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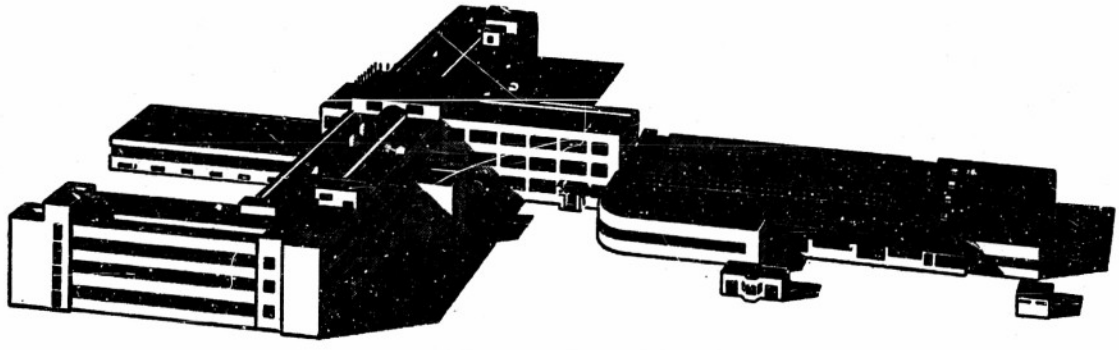
FOURTEENTH INTERIM REPORT

INFRARED PHOTOCONDUCTORS

N6onr-23603

April 15, 1953 - July 15, 1953



DAVID SARNOFF RESEARCH CENTER

PRINCETON, NEW JERSEY

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I. Introduction

Long wavelength impurity photoconductive response at temperatures as high as 77°K (liquid nitrogen) was found to occur in suitably doped germanium as described in Interim Report #13. This response involves electron transitions of relatively high energy levels of multilevel impurities after the low energy levels have been balanced out by impurities of the opposite type. For example, if pure gold is added to germanium the result is a p-type semiconductor which shows almost no change in conductivity upon cooling from room temperature to liquid nitrogen. However, if arsenic is added in proper amount the shallow acceptor levels of the gold will be filled by the donor electrons from the arsenic leaving a deeper level at about 0.15 ev. This material still exhibits p-type conductivity but drops five or six orders of magnitude in conductivity when cooled to liquid nitrogen temperature. At liquid nitrogen, the material shows a long wavelength response which peaks at about 7μ and extends to beyond 10μ.

During the period covered by this report the major part of the work was directed toward a study of germanium incorporating gold (or other multilevel impurity) and a donor impurity. A number of samples of varying composition were investigated for spectral response, variation of conductivity with temperature, and sign of carrier. To obtain further quantitative information on the question of impurity balance, equipment is being prepared for radioactive tracer measurement of germanium.

II. Conductivity Measurements

A. Gold-doped Germanium

Two samples (AA197 and 198) cut from a lower resistivity portion of the crystal which, as described in the last report, previously gave an impurity slope of 0.15 ev and three samples, AA200, 201 and 203, cut from a crystal which had been doped with Johnson and Matthey high purity gold were measured in run 90 in the Collins Cryostat. All samples were p-type as indicated by thermal probe measurements. The results are summarized in the following Table and in Fig. 1.

Gold-Doped Germanium

Cell	Source	Impurity Slope	$\frac{\Delta I}{V}$ at 4°K
AA197	349A	0.18 ev	3.7×10^{-4} μA/volt
AA198	349A	0.16	2.0×10^{-4}
AA200	348L	0.056	1.2×10^{-2}
AA201	348L	0.058	6.6×10^{-3}
AA203	348L	0.056	6.2×10^{-3}

The behavior of cells AA197 and 198 was essentially identical to previously measured samples AA176 and 177 cut from the same crystal (349A). The cells AA200, 201 and 203 were similar to one another but are different from 197 and 198 in that they exhibit a smaller low temperature slope and give indication of two impurity levels; one at about 0.06 ev and one at a higher energy. The difference between the two groups

of cells is probably ascribable to the difference in purity of the two samples of gold used (lower in the case of AA197 and 198) and to the phenomenon of impurity compensation or balance. If the proper amount of n-type impurity is present, the lower lying p-type level due to gold may effectively be removed by impurity compensation. If a smaller amount of foreign impurity is present, this compensation will be incomplete. There was evidence from the present series of measurements that the degree of compensation of the lower lying gold level did change systematically along the crystal.

