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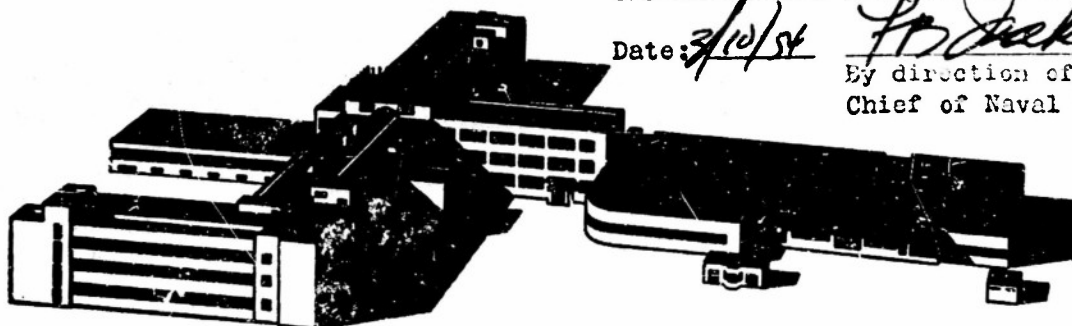
RADIO CORPORATION OF AMERICA

RCA LABORATORIES DIVISION

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Date: 3/10/54

By direction of FR Jackson
Chief of Naval Research (Code 421)



DAVID SARNOFF RESEARCH CENTER
PRINCETON, NEW JERSEY

54AA-16095

FIFTEENTH INTERIM REPORT

INFRARED PHOTOCONDUCTORS

N6onr23603

July 15, 1953 - October 15, 1953

Introduction

The very promising results which have been obtained from the gold/arsenic-doped germanium indicated that the majority of the effort during the period covered by this report be spent on this problem. A spectral response extending out to 10 microns has been obtained with the double-doped germanium cooled to liquid nitrogen temperature. The sensitivity of the material even in its present state is quite good. It is expected with further work that this sensitivity can be markedly increased.

During this period, A. J. Cussen, from Naval Ordnance Laboratory, Corona, California, visited RCA to discuss his measurements on infrared cell AA206 which had been sent to him for evaluation. As described in Section V of the last report, the AA-type cell consists of a gold/arsenic germanium crystal mounted in a liquid nitrogen dewar. This dewar has a silver chloride window and, for convenience, is made demountable. A cross-sectional view of the cell is shown in Fig. 1. The crystal is labelled A; parts B and C are copper blocks and part D is a copper radiation shield. Fig. 2 shows the spectral response of this cell. Cussen was very enthusiastic about the performance of this cell and feels that many groups should be interested in the possibilities of using this type of material for practical infrared detection of radiation out to 10 microns.

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I. Infrared Detectors

The spectral response at 90 cps (5 cps bandwidth) of AA206, shown in Fig. 2, gives the E.N.I. as a function of wavelength. It is seen that the response is practically the same as had been measured in RCA Labs. for our cell, shown as AA205 in Fig. 4 of the last report. On an adjacent page is presented a copy of a tentative data sheet on AA206 as compiled by Cussen. The response of the cell was flat to 1 kcps and down about 3 db at 10 kcps. The cell noise was 1.5 μ V at 90 cps, and 0.2 μ V at 10 kcps.

As a result of Cussen's visit, two more cells of Type AA will be constructed for his evaluation. In addition, he is going to calibrate for our use the response of three germanium crystals in the intrinsic region at room temperature to aid us in putting our response measurements on an absolute basis.

Also, during this period, the results of measurements by H. Levinstein at Syracuse and G. Klingler at Wright Field on cell AA205 were received and indicate that something unknown has happened to this cell. A threshold near 6 microns has been measured by both Levinstein and Klingler, whereas before this cell was sent out, response was measurable out to 10 microns (Fig. 4, last report).

