

UNCLASSIFIED

AD NUMBER	
AD040714	
CLASSIFICATION CHANGES	
TO:	unclassified
FROM:	confidential
LIMITATION CHANGES	
TO: Approved for public release; distribution is unlimited.	
FROM: Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 15 APR 1954. Other requests shall be referred to Office of Naval Research, Washington, DC.	
AUTHORITY	
30 apr 1966, DoDD 5200.10; ntis onr ltr, 26 oct 1977	

THIS PAGE IS UNCLASSIFIED

THIS REPORT HAS BEEN DELIMITED
AND CLEARED FOR PUBLIC RELEASE
UNDER DOD DIRECTIVE 5200.20 AND
NO RESTRICTIONS ARE IMPOSED UPON
ITS USE AND DISCLOSURE,

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

Armed Services Technical Information Agency

Because of our limited supply, you are requested to return this copy WHEN IT HAS SERVED YOUR PURPOSE so that it may be made available to other requesters. Your cooperation will be appreciated.

AD 40714

NOTICE: WHEN GOVERNMENT OR OTHER DRAWINGS, SPECIFICATIONS OR OTHER DATA ARE USED FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED GOVERNMENT PROCUREMENT OPERATION, THE U. S. GOVERNMENT THEREBY INCURS NO RESPONSIBILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE GOVERNMENT MAY HAVE FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE SAID DRAWINGS, SPECIFICATIONS, OR OTHER DATA IS NOT TO BE REGARDED BY IMPLICATION OR OTHERWISE AS IN ANY MANNER LICENSING THE HOLDER OR ANY OTHER PERSON OR CORPORATION, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE OR SELL ANY PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.

Reproduced by
DOCUMENT SERVICE CENTER
KNOTT BUILDING, DAYTON, 2, OHIO

**NOTICE: THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE
NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING
OF THE ESPIONAGE LAWS, TITLE 18, U.S.C., SECTIONS 793 and 794.
THE TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN
ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.**

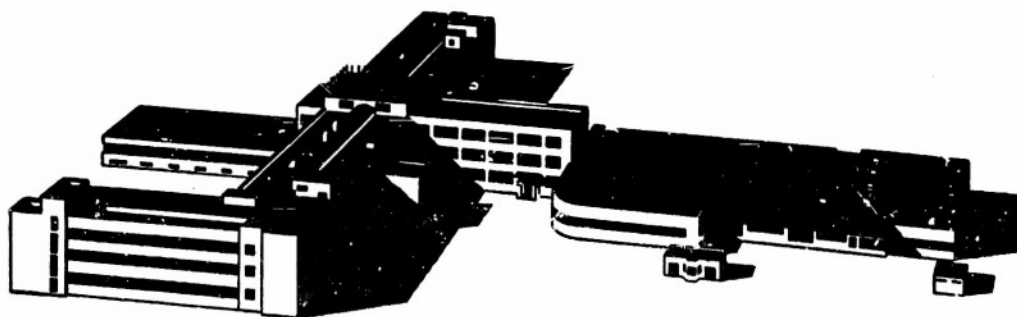
AD No. **40714**
ASTIA FILE COPY

EXTRA COPY

CONFIDENTIAL



RADIO CORPORATION OF AMERICA RCA LABORATORIES DIVISION



DAVID SARNOFF RESEARCH CENTER
PRINCETON, NEW JERSEY

EAUCX23455-34

CONFIDENTIAL

SEVENTEENTH INTERIM REPORT

INFRARED PHOTOCONDUCTORS

N6onr23603

January 15, 1954 - April 15, 1954

Work done by:

E. E. Hahn
A. G. Morris
G. A. Morton
M. L. Schultz

Technical Supervision by:

G. A. Morton

CONFIDENTIAL

54WCL3455-34

CONFIDENTIAL

I. Measurements on Germanium

A. Optical Studies

The crystals described in the following table were investigated during this period:

TABLE I

<u>Crystal</u>	<u>Source</u>	<u>Dope Treatment</u>	<u>Impurity Slope (ev.)</u>
AA207	349A	Au*	.17
AA237	353L	Au-As	.14
AA220	350L	Au-As	.09
AA284	254A	As-Au diffused	
AA301	349A	Au*- annealed	.16
AA280	362L	Cu-Sb	.42
AA202	348L	Au	.06
AA234	353L	Au-As	.13
AA300	348L	Au- annealed	.05

*Possibly impure gold

1. Correlation of Thermal and Optical Activation Energies

The photoconductive response of AA207, AA237 and AA220 was measured at liquid nitrogen temperature. The thermal slopes of these crystals in this temperature range were 0.17 ev, 0.14 ev, and 0.09 ev., respectively. The resistance at liquid nitrogen temperature was 1.8×10^6 ohms, 1.3×10^5 ohms and 3.2×10^4 ohms, respectively, and the crystals were of comparable geometry. All three crystals exhibited identically shaped photoconductive response curves in the region between 5 to 10 microns; consequently the optical activation energy is the same for all three crystals. (The intrinsic peak was 2.5, 2.0, and 0.8 orders, respectively,

CONFIDENTIAL

CONFIDENTIAL

2.

above the peak impurity response; these differences may be due to surface effects and have not been investigated.)

As discussed elsewhere in this report, a crystal similar to AA220, exhibited a larger thermal slope (0.13 ev) after annealing, whereas a crystal having a thermal slope of 0.16 ev showed no change in slope after a similar anneal.

2. Gold Diffused Arsenic-Doped Germanium

As described elsewhere in this report, AA284 was originally an arsenic-doped germanium crystal. After a gold diffusion treatment, the crystal became p-type and the spectral response of the photoconductivity was measured at liquid nitrogen temperature. A response out to 8 microns was measurable and the general shape of the response was similar to a typical 0.18 slope gold-arsenic-doped germanium crystal, although the signal was weak. Thus it would seem feasible to make crystals having response in the region of interest at liquid nitrogen temperatures by the diffusion of gold into arsenic-doped germanium.

3. Effects Due to the 0.05 ev Level of Gold

In accordance with the energy level scheme proposed in earlier reports for gold-doped germanium, it is felt that gold has at least two acceptor levels associated with each gold atom impurity; these levels are thought to be about 0.05 ev and 0.18 ev above the valence band. These levels are postulated as being dependent in the sense that the 0.18 level can only exist when an electron is trapped on the 0.05 ev level belonging to the same gold atom impurity.

CONFIDENTIAL

CONFIDENTIAL

3.

The primary reasons for this model include the fact that the thermal slope of 0.05 ev is consistently found in these laboratories when germanium is carefully doped with high purity gold. This thermal slope is unaffected by annealing operations or different surface treatments. If impure gold or germanium is used, or if arsenic is added to pure gold-doped germanium, the thermal slope increases to about 0.18 ev. Crystals of the latter type have been investigated by groups at other laboratories. With additional arsenic present, one of these groups has demonstrated the existence of a level, believed to be due to gold, at about 0.2 ev below the conduction band. Three levels for a substitutional gold atom impurity in the germanium lattice is not inconceivable since the gold valence differs by three from germanium. Then in pure gold-doped germanium only the shallowest level will initially be thermally filled with electrons on heating from low temperatures giving rise to a 0.05 ev slope. In gold-doped germanium crystals containing sufficient n-type impurities either intentionally added, or already present, or from the gold, these shallowest levels may already be filled by electrons so that the next 0.18 ev level will be thermally filled on heating. And so on.

In order to substantiate this model, it is necessary to show that the 0.05 ev level is due to gold impurity and is a dependent level in the sense discussed above.

If the levels are dependent, then for a 0.18 ev slope crystal the following should obtain. At room temperature both

CONFIDENTIAL

CONFIDENTIAL

4.

the 0.18 ev and 0.05 ev levels are filled with electrons. A single absorption band should exist near the intrinsic corresponding to exciting electrons from the 0.18 ev level to the conduction band. (If the levels are independent, another absorption should exist corresponding to a similar transition for the 0.05 ev level.) On cooling to liquid nitrogen temperatures, only the 0.05 ev levels are filled with electrons and the first absorption described above should disappear. None of these absorptions were found in measurements on AA237 and AA234. The primary reasons are probably the low concentration of these levels and the thermal broadening of the intrinsic edge.

Similar effects might conceivably exhibit a fine structure on the intrinsic photoconduction response. Measurements on AA207 were again unsuccessful probably because the intrinsic photoconduction edge is so naturally broad.

The photoconductive response at liquid helium temperature of crystal AA300 was measured during this period. The results given in Fig. 1 show that there is a definite response beyond the normal range of photoconduction for a typical 0.18 ev thermal slope crystal (shown dotted). The appearance of the curve for AA300 suggests that a large number of the 0.05 ev levels were already filled in the "dark" by the background radiation or by a balancing due to donor impurities allowing holes to be freed from 0.18 ev levels so that the curve appears as a superposition of the response due to two independent levels. It is proposed to measure next the response of a

CONFIDENTIAL

CONFIDENTIAL

5.

gold-indium-doped germanium crystal in which the effect of the indium is to keep electrons off of all gold levels at low temperature.

It is felt that intensity measurements and an analysis of the kinetics of transitions in 6 to 14 micron region for the model described above for gold-doped germanium will have further bearing on the question of the dependency of these levels. Such an analysis is now under discussion among this group.

