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DEVELOPMENT OF TECHNIQUES FOR
PREPARING HIGH-PURITY SINGLE-CRYSTAL
GALLIUM PHOSPHIDE AND ALLOYS OF
GALLIUM PHOSPHIDE AND INDIUM PHOSPHIDE

to

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

July 15, 1961

Subcontract No. 212 of Prime
Contract No. AF 19(604)-5200

by

J. F. Miller, R. T. Bate, H. C. Gorton,
R. C. Himes, and H. L. Goering

Period Covered
July 15, 1959 through July 15, 1961

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5 0 5 K I N G A V E N U E C O L U M B U S I , O H I O

July 27, 1961

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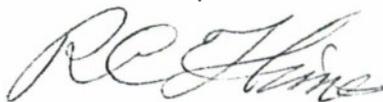
Dear Mr. Harman:

Enclosed are ten copies of the Final Report on your project, "Development of Techniques for Preparing High-Purity Single-Crystal Gallium Phosphide and Alloys of Gallium Phosphide and Indium Phosphide". The report summarizes results of the research for the period July 15, 1959 through July 15, 1961.

It will be noted that electrical properties of the GaP crystals grown from solution by the Bridgman method under only 2 atmospheres' pressure of phosphorus vapor compare favorably with those of crystals grown from the melt by others in much more elaborate equipment. Also, results of diode studies indicate that crystals of reasonably good quality were grown from the vapor phase. Further research on these two promising methods is recommended.

It has been a pleasure to carry out this research for you. We look forward to continuing association in such endeavors.

Sincerely yours,



R. C. Himes, Chief
Physical Chemical Research

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DEVELOPMENT OF TECHNIQUES FOR PREPARING HIGH-PURITY SINGLE-CRYSTAL GALLIUM PHOSPHIDE AND ALLOYS OF GALLIUM PHOSPHIDE AND INDIUM PHOSPHIDE

by

J. F. Miller, R. T. Bate, H. C. Gorton,
R. C. Himes, and H. L. Goering

INTRODUCTION

This report is the Final Report on the research project, "Development of Techniques for Preparing High-Purity Single-Crystal Gallium Phosphide and Alloys of Gallium Phosphide and Indium Phosphide". The report covers work done in the period of July 15, 1959 through July 15, 1961.

The melting points and dissociation pressures of GaP and the GaP-InP alloys are high (up to $\sim 1510^{\circ}\text{C}$ and ~ 35 atmospheres, respectively). To crystallize the materials from stoichiometric melts, it is necessary to work simultaneously at the elevated temperatures and pressures. Since temperature and pressure requirements for growth of crystals from solution are much less severe, the development of such methods is desirable. In this research, emphasis has been placed on development of methods for crystallizing GaP and the GaP-InP alloys from metal-rich solutions.

MATERIAL PREPARATION AND CRYSTAL GROWTH

Four general methods for the preparation and crystallization of GaP and the GaP-InP alloys were investigated: (1) horizontal zone melting, (2) the Bridgman method, (3) the Czochralski or crystal-pulling technique, and (4) the solute-buildup method. In this work, pressure of phosphorus vapor has not (intentionally) exceeded 5 atmospheres, and maximum solution temperatures have been generally in the range 1000 to 1400°C .

Zone Melting

Horizontal zone melting was most successfully applied to the crystallization of InP-rich alloys. Alloy ingots, which were crystallized at low rates (ca. 0.05 inch per hour) by zone leveling under 3 atmospheres' pressure of phosphorus vapor, were sound, and X-ray diffraction data indicated that they were also reasonably homogeneous. Figure 1 is a schematic diagram of the zone-melting apparatus. Ingots of GaP and GaP-rich alloys which were crystallized by this method generally contained high concentrations of gallium inclusions. In this latter work, observation and control of the process were made difficult by the rapid formation of opaque films on the reaction ampoule walls at the required high operating temperatures. Considerable difficulty was also experienced in regard to establishment of desired thermal-gradient patterns at these high temperatures.

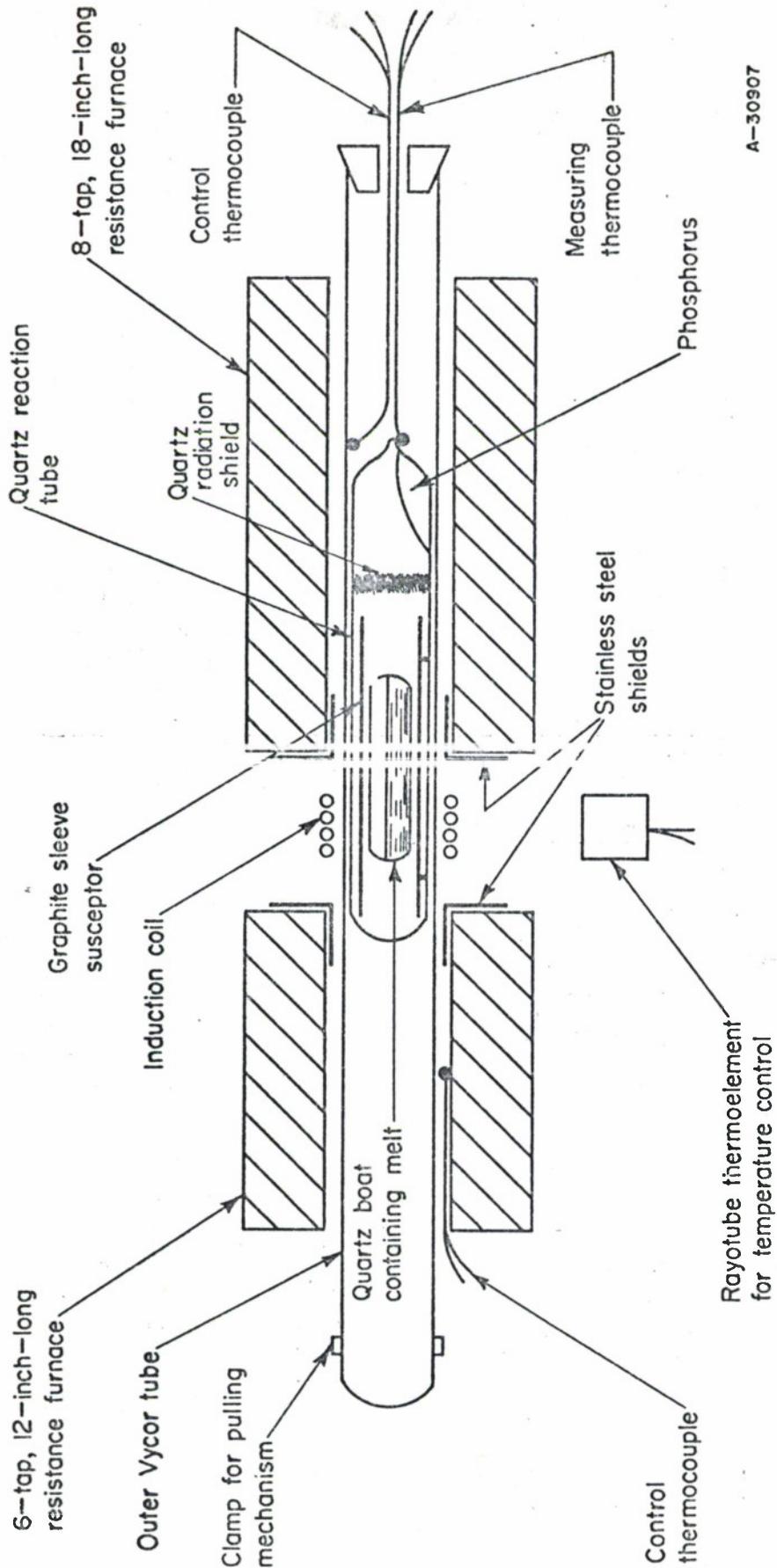


FIGURE 1. ZONE-MELTING APPARATUS

Bridgman Method

In this research, the Bridgman method yielded the largest GaP crystals, and the crystals of best physical quality. Figure 2 is a schematic diagram of the Bridgman crystal-growth apparatus. As is indicated in Table 1, sound ingots were prepared under 2 to 5 atmospheres' pressure of phosphorus vapor and with maximum melt temperatures in the range 1350 to 1385°C.

A difference was noted with respect to quartz and graphite as container materials. In quartz, where area of vapor-liquid contact is restricted to that of the exposed surface of the melt, little or no compound is formed under typical conditions given in the table. However, in graphite, where diffusion of phosphorus through the wall of the container increases effective area of vapor-liquid contact, sound ingots are obtained. Crystallization rate appears to be determined by the rate of dissolution of phosphorus, or by the rate of diffusion of the solute species.