To test the compensation hypothesis, crystal 350L was grown with deliberately added n-type impurity (e.g., arsenic) along with gold and was cut into nine rods. The dark conductivity of these rods was measured as a function of temperature to 77°K. The undoped portion and the first arsenic-added portion (cell AA217) remained saturated to 77°K. The remainder of the samples showed activation energies ranging from 0.09 ev to 0.14 ev. The results are shown in Fig. 2. A silhouette of 350L is also included which shows the relative positions of the samples, and, marked by arrows, the points where the arsenic was added.

In run 92, three of these samples were measured to 4°K. The results are given in Fig. 3.

B. Other Germanium Crystals

The Group Ib elements Cu, Ag and Au appear very interesting as impurities in germanium since both theory and experiment indicate that impurity ionization energies of about 0.1 ev are realizable with these elements. Results on copper- and gold-doped crystals have already been reported. During this period, five samples cut from a germanium crystal heavily doped with silver were measured in the Collins Cryostat. Only the most dilute of these samples showed a significant temperature dependence of conductivity. The others apparently contained such a high concentration of impurity that they were degenerate over the entire temperature range down to 4°K.

The cooling curve for the dilute sample indicated the presence of three impurity levels. The ionization energy of the lowest lying level was found to be 0.011 ev. No estimate of the positions of the other levels can be obtained from the cooling curve since the effects of temperature dependence of mobility and of the lowest lying level partially mask their contributions. It may be that the three levels observed correspond to the three stages of ionization of silver behaving as a lithium-like substitutional impurity. If this is the case, it should be possible to effectively remove the lower levels by adding the appropriate amount of an n-type impurity to the crystal.

A germanium crystal doped with vanadium was measured for the transistor group. It has an activation energy of 0.02 ev;

this is larger by a factor of 2 than for arsenic, for example, and may be due to its unfilled 3d shell.

III. Spectral Response Measurements

The spectral response of AA215 (from the fourth arsenic-added region of 350L) with activation energy 0.12 ev and AA221 (from the second arsenic-added region of 350L) with activation energy 0.09 ev was measured at 77°K. For both, the impurity response peaked at 5.5μ and was down about 35 db at 10μ. The impurity response on the short wavelength side of this peak was slowly varying and, at most, 6 db below the peak. The results are shown in Fig. 4.

Up to the present no certain correlation between optical threshold energies and thermal activation energies for gold-arsenic-doped germanium has been found.

IV. Hall Coefficient Measurements

A test run (88) was made with holder #D for Hall and conductivity measurements in the Collins. An indium-doped crystal (AA170) was measured using a standard d.c. circuit. The results indicated that Hall and conductivity measurements can be made in the Collins in about 7 hours covering the range from 300°K to 4°K. Improvement of the system involves the use of a high impedance detector and better knowledge of the temperature of the sample. It is planned to use a Beckman Ultraohmer as a detector in the next run.

The holder of the sample in the Hall effect equipment has been modified to allow the temperature of the sample to be measured, at high temperatures, by the thermocouples soldered directly on the sample and, at low temperatures, by an Allen-Bradley resistor soldered directly to the sample.

V. Infrared Dectector

The construction of a detector for distant objects at slightly above ambient temperature was completed. The sensitive element is a (gold-arsenic-doped) germanium crystal cooled to liquid nitrogen temperature. A seven inch parabolic mirror is used to image the object onto the cell.

Three such liquid nitrogen cell holders have been constructed. One is for use with our infrared detector system and the other two are for tests at other laboratories (Wright Field and Bureau of Standards). The unit AA205 has been shipped to Wright Field, and unit AA206 to Bureau of Standards. The germanium crystals used in these units are from crystal 349A which was grown by our transistor group as a gold-doped crystal; the gold used, however, was not particularly pure so that probably some compensation occurred to produce a crystal more nearly akin to the gold-arsenic-doped crystals discussed elsewhere in this report.