At liquid nitrogen temperatures, the conductivity of a typical 0.05 ev slope crystal is just beginning to fall into the straight line portion having the 0.05 ev slope in a plot of log conductivity versus inverse temperature. The photoconductivity of AA202 was measured at liquid nitrogen temperature and exhibited response beyond the intrinsic edge to about 2.5 microns. Upon pumping on the liquid nitrogen, with a subsequent lowering of the temperature, the measurements resulted in a flat response out to about 4 microns. This indicates that a 0.05 ev level is too shallow to provide efficient photoconduction at liquid nitrogen temperatures. However, this result plus the general behavior of the 0.18 ev slope crystals would suggest that an efficient photoconductor could be made to work at liquid nitrogen temperatures in the desired 8 to 13 micron region if the proper energy level could be introduced by chemical impurities.

4. Copper-Doped Germanium

The 0.04 ev level due to copper in germanium is well known. The existence of a 0.25 level due to copper has been postulated by BTL from lifetime measurements. In accordance

CONFIDENTIAL

CONFIDENTIAL

6.

with the model outlined for gold impurity above, copper may be expected to have more than one dependent level associated with it. Photoconduction response measurements were made on AA280 in which the antimony has balanced out part of the copper impurity (the 0.04 ev level at least). At liquid nitrogen temperature, this crystal exhibited signal above noise out to 3.5 microns. This threshold is in fair agreement with the 0.4 ev thermal slope of this crystal. It is, therefore, reasonable to suggest that there is a level associated with copper lying somewhere near the middle of the forbidden gap. This is, of course, too deep to be of interest as a detector for the 8 to 13 micron region.

B. Thermal Measurements on Germanium

1. Gold-Doped Germanium

a. Annealed Samples

Germanium crystals doped with high purity gold only have been found to exhibit a low temperature impurity slope of about 0.05 ev while those doped with gold and arsenic have shown slopes ranging between about 0.09 ev and about 0.18 ev. There is a possibility that the 0.05 ev level is due to a foreign impurity (e.g., Cu) rather than to gold since it has not been reported by any other laboratory. For gold-arsenic-doped samples, the photoconductive threshold has always been the same even though the impurity slopes have varied by as much as a factor of two.

CONFIDENTIAL

CONFIDENTIAL

7.

In order to obtain information which might have some bearing upon these two features of the behavior of gold-doped germanium, the effect of annealing has been investigated. Three typical samples:

AA300 - gold only, 0.056 ev slope

AA301 - gold-arsenic, 0.16 ev slope

AA302 - gold-arsenic, 0.10 ev slope

were annealed for 48 hours at 500°C in an argon atmosphere. After annealing, the samples were mounted and measured in the Collins Cryostat. The gold-only-doped sample showed essentially no change upon annealing. This is illustrated in Fig. 2 in which the log conductivity versus $1/T$ curves for the annealed and a similar unannealed sample almost exactly superimpose throughout. This behavior definitely rules out the possibility that the 0.05 ev slope is due to the presence of copper since such an annealing treatment on a copper-doped sample would reduce the effective copper concentration to about 10^{13} cm^{-3} .

Sample AA301 showed no change of slope upon annealing but did show an increase of conductivity at low temperatures by a factor of about 1.7. This may be due to an increase of mobility as a result of decreasing the concentration of lattice imperfections by annealing. Curves for the annealed and unannealed samples are illustrated in Fig. 3. The slightly higher conductivity of the annealed gold-only sample at low temperatures may also represent an effect of annealing upon the mobility.

CONFIDENTIAL

Sample AA302, in the intermediate temperature range, underwent an increase in slope from 0.10 to 0.13 ev as a result of annealing. This is shown in Fig. 4. This result suggests that, in some manner or other, the abnormally small thermal activation energy observed for some gold-arsenic-doped samples is associated with some type of lattice imperfection which may be removed more or less completely by annealing. It might be expected that still longer annealing times would result in a further increase of the thermal slope until it reached the optical activation energy. The tailing off, at low temperatures, of the conductivity curves, both for the annealed and for the unannealed sample, is difficult to interpret. It is probably associated with a small residual concentration of accidental impurity since, in a given crystal, it becomes more prominent as one proceeds toward the bottom of the crystal.

b. Diffused Samples

The ease with which copper can be introduced into germanium by diffusion suggests the possibility that gold might similarly diffuse rapidly into germanium. If this is the case, diffusion might provide a convenient, easily controlled method of preparing samples of partially compensated gold-doped germanium for use as infrared photoconductors.

Two exploratory experiments have been performed. In one, gold was diffused into a bar of 10 ohm cm arsenic-doped germanium (AA284) and in the other, gold was diffused into a bar of 40 ohm cm p-type undoped germanium (AA299). A thin

CONFIDENTIAL

9.

layer of gold was deposited on the surfaces of the freshly etched bars by immersion in a dilute solution of gold chloride. Diffusion was carried out in an argon atmosphere at 750°C for 3-1/4 hours.

After diffusion, AA284 was 15 ohm cm p-type and AA299 was 10 ohm cm p-type. Measurement of the temperature dependence of conductivity of AA284 gave a curve which had a slope of 0.15 ev down to about 140°K and one of 0.10 ev between 140°K and 90°K. The measurements were not carried below this latter temperature. The sample was then remounted to permit spectral response measurements, the results of which are discussed elsewhere in this report.

When the spectral response measurements were completed, the sample was unmounted and given several etch treatments. After each, the conductivity type was determined by means of a thermal probe. During the course of this treatment, a transition from p- to n-type conductivity was observed. Under the conditions of the diffusion experiment, the gold penetrated only part way into the interior of the bar. A rough value of the diffusion constant of gold in germanium at 750°C may be computed from the depth of the p-n junction below the original surface, the arsenic concentration in the original sample, the diffusion time and from an estimate of the surface concentration of gold. The value so obtained is about $2 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$.

Since the distribution of gold in the two samples prepared by diffusion is non-uniform, no quantitative significance can be attached to their detailed behavior. However, some conclusions may be drawn from a qualitative comparison of the

CONFIDENTIAL

behavior of the two samples. The ratio of the room temperature conductance to that at liquid nitrogen temperature was 4×10^4 for AA284 (gold-arsenic) and 7.2 for AA299 (gold-only). There appears to be a significant difference in the behavior of the partially compensated sample as compared with the uncompensated sample. This difference is similar to that which has been found for grown gold-doped crystals. These results are, therefore, consistent with the hypothesis that the 0.05 ev level found for uncompensated gold-doped germanium is due to gold and not to some foreign impurity. Further work on the diffusion of gold into germanium is planned.

2. Copper-Arsenic-Doped Germanium

The study of copper-antimony-doped germanium described in the Sixteenth Interim Report indicated some distinct differences between this material and copper-only doped germanium. These differences were such as to indicate the possible existence of levels due to copper in addition to the well known level at 0.045 ev. In order to investigate further the possible multi-valent behavior of copper as an impurity in germanium, the copper-arsenic-germanium system was studied during this period. A summary of all of the samples measured in this investigation is presented in Table I. Some typical curves of log conductivity versus $1/T$ are given in Fig. 5.

CONFIDENTIAL

11.

TABLE I
Copper-Doped Germanium

Cell	Impurity	Conductivity Type	ρ_{300}°	$\frac{\rho_{77}^{\circ}}{\rho_{300}^{\circ}}$	Impurity Slope	$\frac{\Delta I}{V}$ at 4°K *
AA277	Cu-As Diffused	p	38.6 ohm cm	6.4	0.052 ev	5.5×10^{-5} μ A/volt
AA287	Cu-Sb	p	5.9	17.7	0.062 0.045	3.1×10^{-5}
AA291	Cu	p	1.57	0.28	0.045	1.1×10^{-1}
AA294	Cu-As	p	4.60	0.43	0.051 0.047	2.5×10^{-3}
AA295	Cu-As	p	6.00	0.95	0.056 0.045	8.4×10^{-4}
AA296	Cu-As	p	2.4	0.96	---	---
AA297	Cu-As	p	1.31	0.81	0.058 0.044	1.5×10^{-3}
AA304	Cu-As Annealed 1.5 hr.	p	7.0	2.8	0.057 0.047	2.7×10^{-4}
AA305	Cu-As Annealed 3.0 hr.	p	4.1	2.2	0.056	7.8×10^{-4}
AA306	Cu-As Annealed 6.0 hr.	p	11.9	19.5	0.059	6.3×10^{-5}
AA307	Cu-As Annealed 12.0 hr.	p	3.7	2.2	0.059 0.049	6.9×10^{-4}
AA313	Cu-As Annealed 28.5 hr.	p	7.2	63.1	0.081	9.1×10^{-5}
AA314	Cu-As Annealed 57.5 hr.	n	2.5	0.46	0.014	1.2×10^{-2}

*Response to room temperature radiation.

CONFIDENTIAL

a. Grown Crystal

Several samples were cut from crystal 363L which contained a copper-only section and two copper-arsenic sections containing different concentrations of arsenic. The entire crystal was p-type.

AA291, cut from the copper-only section had a resistivity of 1.6 ohm cm and an impurity slope of 0.045 ev. There was no detectable deviation from this slope over the entire range of the exponential portion of the curve. The behavior of this sample is typical of copper-doped germanium.

