and attaching a vacuum pump to the filling tube in order to reduce the pressure on the liquid helium to obtain lower temperatures.

SECURITY INFORMATION

## SECURITY INFORMATION

2.

b. A sample chamber and guide tube. The sample chamber is located near the bottom of the helium chamber and has vacuum tight silver chloride windows on the sides. A sample is placed in this chamber by mounting the sample on a sample holder tube and inserting it from the top of the cryostat through the guide tube. The electrical leads pass up through the sample holder tube and through vacuum tight lead-ins to the electrical equipment. This system is filled with helium gas at a low pressure. The gas provides good heat conduction from the sample to the liquid helium chamber. Provision is made for measuring the pressure of this system to detect temperature changes of the sample at low temperatures.

c. A liquid nitrogen reserve tank having a filling tube and an exhaust tube. The liquid helium chamber is supported by its filling and exhaust tubes which, along with the guide tube, pass vertically through the liquid nitrogen tank.

d. A liquid nitrogen jacket having a filling tube and an exhaust tube. This jacket surrounds the liquid helium chamber and extends up to the liquid nitrogen reserve. Provision is made for installing various metal aperture disks opposite the silver chloride windows on the liquid helium chamber.

SECURITY INFORMATION

## SECURITY INFORMATION

3.

- e. A vacuum jacket. The two chambers and the liquid jacket are insulated by this common vacuum jacket. Rock salt windows are provided on the outer can of this jacket opposite the liquid nitrogen apertures. The lower end of the outer can is demountable in order to get to the liquid nitrogen apertures.
4. Parts (a), (b) and (c), described above, are one unit and can be removed from the liquid nitrogen jacket so that variations in the design of the sample holder proper can be made if necessary.
5. O-ring seals are used for the two demountable joints described above and also for vacuum sealing the rock salt windows. The number of such demountable joints has been kept to a minimum and occur only at points which are at room temperature.
6. A cloth bellows connection is made between the Leiss and the window of the cryostat. The dry nitrogen gas system in the monochromater (see next section) will thus keep the rock salt window surface in good condition.
7. Using the present design, measurements can be made of the spectral response and the absolute response of the photoconductivity and the spectral transmission of a sample. With a tight vacuum jacket, the cryostat is self-contained and portable.

SECURITY INFORMATION

# SECURITY INFORMATION

4.

## B. Accessories for the External Cryostat

### 1. Sample Mounting

For the purpose of mounting germanium samples (at present) on the sample holder tube, a specially constructed six prong plug and socket is being developed. The germanium crystal, in the form of a bar, is mounted on the plug by means of the two end current leads. Two conductivity and two Hall probes are then attached to the bar. These sample mounts are constructed using non-magnetic and non-superconducting materials and solder.

### 2. Transfer Equipment

In order to fill the external cryostat with liquid helium, a four liter dewar has been prepared with unsilvered slits to observe the helium level. A pyrex vacuum jacketed transfer tube has been constructed.

### 3. Silver Chloride Windows

The practical usefulness of the external cryostat depends primarily upon the availability of an infrared transparent window which is vacuum tight at very low temperatures. To fulfill this requirement, two types of window design are being investigated.

The first type consists of a dome-shaped disk of silver chloride held at its edge against a silver cylinder by specially designed pressure springs, the vacuum seal occurring at the pressure contact between the cylinder and the silver

SECURITY INFORMATION



## SECURITY INFORMATION

5.

chloride. This type of window is described in Jour. Opt. Soc. Am. 39, 786 (1949). An initial test of this type of window failed because of a poor seating surface on the cylinder. Another test holder is being constructed for this type in which the seating surface is more accessible.

The other type of window consists of a dome-shaped disk of silver chloride melted at its edge onto a silver ring which is then soldered in place. Five windows of this type were tested during this period. The successful procedure was to form the silver chloride - silver ring seal by induction heating of the ring and then to soft solder the ring into the test holder by induction heating at a lower temperature. Three windows were defective because of difficulties encountered in their preparation which have now been overcome. One window remained vacuum tight after three slow coolings to  $77^{\circ}\text{K}$  as well as after quenching to  $77^{\circ}\text{K}$  from room temperature. Another window remained tight after being held at  $77^{\circ}\text{K}$  for one hour. A subsequent test for vacuum tightness is planned for a window cooled to  $4^{\circ}\text{K}$ .

The purpose of the dome shape for the silver chloride is to allow for contraction upon cooling without necessary movement at the edge of the window. Clear dome-shaped pieces of silver chloride are pressed from silver chloride sheets in a die constructed for this purpose. It was found to be essential

SECURITY INFORMATION

## SECURITY INFORMATION

6.

to have a silver mirror surface on the faces of the die coming in contact with the silver chloride.

### C. Monochromator and Associated Equipment

The construction of the optical unit housing the thermocouple and focusing mirrors was completed just at the end of this period. In addition to the features of this unit described in the last report, provision has been made to circulate dry nitrogen through both this unit and the monochromator.

SECURITY INFORMATION

# SECURITY INFORMATION

7.

## II. Measurements on Germanium

### A. Behavior of High Purity Germanium

In the final stages of the purification of germanium, portions of the ingots often exhibit cooling curves which show a monotonic decrease of conductivity with decreasing temperature and which have large (0.1 - 0.3 ev.) slopes in the impurity range. For a time, it was felt that this represented the normal behavior of very high purity germanium. However, attempts to measure the Hall coefficients of such specimens have yielded anomalous results even at room temperature. The sign and magnitude of the Hall voltage do not behave in the expected manner upon reversal of the magnetic field and, in addition, the apparent conductivity of the samples depends upon the magnitude and orientation of the magnetic field in a manner which cannot be accounted for by the magneto-resistive effect.

In the further investigation of the behavior of such samples, one was provided with potential probes so located that a line joining them was nearly at right angles to the line joining the current leads. If, as was suspected, the abnormal behavior in the Hall experiments was due to the presence of inhomogeneities in the samples, this arrangement of probes would be expected to accentuate the effect of such inhomogeneities. The specimen was found to be ohmic at room temperature but, as the temperature was lowered, the apparent conductivity, as determined

SECURITY INFORMATION

## SECURITY INFORMATION

8.

by means of these probes, was found to be a function of the direction and of the magnitude of the current as well as of the temperature. The non-ohmic behavior became more pronounced, the lower the temperature was.

The behavior which is observed for these samples is almost certainly not that characteristic of a homogeneous semiconductor and appears to be the result of the presence of regions of different conductivity and possibly of different conductivity type distributed throughout the bulk of the germanium. Such conductivity fluctuations would be the result of an inhomogeneous distribution of residual foreign impurities or of lattice imperfections or of both. Analysis of cooling curves has indicated that in high purity germanium the concentrations of p- and n-type impurities are approximately equal. Spatial fluctuations of impurity densities in such material might well lead to spatial fluctuations of conductivity type. The electrical conductivity of such samples would be characteristic of a complicated system of p-n junctions rather than of the bulk properties of the germanium.

If this hypothesis is correct and if the magnitude of the fluctuations is greater than that to be expected from purely statistical considerations, the magnitude of the anomalies may well be reduced by an annealing heat treatment. Such treatment would be expected to (a) reduce the concentration of lattice imperfections and (b) reduce inhomogeneities in the density of

SECURITY INFORMATION

## SECURITY INFORMATION

9.

foreign impurities by diffusion. Annealing experiments with this result in mind are planned.

Although the impurity concentration of samples exhibiting anomalous conductivity behavior cannot be determined from an analysis of the cooling curves, such samples, nevertheless, are undoubtedly very pure and are suitable for use in controlled impurity addition experiments. A normal high purity sample is characterized by a cooling curve which drops from room temperature with the intrinsic slope to a minimum in conductivity which is one to two orders of magnitude lower than the room temperature value. At lower temperatures, a conductivity maximum will occur and finally an impurity slope of about 0.01 or 0.04 ev. will be displayed. The photoconductivity excited by room temperature radiation with the sample at 4°K will be small and of the order of magnitude of  $10^{-3}$  to  $10^{-4}$   $\mu\text{A/volt}$ . An example of such a curve is illustrated in Fig. 1 for cell AA89.

