order parameter S is nearly unity. Values of γ and ϵ are determined by the data. The plotted points of Figs. 6 and 7 represent observations, and the curves are graphs of Eqs. (11) and (12).

It will be noted that the data are consistent with the assumption, introduced earlier, that the processes of nuclear growth and ordering within nuclei are simultaneous in specimens quenched from above T_c.

In conclusion the authors acknowledge with gratitude their indebtedness to Dr. Charles D. Coxe and his associates of Handy and Harmon, who prepared the specimen material; to Professor Victor K. La Mer of Columbia University for helpful advice on nucleation theory; and to Mr. Leonard Weisberg of this laboratory, who devised the radiation furnace and assisted in many of the measurements.

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Electrical Properties of Gallium Antimonide*

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Data are presented on the conductivity and Hall coefficient of several samples of GaSb over the temperature from −196°C to 650°C. The lowest room-temperature conductivity obtained was 12 ohm^{-1} cm^{-1}. All material produced from zone-purified components was *p*-type. *N*-type material was produced by doping with tellurium, as were *p-n* junctions. The intrinsic band gap is estimated from junction rectification data to be 0.78 ev at −196°C. The mobility of electrons was found by measurement on *n*-type material to be several times greater than the hole mobility. The mobilities of both holes and electrons are found to vary approximately as $T^{-\frac{3}{2}}$ in the lattice scattering range.

INTRODUCTION

CONSIDERABLE interest in the semiconducting properties of intermetallic compounds, particularly those formed by the combination of a group three and a group five element, has developed during the last several years.[1–3] Leifer and Dunlap[4] have recently published the results of their studies of the properties of a relatively pure sample of *p*-type GaSb. The present work includes several *p*-type samples, the purest of which is comparable to that of Leifer and Dunlap, as well as an *n*-type sample. Hall effect and conductivity measurements were made over the temperature range from −196° to 650°C. In addition, the current-voltage characteristics of a grown *p-n* junction were measured at room temperature and at −196°C.

PREPARATION OF MATERIALS

GaSb was formed by the direct combination of the zone-refined components[5,6] in approximately stoichiometric properties. It was found that this could be done most conveniently by mixing the purified components in the zone-refining boat and permitting the reaction to occur as the first molten zone was passed through the charge. Any excess of either component is quickly transported to the end of the ingot. Since gallium exhibits some tendency to wet the silica boats employed, a slight excess of antimony was usually added to insure complete reaction of the gallium.

Zone-refining of antimony and GaSb and subsequent GaSb crystal growing by the Czrochralski method were carried out under a purified hydrogen atmosphere. Electrolytic hydrogen, freed of oxygen and water by passing successively through a catalytic purifier, a high-voltage discharge, a $CaSO_4$ drying tower, and a liquid nitrogen cooled trap, was passed continuously over the charge. The resulting ingots of both antimony and GaSb exhibited a very clean, mirror-like surface as compared to the dull matte surface obtained with less pure hydrogen.

All of the material produced in this fashion exhibited *p*-type conductivity, the value depending upon the purity of the gallium employed. The less pure GaSb samples were prepared from relatively impure gallium which had not been zone-refined. These facts, together with the observation that the purity of GaSb made from the same gallium after zone-refining was as high as any produced, indicates the presence in at least some gallium of an impurity which is not effectively removed from the compound by the zone-refining process.

N-type material and *p-n* junctions were prepared by doping with an alloy of about one atomic percent tellurium in GaSb when growing crystals.