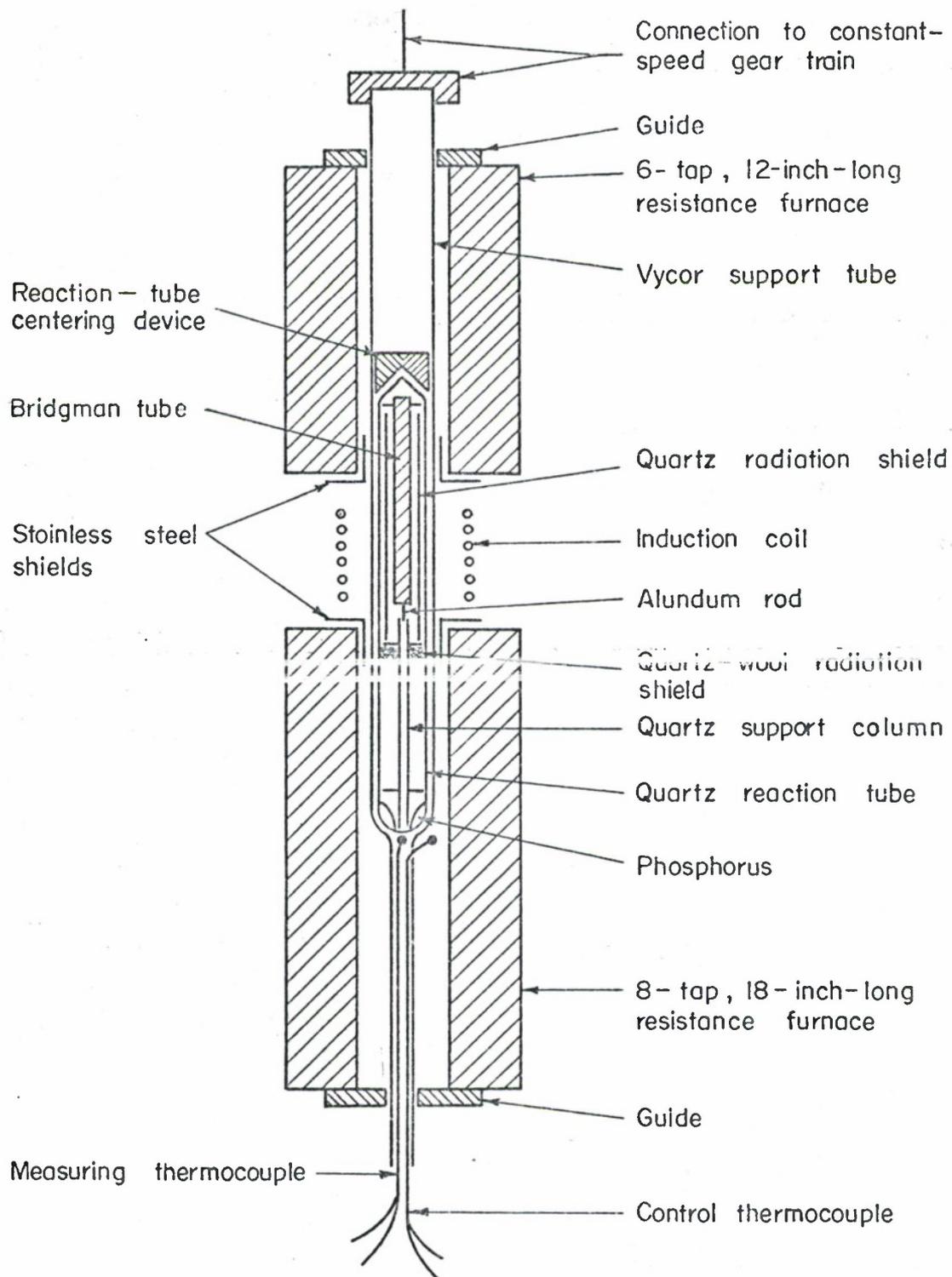
In later experiments, as is also indicated in the table, some improvement was realized by reacting the elements for a period of time prior to the drop. Crystals present in ingots so prepared were large (up to 4 x 7 x 2 mm). It was not determined whether crystal growth occurred during the reaction period or not. However, it does appear that large crystals of GaP can be obtained consistently by this procedure.

Several sound ingots of the GaP-InP alloys were also prepared by Bridgman crystallization at very low dropping rates. However, several factors militate against use of this method for the preparation of alloy specimens. Under the normal freeze conditions, significant segregation of the components occurs and concentration gradients are present in specimens from the ingots. In addition, the melting point of the remaining liquid changes through the run and, since the process cannot be observed directly, control is difficult.

Crystal Pulling

Experiments on the crystallization of GaP by the Czochralski technique were moderately successful. Sound polycrystalline ingots of GaP up to 4-1/2 inches long and 3/16-inch diameter were prepared by this method under only 1 to 3 atmospheres pressure of phosphorus vapor. Permissible crystal growth rates (up to 7/8 inch per hour) were higher than for the Bridgman method, presumably because of the larger area of liquid-vapor interface and the shorter diffusion path. Crystals present in some sections of the ingots were columnar, indicating that conditions favoring propagation of existing crystals were maintained at times and, therefore, that growth of large crystals from solution by this method should be possible.

Figure 3 is a schematic diagram of the Gremmelmaier-type crystal puller used initially. The redesigned crystal puller used in later work is shown in Figure 4. In the redesigned puller, the crucible is supported and rotated magnetically, and the seed crystal, along with the quartz envelope to which it is rigidly attached, is raised and lowered mechanically. Several advantages are seen for this arrangement: (1) both rotational and translational movement are smoother because of the short bearing-to-crucible linkage, and (2) particles of graphite from the bearings cannot drop into the melt.



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FIGURE 2. BRIDGMAN CRYSTAL-GROWTH APPARATUS

TABLE 1. EXPERIMENTS ON GROWTH OF GaP CRYSTALS BY THE BRIDGMAN METHOD

| GaP Ingot | Container Material | Pressure of Phosphorus Vapor, atm | Approximate Maximum Melting Temperature, °C | Dropping Rate, inch/hr | Description of Ingot Obtained(a) |
|-----------|---------------------------|-----------------------------------|---|------------------------|---|
| 9 | Graphite | 1 | 1405 | 1/4 | High concentrations of gallium metal inclusions; several transparent regions along sides |
| 11 | Graphite | 2 | 1460 | 1/4 | Transparent except for cap and several small regions near center; small inclusions of gallium in transparent regions; R_H , +400 cm ³ /coulomb; ρ , 10 ohm-cm; μ_H , 40 cm ² /v-sec; α , +100 μ v/deg; n_h , $1.6 \times 10^{16}/\text{cm}^3$ |
| 12 | Quartz | 5 | 1450 | 1 | Predominantly free gallium metal |
| 13 | Graphite | 5 | 1385 | 1/4 | Transparent and sound except for a small region in the middle which contained gallium metal inclusions; R_H , +120 cm ³ /coulomb; ρ , 4.2 ohm-cm; μ_H , 32 cm ² /v-sec; α , +145 μ v/deg; n_h , $4.8 \times 10^{16}/\text{cm}^3$ |
| 14 | Quartz | 5 | 1385 | 1/4 | Predominantly free gallium metal |
| 47(b) | Graphite (large diameter) | 4 | ~1500 | 1/4 | Predominantly free gallium metal |
| 51(b) | Graphite (large diameter) | 2 | 1350 | 1/4 | Sound, large crystals |

(a) Electrical measurements made at room temperature on transparent sections.

(b) Reacted 8 hr prior to drop.