### B. Heat Treatment

Some additional work has been done during this period on the study of the thermal and photoconductive behavior of heat treated germanium samples. Portions of cells AA86 and AA87 which had previously been measured after quenching from 830°C were annealed at 450°C for 72 hours. The samples after quenching had given cooling curves characteristic of a high impurity content in that they were already below the intrinsic range at room

SECURITY INFORMATION

## SECURITY INFORMATION

10.

temperature. After annealing, both samples showed an intrinsic drop below room temperature which in the case of cell AA89 was by nearly two orders of magnitude. In both cases, a well defined impurity slope of about 0.04 ev. was observed. The results are summarized in Table I, and a comparison of the cooling curves for one of the samples before and after annealing is given in Fig. 1. The high concentration of centers introduced by quenching has been greatly reduced by annealing. The reduction in the magnitude of the photocurrent accompanying the decrease in concentration of centers is outstanding in this example.

- In another experiment, cell AA84 which showed the anomalous high purity behavior discussed above, was cut into two parts, both of which were then quenched from 550°C. Such treatment should lead to the introduction of a much smaller concentration of centers than did quenching from higher temperatures (cells AA86 and AA87). The cooling curves, one of which is illustrated in Fig. 2, for the two samples were practically identical and are typical of germanium with a moderately small impurity content. There was a small intrinsic drop below room temperature followed by a rise to a conductance considerably above the room temperature value and finally a drop with an impurity slope of 0.046 ev. The magnitude of the photocurrent observed is characteristic of samples with a moderate impurity content. The results are summarized in Table I.

SECURITY INFORMATION

# SECURITY INFORMATION

11.

TABLE I

| <u>Cell</u> | <u>Impurity or<br/>Heat Treatment</u> | <u>Intrinsic Drop<br/>from Room Temp-<br/>erature (a)</u> | <u>Impurity<br/>Slope</u> | <u><math>\frac{\Delta I}{V}</math> at 4°K<br/>(b)</u> | <u><math>\frac{\Delta I}{I_D}</math></u> |
|-------------|---------------------------------------|-----------------------------------------------------------|---------------------------|-------------------------------------------------------|------------------------------------------|
| AA84        | Annealed at 450°C                     | Anomalous                                                 | -----                     | $4 \times 10^{-7} \mu A /$<br>volt                    | 0.3                                      |
| AA86        | Quenched from 830°C                   | None                                                      | ~0.03 ev                  | $3.0 \times 10^{-2}$                                  | 40                                       |
| AA87        | " " "                                 | "                                                         | 0.028                     | $1.5 \times 10^{-2}$                                  | 75                                       |
| AA89        | AA86 Annealed at<br>450°C             | 0.014                                                     | 0.047                     | $1.1 \times 10^{-4}$                                  | 6.6                                      |
| AA90        | AA87 Annealed at<br>450°C             | 0.47                                                      | 0.041                     | $1.4 \times 10^{-2}$                                  | 128                                      |
| AA91        | AA84 Quenched from<br>550°C           | 0.63                                                      | 0.047                     | $6.3 \times 10^{-2}$                                  | 71                                       |
| AA92        | AA84 Quenched from<br>550°C           | 0.53                                                      | 0.045                     | $2.4 \times 10^{-2}$                                  | 112                                      |
| AA94        | Gallium                               | None                                                      | 0.013                     | 3.0                                                   | 117                                      |
| AA95        | Arsenic                               | None                                                      | Multiple                  | $1.2 \times 10^{-2}$                                  | 3.5                                      |

(a) This column gives the ratio of the conductivity at the minimum to that at room temperature.

(b) The values of  $\Delta I/V$  are those due to room temperature radiation from the top of the Collins Cryostat.

## C. Doped Samples

One sample each of germanium doped with gallium and with arsenic were obtained from the transistor group. The significant results obtained from measurements on these samples are given in Table I. The results from the arsenic doped sample are probably without much significance since the cooling curve gave an indication of three distinct impurities.

# SECURITY INFORMATION

## SECURITY INFORMATION

12.

The gallium sample is noteworthy in that it gave the largest photoconductive response to room temperature radiation of any of the germanium samples thus far measured.

SECURITY INFORMATION



## SECURITY INFORMATION

13.

### III. Quantitative Determination of Impurity Content by Means of Cooling Curves

The temperature dependence of the electrical conductivity of a semiconductor containing singly ionizable donor and acceptor impurities has been investigated theoretically. This temperature dependence arises from the variation with temperature of both the concentration and mobility of current carriers. The analysis leads to a fourth degree equation in temperature describing the concentration of current carriers in the conduction band (for n-type semiconductor) or filled band (for p-type semiconductor). The coefficients of powers of  $T$  in this relation are related to the concentration of donor and acceptor impurities and the current carrier activation energies. The coefficients can be evaluated by fitting a calculated curve to the experimental measured curve of conductivity vs temperature. This, in turn, permits quantitative evaluation of impurity concentration and carrier activation energy.

The model assumed for the semiconductor is the conventional one shown schematically in Fig. 3. There are  $n_D$  donors per cubic centimeter at an energy  $E_D$  below the conduction band and  $n_A$  acceptors per cubic centimeter at an energy  $E_A$  above the filled band. These impurities are assumed to be singly ionizable so that only one carrier can be excited from each. The impurity gallium or arsenic in germanium is an example of this type of impurity.

SECURITY INFORMATION

## SECURITY INFORMATION

14.

The effective density of states for electron current carriers in the conduction band is taken as

$$N_C = 2 \left( 2\pi m \frac{kT}{h^2} \right)^{3/2} = 4.84 \times 10^{15} T^{3/2} \text{cm}^{-3}$$

for germanium.

A number of simplifying assumptions are made at this point. Spherical energy surfaces in the crystal momentum space near the bottom of the conduction band are assumed. The effective mass of the carrier is taken to be equal to the electronic mass. The same assumptions are also made for hole current carriers in the filled band.

Actually, the states at the edge of the band are probably partially degenerate. The carrier concentration and mobility due to thermal scattering are undoubtedly affected by such degeneracy. This, however, will not be considered in the present report.

The concentration  $n$  of electron current carriers in the conduction band distributed in the  $N_C$  states is given by:

$$n = N_C \exp(-E_F/kT)$$

where  $E_F$  is the energy difference between the Fermi level and the conduction band.

Similarly, the concentration  $p$  of hole current carriers in the filled band is given by

$$p = \frac{N_C^2 \exp(-E_g/kT)}{n}$$

SECURITY INFORMATION

## SECURITY INFORMATION

15.

The concentration of ionized donors  $n_D$  and ionized acceptors  $n_A$  can then be calculated to be the following:

$$n_D = N_D - N_D [1 + K_D/2n]^{-1} = N_D K_D / (2n + K_D)$$

$$n_A = N_A K_A / (2p + K_A)$$

where  $K_D$  and  $K_A$  are equilibrium constants given by

$$K_D = N_C \exp(-E_D/kT)$$

$$K_A = N_C \exp(-E_A/kT)$$

The factor 2 in these expressions arises from the fact that the carrier may have either spin when bound to an impurity.

The condition of electrical neutrality in the crystal requires that

$$n - p = n_D - n_A$$

Substituting the values which were derived for  $n_D$  and  $n_A$  into this expression gives:

$$n - p = N_D K_D / (2n + K_D) - N_A K_A / (2p + K_A) \quad (1)$$

This, together with the relation

$$np = N_C^2 \exp(-E_G/kT) , \quad (2)$$

serves to determine  $n$  or  $p$  as a function of temperature. The combined equation derived from this pair is a fourth degree equation in  $T$ . Consequently, its solution is difficult. However, it is possible, in certain temperature ranges, to make simplifying assumptions which lead to an easy evaluation of the necessary coefficients.

SECURITY INFORMATION

## SECURITY INFORMATION

16.

At high temperatures, the righthand side of Eq. 1 becomes negligibly small. Hence:

$$n = p = N_C \exp(-E_G/kT)$$

The same equation applies under other conditions when the crystal behaves as an intrinsic semiconductor. Such conditions are when  $N_D = N_A = 0$  or when there is a true balance  $N_A = N_D$  and  $E_D = E_A$ .

At somewhat lower temperatures, the expression for  $n$  reduces to

$$n = N_D - N_A$$

where  $N_D$  is assumed to exceed  $N_A$ .