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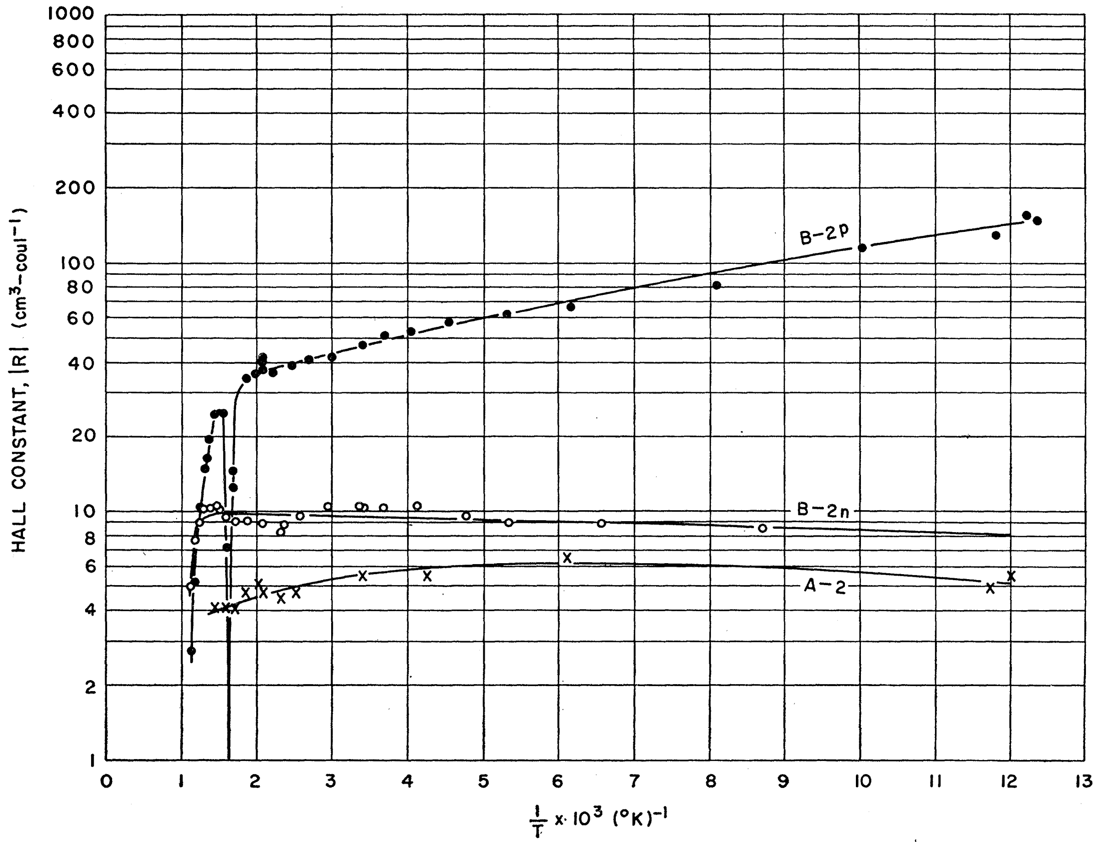

FIG. 1. The conductivity of gallium antimonide as a function of reciprocal temperature.

EXPERIMENTAL PROCEDURE

The conductivity and Hall coefficient of samples with dimensions of approximately 1.0 cm by 0.1 cm by 0.3 cm was measured over the temperature range from −196°C to 650°C in a vacuum furnace. The samples were supported on a lavite sample-holder mounted inside a mica-lined heavy-wall copper cavity. Mica lining was employed to avoid evaporation of copper onto the specimens at the higher temperatures. A vacuum of about 10^{-5} mm of Hg was maintained during measurements.

The temperature was determined with a calibrated chromel-alumel thermocouple mounted in the sample chamber. A second thermocouple in good thermal contact with the heater windings was employed in conjunction with a photoelectrically controlled thyratron for temperature control. With this circuit the temperature of the sample could be maintained constant to ±0.02°C over long periods. Temperatures below room temperature were obtained by immersing the entire vacuum furnace in liquid nitrogen and supplying sufficient heat to reach the desired temperature.

Potential contacts to the specimen for conductivity and Hall coefficient measurements were made with stainless steel whiskers. After being placed in pressure contact with the sample, the probes were lightly welded by a high-voltage discharge from a Tesla coil. This resulted in a quite stable, low resistance, nonrectifying contact of very small area. Remeasurement of a sample at low-temperature after heating to the highest temperature indicated the absence of any effect of the contacts upon the bulk properties. Current contacts to the specimens were large-area stainless steel springs. All potential measurements were made with a Wenner thermo-free potentiometer.

The magnetic field employed in determining the Hall constant was produced by an electromagnet. The field was controlled by an electronic controller to an accuracy of ±0.02 percent, and could be varied from zero to 5000 oersteds. No dependence of Hall constant upon field strength was found in the purest specimens for fields from 200 to 2500 oersteds.

Samples were cut from grown crystals with either a diamond or a carborundum saw and were etched with a dilute HCl-HNO_3 etch. A more concentrated solution of the same acids acts as a chemical polish. It was found possible to achieve a concentration such that a *p-n* junction could be located visually because of the difference of polishing activity between *n*-type and *p*-type materials.