The behavior of the samples AA294-AA297 cut from the double-doped sections of the crystal differs significantly from that of the sample from the copper-only doped section in several ways. (1) The room temperature resistivity is increased (except for AA297). (2) The maximum conductivity occurs at a higher temperature for the compensated samples. A convenient index, from the point of view of the possible utilization of such materials as impurity photoconductors at liquid nitrogen temperature, of the behavior of the samples in and near the impurity saturation range, is the ratio of the resistivity at liquid nitrogen temperature to that at room temperature. This ratio is considerably larger for the double-doped samples than for the copper-only doped sample. From conductivity measurements alone, it is impossible to decide how much of this difference is due to a change in mobility as a result of the presence of the compensating impurity and how much is due to a difference

in the temperature at which carriers begin to condense out on impurities. (3) In the impurity range, the double-doped samples show two distinct regions in which the impurity slopes are slightly different. Above about 40°K , the average value of the slope is 0.055 ev, while below this temperature it is 0.045 ev. This latter value agrees with that found for copper-only doped samples. The significance of the double slope is not at present understood. (4) The magnitude of the impurity photoconductivity of the double-doped samples at 4°K is about two orders of magnitude less than that of the copper-only doped sample. This difference probably depends upon two factors; a difference in the net impurity concentration and a difference in mobility for the two types of samples.

b. Annealed Samples

The resistivities and the details of the log conductivity versus $1/T$ curves for the double-doped samples from crystal 363L indicate that the compensation of copper by arsenic is far from complete. It is known from published results that the effective concentration of copper in germanium can be reduced by annealing at temperatures in the neighborhood of 500°C . If this is so, controlled annealing of copper-rich copper-arsenic-doped germanium should permit a close approach to complete compensation. Prolonged annealing should lead to overcompensation and conversion to n-type conductivity.

Seven bars were cut from a single wafer which had been sliced from crystal 363L. One of these, AA296, was mounted and

CONFIDENTIAL

14.

tested without any further treatment. The remaining six, AA304 - AA307, AA313 and AA314, were annealed at 500°C in an argon atmosphere for times ranging from 1.5 to 57.5 hours. After annealing, the bars were etched, tested for conductivity type with a thermal probe and then mounted for conductivity measurements. The sample, AA314, annealed for the longest time was n-type with an impurity slope of 0.014 ev which is characteristic of arsenic. All others were p-type.

Annealing produced a considerable increase in the room temperature resistivity of the p-type samples. However, no correlation between the annealing time and the final resistivity was found. The general features of the conductivity curves of the unannealed samples and of the p-type annealed samples are similar. Both show double slopes in the impurity range. The ratio, ρ_{77}/ρ_{300} , is considerably larger, however, for the annealed than for the unannealed samples. In two cases, AA306 and AA313, the value of the ratio is large enough so that there is some hope of finding useful photoconductive sensitivity at liquid nitrogen temperature. This is currently being investigated. The photoconductive response of the annealed samples at 4°K is about one order of magnitude smaller than that of the unannealed samples.

It is of interest to note that the copper-antimony doped sample, AA287, discussed in the Sixteenth Interim Report (see Fig. 3 of that report) exhibits a behavior very much like that of the copper-arsenic-doped samples being discussed here. This similarity lends weight to the supposition that the features

CONFIDENTIAL

of behavior mentioned above are really characteristic of p-type compensated copper-doped samples.

c. Diffused Sample

The diffusion of copper into germanium proceeds rapidly at moderate temperatures. Since values of the diffusion constant and of the solubility of copper in germanium have been reported in the literature, it should be possible by appropriate choice of time and temperature of diffusion to produce a desired copper concentration. If copper is diffused into germanium containing a known concentration of n-type impurity, any desired degree of compensation should be attainable.

One experiment of this type has been performed. A bar cut from 10 ohm cm n-type arsenic-doped germanium was coated with copper by immersion in a dilute CuSO_4 solution. This copper was diffused into the bar by heating at 625°C for about five hours in an argon atmosphere. The germanium was converted to p-type by this treatment. After mounting, the conductivity was determined over the range from room temperature to about 30°K . At room temperature, the sample was in the intrinsic range and had a resistivity of about 39 ohm cm. Evidently the sample is almost exactly compensated. The impurity slope at low temperatures was found to be 0.052 ev. The behavior of this sample appears to be intermediate between that of copper-doped germanium and of the grown copper-arsenic-doped material. Although the impurity range exhibits only a single slope, the magnitude of this slope is somewhat larger than that characteristic of copper only.

CONFIDENTIAL

16.

The photoconductive response at 4°K was small as would be expected for a sample with a very small net impurity concentration.

d. High Temperature Behavior

Most of the previous discussion concerning compensated copper-doped samples has dealt with their low temperature behavior. There is one feature of their behavior in the neighborhood of room temperature which may be of significance. In Fig. 6 are plotted the high temperature portions of the conductivity curves for a number of copper-doped germanium samples. Consider first the curve for AA175. This is a sample of copper-only-doped germanium ($\rho_{300} = 5.5$ ohm cm) obtained from an earlier crystal, which has been measured over the temperature range up to 410°K. Above 350°K, this sample is in the intrinsic range. Upon leaving the intrinsic range, the conductivity quickly passes through a minimum and begins to rise due to increasing mobility. This behavior is to be compared with that depicted for AA306 which is a compensated copper-arsenic-doped sample. AA306 does not become intrinsic until 385°K. However, upon leaving the intrinsic range, the slope of the curve decreases very gradually and the minimum is reached only at a very much lower temperature than that for AA175. The difference in behavior between these two samples must, of course, mean that the temperature dependence of mobility and/or the temperature dependence of carrier concentration must be different. Independent determinations of the mobility or carrier concentration as functions of temperature are required in order to decide between these two possibilities.

CONFIDENTIAL

CONFIDENTIAL

17.

If it be assumed that the temperature coefficient of mobility is not very different for the two samples, then the conclusion may be reached that, as AA306 is cooled, carriers begin to condense out even well above room temperature. This may possibly be taken as evidence for the existence of a deep lying level. AA313 (Ge:Cu-As) and AA287 (Ge:Cu-Sb) appear to behave in a similar fashion although, in these cases, the measurements have not been carried above room temperature. In fact, AA287 is a more extreme example of this effect. AA277, the diffused copper-arsenic sample, appears to be intermediate in behavior between the two types.

C. Preparation of Materials

1. Germanium Crystals

363L - 11 g of Ge from T519 plus 12.1 mg of Johnson and Matthey copper. After about 2.5 g of crystal had been drawn, 60.1 mg of heavily arsenic-doped germanium from T322N were added. When 2.4 g more of crystal had been grown, 104.5 mg of T322N were added. Then growth of the crystal was completed.

364L - 8.9 g of Ge from HF147 and 1.0438 of Johnson and Matthey indium. The entire crystal was grown without any further impurity additions. This crystal was grown to provide material to be used in doping other crystals with indium. Its appearance suggested that it was not a single crystal.

365L - 11.9 g of 45 ohm cm Ge plus 43 mg of Johnson and Matthey gold (Laboratory No. 3226). After about 2.5 g of crystal had been drawn, 0.667 g of 364L (Ge:In) were added.

CONFIDENTIAL

CONFIDENTIAL

18.

After about 3.8 g more of the crystal had been drawn, 0.638 g of 364L (Ge:In) was added and the remainder of the crystal was grown. This crystal was grown in order to provide gold-doped germanium in which there occurred no compensation of gold by accidental n-type impurities.

366L - 14.8 g of 45 ohm cm Ge plus 39 mg of Johnson and Matthey gold (Laboratory No. 3226). About 2.5 g of crystal were then drawn. The remainder of the crystal was drawn in four sections. Prior to the growth of each section, material from 364L (Ge:In) was added. The amounts added were 2.6, 3.1, 4.8, and 7.1 mg. This crystal was grown to contain smaller concentrations of indium relative to gold than did 365L since that crystal was found to have a large excess of indium.

2. Diffusion of Volatile Impurities into Germanium

Preparations are being made to attempt to introduce volatile impurities such as S, Se, Te, Cl, Br, I, Cd and Hg into germanium by diffusion. Preparation of crystals doped with such impurities by growth from the melt would be difficult since the volatilities of such impurity elements are so great. Impurities such as these are of interest since they ought to exhibit multivalent behavior similar to that which is believed to exist for gold in germanium. The diffusion will be carried out in evacuated closed systems in which the impurities will be introduced by way of the vapor phase.

CONFIDENTIAL

II. Use of an Integrating Sphere with Cells of Low Absorption

In order to increase the photoconductive signal of a gold-arsenic-doped germanium crystal working at liquid nitrogen temperature, the effect of an "integrating sphere" in the form of a polished copper cylinder surrounding the crystal was investigated. In the impurity region of the response the signal is small because of the small absorption of the gold impurities, being present to a concentration less than about 10^{15} cm^{-3} . The purpose of the shield is to essentially trap the radiation and cause it to pass several times through the crystal.

The action of the "integrating sphere" can be shown, in rough approximation, as follows.

Let L_0 be the infrared flux entering the slit of the "sphere". If the walls are perfectly reflecting, radiation can only be lost by absorption in the cell element and by escape through the entrance slit.

Assume that the cell element is in the form of a long rectangular parallelepiped of

length l

width w

If the absorption is small, it can be assumed to be proportional to the width with a constant of proportionality α . The absorption is also proportional to the area of the element (since the radiation density in the sphere is essentially uniform).