This represents the region where the impurity centers are completely ionized, yet is below the temperature at which the intrinsic transition contributes to the carrier concentration. At still lower temperatures, the expression for the current carrier  $n$  becomes

$$n = \frac{K_D(N_D - N_A)}{2N_A}$$

The genealogy of these approximate equations is given in Fig. 4. It should be pointed out that the approximations are used to evaluate the various parameters. After these have been evaluated, they should be substituted back into Eqs. 1 and 2 and the resultant curve compared with the measured cooling curve.

SECURITY INFORMATION

## SECURITY INFORMATION

17.

The discussion in the preceding paragraphs has dealt with the form of the carrier concentration curve. The carrier concentration must be multiplied by the mobility, which is also a function of temperature, to obtain the conductivity which is the actual experimental quantity measured. The mobility for electrons and holes as a function of temperature is given by the following relation:

$$1/\mu_n = \alpha T^{-3/2} + \beta_n T^2 \quad (3a)$$

$$1/\mu_p = \alpha T^{-3/2} + \beta_p T^2 \quad (3b)$$

The  $T^2$  term in these expressions predominates at high temperatures and represents the effect of lattice scattering.

The experimental variation of conductivity over the region of temperature where carrier concentration is constant with temperature, together with Hall measurements, justifies the assumed temperature dependence of lattice scattering and mobility. It has been assumed that in this high temperature region where the lattice scattering term is predominant  $\mu_n / \mu_p = 2.1$ . At low temperatures, the term containing  $T^{-3/2}$  predominates. This represents the effect of impurity scattering on mobility. The coefficient of impurity scattering for a total concentration of  $N_I$  is given by the Conwell-Weisskopf formula:

$$\alpha = N_I \ln(1 + x^2) / 1.2 \times 10^{18}$$

$$x = 3.4 \times 10^4 T / N_T^{1/3}$$

SECURITY INFORMATION

## SECURITY INFORMATION

18.

Fig. 5 gives the variation of mobility with temperature for a number of different concentrations of impurities.

In carrying out a quantitative determination of impurity concentrations from a measured cooling curve, the first step is to correct for mobility. This is done by using Eq. 3a or 3b (depending upon whether it is an n- or p-type semiconductor). The coefficient  $\beta$  is adjusted until the carrier concentration curve which is obtained by dividing the conductivity curve by mobility does not rise over any of the temperature range. Next, using the approximate expression given above, the quantities  $N_d - N_a$ ,  $N_a$  and  $E_D$  are found. Using these coefficients, the entire curve is fitted to the experimental curve making any adjustments in the coefficients that may be necessary.

In Fig. 6, crosses represent the experimentally measured conductivities for the temperature range indicated. The solid curve represents the product of the equation expressing carrier concentration, and the expression for the mobility. The impurity concentrations and activation energies used are indicated on the figure. It will be seen that an excellent fit is obtained over the entire temperature range. The sample under test was a p-type semiconductor. The dotted and dashed curve represents an attempt to fit the experimental points to a model having only acceptor type impurities. The dashed curve fits over the low temperature

SECURITY INFORMATION

## SECURITY INFORMATION

19.

ranges but predicts too large an intrinsic drop. On the other hand, using a higher acceptor concentration, the dotted curve fits in the intrinsic region but does not fit at all well at low temperature. The dotted and dashed curves are included to indicate the sensitivity of this method of determining impurity concentration.

SECURITY INFORMATION

# SECURITY INFORMATION

20.

## IV. Measurements on Other Materials

### A. Cadmium Antimonide

#### 1. Cooling Curves and Photoresponse

A survey of some of the effects of composition and of heat treatment upon the semiconductivity of cadmium antimonide preparations has been given in the Tenth Interim Report (N6onr23603). During the present period, two of the samples G28 - CdSb and G29 -  $\text{Cd}_3\text{Sb}_2$ , were measured down to 4°K in the Collins Cryostat. The cooling curves obtained are illustrated in Fig. 7.

The  $\text{Cd}_3\text{Sb}_2$  sample shows an exponential decrease of conductivity with increasing reciprocal temperature starting from room temperature. At about 150°K, there is a minimum and at about 75°K a maximum in conductivity which presumably are due to the effect of temperature upon carrier mobility. At temperatures below the maximum, the conductivity decreases with a gradually decreasing slope of the  $\log \sigma - 1/T$  curve. It is reasonable to conclude, from the shape of the cooling curve, that the initial exponential portion of the cooling curve represents the intrinsic conductivity region. Of course, measurements of conductivity at temperatures above room temperature would be required to confirm this supposition.

The compound CdSb shows a quite different behavior. The conductivity decreases with decreasing temperature from room temperature to about 20°K. Below this temperature, the conductivity

SECURITY INFORMATION



## SECURITY INFORMATION

21.

is essentially constant. The slope of the cooling curve in the neighborhood of room temperature, 0.017 ev., is so small that it certainly cannot represent the intrinsic range.

Both compounds gave some indication of a photoconductive response to room temperature radiation when cooled to 4°K. For  $\text{Cd}_3\text{Sb}_2$ , the increase of conductance was about 90  $\mu\text{A}$  per volt and the fractional increase was about  $4 \times 10^{-3}$ . In the case of  $\text{CdSb}$ , the existence of a response was less certain. There appeared to be a slight effect with a fractional change of conductance of about  $6 \times 10^{-4}$ . In both cases, the very high dark conductivity at liquid helium temperature makes the detection of a photoeffect very difficult.

### 2. Analysis of Cooling Curve for $\text{Cd}_3\text{Sb}_2$

The general similarity of the cooling curves for the  $\text{Cd}_3\text{Sb}_2$  samples which have been measured to those of germanium samples suggests that an analysis of such curves much like that carried out for germanium can be performed. This has been attempted for the cooling curve of sample G29.

Since there has been no independent determination for  $\text{Cd}_3\text{Sb}_2$ , of  $E_g$ , the width of the intrinsic gap, the analysis is based upon the assumption that, in the neighborhood of room temperature, the sample is in the intrinsic range. In the neighborhood of the conductivity maximum, the experimental curve was fitted by assuming that the carrier concentration was independent

SECURITY INFORMATION

## SECURITY INFORMATION

22.

of temperature and that the mobility was composed of lattice and impurity scattering terms combined according to:

$$\frac{1}{\mu} = \frac{1}{\mu_L} + \frac{1}{\mu_I}$$

with the temperature dependence of mobility given by:

$$\frac{1}{\mu} = bT^2 + aT^{-3/2}$$

It may be noted that, in order to fit the data, an assumption of lattice scattering varying as  $T^{-2}$  is required as is also the case for germanium. The relative charge carrier concentration  $q$  may now be obtained as function of the temperature from the experimental conductivity data and the above expression for mobility. The absolute concentration cannot be determined since the absolute mobility is not known.

The magnitude of the intrinsic gap may be estimated from the slope of the plot of  $\log (q/T^{3/2})$  against  $1/T$  over the high temperature portion of the range covered by the measurements. This curve turns out to be linear, for G29, down to about 220°K. The value of  $E_g$  so obtained is 0.20 ev. The concentration of charge carriers of either sign, calculated from  $E_g$  with the assumptions that the effective masses of both holes and electrons are equal to the free electron mass and that the concentration of carriers from impurities is negligible, is  $4.9 \times 10^{17} \text{ cm}^{-3}$  at 300°K.

SECURITY INFORMATION

## SECURITY INFORMATION

23.

The charge carrier concentration in the impurity range may be determined from the value of  $q$  at  $300^{\circ}\text{K}$ ; the value of  $q$  in the impurity range and the above mentioned value of the concentration of intrinsic carriers at  $300^{\circ}\text{K}$ . The value obtained is  $3.5 \times 10^{16} \text{ cm}^{-3}$ . If impurities of only one conductivity type are present, this figure would represent the concentration of such impurity. If impurities of both types are present, then this figure represents the excess of the majority over the minority types.

With the assumption as to the temperature dependence of mobility employed above,  $q$  is found to be independent of temperature over the range from about  $110^{\circ}\text{K}$  to about  $55^{\circ}\text{K}$ . Below the latter temperature,  $q$  rises slowly with decreasing temperature. Since it is unlikely that the charge carrier concentration should rise in this manner, this probably means that below  $50^{\circ}\text{K}$  the impurity scattering varies less rapidly than  $T^{3/2}$ . An assumption of mobility proportional to  $T$  gives a  $q$  which is essentially constant over the range from  $50^{\circ}\text{K}$  to  $4^{\circ}\text{K}$ .