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CELL SENSITIVITY

CONDITIONS OF MEASUREMENT

	<u>Uncooled</u>	<u>Cooled</u>		<u>Uncooled</u>	<u>Cooled</u>
A. Time Constant: (μ seconds)		10	Chopping Frequency:		90 cps
1. Rise:			Bandwidth		5 cps
2. Decay:			Humidity:		
B. 500°K Black Body Response:			Cell Temper- ature ($^{\circ}$ C):		-195
1. Noise Equiv- alent Power: (watts/cm ²)		1.2×10^{-8}	Dark Resist- ance (megohms)		1.6
(watts)		1.8×10^{-9}	Load Resist- ance (megohms):		1.0
2. Jones "S" (watts)		1.9×10^{-8}	Cell Current (μ amps):		5.0
3. S T: (μ watt- μ seconds)		1.9×10^{-1}	Cell Noise (μ volts):		0.9
C. Response at Peak of Spectral Curve:			Black Body Flux Density: (μ watts/cm ²) (RMS)		5.85
1. Position of spectral peak in microns:		1.48	Spot Diameter: (mm)		
2. Noise Equiv- alent Power: (watts)		1.8×10^{-12}	Spot Energy: (μ watts - RMS)		0.0295
3. Jones "S" (watts)		2.0×10^{-11}			
4. S T: (μ watt- μ seconds)		2.0×10^{-4}			
D. Sensitivity Contour:					
1. Zone 100 (volts/watt)					
E. Specific Properties:					
1. "S ₁ " (at 148 microns)		(S ₁ and N ₁ not defined for Germanium)	Area (mmxmm):		
2. "N ₁ " (volts)					

CELL CONSTRUCTION

Type: Ge gold-doped
Electrode Material: Indium
Window: AgCl
Method of Prepara-
tion: Coolable

Cell #AA206 - Germanium

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II. Conductivity Measurements

In a continuation of our study of gold/arsenic germanium, crystal 353L was cut into 14 pieces for conductivity and spectral response measurements. An induction hydrogen furnace was semi-permanently set up to alloy broad area indium contacts into the ends of the cylindrical samples. Crystal 353L was a gold-doped germanium melt with arsenic added step-wise three times during the drawing of the crystal. A half-silhouette of 353L is shown in Fig. 3.

In runs 93 and 95, the dark conductance of eleven crystals from 353L was measured as a function of temperature to 4°K. The characteristic behavior of these crystals is shown in Fig. 3. The activation energy of the arsenic-free section was 0.048 ev whereas, for the crystals containing arsenic, it varied from 0.10 to 0.14 ev.

It is planned to summarize the present results on gold/arsenic germanium in the next report.

In order to measure the temperature dependence of the conductance of germanium crystals above room temperature, a helium furnace was set up. So far, measurements into the intrinsic range have only been made on two crystals, both from 353L.

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III. Spectral Response Measurements

The spectral response of two crystals from crystal 354L was measured at liquid nitrogen temperature. Crystal 354L is a zinc-doped germanium melt with arsenic added step-wise three times. Both crystals exhibited a much sharper impurity threshold than the gold/arsenic germanium. Subsequent measurements have indicated the presence of short wavelength scattered light in the Leiss at settings of the prism corresponding to the "response" described above; the zinc/arsenic crystals have not yet been reexamined.

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IV. Preparation of Germanium Samples

In this period the preparation of Ge passed through several changes.

The first of the intentionally double-doped crystals (349L), with Au and As, was prepared, following observations on the behavior of "chemically pure" gold compared to the extremely refined Johnson and Matthey Au.

Since the first crystal had insufficient As, another (350L) was grown, in which the As was added step-wise. This was repeated (353L) in an attempt to get the transition from "p" to "n" type occurring in one crystal.

Work was done to further the compensation concept by preparing a ZnAs double-doped crystal (354L) (by step-wise addition). In this case, perhaps in part due to the volatility of the Zn, the expected "p" to "n" transition occurred near the middle of the crystal.

A crystal containing Ag was prepared, but the behavior of this doping material still appeared anomalous.

The additions were mostly made through a Σ fitting on the viewing side-arm, in more than 6 crystals this proved very satisfactory, for additions greater than ~ 5 mgms.

In order to get a homogeneous melt from which to draw the double-doped crystals, the seed and crystals were rotated at 100 r.p.m. - well within the range of 15 to several hundred r.p.m. used by other workers. To avoid introduction of foreign

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materials, a new type of furnace tube head was machined from Teflon.

Toward the end of this period, the furnace in the "penthouse" lab was set up in preparation for the radioactive tracer dopings.

The grinder obtained for cutting radioactive crystals was put into use on inert materials to avoid the delay between preparing and testing crystals, which often occurred when others did the cutting for us.

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V. Radioactive Tracer Measurements

A. Introduction

The reasons underlying the commencement of radioactive tracer measurements of impurity concentrations in germanium have been summarized in Interim Report No. 14. A brief outline of the principal steps involved in the determination as planned has also been presented there. The effort on this problem during the present period has been concerned with assembling the equipment necessary and developing the techniques required for carrying out some of the steps of the procedure.