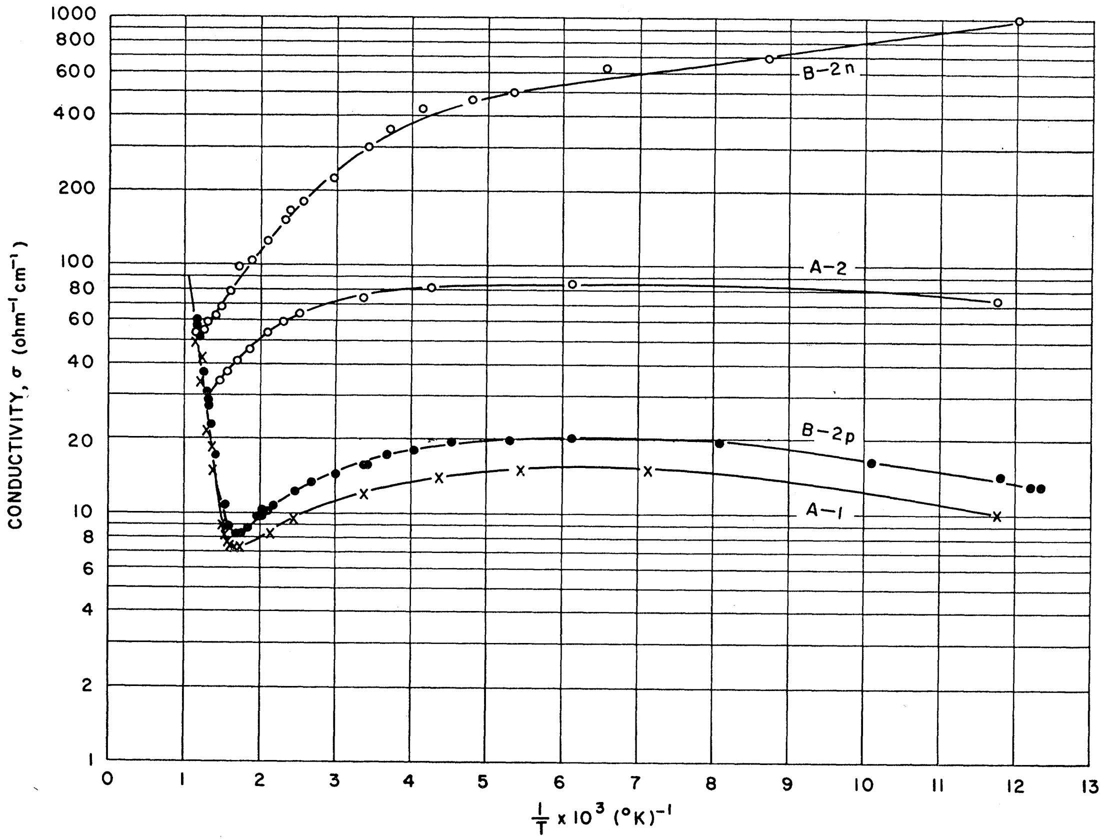

FIG. 2. The Hall coefficient of gallium antimonide as a function of reciprocal temperature.

For measurement of *p-n* junction characteristics, contacts were soldered to samples with pure indium solder, using a zinc chloride flux. This results in mechanically reliable, nonrectifying contacts.

RESULTS AND DISCUSSION

A. Conductivity and Hall Coefficient

Conductivity and Hall coefficient data on several samples, both *n*-type and *p*-type, are shown in Figs. 1 and 2, respectively. All samples except that designated *A*-1 were single crystals; all except *B*-2*n* were *p*-type. Samples *A*-1 and *B*-2*p* are shown for comparison with the results of Leifer and Dunlap.[4] The purity is very similar to theirs, illustrating the observation that various workers have obtained essentially the same limiting purity.

An impurity activation energy of 0.025 ev is calculated from the Hall coefficient *vs* temperature of sample *B*-2*p*, in good agreement with the previous results.[4] The Hall coefficients of samples *A*-2 and *B*-2*n*, containing respectively 1.2×10^{18} and 7×10^{17} impurities per cm^3, however, indicate that at this concentration the impurities are completely ionized at temperatures as low as −196°C. This implies an activation energy not greater than approximately 0.01 ev at this concentration.