It may be concluded that, although from this analysis no very precise statement as to the dependence of charge carrier concentration upon temperature below about  $100^{\circ}\text{K}$  can be made,  $q$  appears to be essentially constant between this temperature and  $4^{\circ}\text{K}$ . In other words, the impurity behaves as though it had zero activation energy. The photoconductive response observed in the

## SECURITY INFORMATION

## SECURITY INFORMATION

24.

cryostat with this sample must, therefore, have been intrinsic response corresponding to the 0.20 ev. gap.

### B. Zinc Antimonide

Since the cadmium-antimony system has shown interesting semiconductor properties, it is likely that other similar systems will also be of interest. Preliminary investigation of one such, the zinc-antimony system, has been carried out.

The first sample to be investigated was an alloy junction formed by melting zinc in contact with a solid piece of antimony. This sample yielded the cooling curve illustrated in Fig. 8. Starting from room temperature, the conductance first rose to a maximum at 268°K; then dropped rapidly and passed through a minimum at 254°K; a maximum at 243°K; a minimum at 191°K and then gradually rose. This behavior, although rather complicated, indicated that the system warranted further investigation.

Two homogeneous, polycrystalline preparations having compositions corresponding to  $\text{ZnSb}$  and  $\text{Zn}_3\text{Sb}_2$  were next measured. The cooling curves obtained are given in Figs. 9A and 10A. The sample of  $\text{ZnSb}$  showed a negative temperature coefficient of conductance throughout except for a small drop and subsequent rise in the region in which the alloy junction sample showed the large decrease in conductance. The  $\text{Zn}_3\text{Sb}_2$  sample gave a curve very similar to that of the junction sample except that the intermediate minimum and maximum did not appear and that

SECURITY INFORMATION

## SECURITY INFORMATION

25.

the homogeneous sample showed a larger drop in conductance than did the junction sample.

The effect of heat treatment upon the behavior of the samples has been investigated to some extent. One sample of each composition was annealed in vacuum at 400°C for about 92 hours. The cooling curves for the annealed samples are presented in Figs. 9B and 10B. Annealing had relatively little effect upon ZnSb but resulted in almost complete disappearance of the rapid drop in conductance displayed by unannealed  $\text{Zn}_3\text{Sb}_2$ . This behavior is reminiscent of that displayed by the cadmium antimonides.

In some respects, the behavior of the zinc antimonides is rather puzzling. ZnSb has given no clear-cut indication of semiconduction, although the results of measurements upon a single preparation should, by no means, be taken to be conclusive. The rapid drop of conductance observed for  $\text{Zn}_3\text{Sb}_2$  might be evidence of semiconductor behavior but it is somewhat difficult to understand why the room temperature conductivity is so high, about  $10^3(\text{ohm cm})^{-1}$ , in view of the rather large slope, 0.8 ev., of the curve. One possible explanation might be the following. Complete combination of zinc and antimony to form the compound may not have occurred under the conditions of preparation of the sample. That this might well be the case is indicated by the results of the annealing experiment described above. The sample would then consist of a mixture of compounds, of which one component is a semiconductor,

SECURITY INFORMATION

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26.

having a positive temperature coefficient of conductance and the other a metal which would have a negative temperature coefficient. If there is effectively a series arrangement of metal and semiconductor, the metallic component might dominate at high temperatures and give rise to the ascending portion of the curve observed just below room temperature. At lower temperatures, the semiconductor component would dominate and would be responsible for the descending portion of the cooling curve. The final ascending portion of the curve below about 200°K could then be explained as being the result of an increase of charge carrier mobility with decreasing temperature. Since this possible explanation is purely speculative, it is clear that further experimental work is required to clarify the electrical behavior of the zinc antimonides.

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27.

## V. Photoconductor Material Preparation

### A. Germanium

During the present period, a series of purification crystallizations have been carried out in order to build up a stock of material suitable for doping experiments. A total of ten 50 gram crystals have been drawn which have yielded approximately 75 grams of germanium of suitable purity. This is sufficient for three or four doping experiments. It is planned to investigate zinc as added impurity in the next series of doping experiments.

### B. Cadmium Antimonide

Two attempts to grow single crystal specimens by means of the Kyropoulos technique have been made. One outstanding difficulty with the method is the volatility of the material at its melting point. Considerable sublimation of material to cooler portions of the furnace tube occurred. If there is dissociation of the compound in the melt, then, since cadmium and antimony have different vapor pressures, the composition of the melt will change with time and a crystal drawn from the melt will have a variable composition. In spite of this obvious objection to the method, the attempt was made. Satisfactory crystal growth appears possible with this method although, for extraneous reasons, no completely single crystals were obtained. Electrical measurements upon the material have not yet been made.

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28.

## C. Zinc Antimonide

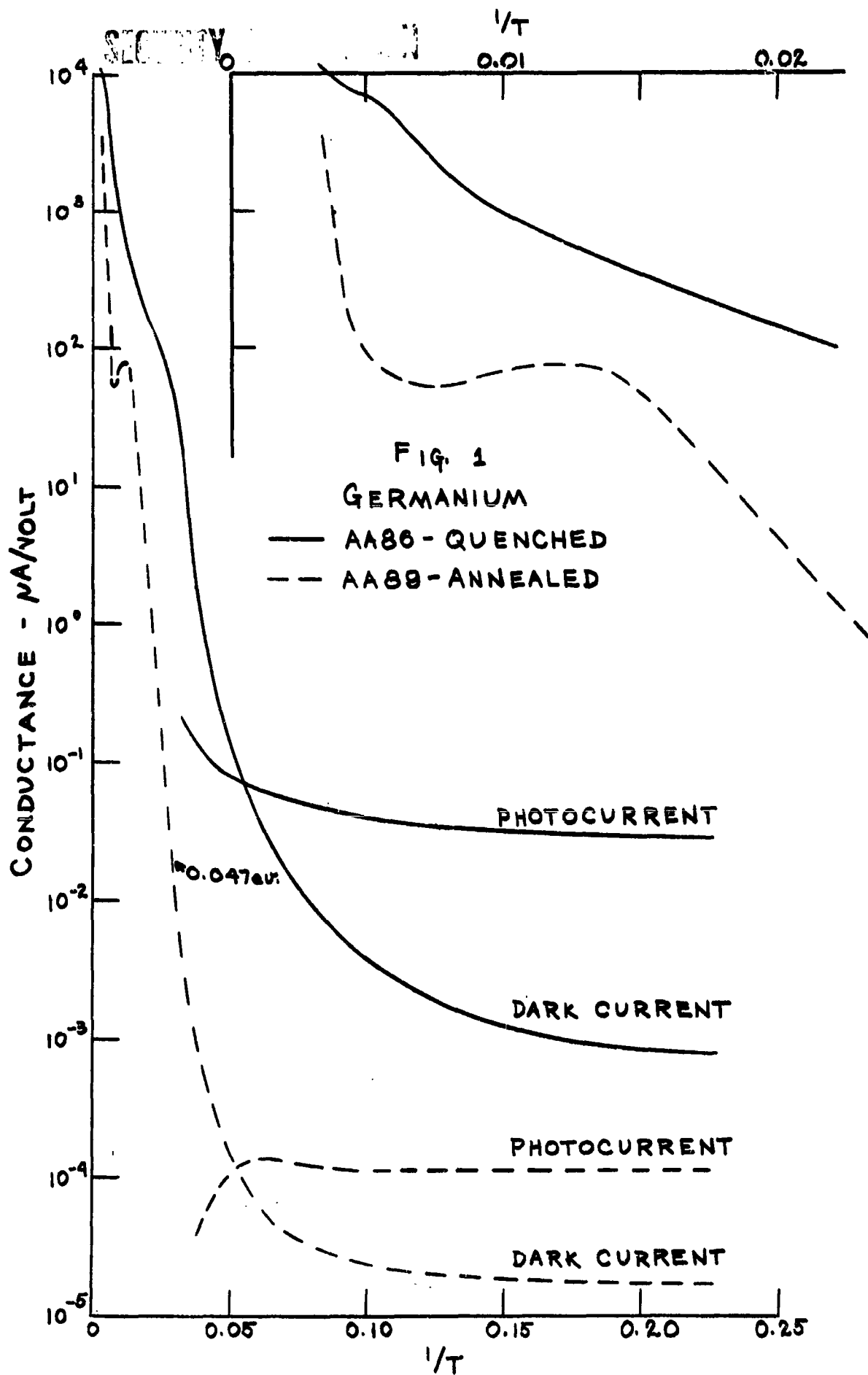
The method of preparation of the samples was essentially identical to that previously described for cadmium antimonide. It involved melting, in a sealed-off evacuated tube, appropriate amounts of Johnson & Matthey Co. zinc and antimony and then allowing the melt to solidify to a polycrystalline ingot after thorough mixing. The two preparations made had the compositions:

|                                   |                          |
|-----------------------------------|--------------------------|
| ZnSb:                             | 49.99 atomic percent Zn  |
|                                   | 50.01 atomic percent Sb  |
| Zn <sub>3</sub> Sb <sub>2</sub> : | 59.99 atomic percent Zn  |
|                                   | 40.01 atomic percent Sb. |

