PHYSICAL REVIEW VOLUME 121, NUMBER 4 FEBRUARY 15, 1961

Electrical Properties of n-Type GaSb

ALAN J. STRAUSS
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts*

(Received October 3, 1960)

The electrical conductivity and Hall coefficient of n-type GaSb doped with Se or Te have been measured, in most cases at 77° and 300°K, for samples with net donor concentrations between about 6×10^{16} cm^{-3} and 2×10^{18} cm^{-3}. In general, the data are consistent with the two-band model which Sagar has proposed for the conduction band of GaSb, but systematic differences are observed between the properties of Se-doped and Te-doped samples. It seems likely that these differences are associated with impurity conduction of the metallic type. For the Te-doped samples, the electron mobility at 77°K apparently varies in an anomalous manner with increasing impurity concentration.

INTRODUCTION

THE electrical properties of n-type GaSb doped with tellurium have been investigated by Sagar,[1] who measured the Hall coefficient (R_H), conductivity (σ), and piezoresistance as functions of temperature and also determined the dependence of R_H and σ on hydrostatic pressure. Sagar found that his results could not be explained solely on the basis of the spherically symmetric conduction band with energy minimum at $k=0$ and effective mass of 0.047 m_0 which had been deduced by Zwerdling *et al.*[2] from their data on the infrared absorption of p-type GaSb. He proposed, therefore, an additional conduction band with minima lying at a slightly higher energy ($\sim$0.075 ev) along the $\langle 111\rangle$ directions in k space. He suggested that this band might resemble the $\langle 111\rangle$ band in germanium, with a density of states about 40 times that of the lower band. By assuming different mobilities for the electrons in the two bands, he could explain the observed electrical properties of n-type GaSb in terms of changes in the distribution of electrons between the bands.

In the present investigation, the Hall coefficient and electrical conductivity of n-type GaSb have been measured, in most cases at room temperature and at 77°K, for Se-doped as well as for Te-doped samples. In general, the data are consistent with the two-band model proposed by Sagar. Systematic differences, however, have been observed between the properties of Se-doped and Te-doped samples. Furthermore, although the data for Te-doped samples agree with Sagar's experimental results, it has been found that some features of these data are not explained by his band model. Therefore, it appears that the character of the donor impurities, as well as the conduction-band structure, plays an important role in determining the electrical properties of n-type GaSb which contains relatively high donor concentrations ($>10^{17}$ cm^{-3}). In particular, impurity conduction of the metallic type, which was neglected by Sagar, is probably significant.

EXPERIMENTAL

Samples for Hall and conductivity measurements were cut from crystals which had been pulled from the melt, in a hydrogen atmosphere, in approximately the [111] direction. The raw material used was zone-refined p-type GaSb (supplied by United Mineral and Chemical Corporation) which, like all high purity GaSb currently available, contained a free hole concentration of approximately 10^{17} cm^{-3} at room temperature; sufficient Se or Te was added to the melt to obtain n-type crystals with excess donor concentrations ranging from about 6×10^{16} cm^{-3} to about 2×10^{18} cm^{-3}. The samples were rectangular parallelepipeds 1–2 mm thick, 3–5 mm wide, and 10–15 mm long. Two potential leads were ultrasonically soldered with indium to each of the long sides of each sample, so that duplicate Hall and conductivity measurements could be made. Data for a sample were rejected unless the duplicate results agreed to within 10%. Conventional dc potentiometric techniques were used to make the voltage measurements, while the magnetic field of approximately 7800 gauss was monitored with a rotating coil fluxmeter. In most cases measurements were made only at room temperature and at 77°K, but for five of the Se-doped samples detailed measurements were made between 77° and approximately 350°K by using automatic switching and recording apparatus to obtain the data as the samples were allowed to warm up slowly from liquid nitrogen temperature.