Figure 3 shows the mobility values computed from the measured Hall coefficients and conductivities. Sample *B*-2*p* exhibits the expected $T^{-\frac{3}{2}}$ dependence

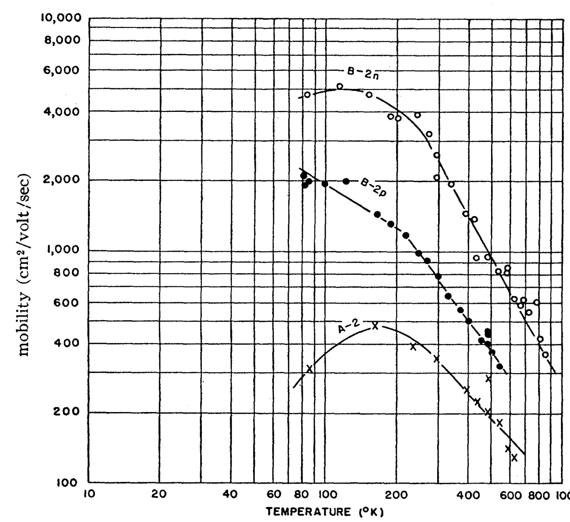

FIG. 3. The mobility of charge carriers in gallium antimonide.

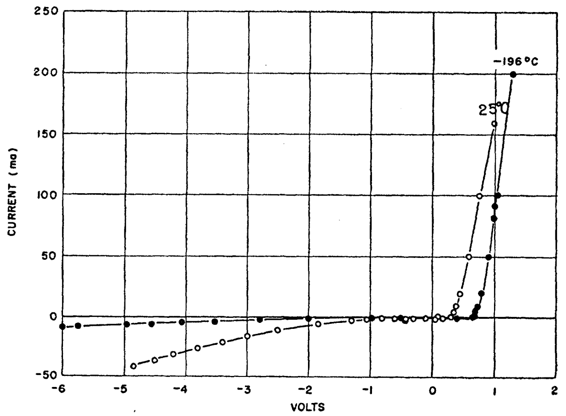

FIG. 4. A *p-n* junction rectification characteristic at room temperature and −196°C.

of mobility upon temperature in the higher temperature region where lattice vibrations are the dominant scattering mechanism. In the somewhat less pure sample, *A*-2, however, the mobility appears to depend slightly less strongly upon temperature, while the electron mobility in sample *B*-2*n* appears to depend somewhat more strongly upon temperature.

The ratio of electron to hole mobility may be computed in sample *B*-2*p* by the method discussed by Shockley.[7] This leads to a value of 6.5 as compared to the ratio of 2.3 for the mobility of majority carriers in sample *B*-2*n* to that in sample *B*-2*p* at the temperature of the Hall reversal. This is considered reasonable agreement in view of the lower purity of the sample *B*-2*n* and the dependence of mobility upon purity.

The chief problem at present in this work appears to be the preparation of GaSb of purity comparable to that of germanium. A limiting purity of about 10^{17} carriers per cm^3 has been obtained by several workers.[1,4,8] This is believed to be the result of a slight deviation of the composition from stoichiometry rather than a chemical impurity effect, since the results of the various laboratories agree so closely. Further, it has been found in the course of the present investigation by analysis of the distillate from previously zone-refined GaSb heated under vacuum that antimony is evaporated preferentially. Several samples collected at various distillation temperatures above the melting point showed antimony contents of from 75 to 95 atomic percent in the distillate. This is in agreement with the observed *p*-type conductivity in the present materials.

B. *p-n* Junction Rectification

Several *p-n* junctions were grown from the melt by doping an initially *p*-type melt with tellurium when the crystal was partly grown. Figure 4 shows the dc characteristic of one of these junctions as measured at room temperature and at −196°C. Although photosensitivity of the junction was noted at high levels of illumination, no difference could be observed between measurements in darkness and in room light. Consequently, most measurements were carried out in room light.

Rectification ratios at one volt of about 200 and 500 were observed at room temperature and −196°C respectively. However, considerable "softening" of the reverse characteristic is found with no well-defined saturation region. This and the rather low photosensitivity are believed to be manifestations of the existence of a small minority carrier lifetime in this material.

The width of the forbidden energy gap, E_g, may be determined from the forward *p-n* junction characteristic in the region where the current becomes linear with voltage. Here the applied voltage is greater than E_g, so the current is limited only by the ohmic resistance of the specimen. Extrapolating this region back to the zero-current axis, one obtains the voltage required to overcome the barrier at the junction, i.e., E_g. Performing this extrapolation on the low-temperature data shown in Fig. 4, one obtains a value for E_g of 0.78 ev. This compares very well with the value of 0.77 ev calculated from Leifer and Dunlap's[4] values of E_g at room temperature and α, the temperature coefficient of E_g.

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