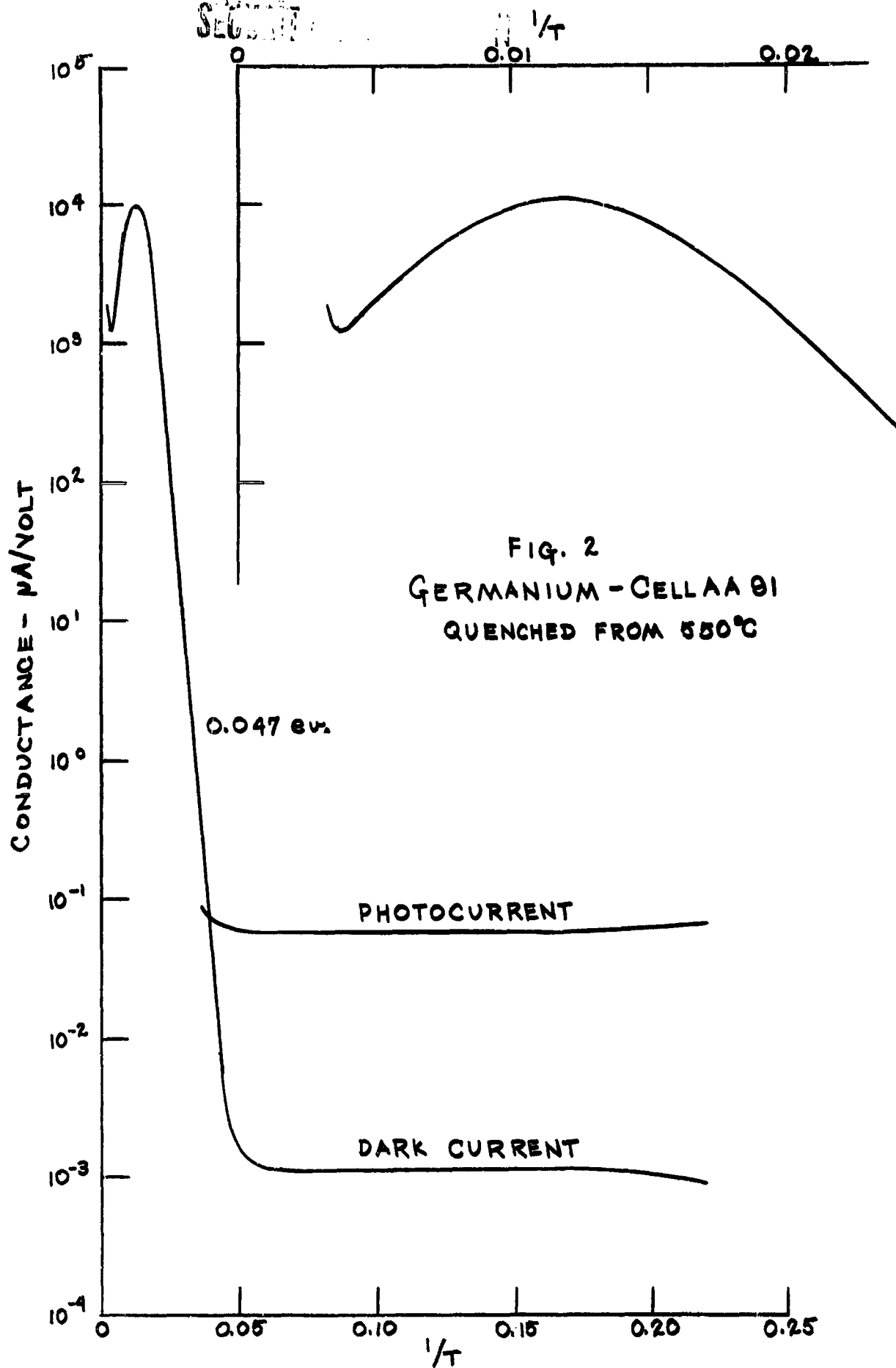
The annealed samples were prepared by taking portions of the original preparations and heating them in sealed-off evacuated tubes for about 92 hours at about 400°C and finally cooling them slowly to room temperature.

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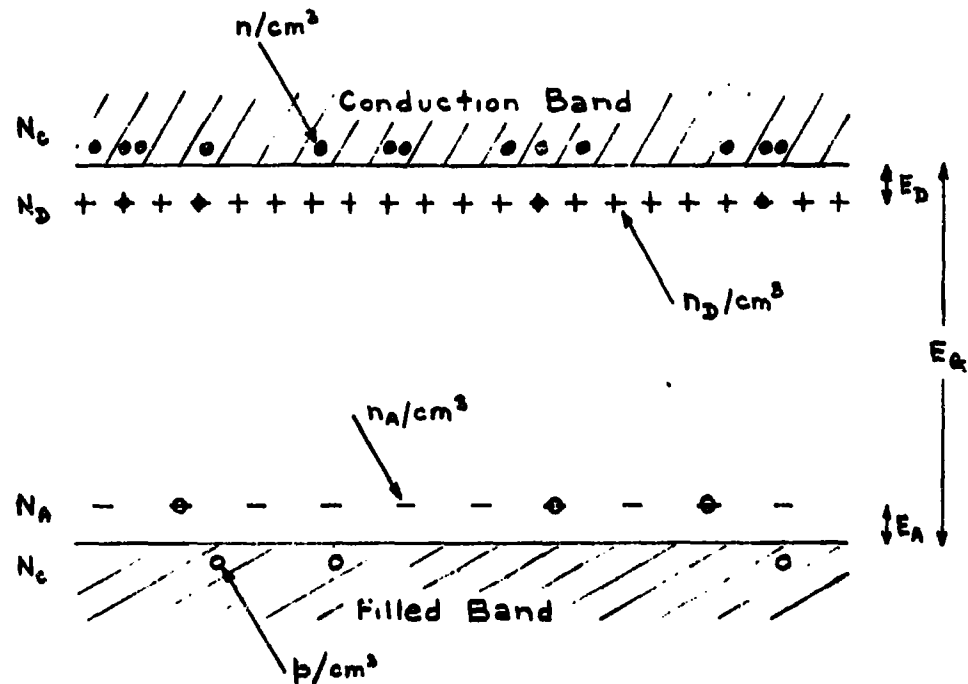




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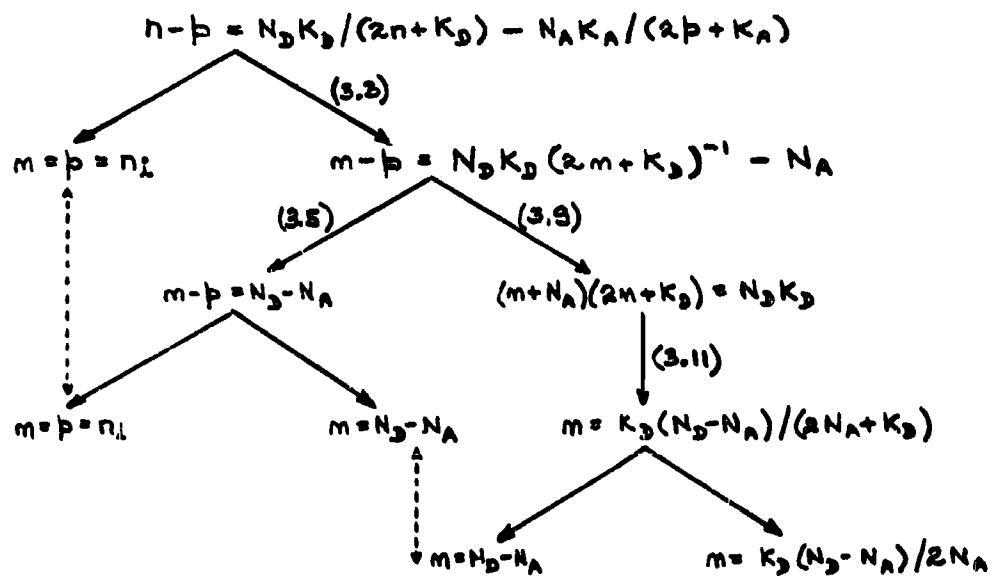