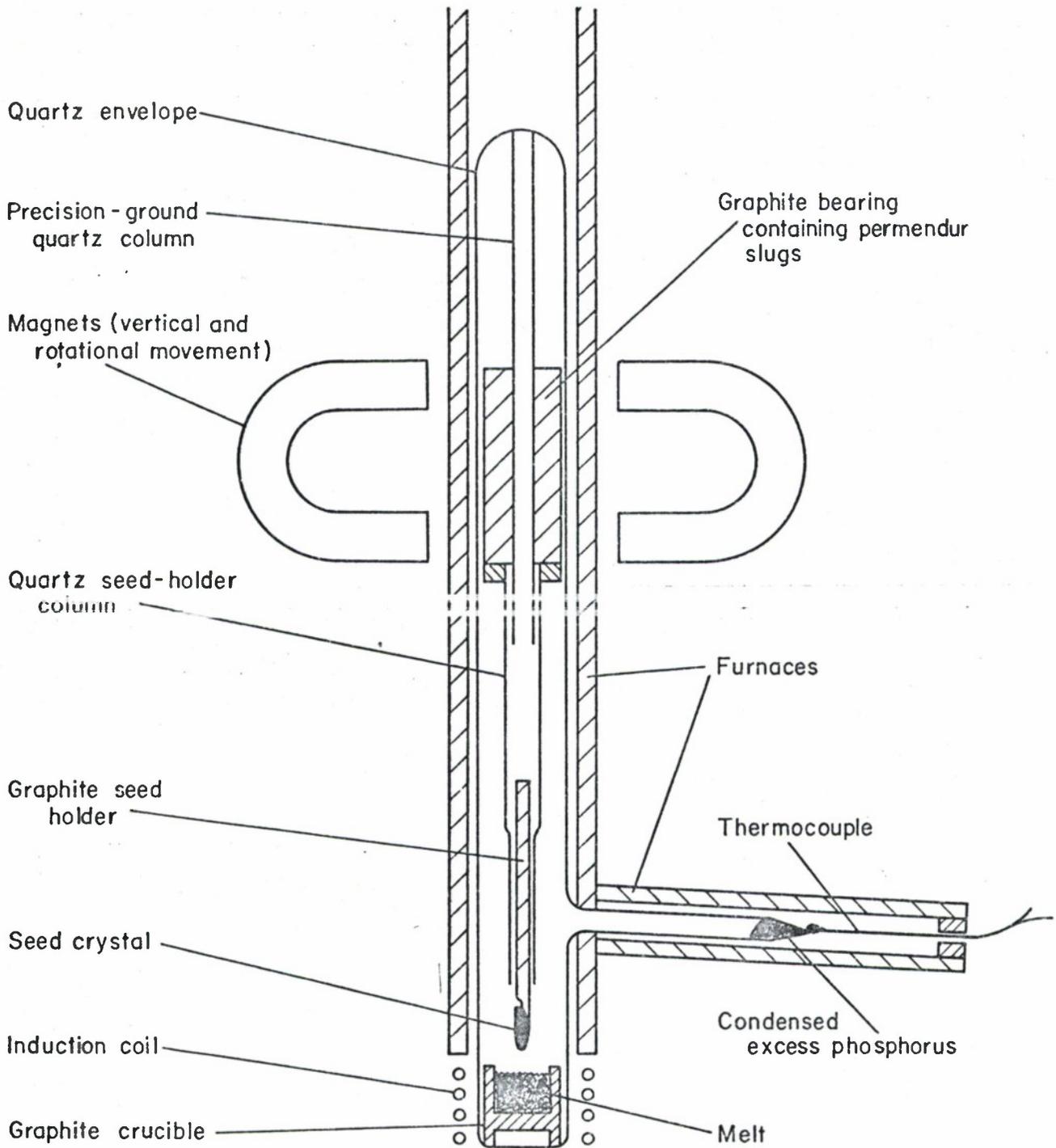


FIGURE 3. SCHEMATIC DIAGRAM OF GREMMELMAIER-TYPE CRYSTAL PULLER

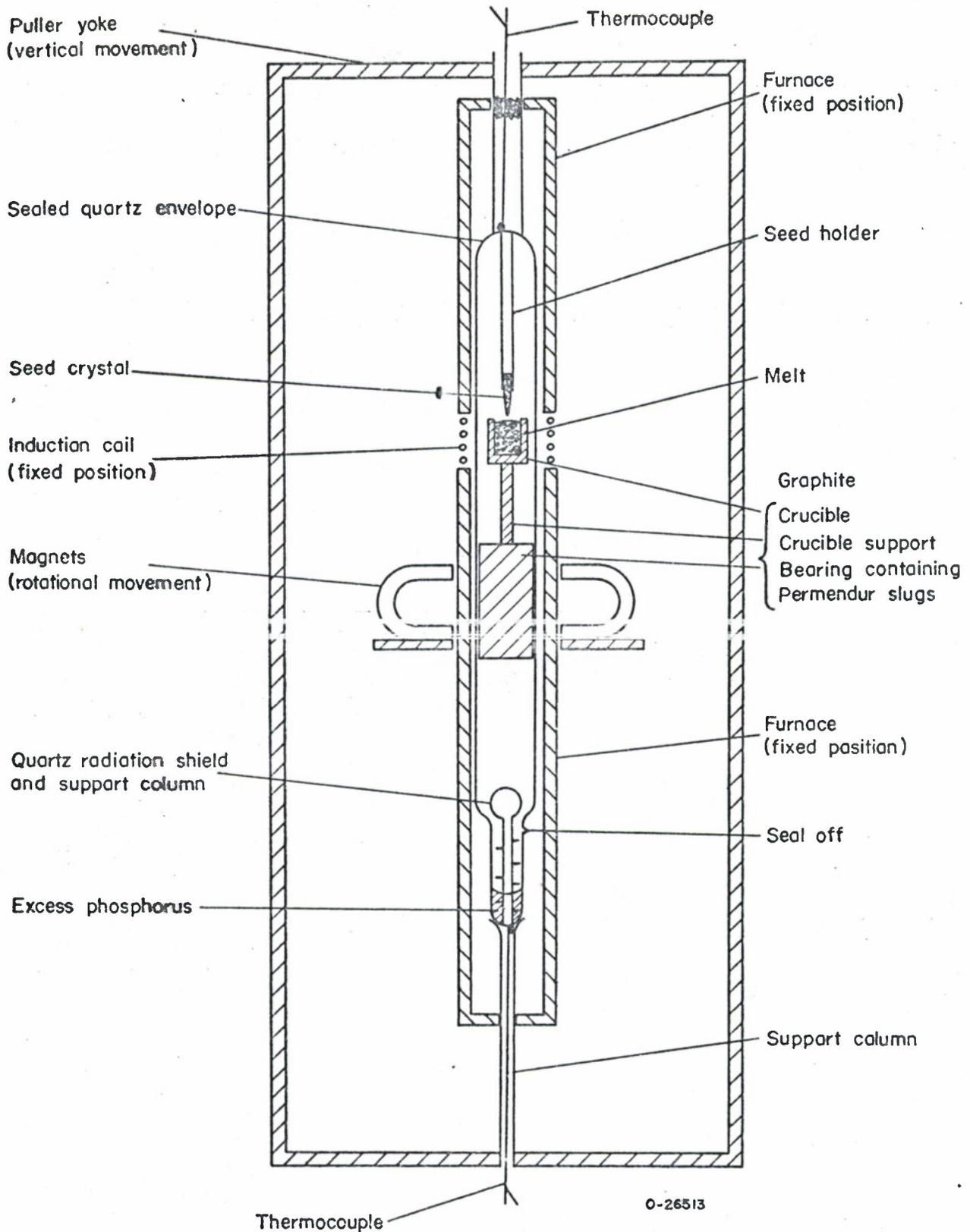


FIGURE 4. SCHEMATIC DIAGRAM OF EXPERIMENTAL GaP CRYSTAL PULLER

No experiments were conducted on growth of alloy crystals by the Czochralski technique.

Solute-Buildup Method

Experiments on crystallization by the solute-buildup method, which were also concerned only with the crystallization of GaP, were limited in number and were of an exploratory nature. Figure 5 is a schematic drawing of the type of apparatus used for this work. In conducting an experiment by this method, a temperature gradient is established over the length of the melt and held fixed as pressure of phosphorus vapor in the envelope is gradually increased. The resulting gradual increase of phosphorus concentration in the melt leads to (1) precipitation as solubility is exceeded at the cooler end of the boat, and (2) propagation of freezing up the temperature gradient.

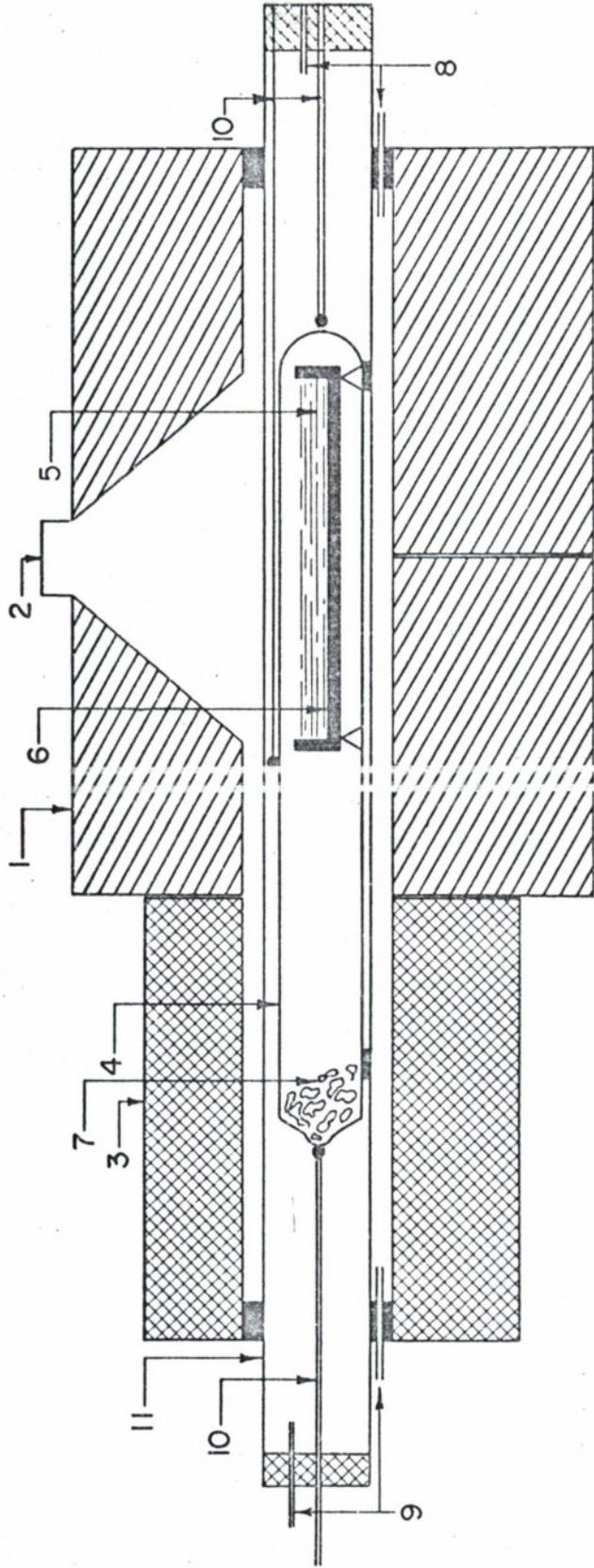
Although sound specimens of GaP were prepared by this method at solution temperatures as low as 930°C and under less than 1-atmosphere pressure of phosphorus vapor, the specimens were small and the yield was low. Nevertheless, the method may merit further consideration.