Furthermore, if the slit length and width are l_s and

CONFIDENTIAL

20.

w_s , respectively, the following relation must obtain:

$$L_o = \rho l_s w_s + \rho 4(lw)(w\alpha)$$

(slit loss) (cell abs.)

where ρ is the radiation density in the "sphere".

The radiation L absorbed by the cell is, therefore,

$$L = L_o \frac{4\alpha lw^2}{l_s w_s + 4\alpha lw^2} .$$

The signal from the cell will be proportional to the responsiveness of the cell q , the voltage applied to it and to the absorbed radiation L .

Thus:

$$S = L_o \frac{Vq}{l^2} \frac{4\alpha lw^2}{l_s w_s + 4\alpha lw^2}$$

On the other hand, the noise is given by:

$$N = \frac{Vk}{l^2} \sqrt{w^2 l}$$

(Note: This involves assumptions which may not be correct in all cases.)

Therefore, the signal to noise ratio R_a is given by:

$$R_a = \frac{L_o q}{k} \frac{4\alpha (w^2 l)^{1/2}}{l_s w_s + 4\alpha w^2 l}$$

Optimizing with respect to cell volume by:

$$\frac{dR_a}{d(lw^2)} = 0 ,$$

it follows that:

$$w = \sqrt{\frac{l_s w_s}{4\alpha l}} .$$

CONFIDENTIAL

Considering the following example:

$$\alpha = 0.1/\text{cm}$$

$$l = 0.75 \text{ cm}$$

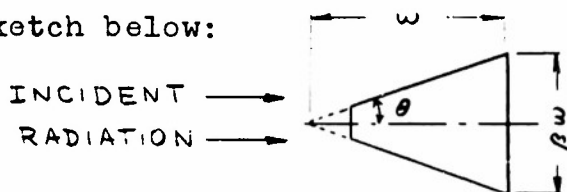
$$l_s = 0.5 \text{ cm}$$

$$w_s = 0.1 \text{ cm}$$

$$w = \sqrt{\frac{.5 \times .1}{4 \times .1 \times .75}} = 0.40 \text{ cm}$$

The advantage gained by the "integrating sphere" can be estimated as follows.

Assume that the detector cell has the shape indicated in the sketch below:



The angle θ is chosen to be the critical angle for the cell material. For germanium, this is about 14° and therefore $\beta = 0.5$. The length of the cell is l_s and the width of the truncated section w_s (small compared to the other dimensions, so that little error is made in assuming the cell triangular in cross-section).

The signal-to-noise ratio for this cell will be

$$R_b = \frac{L q \alpha w}{k \sqrt{\beta w^2 l_s}} = \frac{L q \alpha}{k} \sqrt{\frac{2}{\beta l_s}}$$

The optimum signal-to-noise ratio with the "sphere" is

$$R_a = \frac{L q}{k} \sqrt{\frac{\alpha}{w_s l_s}}$$

CONFIDENTIAL

22.

and

$$\frac{R_a}{R_b} = \sqrt{\frac{\beta}{2\alpha w_s}}$$

For the example above $\frac{R_a}{R_b} \cong 5$.

The response of AA207 at liquid nitrogen temperature was measured with and without the copper cylinder. The results were not very gratifying and a more suitable type of shield was constructed having a port that closely matches the shape of the incoming beam. Measurements were then made of the response of AA301 at liquid nitrogen temperature, first with the shield polished and then with the shield blackened with lamp black. A 6 db increase in signal was found in the impurity region whereas the response in the intrinsic region remained unaltered.

It is believed that still better effectiveness of an "integrating sphere" can be achieved with different positioning of the crystal.

CONFIDENTIAL

III. Measurements on Other Materials

A. Cadmium Chalcogenides

During this period, three samples, one each of CdS, CdSe and CdTe all containing added iodine impurity, were obtained from another group. The conductance of these samples was measured over the range from room temperature to liquid helium temperature. The results are presented in Fig. 7. (Note the change in scale for $1/T$ at 0.05.) Also included in this figure is a previously determined curve for a sample of CdS doped with chlorine. The curves for CdS and CdSe are similar. The magnitudes of the impurity slopes depend both upon the identity of the added impurity and upon the identity of the anion of the host lattice. The slope for CdS(Cl) is 0.038 ev and for CdS(I) is 0.024 ev. That for CdSe(I) is 0.051 ev. From this dependence of impurity slope upon the identity of the impurity and of the anion, it may be predicted that CdSe(Cl) should have an impurity slope of about 0.08 ev. Such material should show photoconductivity in the 8-13 micron band. Its resistivity at liquid nitrogen temperature might be high enough to permit easy detection of such response at this temperature. If samples of such material can be obtained, they will be investigated.

Impurity photoconductivity at liquid helium temperature has been observed both for cadmium sulfide and for cadmium selenide. The magnitudes are: CdS(Cl), 6.7×10^{-2} $\mu\text{A/volt}$; CdS(I), 1.6×10^{-1} $\mu\text{A/volt}$; and CdSe(I), 1.2×10^{-3} $\mu\text{A/volt}$.

CONFIDENTIAL

24.

The sample of CdTe(I) measured showed almost no change of conductance with temperature. Apparently, the impurity concentration in this sample is very high. No long wavelength photoconductivity was observed.

B. Gallium Antimonide

Two polycrystalline samples of gallium antimonide, one p-type with a room temperature resistivity of 0.43 ohm cm and the other n-type with a resistivity of 0.03 ohm cm, were obtained from another group during this period. Gallium antimonide is of interest since it is reported to have an intrinsic gap of approximately the same width as does germanium. The comparison of activation energies of impurities in gallium antimonide with those in germanium might provide a basis for the preparation of a photoconductor with a response which more nearly matches the 8-13 micron atmospheric window than does compensated gold-doped germanium.

The conductivity of the n-type sample was measured between room temperature and 60°K. At some temperature below this point, the resistance suddenly increased by at least an order of magnitude and the sample became non-ohmic. When the sample was subsequently warmed to room temperature, its resistance was much higher than it was originally. It is probable that this behavior was due to the development of a crack, either at one of the contacts or within the bulk of the sample, upon cooling. The data obtained for this sample are summarized in Fig. 8. Near room temperature, the slope of the curve passes

CONFIDENTIAL

CONFIDENTIAL

25.

through a minimum. At somewhat lower temperatures, the slope becomes constant at 0.028 ev and finally it begins to decrease. The behavior near room temperature may represent the effect of the change of carrier mobility with temperature. Above room temperature, the curve should approach the intrinsic range. If the change of conductivity with temperature at lower temperatures is the result of the change of carrier concentration rather than of mobility, and if the impurity responsible for this behavior is analogous to a Group V impurity in germanium, then it might be concluded that the activation energy of an impurity in gallium antimonide is about two or three times larger than that of the corresponding impurity in germanium.

The p-type sample was measured over the temperature range from 435°K to 4°K. The results are plotted in Fig. 9. The behavior in the high temperature region is similar to that found for the n-type sample. At the highest temperatures the sample appears to be approaching the intrinsic range. Below room temperature, the change of conductivity with temperature is gradual. Between room temperature and about 80°K, the conductivity decreases by only a factor of about 2.5. This small change cannot, with certainty, be ascribed to a decrease in carrier concentration. Therefore, the slope of the curve cannot, with any certainty, be taken as a measure of an impurity activation energy. Below 80°K, the conductivity changes by even a smaller factor. It first decreases slightly and then rises somewhat. These changes, almost certainly, are due to mobility changes.

CONFIDENTIAL

CONFIDENTIAL

26.

No impurity photoconductivity was observed for either sample. This is not surprising since the residual conductivity at low temperatures is so large. These samples are much too impure to permit the statement of any clear-cut conclusions relative to impurity activation energies from the present measurements.

CONFIDENTIAL

IV. Equipment

A. Collins Cryostat

During one of the runs of this period requiring the withdrawal of liquid helium from the Collins, the transfer tube froze closed so that no liquid helium was drawn off. Subsequent repair work entailed shortening the transfer tube a few inches; successful transfers were obtained thereafter.

A 15-liter capacity liquid helium storage dewar was ordered and received during this period. The techniques of the transfer and storage of liquid helium was discussed with the low temperature group at Rutgers University. The 15-liter dewar can be filled conveniently in one day's running and then will provide sufficient liquid helium for up to 4 or 5 runs in ordinary dewar equipment. The running time of the Collins will be lessened for the same number of runs in external dewars. The design of the transfer tubing for transferring liquid helium from the Collins to the storage vessel and from the storage vessel to a dewar as well as liquid helium level indicators for the Collins and the storage vessel were begun. Tests of the efficiency of the storage container await construction of the transfer equipment.

B. Leiss Monochromator System

Several minor additions and alterations were made to the Leiss monochromator infrared system. These included a variable position dewar holder for transmission measurements with the small metal liquid nitrogen dewars, an additional

CONFIDENTIAL

28.

step attenuator in the amplifier, and a humidity meter in the thermocouple unit.

A new thermocouple was received and installed during this period to replace the one we had been using since it had opened contact and ceased operating.