- Electron
- Hole
- + Singly Ionized Donor
- Singly Ionized Acceptor

Electronic Energy Level Scheme For Germanium

FIGURE 3

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Genealogy Of Approximate Equations In Text

FIGURE 4

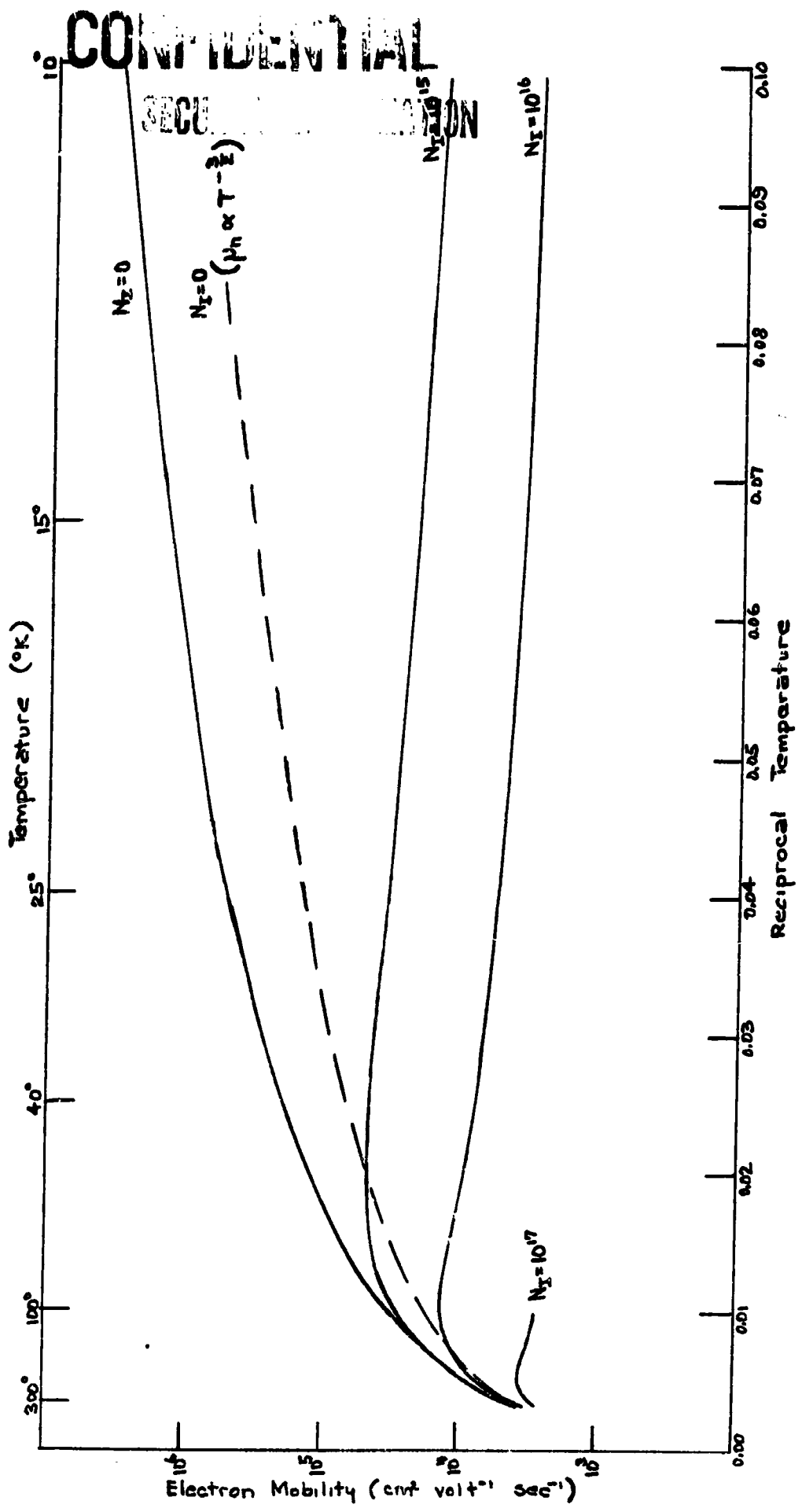


FIGURE 5

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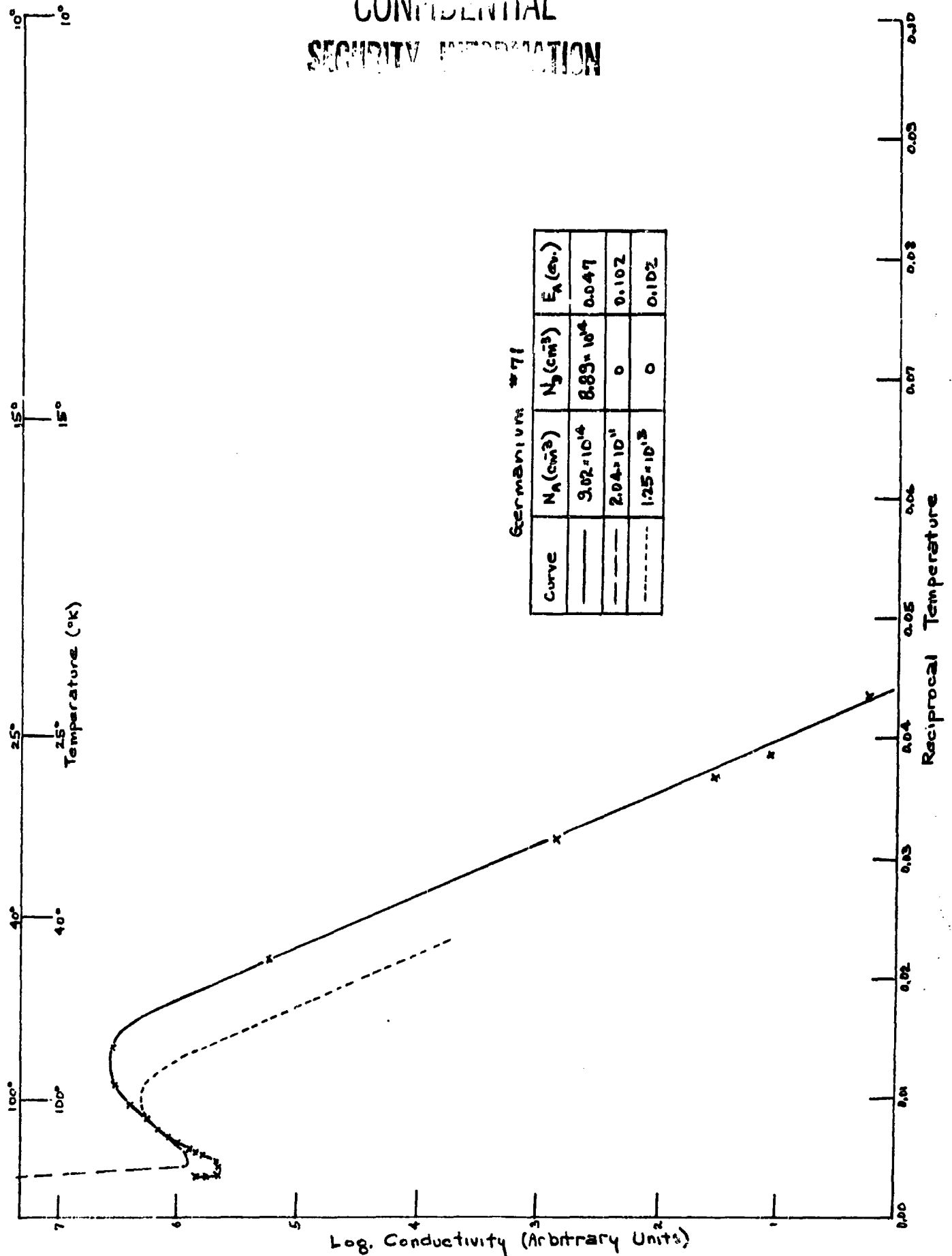