Crystal Growth From the Vapor Phase

In the course of one of the long-term solute-buildup runs (~330 hr at 930 to 1100°C), a number of sizable (~3 x 3 x 3 mm) well-formed GaP crystals were grown in a low-temperature region of the reaction ampoule by deposition from the vapor phase. Results of determinations of rectification characteristics indicated that electrical properties of these crystals were superior (peak inverse voltages as high as 60 volts) to those of Bridgman-grown crystals (peak inverse voltages ~10 volts). Crystal growth of GaP from the vapor phase, therefore, may warrant further consideration.

Gallium Inclusions in GaP

Microscopic inclusions of gallium metal were found to be present in nearly all Bridgman and Czochralski ingots of GaP. The inclusions were generally 2 to 15 microns in diameter, but in some few instances were observed to be larger. A tendency was noted for the inclusions to be arrayed along grain boundaries. An example of this is shown in Figure 6. It is suggested that the gallium is trapped in the grain boundary as the crystals encroach upon one another during growth. The extent to which the inclusions are confined to grain boundaries was not determined.



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- | | | |
|------------------------------|--------------------------------|-----------------------------|
| (1) Two-zone furnace | (5) Metallic solution or melt | (9) Inert-gas outlets |
| (2) Quartz window | (6) Melt container (supported) | (10) Thermocouples |
| (3) Single-zone furnace | (7) Volatile component | (11) Quartz protection tube |
| (4) Quartz reaction envelope | (8) Inert-gas inlets | |

FIGURE 5. SOLUTE-BUILDUP APPARATUS

ELECTRICAL PROPERTIES

Diode Studies

In the course of studies of point-contact diodes prepared from GaP single crystals, it was noted that the onset of radiation from isolated points on the surface of the crystal correlated with discontinuities in the slope of the reverse characteristic such as are shown in Figure 7. It has been deduced that the radiation is associated with the recombination of carriers in the breakdown region of the current-voltage characteristic.

The spectrum of the recombination radiation, which was obtained through use of a diffraction grating attached to a 35-mm camera, is shown in Figure 8. The energy of the radiation is between 1.96 and 2.19 ev, with a peak at 2.12 ev. Operation of the diode in the breakdown region generated sufficient heat in the device to increase its temperature significantly. Since the temperature of the diode was not determined, the mechanism of the recombination cannot be elucidated from these data. However, it is suggested that, with precise temperature measurement and/or control, it may be possible by this method to determine the energy levels involved in the recombination transition.

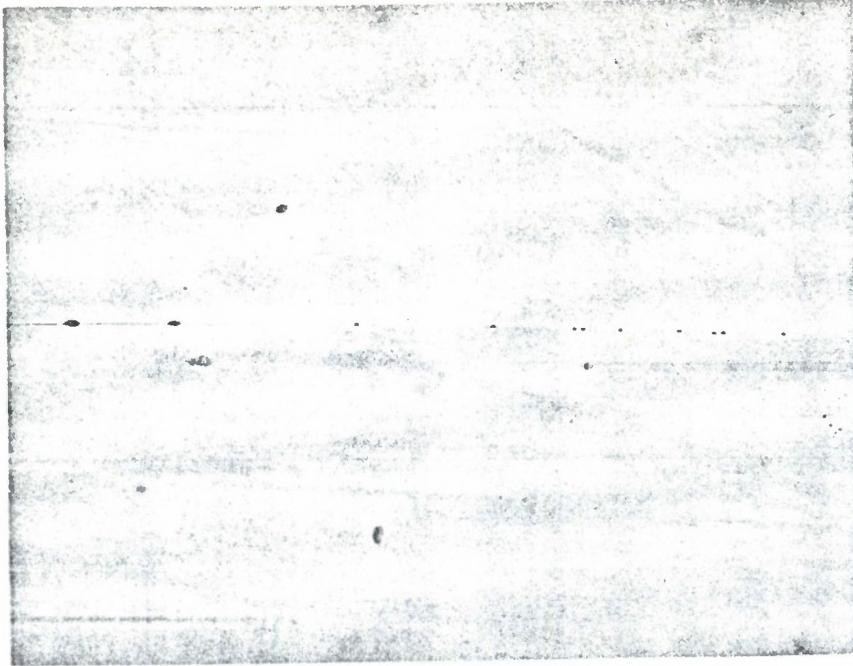
Resistivity and Hall Effect

Results of attempts to evaluate electrical properties of polycrystalline GaP have shown that little reliance can be placed on the values obtained. It is concluded, therefore, that evaluation of electrical properties of GaP should be made solely through study of single-crystal specimens.

Results of a series of measurements which were made on a specimen of polycrystalline GaP (Figure 9) indicate that resistivity is electric-field dependent and show that the measured value depends considerably on contacting procedure. Observed resistivity-versus-temperature characteristics also suggest that contacting procedures strongly influence observation of electrical properties in the range near room temperature, but that these effects tend to diminish in significance (along with grain-boundary effects) as temperature is increased.

Results of measurements on polycrystalline specimens at higher temperatures, where the grain-boundary effects were expected to be negligible, showed that irreversible changes in electrical properties occurred above 350°C. These irreversible changes were attributed to rapid diffusion of the contact material (silver in this case) into the bulk of the specimen, initially along grain boundaries.

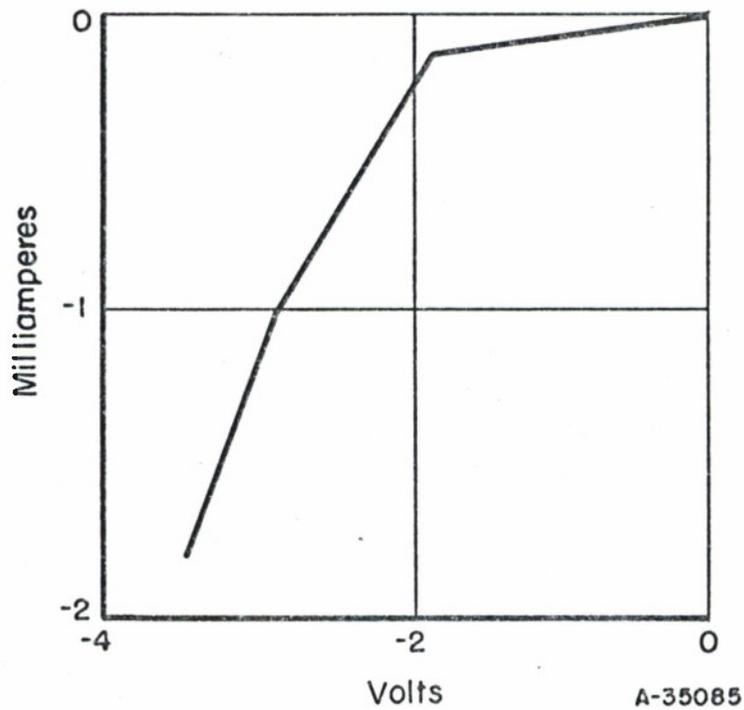
In contrast, measurement of the electrical properties of single-crystal GaP gave reproducible results and showed no dependence of resistivity on current. Results of electrical measurements on a single crystal of p-type GaP are shown in Figure 10. The results indicate some compensation: exhaustion carrier concentration and total ionized-impurity concentration estimated roughly from the Hall data were 1.5×10^{17} and $\sim 10^{19}$ per cm^3 , respectively. An activation energy of 0.05 ev for deionization of acceptors was also calculated from the Hall data.



100X

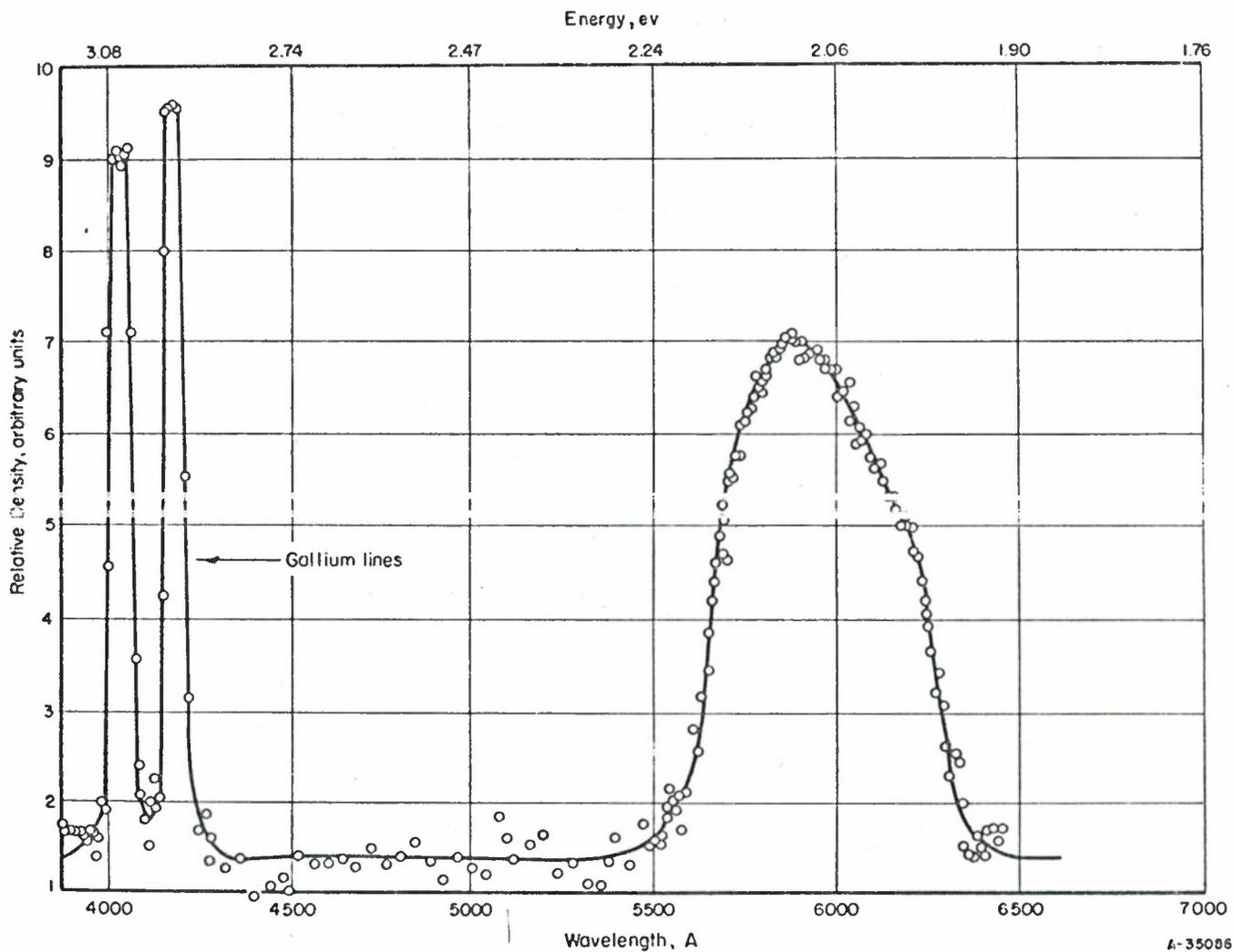
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FIGURE 6. GALLIUM INCLUSIONS ALONG GRAIN BOUNDARY IN GaP