CALCULATION OF ELECTRICAL PROPERTIES

In order to compare the experimental results with theory, Sagar's conduction band model was used to calculate the electrical conductivity (σ), Hall coefficient (R_H), and Hall mobility ($R_H\sigma$) at 300° and 77°K as functions of net donor concentration (N_D'). It was assumed that the donors are completely ionized at both temperatures, so that the total concentration of free electrons is equal to N_D', independent of temperature. (The intrinsic carrier concentrations at both temperatures are negligible compared to the values of N_D' considered.) The values of R_H and σ were calculated according to the usual expressions for two-band

---

* Operated with support from the U. S. Army, Navy, and Air Force.

[1] A. Sagar, Phys. Rev. 117, 93 (1960).

[2] S. Zwerdling, B. Lax, K. Button, and L. Roth, J. Phys. Chem. Solids 9, 320 (1959).

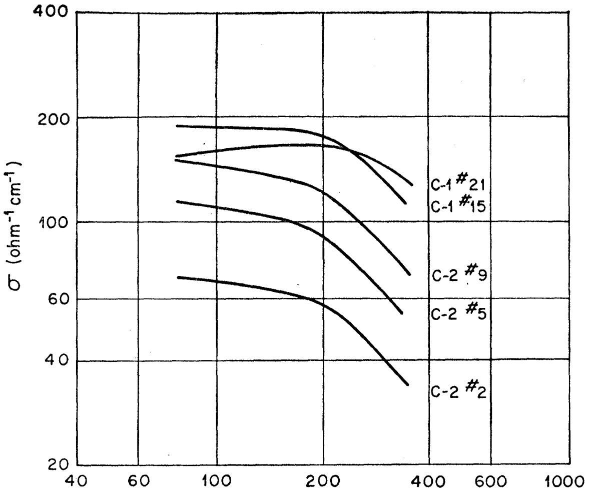

FIG. 1. Electrical conductivity (σ) as a function of temperature for Se-doped n-type GaSb.

conduction:

$$\sigma = e(n_0\mu_0 + n_1\mu_1),$$

$$R_H = -e^{-1}[(n_0\mu_0^2 + n_1\mu_1^2)/(n_0\mu_0 + n_1\mu_1)^2],$$

where n and μ represent the free electron concentration and mobility, respectively, while the subscripts 0 and 1 refer to the conduction bands with energy minima at $k=0$ and along the $\langle 111\rangle$ directions, respectively. The electron concentrations were evaluated according to Fermi-Dirac statistics. The effective mass for the lower band (minimum at $k=0$) was taken as 0.047 m_0, the value obtained by Zwerdling *et al.*[2] Following Sagar, the density of states for the $\langle 111\rangle$ band was assumed to be 40 times that for the lower band, while the difference in energy between the band minima was taken to be 0.074 ev. The mobility ratio μ_1/μ_0 was assumed to have the value of 1/6 estimated by Sagar, while the values of μ_0 at 300° and 77°K were taken as 3300 and 2600 cm^2/v sec, respectively, in order to give a satisfactory fit to the data for the samples of lowest net donor concentration.

RESULTS AND DISCUSSION

The measured values of σ and R_H for five Se-doped samples are shown in Figs. 1 and 2, respectively, for the temperature range 77°–350°K. (The experimental points are omitted for the sake of clarity.) The data are plotted against temperature, rather than against $1/T$, in order to facilitate comparison with Sagar's plots for Te-doped samples. The net donor concentrations (N_D') for these samples have been estimated from the R_H data at 77°K, together with the theoretical R_H vs N_D' curve for 77°K calculated on the basis of Sagar's conduction band model in the manner described above. The estimated N_D' values increase from 1.7×10^{17} cm^{-3} for sample [C-2, No. 2] to 8×10^{17} cm^{-3} for sample [C-1, No. 21].

The temperature dependence of σ and R_H for Se-doped samples qualitatively resembles the temperature dependence measured by Sagar for Te-doped samples. The most striking feature of both sets of data is the increase in R_H with increasing temperature for the samples with highest R_H values—i.e., lowest free electron concentrations. In contrast, for an extrinsic semiconductor exhibiting single band conduction, R_H either decreases with increasing temperature (as additional free carriers are produced by increasing thermal ionization of impurities) or is independent of temperature (if all impurities are already ionized).