C. Dewar Sample Holders

Crystal AA220 was mounted in one of the small liquid nitrogen dewars and the unit was then given to B. Chasnov of Ft. Belvoir for experimental purposes. This was the dewar returned by H. Levinstein at Syracuse University.

A new envelope was made for the small liquid nitrogen dewar in our possession which will permit transmission measurements to be made with the Leiss monochromator system.

Some time was spent in designing a permanently evacuated dewar, similar to the three small metal demountable liquid dewars already built, for holding a gold-arsenic-doped germanium crystal at liquid nitrogen temperatures. These units will be for experimental tests by groups at other laboratories of the effectiveness of this material as an infrared detector in the region of interest as specified by the contract. The final design of these units awaits a determination of the most effective way to mount the crystal so as to utilize photoconductively as much of the incident radiation as possible.

D. Miscellaneous

Seven germanium cells were sent to A. J. Cussen at NOL, Corona, California, for his evaluation of these units as

CONFIDENTIAL

CONFIDENTIAL

29.

possible substandards for absolute radiation measurements. The germanium crystals are photoconductive at room temperature in the intrinsic region and are enclosed in an evacuated glass envelope with a plane glass window.

CONFIDENTIAL

CONFIDENTIAL

30.

V. Miscellaneous Optical Measurements

The transmission of a typical Nesa coating was measured out to 14 microns and averaged 60 to 70% transmission between 5 to 14 microns. The percentage reflection was not known.

The transmission of a CdS crystal was determined to be approximately 45% from the visible red to 13 microns. Attempts to measure the photoresponse of a CdS crystal at liquid nitrogen temperature were unsuccessful due to faulty electrical contacts to the crystal.

eb

7/20/54

CONFIDENTIAL

CONFIDENTIAL

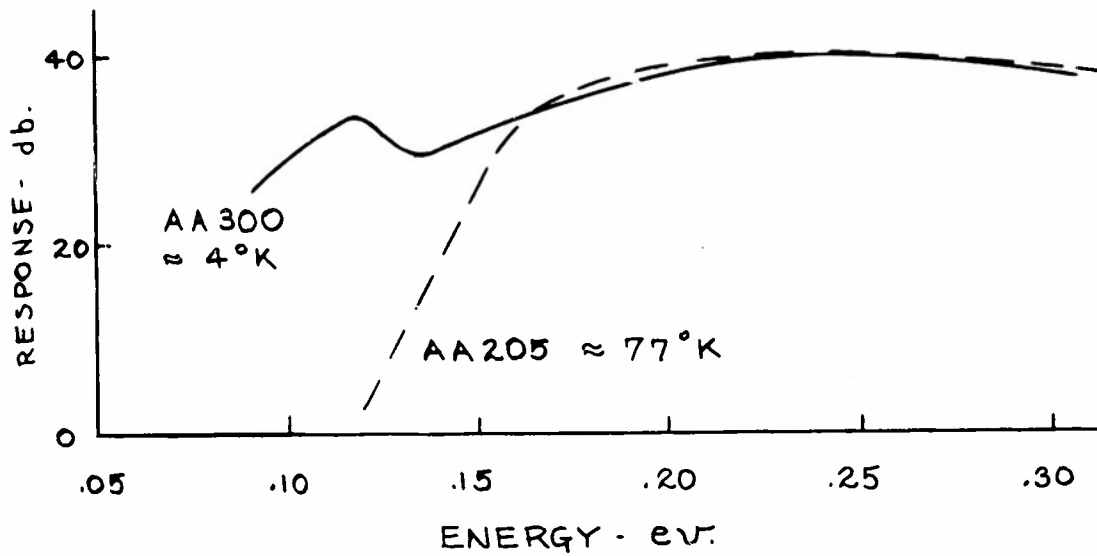
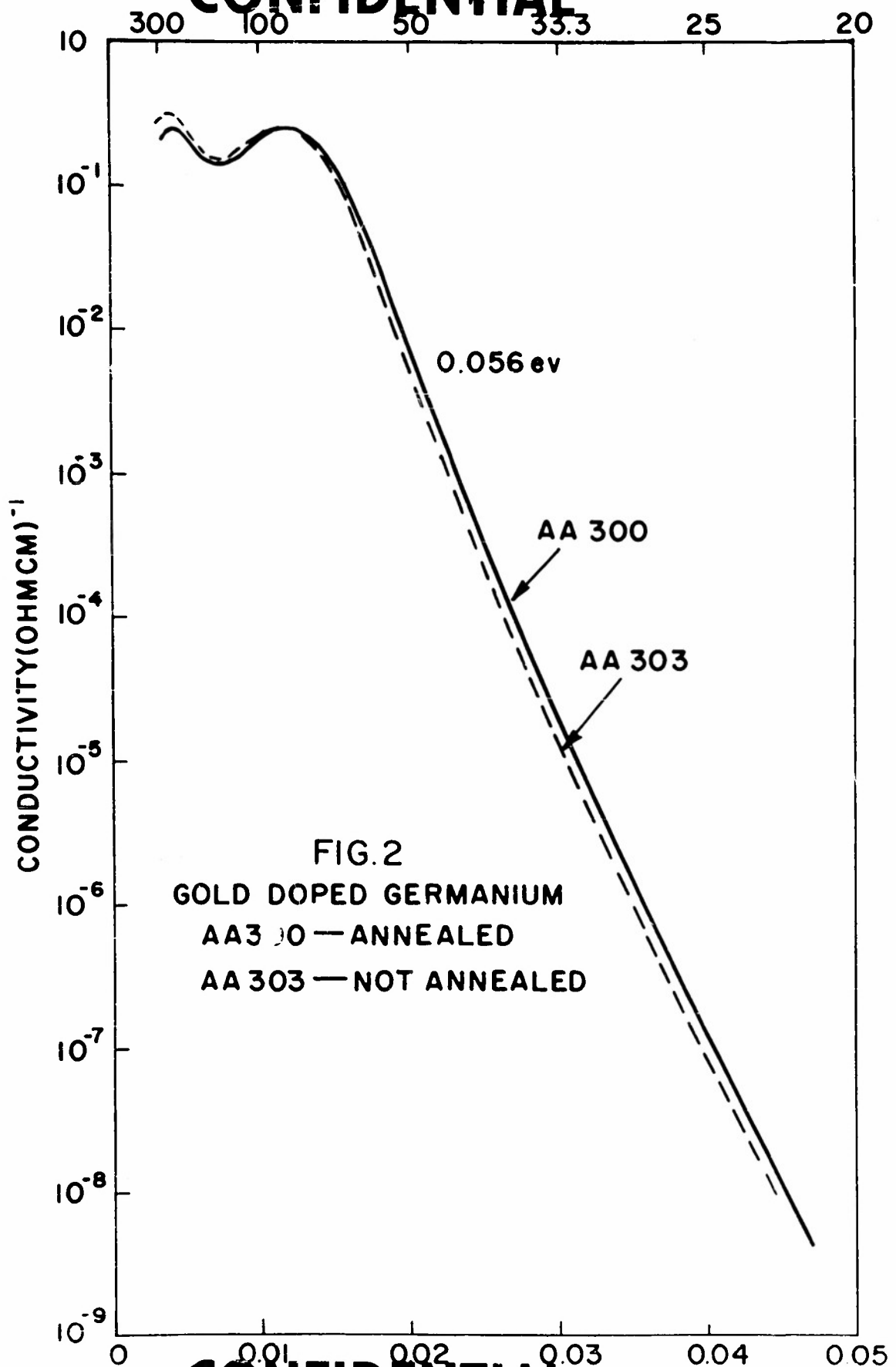