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FIGURE 7. REVERSE CHARACTERISTIC OF GaP POINT-CONTACT DIODE



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FIGURE 8. DENSITOMETER TRACE OF THE FIRST-ORDER SPECTRUM OF RECOMBINATION RADIATION FROM GaP POINT-CONTACT DIODE

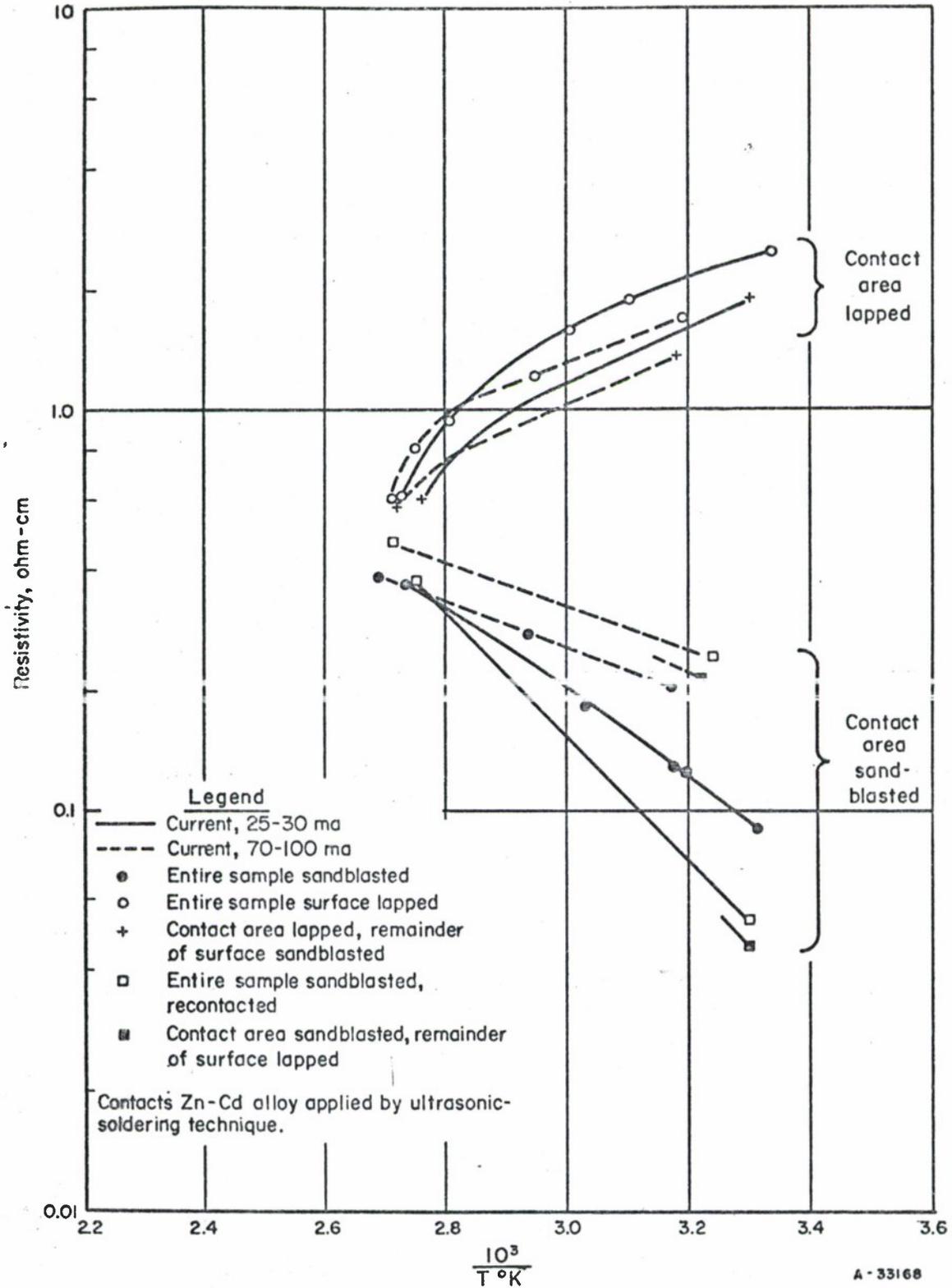
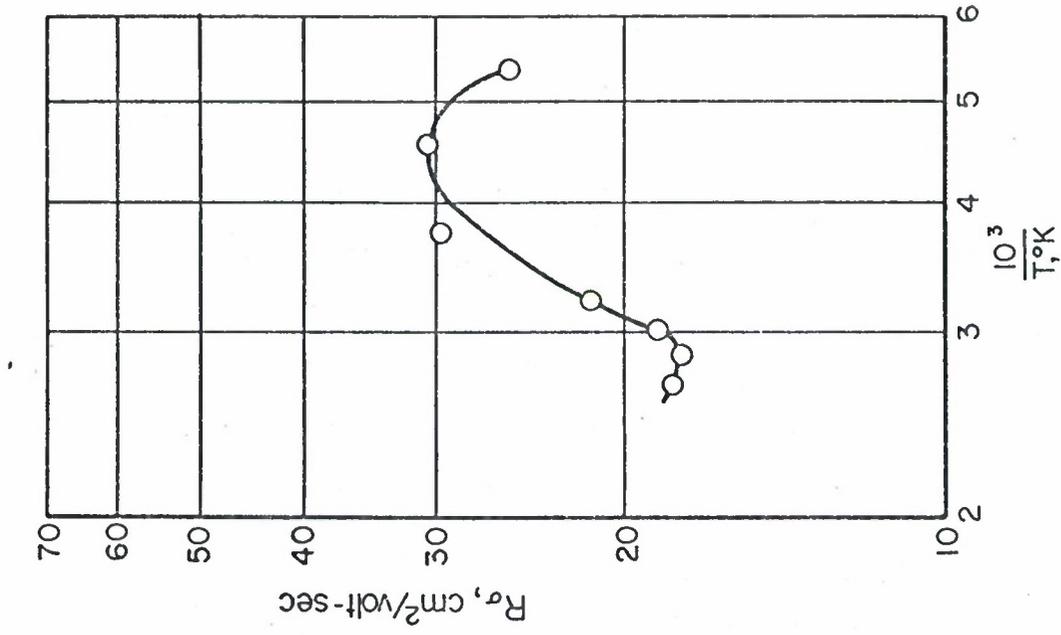
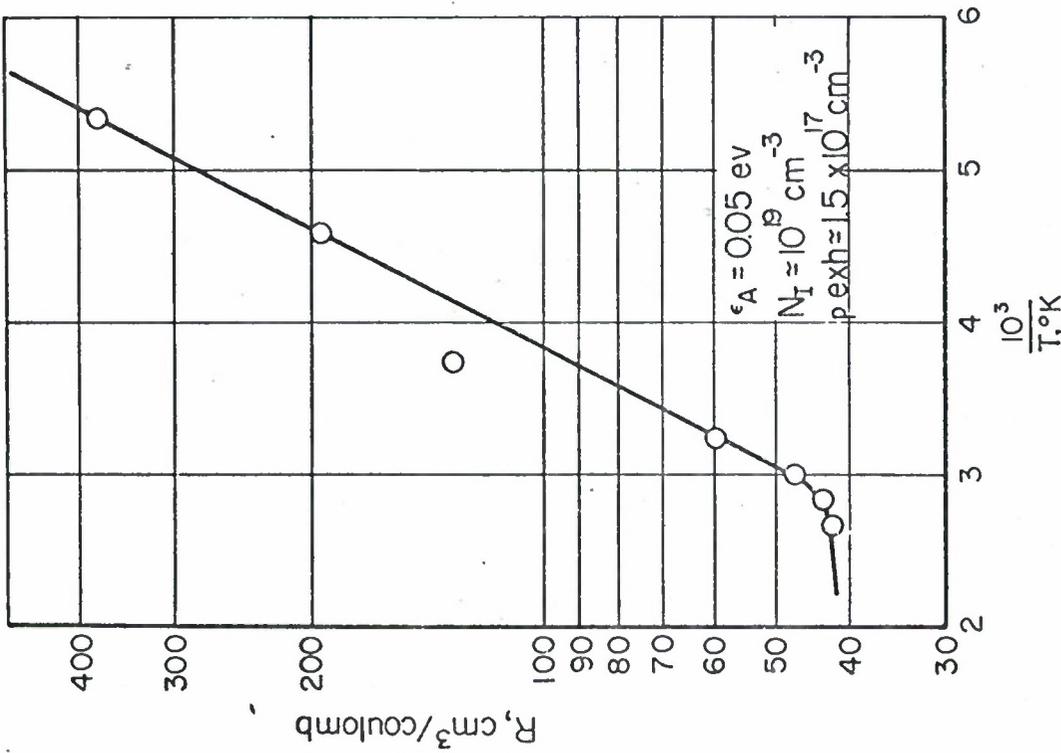