For both Se-doped and Te-doped samples, the temperature dependence of R_H is consistent with Sagar's band model, according to which the changes in R_H reflect changes in the distribution of electrons between the two conduction bands, rather than changes in the total free electron concentration. For sufficiently pure samples, essentially all the free electrons are in the lower band at 77°K, so that $R_H \approx 1/ne$. With increasing temperature, however, some of the electrons are promoted into the higher (low mobility) band, and R_H therefore increases in accordance with the mixed conduction expression given above. The decrease in σ with increasing temperature for these samples is caused primarily by the reduction in the mobility of electrons which are transferred into the higher band, rather than by a decrease in electron mobility in a single band due to increased lattice scattering. For less pure samples, some electrons are in the higher band even at 77°K, so that the distribution of electrons, and therefore R_H and σ, does not change to as great an extent with increasing temperature; for samples containing sufficiently high concentrations of free electrons, the electron distributions and electrical properties are essentially independent of temperature.

Although the general features of the data for Se-doped and Te-doped samples are similar, detailed comparison reveals systematic differences which are surprisingly

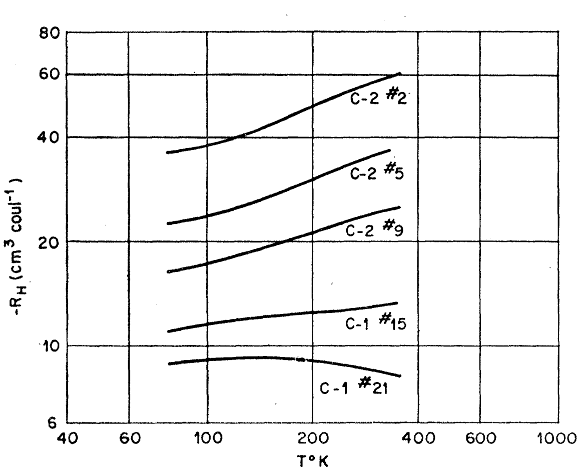

FIG. 2. Hall coefficient (R_H) as a function of temperature for Se-doped n-type GaSb.

large in view of the chemical similarity between Se and Te. These differences are illustrated by Fig. 3, in which $R_H(300°\text{K})/R_H(77°\text{K})$ and $\sigma(77°\text{K})/\sigma(300°\text{K})$ for all samples are plotted against $R_H(77°\text{K})$, and by Fig. 4, in which the Hall mobilities $R_H\sigma(300°\text{K})$ and $R_H\sigma(77°\text{K})$ are also plotted against $R_H(77°\text{K})$. The net donor concentrations estimated from the values of $R_H(77°\text{K})$ range from 6×10^{16} cm^{-3} to 4×10^{18} cm^{-3}. Sagar's data for Te-doped samples, which are in good agreement with the present results, are included in both figures. The dashed lines in Figs. 3 and 4 are theoretical curves derived from the R_H and σ values for 300° and 77°K calculated on the basis of Sagar's conduction band model in the manner described above. It is seen that for high impurity concentrations [i.e., low values of $R_H(77°\text{K})$], Se-doped and Te-doped samples which have the same values of $R_H(77°\text{K})$ differ markedly both in the degree of change in R_H and σ between 300° and 77°K and also in the Hall mobilities at these temperatures. For the purest samples, on the other hand, the differences are minor.

Although no detailed explanation can be given for the differences between the properties of Se-doped and Te-doped samples, since these differences disappear with decreasing donor concentration it seems likely that they are associated with impurity conduction. In the case of degenerate *n*-type Ge, which exhibits impurity conduction of the metallic type (i.e., impurity conduction which does not require the simultaneous presence of acceptor impurities), there are appreciable differences between the Hall mobilities of As-doped and Sb-doped samples[3,4] and also between the characteristics of tunnel diodes prepared from such samples.[4,5] Since Se and Te atoms in GaSb are shallow, singly ionized donors analogous to As and Sb in Ge, differences in impurity conduction due to these atoms in GaSb would not be surprising. Furthermore, it seems certain that impurity conduction does occur in *n*-type GaSb, since the total donor concentrations in even the purest *n*-type samples must exceed 10^{17} cm^{-3}, the acceptor concentration in the raw material used for both the present crystals and those prepared by Sagar. Even at this minimum concentration, impurity conduction of the metallic type would certainly be associated with the lower, low-mass conduction band. For still higher concentrations, metallic impurity conduction would probably also be associated with the higher conduction band, if this band is similar to the ⟨111⟩ band in Ge, as Sagar has suggested; in Sb-doped Ge, the onset of metallic impurity conduction occurs at approximately 10^{17} cm^{-3}, according to Fritzsche's data.[6]