In order to give an idea of the order of magnitude of the amount of impurity (antimony in the first experiments) which must be added in order to produce a suitably doped crystal, some illustrative figures will be given. Suppose it is desired to grow a crystal in which the antimony concentration is about $1 \times 10^{15} \text{ cm}^{-3}$ near the seed end of the crystal. From the value of the segregation coefficient for antimony in germanium (5×10^{-3}), the density of germanium at room temperature (5.35 g/cm^3), the atomic weight of antimony (121.76) and Avogadro's number, a simple calculation gives the result that 7.6×10^{-6} grams of antimony must be present per gram of germanium in the melt.

A bar, suitable for Hall effect measurements, cut from this crystal will have a weight of about 0.35 g and will contain about 1.3×10^{-8} grams of antimony. If the specific activity of the tracer antimony used is about one curie per gram, then the total number of radioactive disintegrations per second in a Hall

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effect sample will be about 500. The actual counting rate to be expected when the radioactivity of such a sample is measured will be smaller than this by a factor determined by the geometry of the counting arrangement and by the efficiency of the counter.

B. Addition of Tracer Antimony to Germanium

The present plan is to add an appropriate amount of tracer antimony by electrodepositing the antimony upon a piece of the pure germanium to be doped.

The electrodeposition of small amounts of antimony has been studied using non-radioactive antimony and a modification of the plating method described by Norwitz.* The antimony must be in the pentavalent state for deposition to occur. The oxidation is accomplished by the addition of a small amount of perchloric acid to a solution of antimony chloride or sulfate in H_2SO_4 -HCl solution. The uniformity of deposition is improved if hydroxylamine hydrochloride is present in the electrolyte. The electrodeposition is carried out using a platinum anode and a current density of about 1 amp. per sq. dm.

Several trial depositions in which the total amount of antimony present in the electrolyte ranged from 0.2 to 0.6 mg were carried out. Recoveries of from about 30% to about 50% of the total antimony were observed. There appeared to be no systematic dependence of efficiency upon total amount of antimony present.

These experiments have demonstrated the feasibility of this method of addition of small amounts of antimony to a germanium melt. There remains to be demonstrated that no foreign impurity

*G. Norwitz, Anal. Chem. 23, 386 (1951)

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is introduced along with the electrodeposited antimony. This will be investigated by preparing a germanium crystal doped with inactive antimony which has been plated out in this manner. A determination of the electrical behavior of this crystal should give an indication of the presence or absence of at least certain types of foreign impurities. Since the electrolyte contains no non-volatile constituents, the probability of contamination of the deposited antimony should be small.

C. Determination of Antimony Concentration in Crystals

The object of the tracer experiment is to compare the charge carrier concentration as determined by measurement of the Hall effect in the impurity saturation range with the impurity concentration as determined by measurement of the radioactivity of the samples upon which the Hall effect measurements have been made.

After the Hall measurements have been made on a given sample, the electrodes will be removed, the sample will be weighed and will then be brought into solution for measurement of the radioactivity. Reproducibility of the counting geometry, it is felt, will be more satisfactory if measurements are made upon a solution of the sample rather than upon the solid sample itself. A tentative procedure for dissolving the samples under conditions such that no loss of either germanium or antimony occurs has been developed. The sample is dissolved by means of a HF-HNO_3 mixture in the presence of an amount of lithium fluoride sufficient to convert the germanium to Li_2GeF_6 and the antimony to LiSbF_4 .

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The excess HF and HNO_3 are removed by evaporation to dryness and the solids are redissolved by adding a definite amount of water. The entire operation will be carried out in a Teflon cup which will serve also as the container to be used in measuring the radioactivity of the solution. This will involve counting of gamma rays emitted by Sb^{124} by means of a scintillation counter employing a thallium activated sodium iodide crystal.

D. Calibration of Radioactivity Measurement

In order to determine the total amount of antimony present in a sample whose radioactivity has been measured, the specific activity of the radioactive Sb^{124} preparation used must be known. Two steps are involved in the determination of this quantity.

(1) The radioactivity, determined under the same conditions of volume and amount of germanium as those employed in the measurement of the Hall effect samples, must be measured upon an aliquot of the Sb^{124} preparation used. (2) A quantitative chemical analysis of an aliquot of the Sb^{124} preparation for total antimony must be made.

An analytical method based upon procedures described by Frederick* and Maren** has been developed in a form suitable for use with radioactive antimony solutions. In summary, the method involves the formation of a colored complex between pentavalent antimony and the dye Rhodamine B. This complex is soluble in solvents such as benzene or toluene in which the

*W. G. Frederick, Ind. Eng. Chem. Anal. Ed., 13, 922 (1941).
**T. H. Maren, Anal. Chem., 19, 487 (1947).