FIGURE 9. RESISTIVITY VERSUS TEMPERATURE FOR POLYCRYSTALLINE SPECIMEN OF GaP



Hall Mobility Versus Temperature for Single-Crystal P-type GaP



Hall Coefficient Versus Temperature for Single-Crystal P-type GaP

FIGURE 10. ELECTRICAL PROPERTIES OF SINGLE-CRYSTAL P-TYPE GaP

Results of electrical measurements on a large ($\sim 10 \times 3 \times 0.6$ mm) single crystal of p-type GaP from an ingot which was prepared by a Bridgman drop at 3/8-inch per hour under only 2 atmospheres' pressure of phosphorus vapor are shown in Figures 11 and 12. Data on the Hall coefficient indicate that exhaustion carrier concentration is $\sim 6 \times 10^{17}$ per cm^3 for this material. The slope of the linear portion of the $T^{3/2}R$ plot corresponds to an activation energy of 0.021 ev. However, if the donor concentration is small, i. e., compensation is only slight, the activation energy for ionization of donors may be twice as large. Using the value obtained by extrapolating the plot to the intercept and assuming $m^* \leq 1$, it can be calculated that the acceptor concentration is larger than the donor concentration by at least a factor of two. The relatively high mobility values (Figure 12) also suggest that compensation effects are minor.

All GaP-InP alloy specimens prepared were polycrystalline. Since no estimate of the importance of grain-boundary effects on electrical properties was obtained, conclusions based on studies of properties of these alloy specimens are of doubtful value. However, measured electrical properties for several alloys are presented in the legend of Figure 13. Hall mobility of electrons for the 31GaP-59InP specimen C appear to be very low. (Composition was calculated from lattice constant, assuming the applicability of Vegard's law.) Low mobilities such as these were observed for a number of alloy specimens. Some possible explanations for the low mobility include (1) large electron effective mass, (2) interband scattering, (3) ionized impurity scattering, (4) effect of polycrystallinity, (5) heterogeneity, and (6) alloy scattering.

OPTICAL PROPERTIES

Optical transmission data, which were obtained for several GaP-InP alloy specimens, are plotted in Figure 13. Absorption cutoffs were at wavelengths corresponding to approximately 1.40, 1.58, and 2.25 ev for specimens containing 12, 31, and 98.9 mole per cent GaP, respectively, as deduced from X-ray data assuming that Vegard's law applies. Additional data and more rigorous analysis of the data would be required to reach firm conclusions regarding the relationship between energy gap and composition in the GaP-InP system.

The transmission spectrum of a specimen of p-type GaP was investigated for wavelengths between ~ 0.5 and 15 microns. Plots of absorption-coefficient data for the material are presented in Figures 14 and 15. Extrapolation of the linear portion of the $\alpha^{1/2}$ versus photon energy (Figure 14) intersects the abscissa at 2.19 ev. This is taken as the minimum energy for indirect transitions and is in good agreement with recent published values. Using the (classical) Drude theory on conductivity and an assumed flat, residual absorption of 6 cm^{-1} at longer wavelengths, a carrier effective mass of 0.11 was estimated from the α versus $\sqrt{\lambda}$ data (Figure 15). However, this value should be regarded as only tentative.