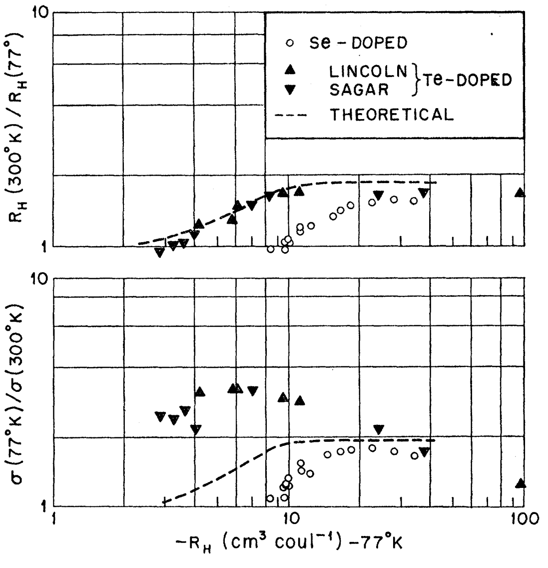

FIG. 3. The ratios $R_H(300°\text{K})/R_H(77°\text{K})$ and $\sigma(77°\text{K})/\sigma(300°\text{K})$ as functions of $R_H(77°\text{K})$ for Se-doped and Te-doped *n*-type GaSb.

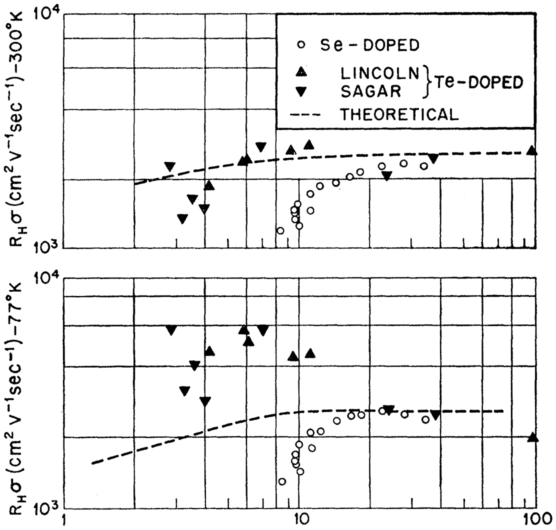

FIG. 4. Hall mobilities at 300° and 77°K as functions of $R_H(77°\text{K})$ for Se-doped and Te-doped *n*-type GaSb.

In view of the uncertainties in a number of the band parameters used in calculating the theoretical curves of Figs. 3 and 4 from Sagar's band model, a detailed comparison between these curves and the experimental data would not be particularly useful at this time. Compensation by the residual acceptors and the probable occurrence of impurity conduction, which were not considered by Sagar, also complicate the situation. Two general comments seem appropriate, however.

For the Se-doped samples, each of the properties plotted in Figs. 3 and 4 exhibits the monotonic decrease with decreasing R_H which is predicted theoretically, but in each case the decrease is more rapid than calcu-

---

[3] P. L. Moody and A. J. Strauss, Semiconductor Symposium of the Electrochemical Society, May, 1960 (unpublished).

[4] Y. Furukawa, J. Phys. Soc. Japan **15**, 730 (1960).

[5] N. Holonyak, I. A. Lesk, R. N. Hall, J. J. Tiemann, and H. Ehrenreich, Phys. Rev. Letters **3**, 167 (1959).