Measurements were made of the spectral response of our unit. The results are given in Fig. 4. Impurity response peaked around 6 microns and was equal to the noise in the system beyond 10 microns. The effect of using a 10 mil thick pure germanium filter (unpolished surfaces) was investigated. Without this filter the intrinsic peak was 48 db above the impurity peak. With the filter present the impurity response was 6 db lower (reflection loss). With the filter cooled, the intrinsic

peak was 45 db above the impurity peak and with the filter at room temperature it was only 19 db above. It would appear that an uncooled germanium filter is useful for absorbing unwanted short wavelength radiation.

Tests with our unit have shown that the temperature of the chopper blade is most critical; spurious signals resulted as the temperature of the chopper blade drifted above and below ambient. It was not thought advisable to thermostat the chopper at this time. The tests did demonstrate, however, that with the cell at liquid nitrogen temperature, a human hand or figure at 25 feet resulted in significant signals.

VI. Recombination Radiation

In run 94 an attempt was made to detect any recombination radiation from a germanium crystal that had undergone an electrical breakdown at helium temperatures.

Crystals AA70 (Bismuth n-type) and AA150 (Arsenic n-type), in the form of circular disks, were mounted with their faces separated by about 0.040 inches and parallel to each other. These samples were placed in a brass cup to shield them electrostatically and from the radiation from the warm upper parts of the Collins. Using a simple dc circuit to effect breakdown in one crystal, the other crystal exhibited a change in conductance that was independent of the direction of the breakdown field.

It is felt that the effect may be due to recombination radiation; however, it was not distinguished from a pure heating effect.

VII. Equipment

The construction of Collins Holder #4 was completed during this period. This holder consists of a copper gas thermometer bulb, with provision for soldering samples directly to the bulb, and an absolute pressure gauge for the gas thermometer pressure indicator. The use of this gauge eliminates the laborious calibration calculations required previously for each run. Although the samples cannot be illuminated during the run, it is felt that any uncertainty in the sample temperature has been eliminated. In the holder used previously, the samples could be exposed to room temperature radiation from the top sections of the Collins dewar by opening a flap above the samples; however, in this holder the samples were not in contact with the gas thermometer bulb but were brought into equilibrium with it through the thermal conductivity of the surrounding helium gas.

In run 91, the new gas thermometer was used to calibrate two copper-constanton thermocouples to low temperatures and two Allen-Bradley resistors at low temperatures. The latter thermometers are to be used in the Hall measurement equipment at low temperatures.

A thermal probe was constructed to determine the type (n or p) conductivity of a crystal.

A circuit was built for measuring the deviation of a sample from a linear voltage-current relation; provision is also made for presenting the voltage-current relation on an oscilloscope. This device is for use in studying contacts on crystals.

VIII. Analysis of Conductivity Curves

In fitting experimental conductivity-versus-temperature curves for chemically doped germanium, it was initially necessary to use a model of a semiconductor in which impurities of both types (n and p) are present in concentrations within several or sometimes one order of magnitude of each other. For example, for an arsenic-doped germanium sample, the donor concentration N_D was 10.1×10^{15} cm^{-3} and the acceptor concentration N_A was 3.1×10^{15} cm^{-3}. The electron concentration around room temperature had its saturation value of $N_D - N_A$. By "acceptor" is meant an electron trap - not necessarily a chemical impurity. In this initial model the traps can lie anywhere in the forbidden band as long as they are below about 0.2 ev from the bottom of the conduction band. The discrete donor level was 0.0078 ev below the conduction band.

Several subsequent models have been found that result in identical mathematical forms as the initial model, over the temperature range measured. These are: (a) donors and traps at the same level. For the example cited, 7.0×10^{15} cm^{-3} donors and 3.1×10^{15} cm^{-3} traps lying 0.0078 ev below the conduction band. (b) Ionized donors with a discrete level of traps. For the example cited, 7.0×10^{15} cm^{-3} donors near the bottom of the conduction band (always ionized) and 10.1×10^{15} cm^{-3} traps lying 0.0078 ev below the conduction band.