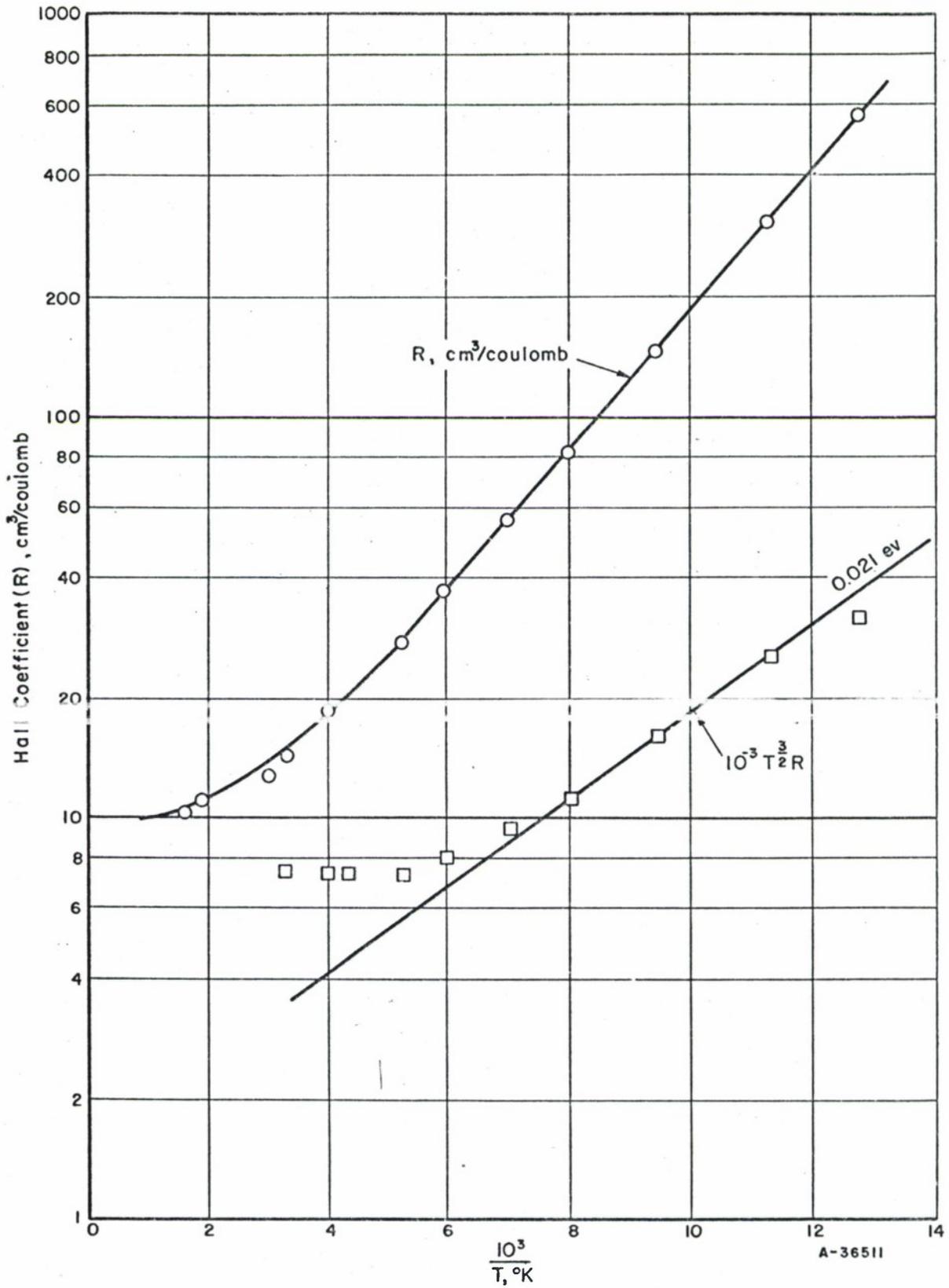


FIGURE 11. HALL COEFFICIENT VERSUS TEMPERATURE FOR SINGLE-CRYSTAL P-TYPE GaP

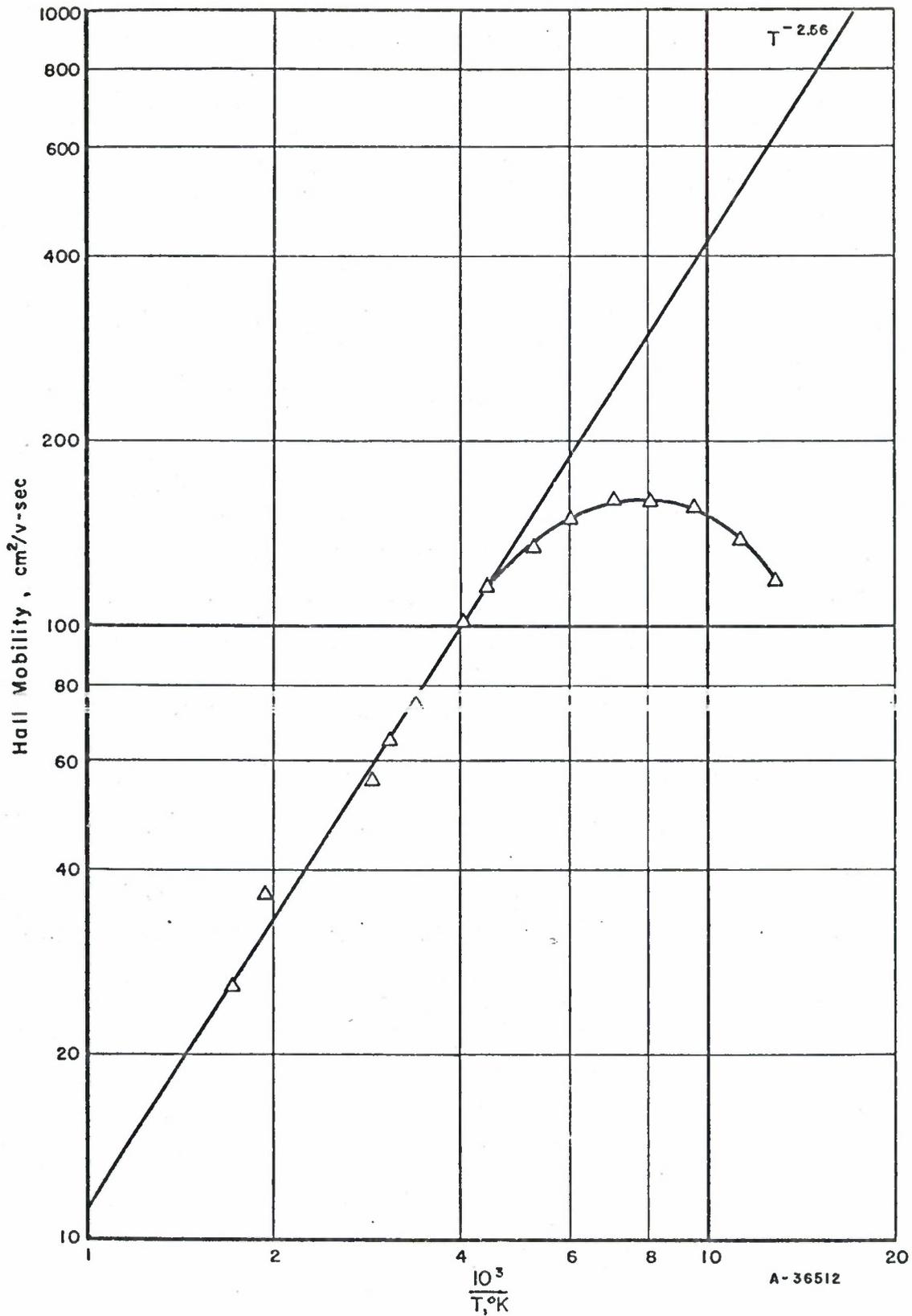
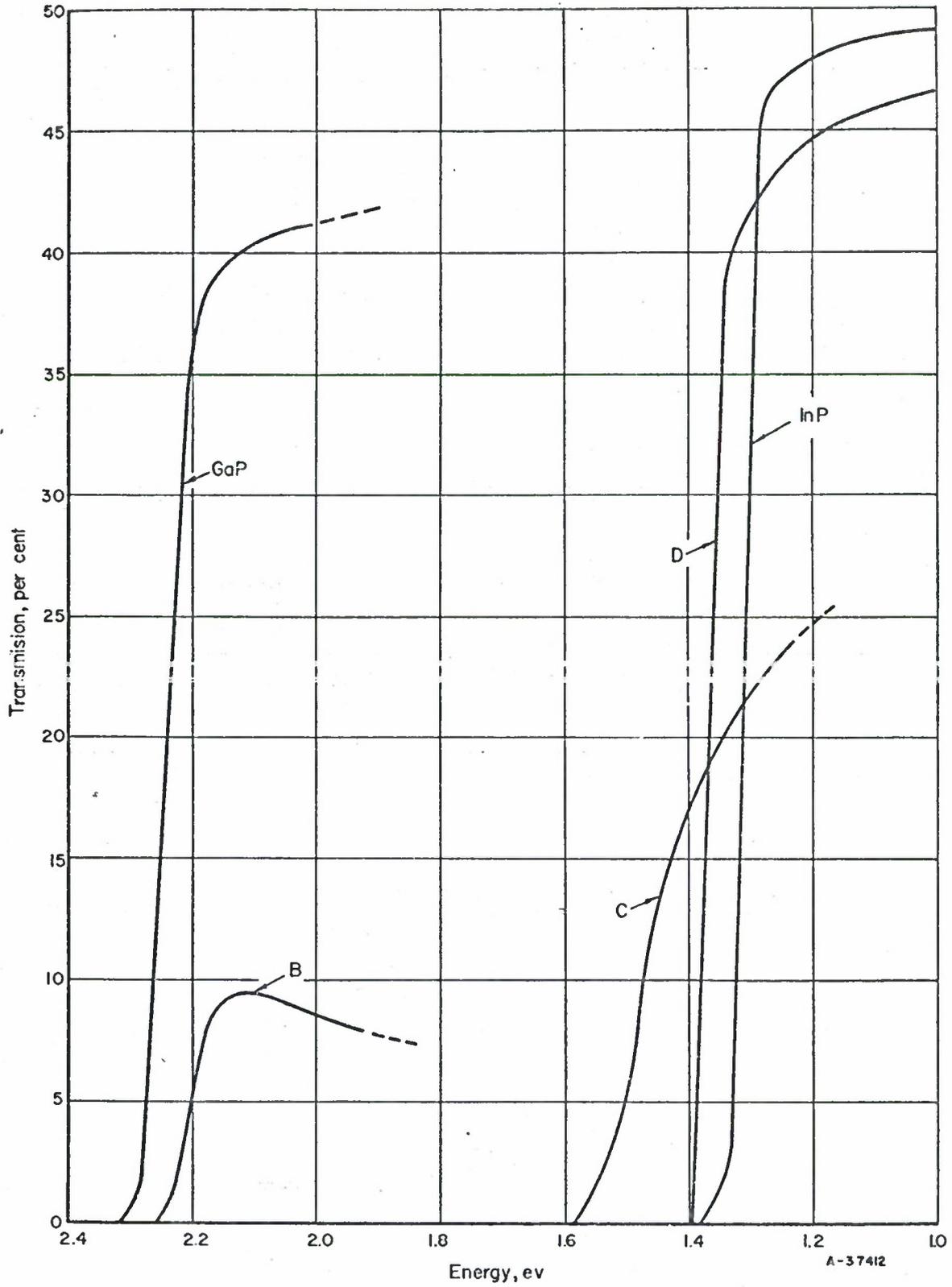


FIGURE 12. HALL MOBILITY VERSUS TEMPERATURE FOR SINGLE CRYSTAL P-TYPE GaP

| | <u>Legend</u> | | | | |
|--|----------------------|----------------|--------------------|----------------------|----------------------|
| | GaP | B | Specimen | | |
| | C | D | E | F | G |
| Thickness, cm | 0.081 | 0.165 | 0.015 | 0.044 | 0.044 |
| Composition, molar ratio by Vegard's law | GaP | 98.9GaP-1.1InP | 31GaP-69InP | 12GaP-88InP | InP |
| X-Ray Lattice Constant, a_0 , Å | 5.4512 | 5.4558 | 5.74 | 5.817 | 5.8689 |
| Resistivity, ρ , ohm-cm | 4.2 | -- | 0.29 | 0.11 | 2.2×10^6 |
| Hall Coefficient, R, $\text{cm}^3/\text{coulomb}$ | +120 | -- | -16 | -92 | -4.6×10^8 |
| Hall Mobility, μ , $\text{cm}^2/\text{volt-sec}$ | 32 | -- | 54 | 840 | 210 |
| Carrier Concentration, n, cm^{-3} | 4.8×10^{16} | -- | 4×10^{17} | 6.8×10^{16} | 1.4×10^{10} |