FIG. 1

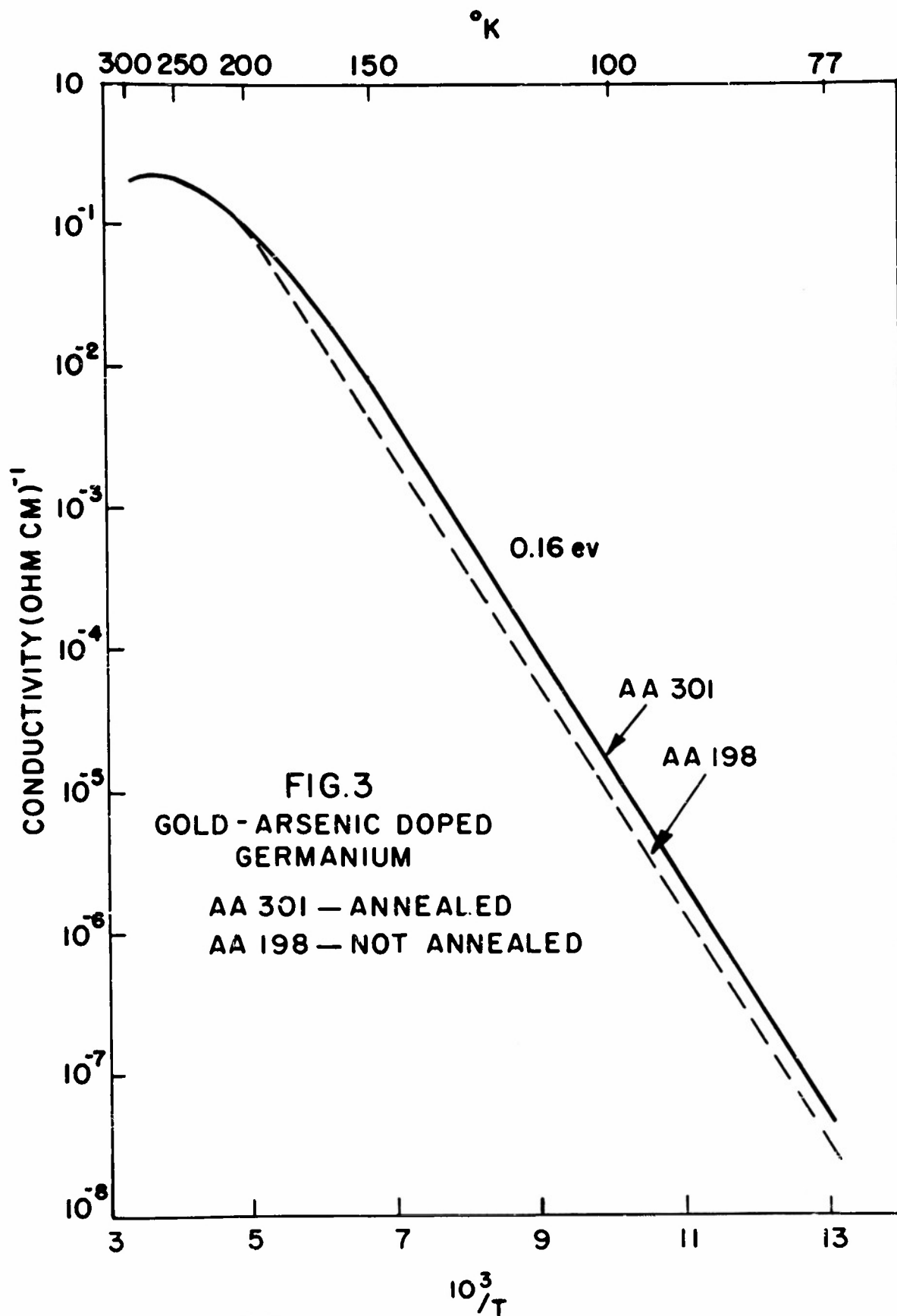
CONFIDENTIAL

CONFIDENTIAL



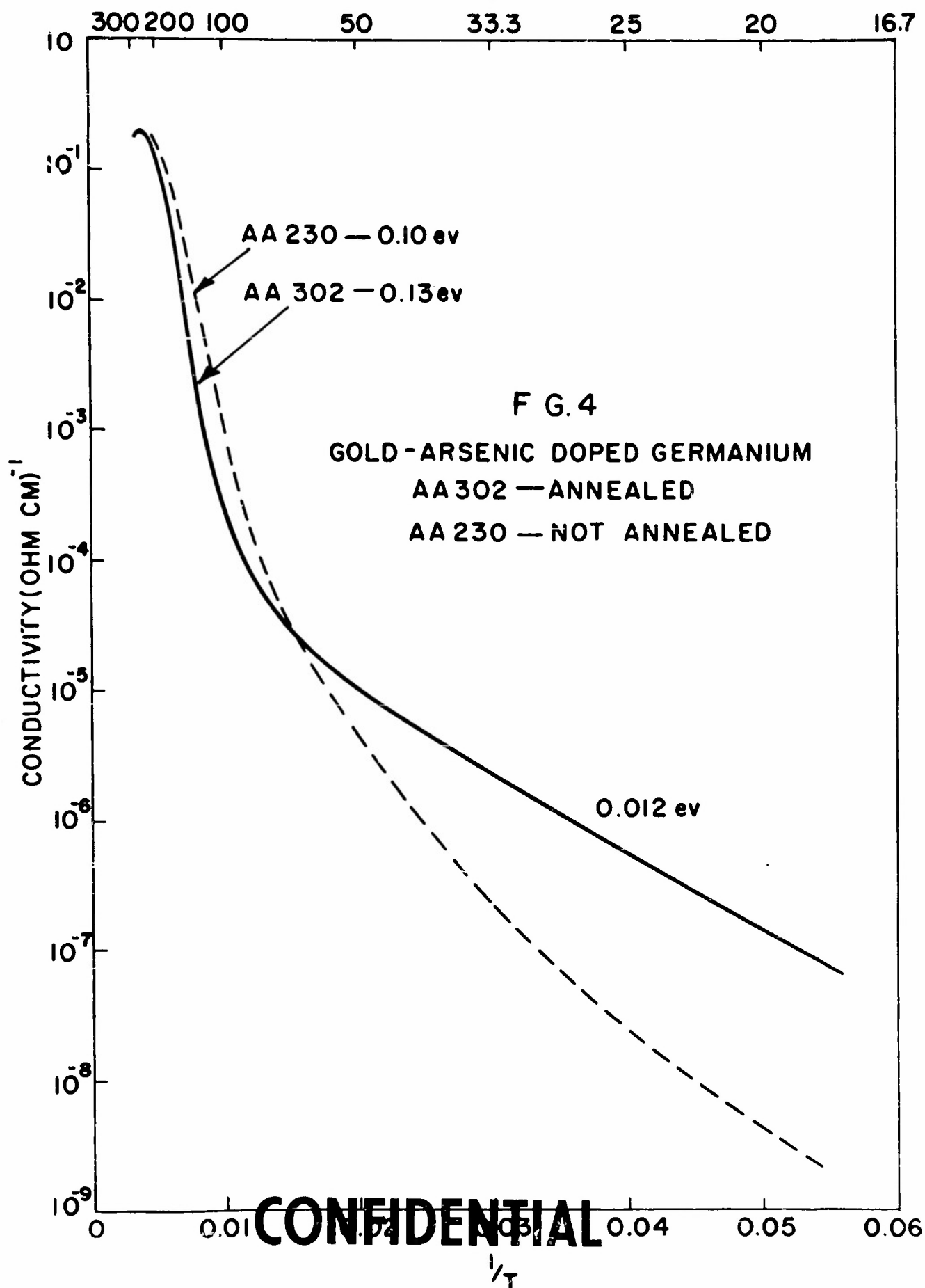
CONFIDENTIAL

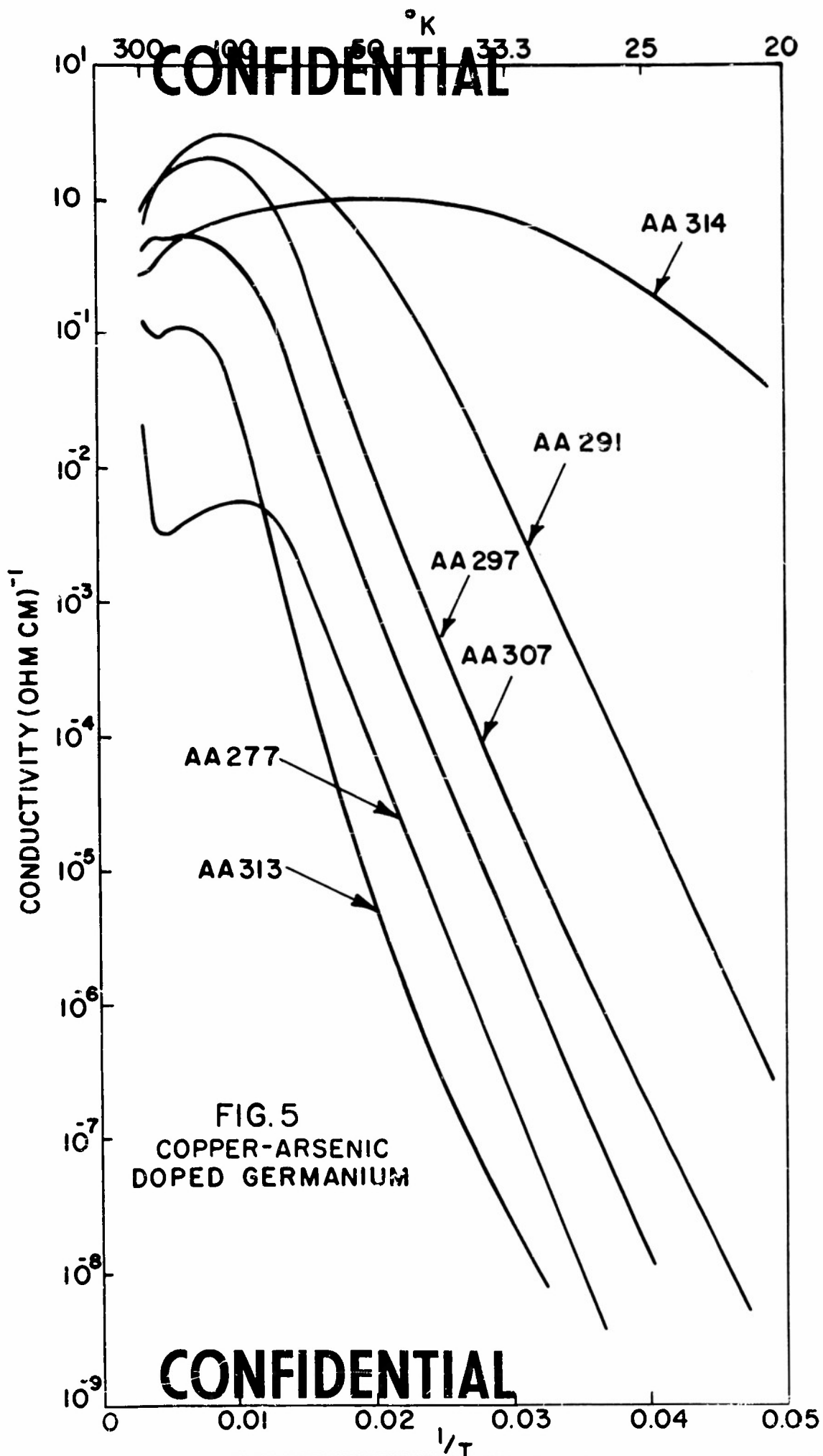
CONFIDENTIAL



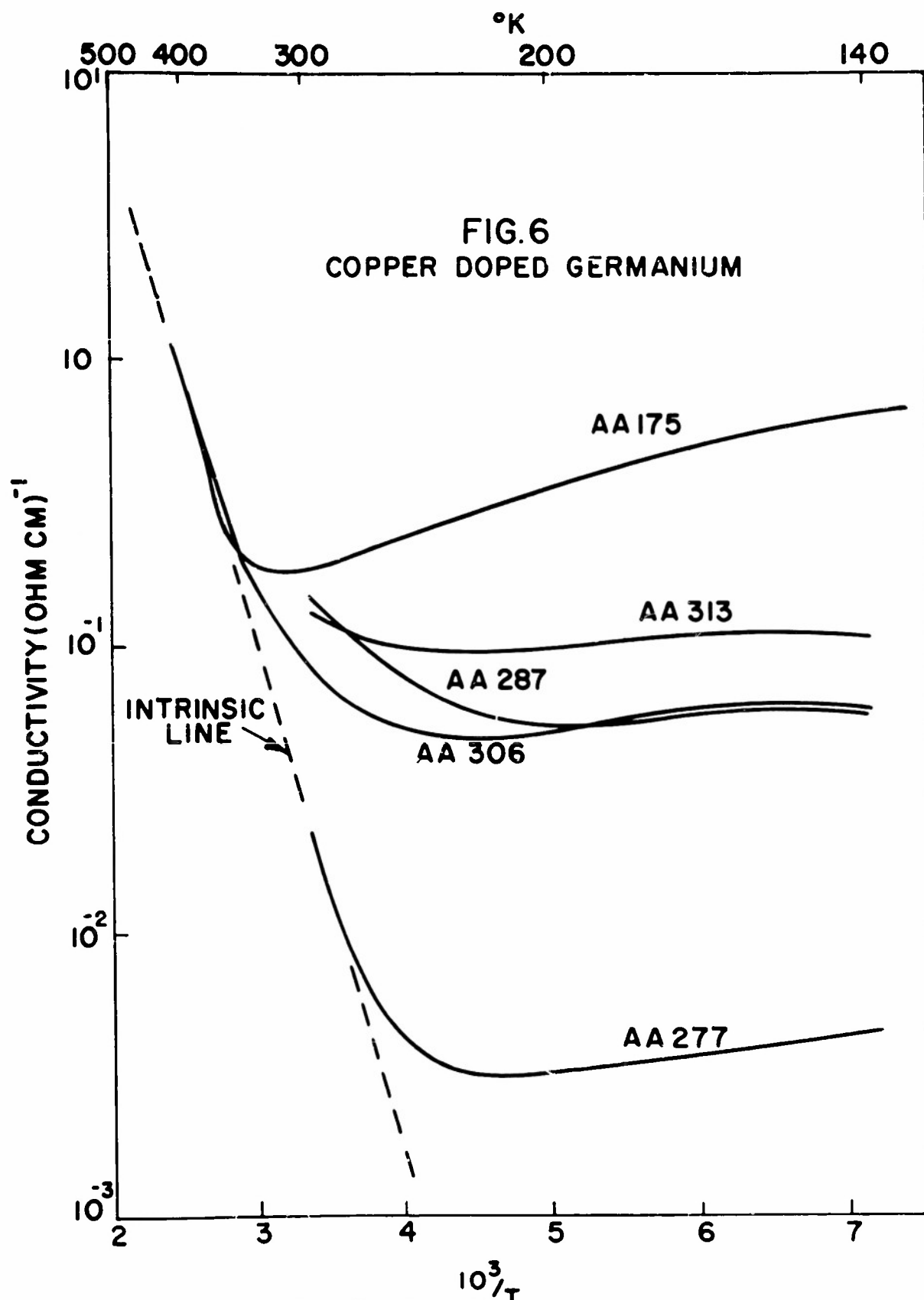
CONFIDENTIAL

CONFIDENTIAL



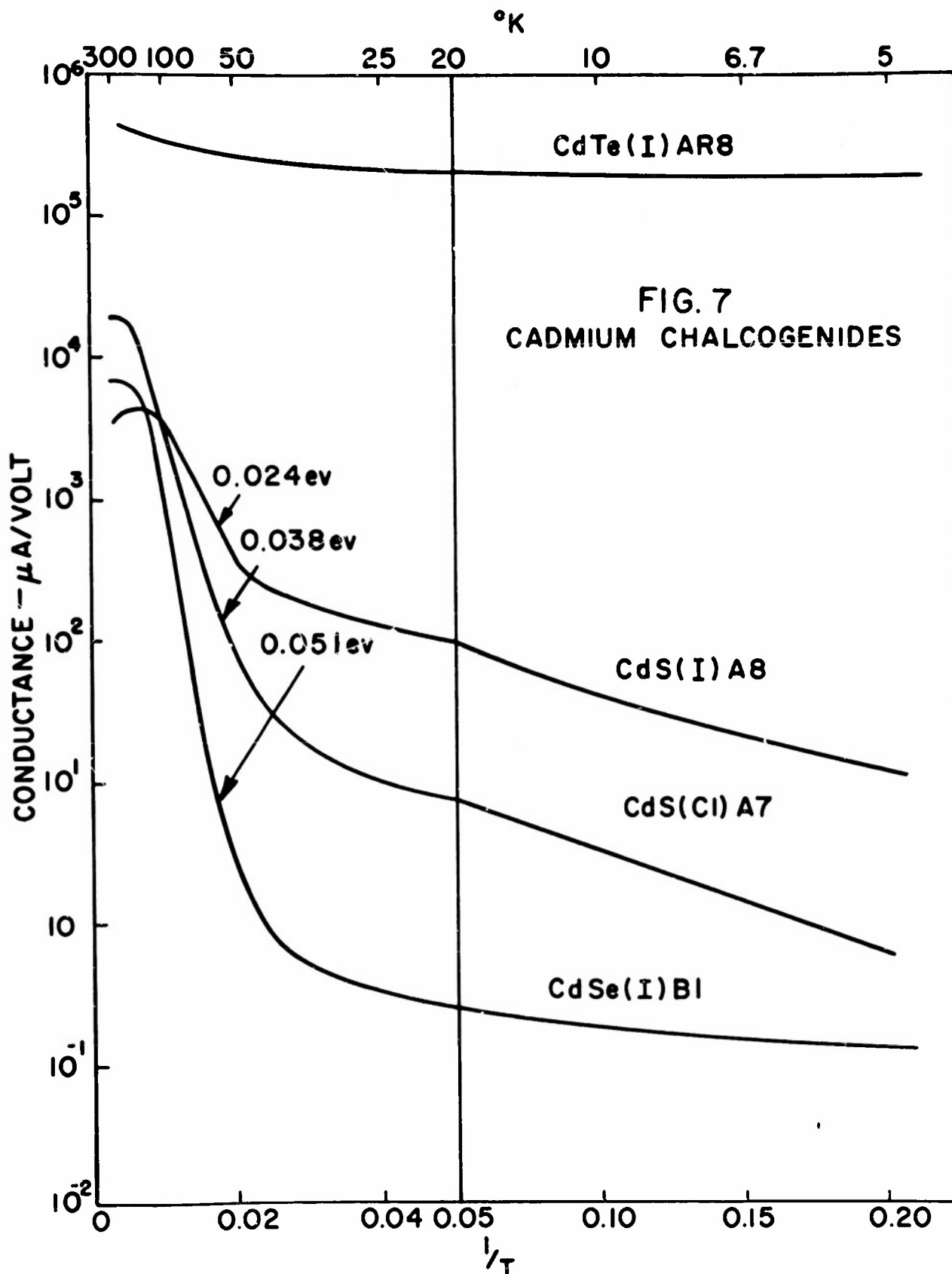


CONFIDENTIAL



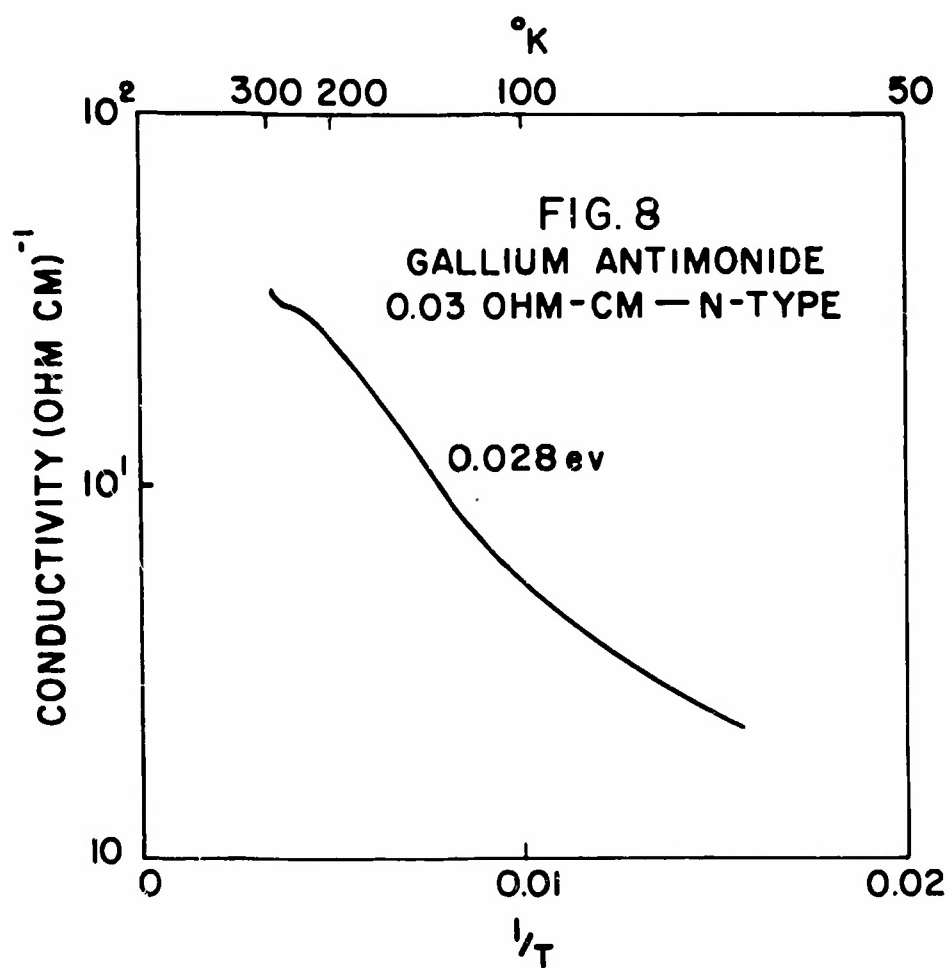
CONFIDENTIAL

CONFIDENTIAL



CONFIDENTIAL

CONFIDENTIAL



CONFIDENTIAL

CONFIDENTIAL

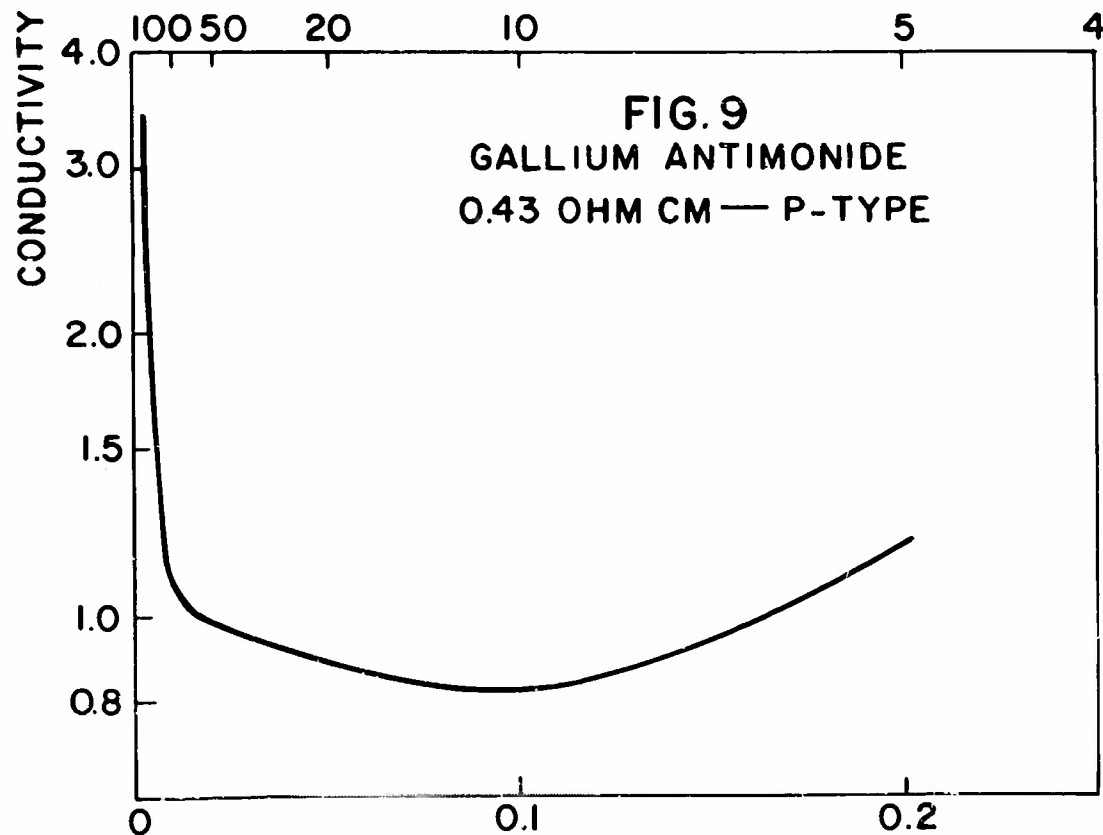
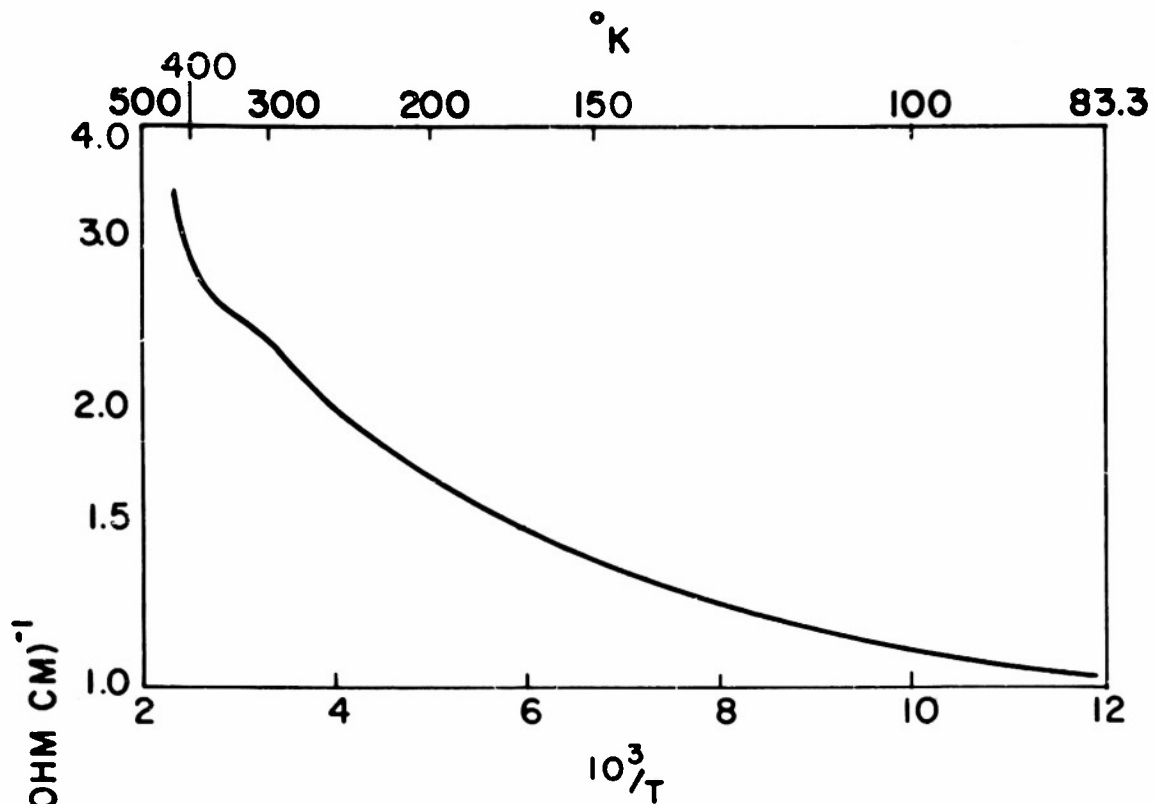


FIG. 9
GALLIUM ANTIMONIDE
0.43 OHM CM — P-TYPE

CONFIDENTIAL

AWCR 3455-34

Armed Services Technical Information Agency

Because of our limited supply, you are requested to return this copy WHEN IT HAS SERVED YOUR PURPOSE so that it may be made available to other requesters. Your cooperation will be appreciated.

AD

40714

NOTICE: WHEN GOVERNMENT OR OTHER DRAWINGS, SPECIFICATIONS OR OTHER DATA ARE USED FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED GOVERNMENT PROCUREMENT OPERATION, THE U. S. GOVERNMENT THEREBY INCURS NO RESPONSIBILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE GOVERNMENT MAY HAVE FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE SAID DRAWINGS, SPECIFICATIONS, OR OTHER DATA IS NOT TO BE REGARDED BY IMPLICATION OR OTHERWISE AS IN ANY MANNER LICENSING THE HOLDER OR ANY OTHER PERSON OR CORPORATION, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE OR SELL ANY PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.

Reproduced by
DOCUMENT SERVICE CENTER
KNOTT BUILDING, DAYTON, 2, OHIO