Another model that results in similar, although not mathematically identical, behavior is to have 10.1×10^{15} cm^{-3}

donors at 0.0078 ev with a uniformly distributed background of about 2×10^{15} cm^{-3} traps.

The effect of the excited states of donors was investigated. It was found that thermally these states have little effect on the temperature variation of the carrier concentration over the temperature range considered.

The tracer experiments discussed in Section IX are aimed toward information which may help in distinguishing between these models.

IX. Radioactive Tracer Measurements

The decision to undertake some radioactive tracer measurements of impurity concentrations in germanium has recently been reached for the following reasons.

(1) It has been pointed out, both in this report (Sect. VIII) and in previous reports, that in order to fit the experimental conductivity versus inverse absolute temperature curves for germanium doped with adjacent column impurities, it appears to be necessary to assume that both donors and acceptors are present. The concentration of the minority type which must be assumed in order to obtain a satisfactory fit between the experimental results and the calculated curves based on any of several semiconductor models is often within an order of magnitude of that of the majority type over a considerable concentration range. This result suggests that the concentration of the minority center, either a chemical impurity or a charge carrier trap, is somehow determined, at least approximately, by the concentration of deliberately added impurity.

Since the concentration of charge carriers in the impurity saturation range, as determined, for example, by measurement of the Hall effect, depends upon the magnitude of the excess of donors over acceptors or vice versa, a comparison of the charge carrier concentration with that of the added impurity determined by an independent method should give information from which a mechanism to account for the observed impurity compensation could

be devised. The only method having sufficient sensitivity for the determination of the minute impurity concentrations encountered is one involving the measurement of the radioactivity of the impurity either after activating the grown crystal containing the impurity by exposure to a strong neutron flux or after adding a radioactive impurity to the germanium prior to growth of the crystal. The former method requires access to a nuclear reactor and is, therefore, less convenient than the latter.

2. Radioactive tracers should prove to be useful, also, in the investigation of those samples, e.g., gold-doped germanium, in which two impurities of opposite type appear necessary for the development of desirable photoconductive properties. The use of two radioactive impurities having radiations which could be measured separately in the presence of one another would permit the determination of electrical properties as function of the relative and absolute amounts of the two impurities.

A survey of the available radioisotopes indicated that antimony 124 ($T_{1/2}$= 60 days) would be most convenient to use in the initial experiments. Silver 110 is another suitable tracer.

The system: antimony 124 - germanium has already been studied* The conclusion drawn by the authors as the result of

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*Pearson, Struther and Theuerer, Phys. Rev., 77, 809-813, (1950).

measurement of the Hall effect and of the radioactivity of germanium doped with Sb^{124} is that in the impurity saturation range there is one conduction electron furnished per antimony atom present. Actually, the average value of the ratio of the concentration of conduction electrons at room temperature to the concentration of antimony atoms as estimated from their data is 1.5±0.2. This indicates that their data are of relatively low precision and that, therefore, their conclusion ought to be considered as being only approximately valid. The major objections to their experimental techniques are:

(1) The measurements were made upon polycrystalline ingots rather than upon single crystals; (the grain boundaries present would have an effect on both the electrical characteristics of the specimens and on the uniformity of distribution of solute atoms);

(2) The method used for the calibration of the counting rates of the samples measured in terms of the number of antimony atoms present;

(3) The method used for determining the corrections to be applied to the observed counting rates in order to take into account the absorption by the radiation in the sample being measured; and

(4) A Geiger Counter was used to measure the radioactivity of the samples.

An outline of the procedure planned for measurements with tracer antimony-doped germanium includes the following steps:

1. Purification of the germanium to be used by growth of single crystals.
2. Addition of an appropriate amount of tracer antimony by electrodeposition upon a piece of purified germanium.
3. Growth of single crystals by pulling from the melt consisting of germanium plus tracer antimony.
4. Check gross uniformity of distribution of antimony in the crystal (i.e., insure absence of striations) by making radio-autographs of cut sections.
5. Measurement of Hall effect and conductivity as function of temperature upon bars cut from doped crystal.
6. Measurement of radioactivity of samples whose electrical properties have been measured. It is planned to dissolve the germanium under conditions such that there is no loss of either antimony or germanium during the process. The gamma radiation from this solution, diluted to a standard volume in a standard container, will be measured by means of a scintillation counter employing a NaI-Tl crystal.
7. Determination of specific activity of the Sb^{124} preparation used. This involves two steps: (a) measurement of the radioactivity of an aliquot of the stock Sb^{124} solution under the same conditions as those used in measurement of

the germanium samples, and (b) determination of total antimony in another aliquot by a quantitative chemical analytical method. The method to be used involves the formation of a colored complex between antimony and the red dye Rhodamine B and the measurement of the optical transmission of a solution of this complex in an organic solvent. The method is calibrated by carrying out the determination on a series of samples containing known amounts of antimony. Its sensitivity is such as to permit its use in the microgram range.

The experimental work thus far carried out on this problem has consisted of preparation of the radiochemistry laboratory for the various operations involved. A crystal growing furnace with the necessary associated equipment is being set up; a diamond saw is being modified so as to permit cutting of radioactive crystals without spreading contamination about the laboratory and equipment is being constructed and assembled for the various chemical operations involved.