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dye itself is insoluble. The complex is formed in an aqueous phase in the presence of an excess of dye and is then subsequently extracted by equilibration with a definite volume of organic solvent. The optical transmission of the organic solution of the complex is then measured in a simple photoelectric filter photometer. The method is calibrated by determination of the transmission of a series of samples containing known amounts of antimony. This has been done for amounts of antimony up to about 30 micrograms. From the scatter of the calibration points about a line drawn through them, the precision of the method has been estimated to be about 2% for amounts of antimony in the range between 5 and 30 micrograms.

One point which will have an, at present, unknown effect on the overall precision of the radioactive determination of the antimony concentration in the doped germanium should be mentioned. As indicated in section A, a doped germanium sample whose radioactivity is to be measured will contain about 10^{-8} grams of antimony. In order to eliminate any possible non-linearity of the radioactive count with amount of antimony, the calibration radioactivity measurement of Section D(1) should be made upon a sample containing about the same amount of Sb^{124} as do the unknowns. Since, however, the colorimetric antimony determination cannot be used below the microgram range, the chemical analysis must be made at a concentration level about two orders of magnitude higher than that at which the radioactivity is measured. Although no serious difficulty is expected in going from the microgram to

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the sub-microgram level, the possibility of radiocolloid formation or of adsorption of significant amounts of antimony upon the walls of the containing vessels must be kept in mind as possible sources of error.

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VI. Equipment

1. Infrared Detector, Type AA

The detector shown in Fig. 1 was originally designed for use with a parabolic mirror as a means for testing the usefulness of the gold/arsenic germanium crystals under near-practical conditions. Because of the difficulties encountered with spurious signals from the chopper blade, as described in Section V of the last report, this phase of the work has been discontinued.

However, a more compact cell holder for use at liquid nitrogen temperatures is being designed for use with gold/arsenic germanium. The f-number of this holder will be smaller to enable it to be used more readily for laboratory measurements. This will result in more efficient shielding of the crystal. Two of these cells will go to Cussen at N.O.L., one to the Army Engineer Board and one will be used in this laboratory. Demountable construction will permit the evaluation of different crystals under identical conditions.

2. Far Infrared

As a result of a visit to the Ohio State University Research Foundation, a metal dewar system for operation with liquid helium in their grating spectrometer was designed and is now being built for the purpose of making spectral response measurements in the region from 40 microns to 140 microns.

3. Optical and Electrical

An angle iron frame table has been designed and is under construction in the Model Shop for use as a bench for all

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the infrared optical equipment (Leiss monochromator, standard black body, dewar) and associated electrical equipment. A high vacuum line using an oil diffusion pump is also being installed on the table as a dynamic system for the evacuation of the various dewars to be used for the infrared measurements at low temperatures.

The metal dewar for measurements of photoconductive response and transmission at 4°K described in the Eleventh Interim Report was received from the Model Shop. Some time was spent in leak testing and re-soldering several joints.

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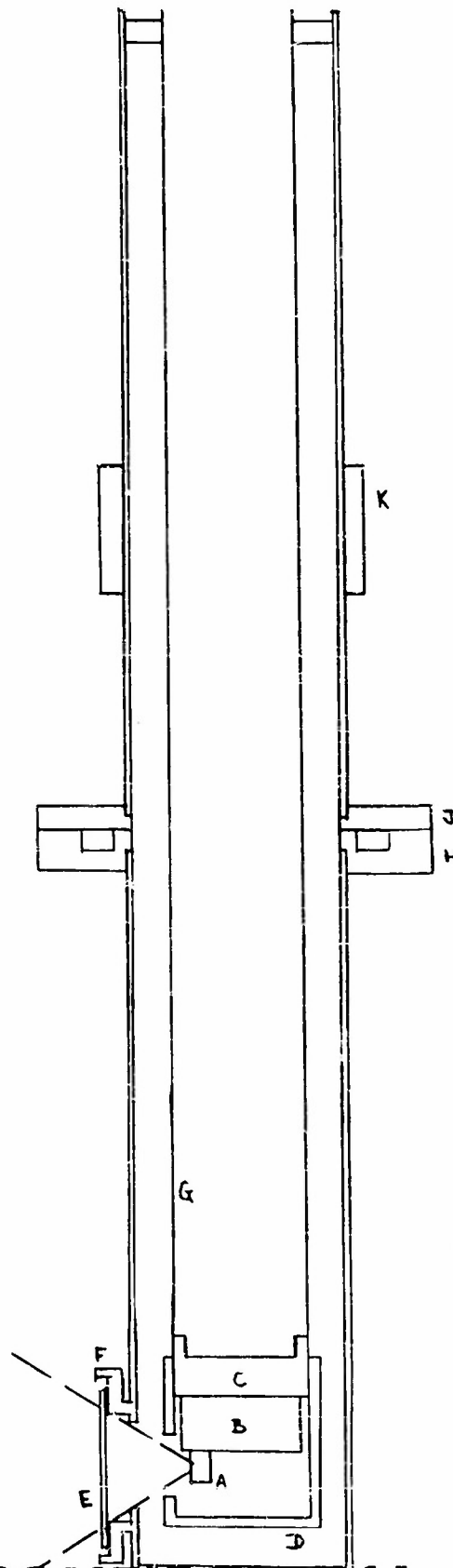