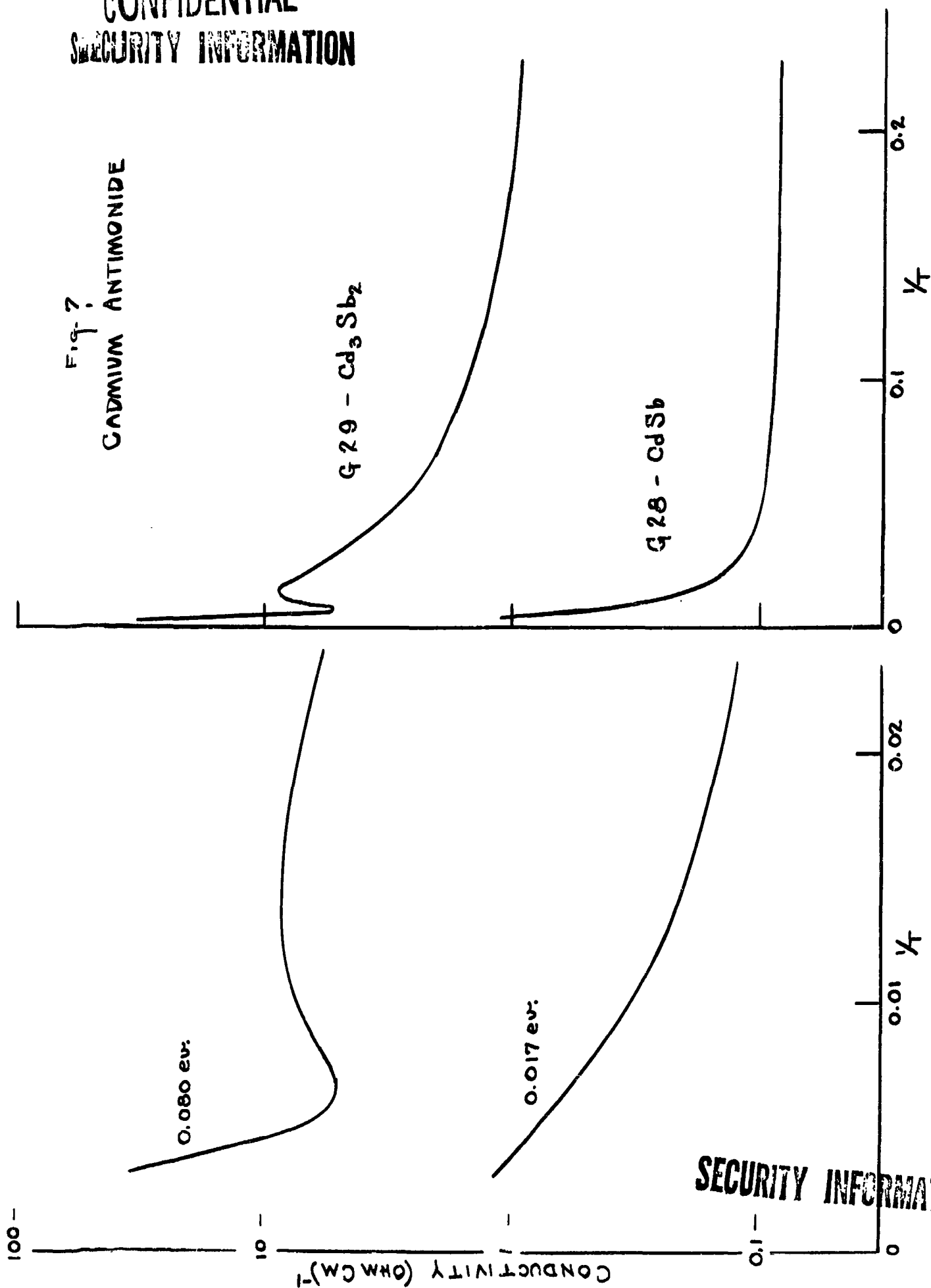


FIGURE 6

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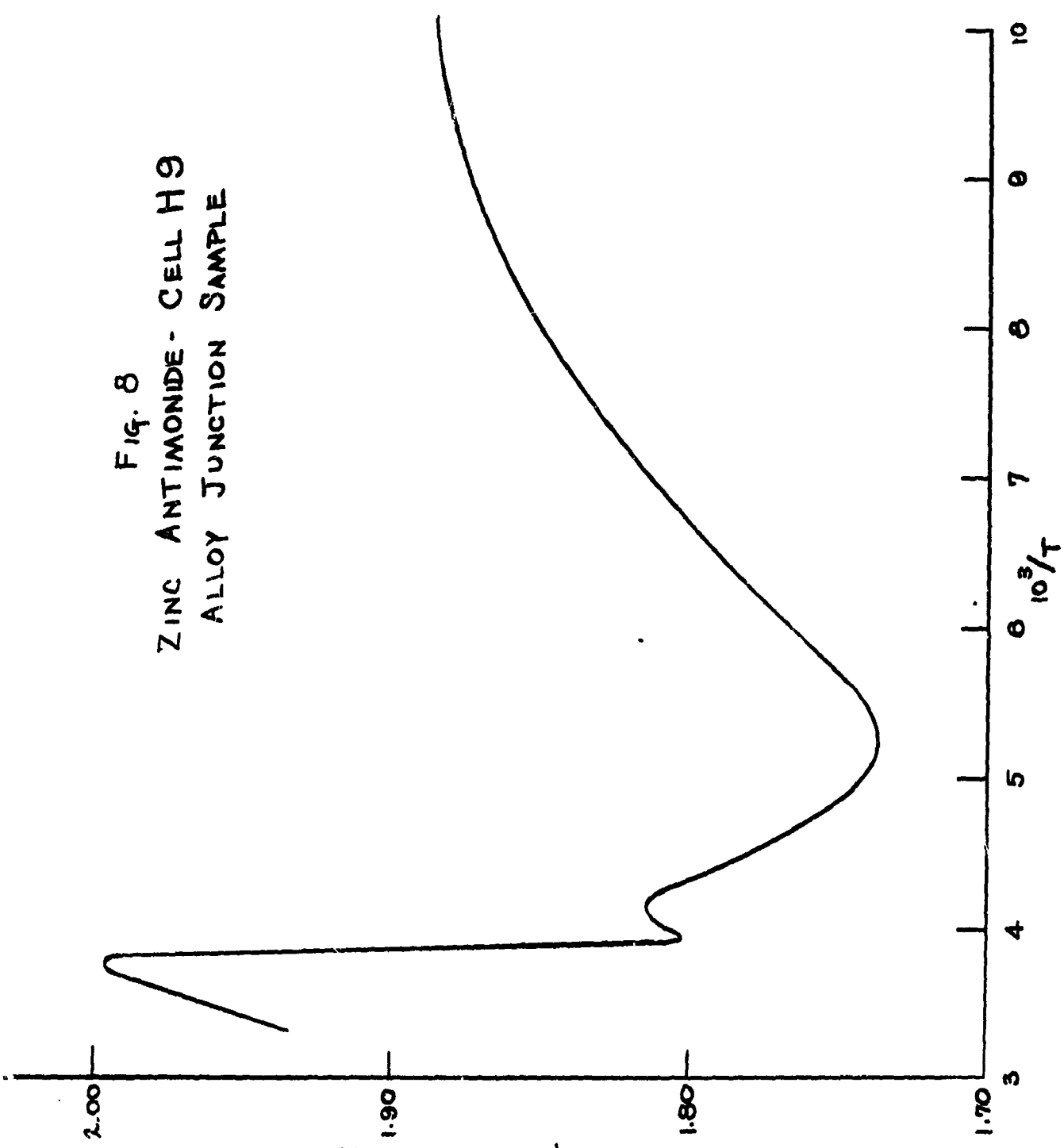
Fig. 7  
CADMIUM ANTIMONIDE



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Fig. 8  
ZINC ANTIMONIDE - CELL H9  
ALLOY JUNCTION SAMPLE