[6] H. Fritzsche, J. Phys. Chem. Solids **6**, 69 (1958).

lated. The discrepancies between theory and experiment could probably be removed by adopting somewhat different values for the band parameters, without making any radical revision in Sagar's model. It should be noted, for example, that the band parameters were taken to be independent of impurity concentration. The usual decrease in electron mobility in each conduction band with increasing impurity concentration would therefore cause the observed Hall mobilities to decrease more rapidly with decreasing R_H than predicted.

For the Te-doped samples, both $R_H(300°\text{K})/R_H(77°\text{K})$ and $R_H\sigma(300°\text{K})$ vary with $R_H(77°\text{K})$ in approximately the manner predicted by theory. This agreement is to be expected, since several of the band parameter values used in the calculations were adopted by Sagar in order to fit his data on Te-doped samples. Surprisingly, however, both $\sigma(77°\text{K})/\sigma(300°\text{K})$ and $R_H\sigma(77°\text{K})$ first increase markedly with decreasing R_H, rather than decreasing monotonically as predicted. At 77°K, therefore, the electron mobility in one or both conduction bands appears to increase at first with increasing Te concentration, rather than decreasing in the usual manner. No explanation has been found for this anomalous increase in mobility. Although the increase might be connected with impurity conduction, it should be noted that in the case of Ge the Hall mobility decreases continuously with increasing impurity concentration throughout the degenerate range.[3,4]

ACKNOWLEDGMENTS

The author is indebted to P. L. Moody and R. L. MacLean for their assistance in growing the GaSb crystals used in this investigation and to Mrs. M. C. Plonko for her assistance in making the electrical measurements. He is also grateful to Dr. A. Sagar for communicating his results prior to publication.

PHYSICAL REVIEW VOLUME 121, NUMBER 4 FEBRUARY 15, 1961

Friedel Sum Rule for a System of Interacting Electrons

J. S. Langer
Carnegie Institute of Technology, Pittsburgh, Pennsylvania

and

V. Ambegaokar*
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

(Received October 3, 1960)

The Friedel sum rule is derived for a system of interacting electrons in a periodic potential.

I. INTRODUCTION

In a recent paper[1] one of the authors (J. S. L.) has derived an expression for the impurity-resistance of a metal using as a model an interacting Fermi fluid and randomly placed scattering centers. As expected, the current-carrying excitations of the fluid had wave numbers just at the Fermi surface and were scattered by screened impurities. The usual independent-electron approximation was replaced by the assumption that these single-particle-like excitations do not interact strongly among themselves. A graphical prescription was given for calculation of the relevant impurity-scattering amplitude.

Needless to say, it is not practicable to evaluate this amplitude in perturbation theory including exchange effects and allowing for an arbitrarily strong scattering potential. Thus, it is highly desirable to know certain general relationships pertaining to this scattering process which may be useful in semi-phenomenological analyses of metallic properties. For example, the Friedel sum rule[2,3] relates the total charge displaced in the field of a fixed impurity to the scattering by that impurity of a free electron at the Fermi momentum k_F. In particular, the rule states that the number of displaced electrons N_D is given by

$$N_D=\frac{2}{\pi}\sum_l(2l+1)\delta_l(k_F), \qquad (1)$$

where the δ_l are the scattering phase shifts. This rule has been used by Kohn and Vosko[4] to deduce some features of the screening of solute atoms in dilute alloys from the known residual resistivity of these materials. They then were able to explain certain results of nuclear resonance experiments and to lend support to the theory of a sharp Fermi surface in metals.

The question of the nature of the Fermi surface is

---

* Present address: Institute for Theoretical Physics, Copenhagen, Denmark.

[1] J. S. Langer, Phys. Rev. **120**, 714 (1960), hereafter referred to as I.

[2] J. Friedel, Phil. Mag. **43**, 153 (1952).

[3] The sum rule has been proven for independent Bloch electrons in the case of spherical energy surfaces by L. M. Roth, Tech. Rept. 267, Cruft Laboratory, Harvard University, Cambridge, Massachusetts, 1957 (unpublished).

[4] W. Kohn and S. H. Vosko, Phys. Rev. **119**, 912 (1960).