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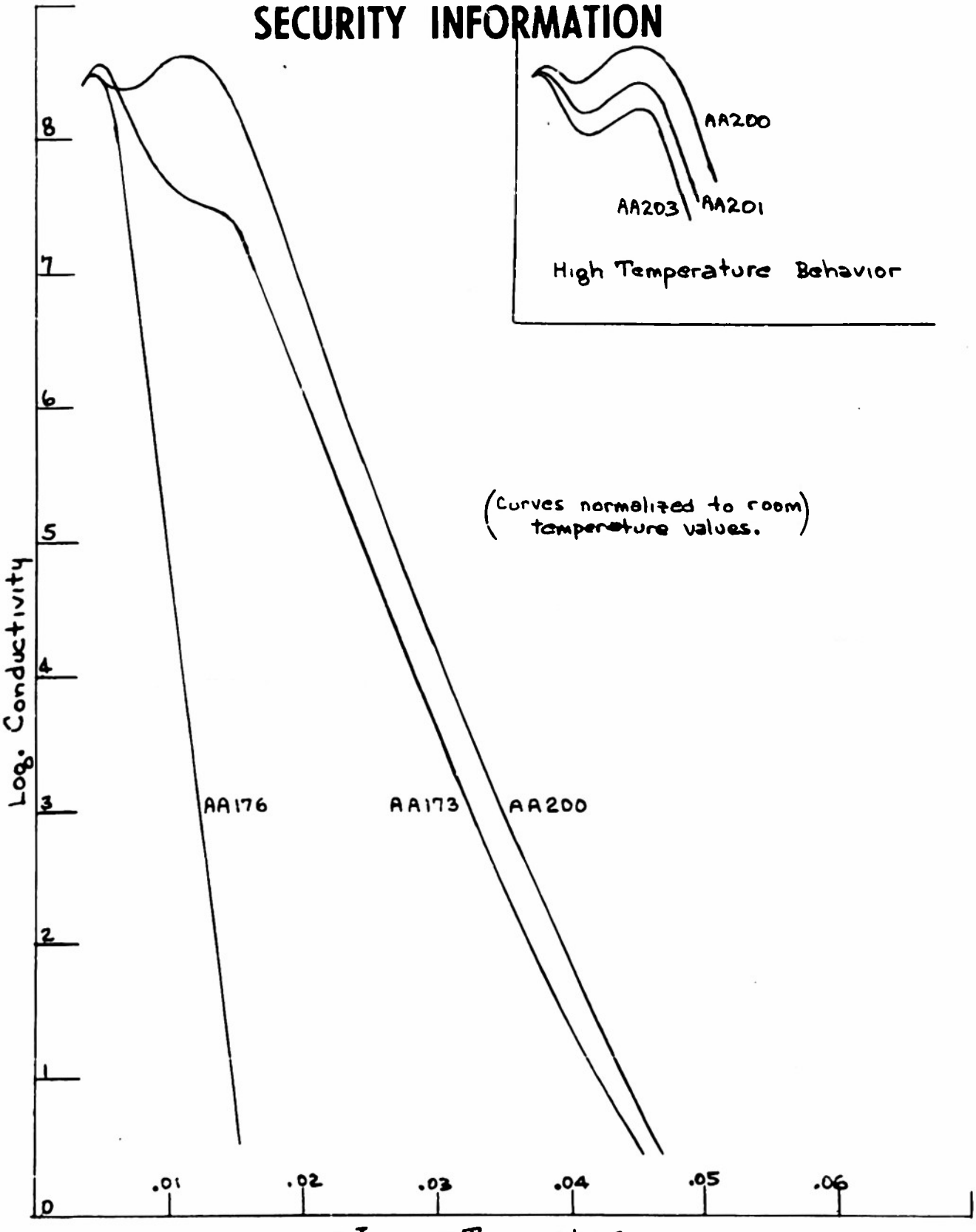