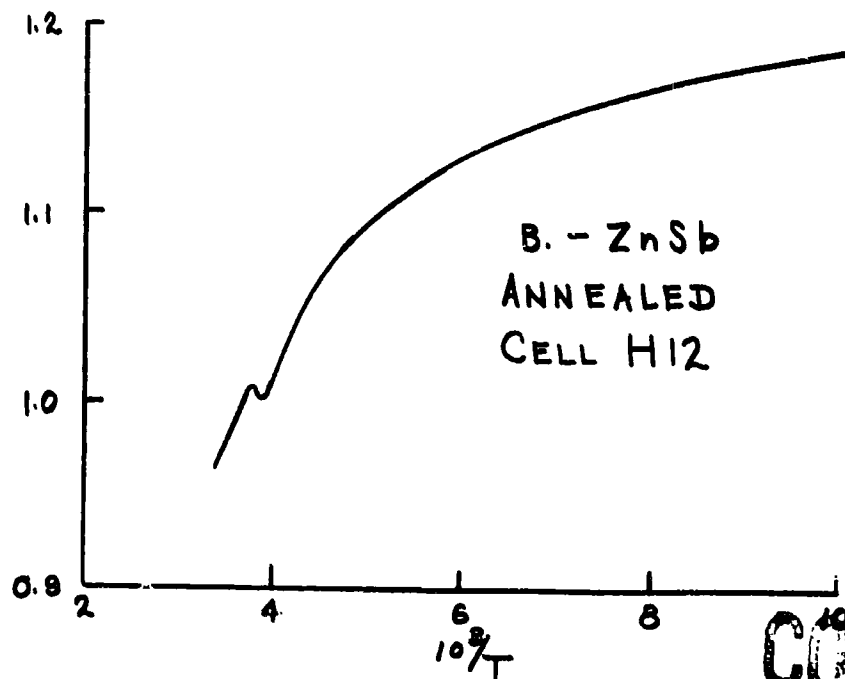
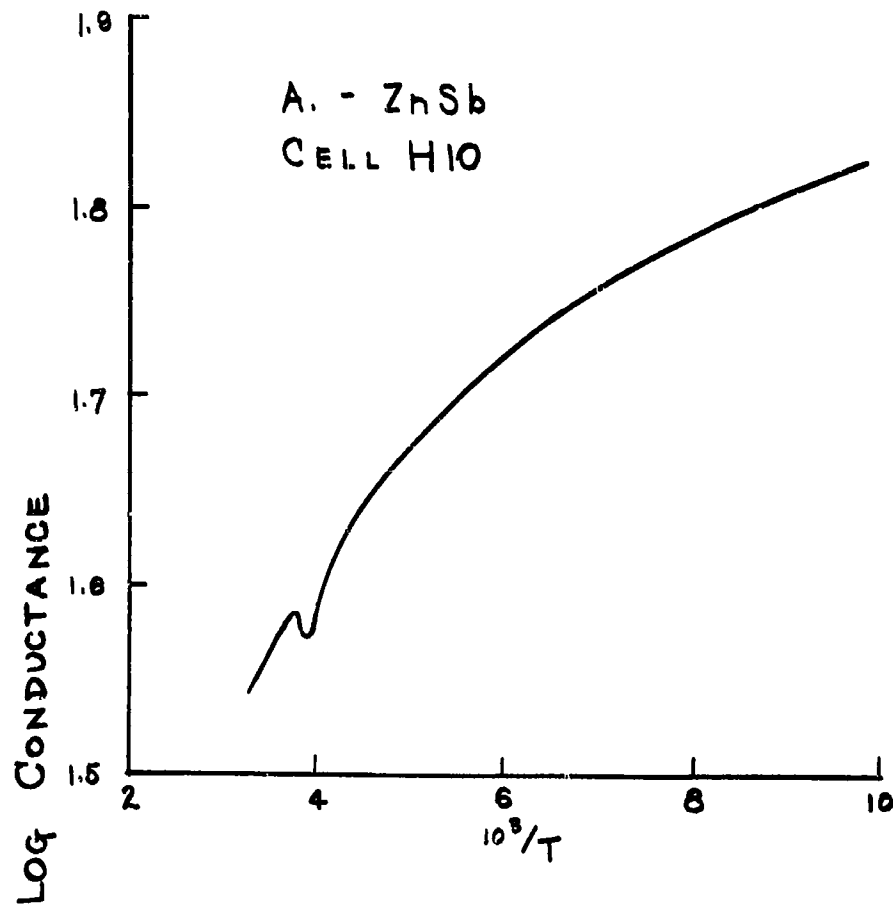
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Fig. 9  
ZINC ANTIMONIDE

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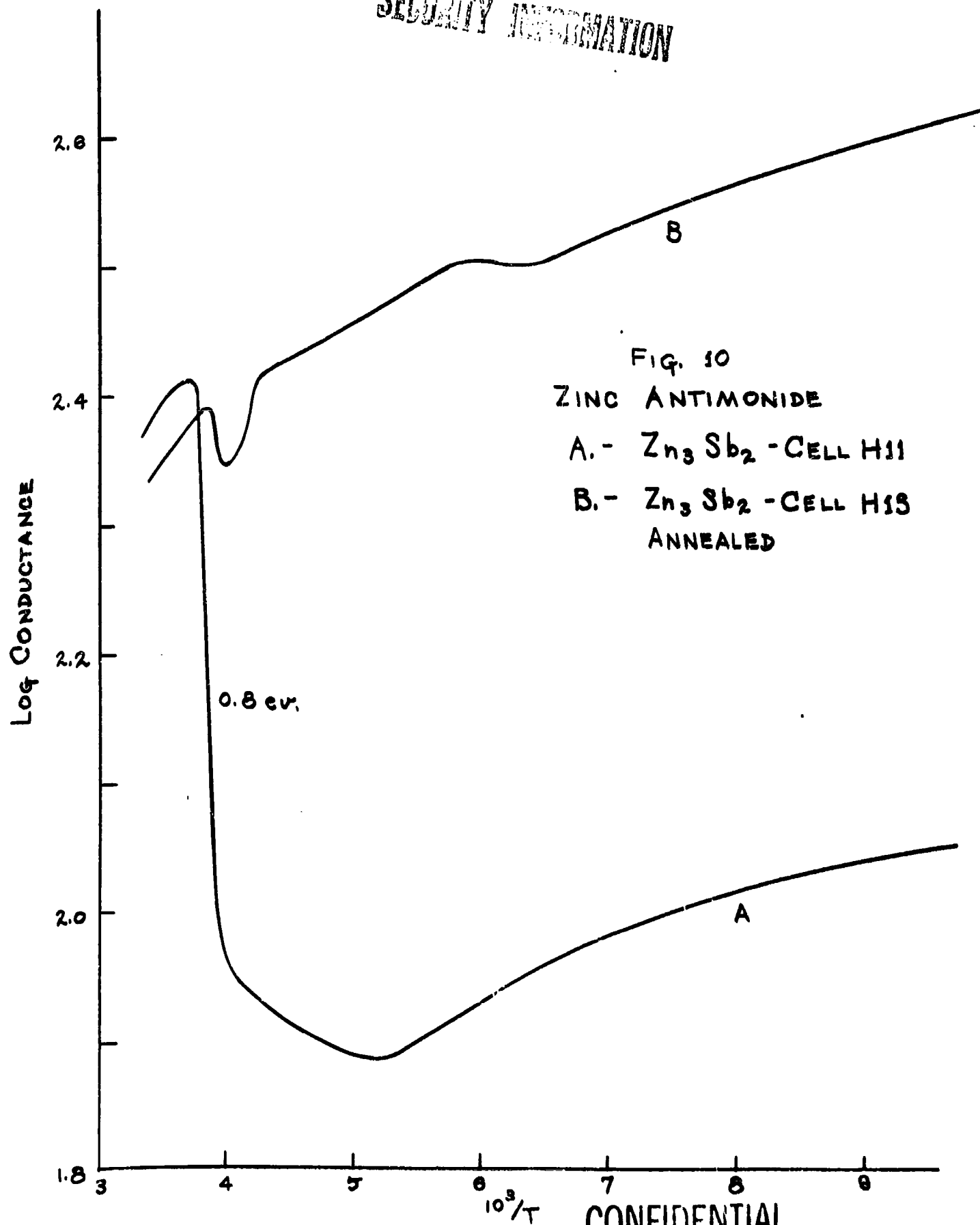


FIG. 10  
ZINC ANTIMONIDE  
A. - Zn<sub>3</sub>Sb<sub>2</sub> - CELL H11  
B. - Zn<sub>3</sub>Sb<sub>2</sub> - CELL H13  
ANNEALED

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