FIGURE 13. OPTICAL TRANSMISSION DATA FOR GaP-InP ALLOY SPECIMENS



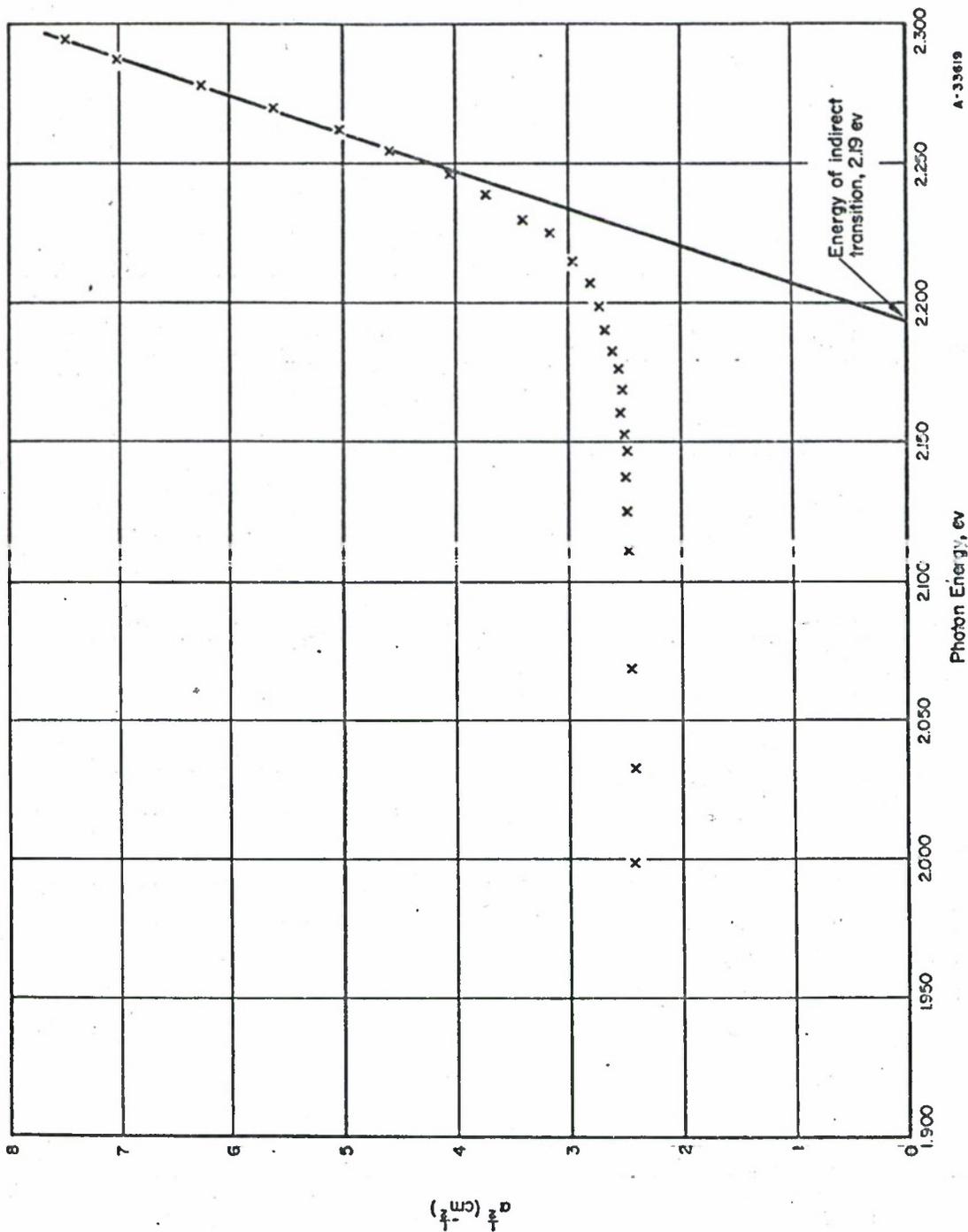
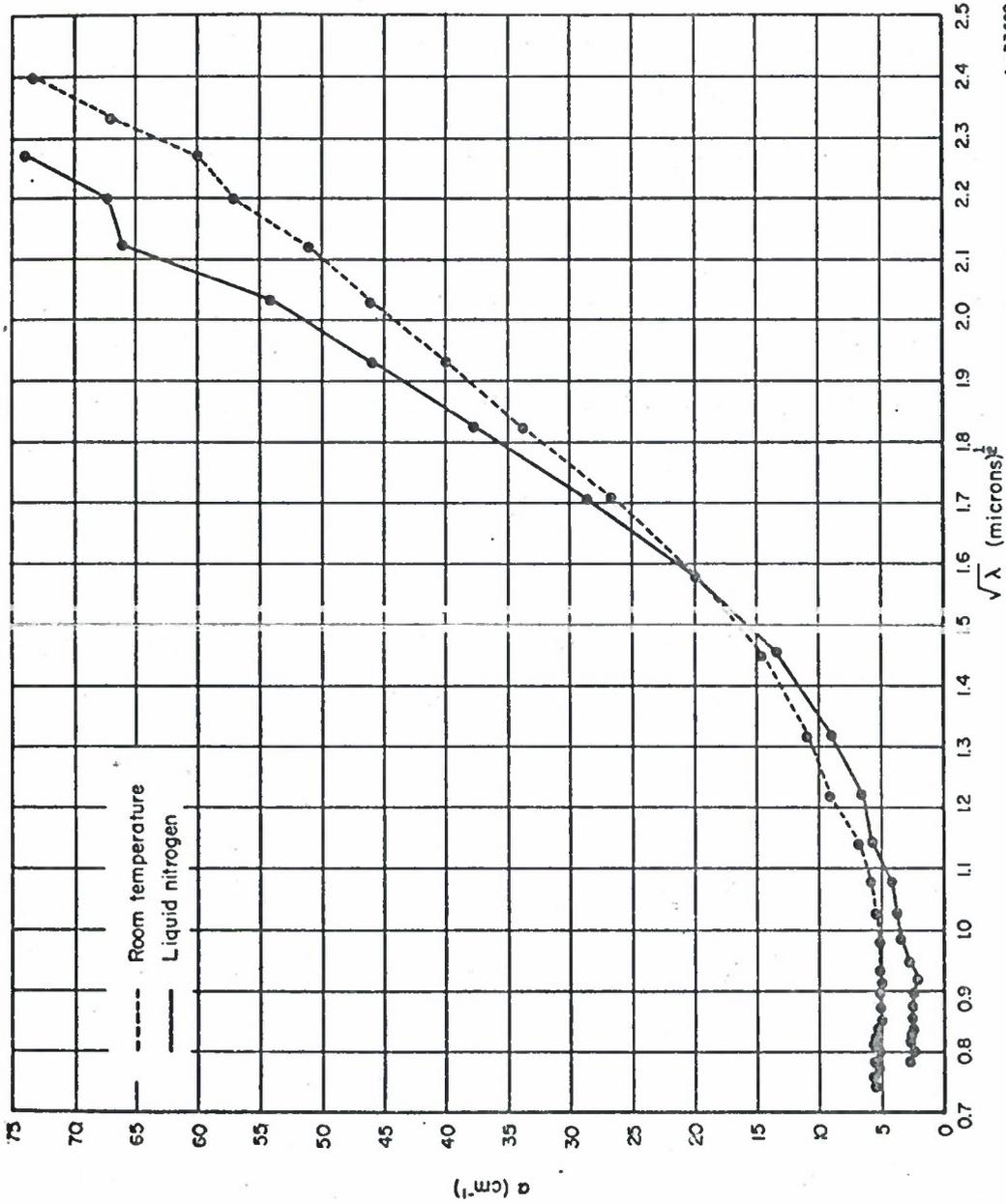


FIGURE 14. SQUARE ROOT OF ABSORPTION COEFFICIENT VERSUS PHOTON ENERGY FOR POLYCRYSTALLINE P-TYPE GaF

Specimen from Ingot 13.



A-33620

FIGURE 15. ABSORPTION COEFFICIENT VERSUS SQUARE ROOT OF WAVELENGTH FOR POLYCRYSTALLINE P-TYPE GaF

Specimen from Ingot 13.

PAPERS PRESENTED OR PUBLISHED

On the basis of work summarized in this report, the following papers were presented or published:

- (1) J. F. Miller, R. C. Himes, and H. L. Goering, "Preparation of Gallium Phosphide Under Moderate Pressures of Phosphorus Vapor", presented at the 118th Meeting of the Electrochemical Society, Houston, Texas (October 10, 1960).
- (2) E. P. Stambaugh, J. F. Miller, and R. C. Himes, "Growth of Refractory III-V Compounds and Alloys From Solution", presented at the AIME Technical Conference on Metallurgy of Elemental and Compound Semiconductors, Boston, Massachusetts (August 29, 1960).
- (3) H. C. Gorton, J. M. Swartz, and C. S. Peet, "Radiative Recombination in Gallium Phosphide Point-Contact Diodes", Nature, 188, 303 (October, 1960).

SPECIMENS PROVIDED FOR SPONSOR

In the 2-year period covered by this report, a number of crystals of various metals and semiconductor materials were sent to the Sponsor for use in various research programs conducted at the Lincoln Laboratory.

RECOMMENDED FUTURE WORK

Electrical properties of GaP crystals grown from solution by the Bridgman method under only 2 atmospheres' pressure of phosphorus vapor compare favorably with those reported in the literature for crystals grown from the melt under 20 to 35 atmospheres' pressure of phosphorus vapor. Relatively large crystals were present in ingots which were crystallized from solution in the latter part of the program. It is believed that this method can be developed to yield consistently crystals of device size. Continuation of work on development of this method for growth of GaP crystals is recommended.

Results of diode studies indicate that GaP crystals of good quality (breakdown voltages up to 60 v) were grown from the vapor phase. Further work on this method, possibly including investigation of epitaxial crystal growth, is desirable and is also recommended.

Data upon which this report is based are recorded in Battelle Laboratory Record Books 14867, pp 74-100; 16707, pp 1-58.

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| 13. ABSTRACT <p>This report describes the work accomplished on the development of techniques for preparing high-purity single-crystal gallium phosphide and alloys of gallium phosphide and indium phosphide and during the period from 15 July 1959 through 15 July 1961. It was found that the melting point and dissociation pressures of GaP and the GaP-InP alloys are high (up to ~1510°C and ~35 atmospheres, respectively). To crystallize the materials from stoichiometric melts, it is necessary to work simultaneously at the elevated temperatures and pressures. Since temperature and pressure requirements for growth of crystals from solution are much less severe, the development of such methods is desirable. In this research, emphasis has been placed on development of methods for crystallizing GaP and GaP-InP alloys from metal-rich solutions.</p> | | | |
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