FIG. 1

Dewar for AA206

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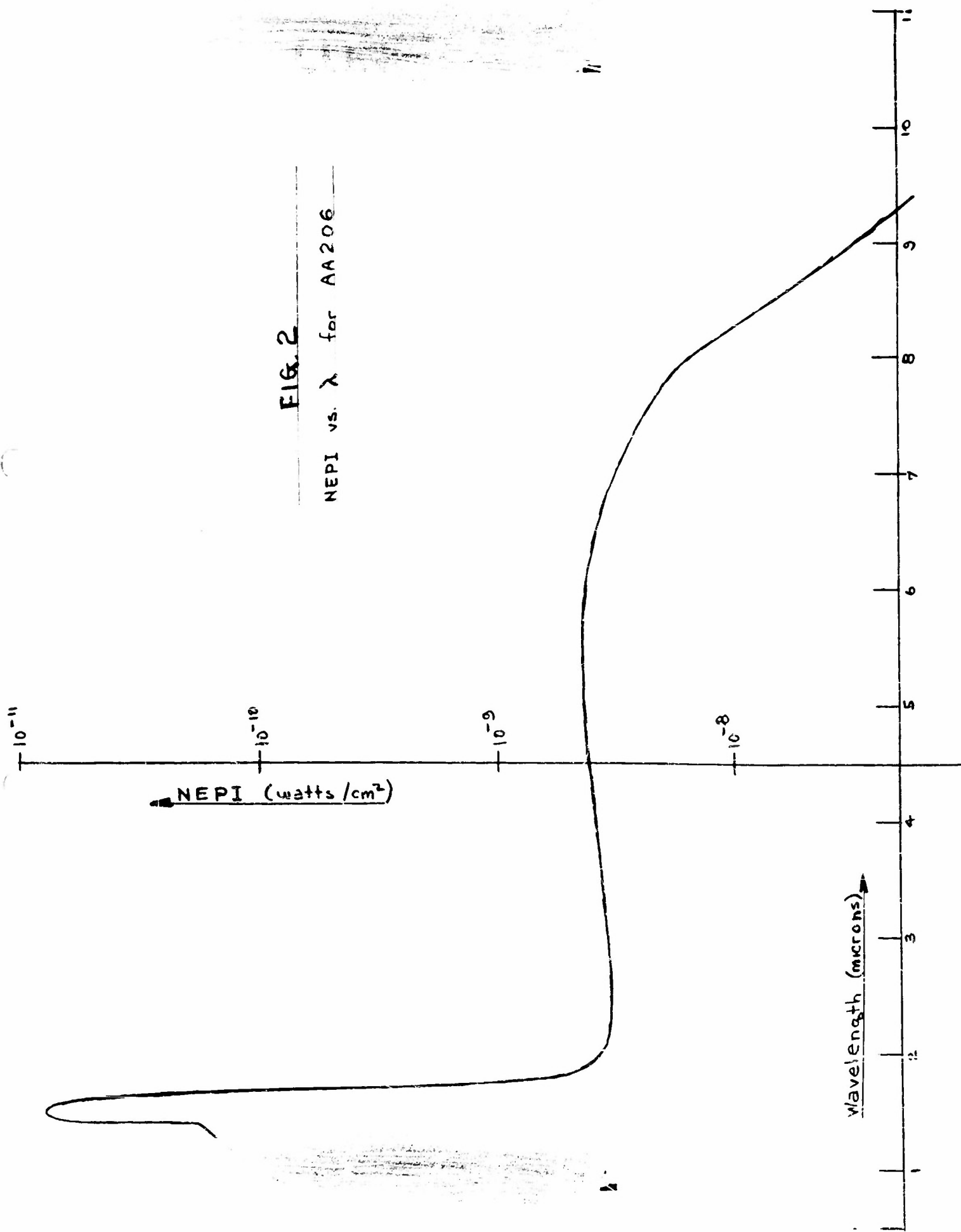


FIG. 2

NEPI vs. λ for AA206