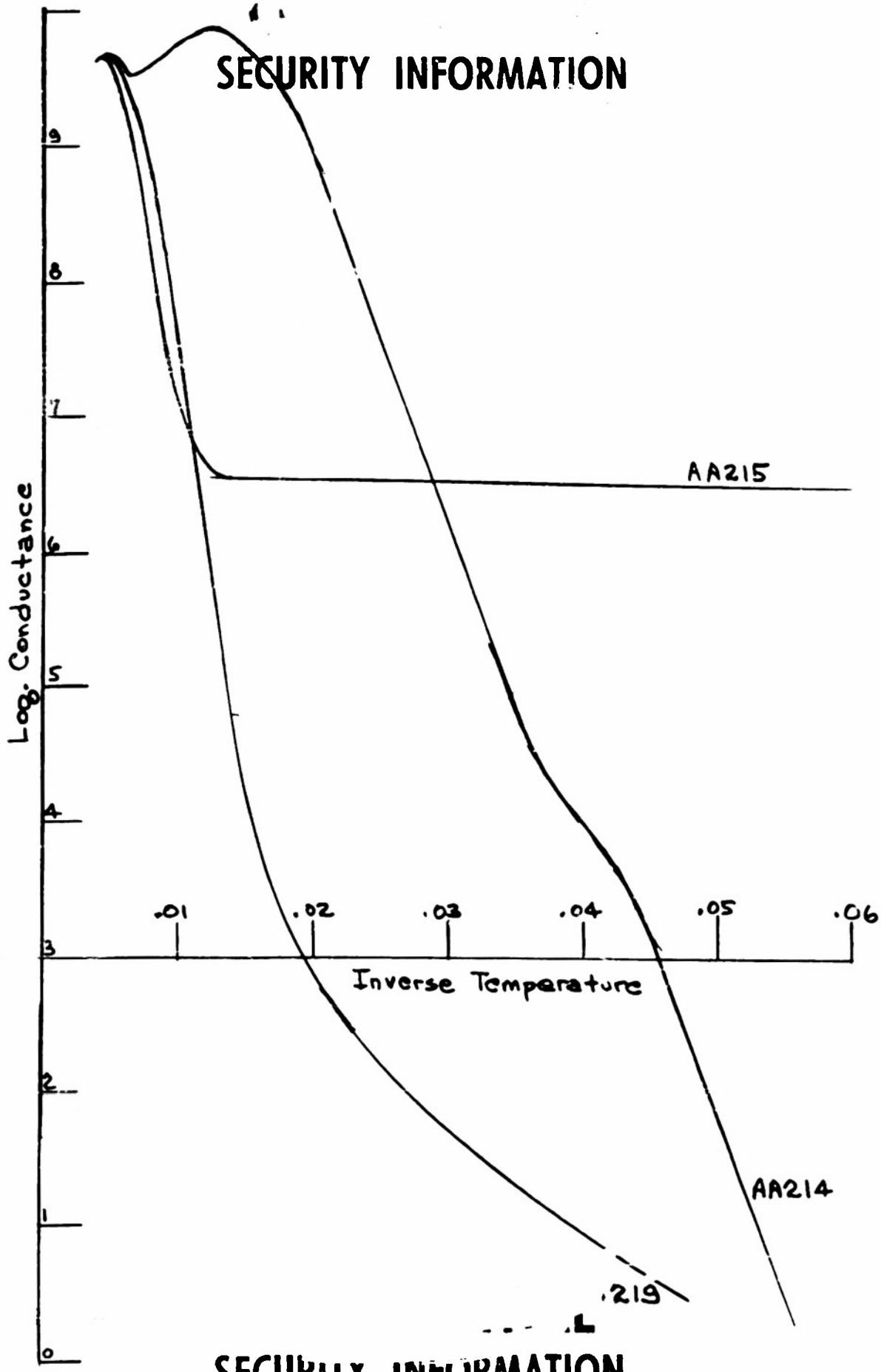
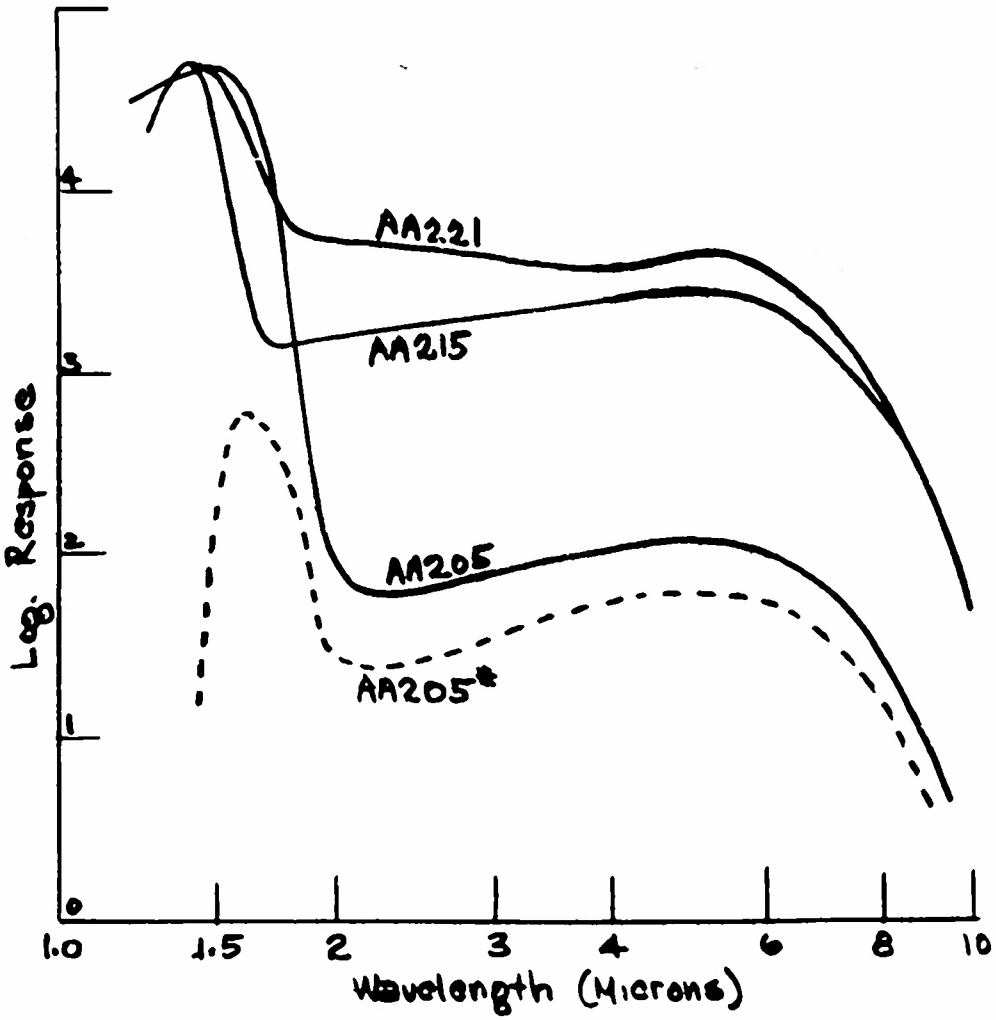


Fig. 1





*With germanium window

FIG 4