Galvanomagnetic Effects in p-Type Indium Antimonide*

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The conductivity and Hall effect of p-type InSb have been measured as a function of magnetic field strength and of temperature. The behavior of the Hall coefficient and the magnetoresistance at 78°K is consistent with a valence band which consists of two bands with different effective masses and has degenerate maxima at the center of the Brillouin zone. Negative magnetoresistances have been observed at liquid helium temperatures; the effect is positive, however, for very pure samples when the magnetic field strength exceeds $\sim 10^3$ gauss. The conduction mechanism in this temperature range is still poorly understood.

INTRODUCTION

WHILE n-type InSb shows rather unique properties, the p-type material follows more closely the "conventional" pattern established by the work on silicon and germanium. The transport phenomena and optical characteristics are not strikingly different from those of other semiconductors. This is mainly due to the fact that the mobilities and the effective masses have a more "familiar" order of magnitude.

Although the list of publications on p-type InSb is of considerable length, there are still a number of open questions; the most important of these are the detailed shape of the valence band and the negative magnetoresistance at very low temperatures.

Cyclotron resonance experiments[1] showed two resonance lines corresponding to effective masses $m_{h1}=0.18\ m_0$ and $m_{h2}>1.2\ m_0$; these masses were tentatively associated with holes. Conductivity and Hall effect results can be fitted with[2] $m_h=0.17\ m_0$ or[3] $m_h=0.15\ m_0$ (in the temperature range 100–300°K). From thermoelectric power data (at higher temperatures) values of $0.18\ m_0$,[4] $0.13\ m_0$,[5] and $0.1\ m_0$ [6] have been deduced. The cyclotron resonance value m_{h1} is usually accepted as the best one; using this figure, one calculates an impurity activation energy which agrees very well with experiment.[2,7] (The larger mass m_{h2} does not fit in with theory, nor is it confirmed by other experimental observations.)

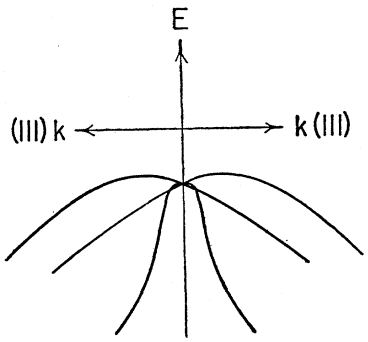

FIG. 1. Proposed valence band structure for a zincblende lattice (references 8 and 9).

The band structure has been studied by several investigators. Theoretical treatments[8–11] agree on the existence of 3 bands: one with a heavy mass corresponding to m_{h1}, another with a much smaller effective mass degenerate with the first at the center of the Brillouin zone, and a third band at considerably lower energy. Both Dresselhaus and Kane conclude that the heavy mass band is anisotropic; Kane[8] puts the maxima, however, very close to the center of the zone (see Fig. 1).

A number of experimental results support Kane's picture of the valence band. The cyclotron resonance observations[1] indicate somewhat anisotropic masses. Roberts and Quarrington[12] conclude from their optical data that indirect transitions between valence and conduction band are involved. These data have also been analyzed by Blount *et al.*[13] and by Potter.[14] They come to the conclusion that the maxima are away from $\mathbf{k}=0,0,0$ along the [111] axis. A similar conclusion is reached by Keyes[15] who measured the pressure dependence of the conductivity. The results of Hrostowski *et al.*[2] also seem to indicate nonspherical energy surfaces at the top of the valence band.

There are, however, a number of experiments which favor an isotropic heavy-hole mass. Dumke[16] was able to fit the optical absorption edge assuming the maximum of the valence band at $\mathbf{k}=0,0,0$. Recent measurements of the elastoresistance of InSb [17] suggest a valence band similar to that of Ge and Si (warped surfaces with one maximum at the center of the zone).

The existence of the small-mass band is generally

* Research sponsored by Office of Naval Research.

[1] Dresselhaus, Kip, Kittel, and Wagoner, Phys. Rev. **98**, 556 (1955).
[2] H. J. Hrostowski *et al.*, Phys. Rev. **100**, 1672 (1955).
[3] R. G. Breckenridge *et al.*, Phys. Rev. **96**, 576 (1954).
[4] H. Weiss, Z. Naturforsch. **11a**, 131 (1956).
[5] H. P. R. Frederikse and E. V. Mielczarek, Phys. Rev. **99**, 1889 (1955).
[6] J. Tauc and M. Matyas, Czechoslov. J. Phys. **5**, 383 (1955).
[7] H. Fritzsche and K. Lark-Horovitz, Phys. Rev. **99**, 400 (1955).
[8] E. O. Kane, J. Phys. Chem. Solids **1**, 249 (1957).
[9] G. Dresselhaus, Phys. Rev. **100**, 580 (1955).
[10] R. H. Parmenter, Phys. Rev. **100**, 573 (1955).
[11] F. Herman, J. Elec. **1**, 103 (1955).
[12] V. Roberts and J. E. Quarrington, J. Elec. **1**, 152 (1955).
[13] E. Blount *et al.*, Phys. Rev. **101**, 563 (1956).
[14] R. F. Potter, Phys. Rev. **103**, 861 (1956).
[15] R. W. Keyes, Phys. Rev. **99**, 490 (1955).
[16] W. P. Dumke, Bull. Am. Phys. Soc. Ser. II, **2**, 185 (1957).
[17] R. F. Potter, Phys. Rev. **108**, 652 (1957).

TABLE I. Characteristics of p-type samples.

	R_{78} $\left(\frac{\text{cm}^3}{\text{coul}}\right)$	$(R\sigma)_{78}$ $\left(\frac{\text{cm}^2}{\text{volt-sec}}\right)$	Magneto-resistive ratio: $\left(\frac{\text{trans.}}{\text{long.}}\right)$	$R_{4.2}$ $\left(\frac{\text{cm}^3}{\text{coul}}\right)$	$\sigma_{4.2}$ ($\text{ohm}^{-1}\,\text{cm}^{-1}$)	$(R\sigma)_{4.2}$ $\left(\frac{\text{cm}^2}{\text{volt-sec}}\right)$	$R_{1.7}$ $\left(\frac{\text{cm}^3}{\text{coul}}\right)$	$\sigma_{1.7}$ ($\text{ohm}^{-1}\,\text{cm}^{-1}$)	$(R\sigma)_{1.7}$ $\left(\frac{\text{cm}^2}{\text{volt-sec}}\right)$
O(100)	225	2580	>10						
P(110)	285	2450	>10						
Q(100)									
etched	2100	5320	54	3660	2.5×10^{-3}	9	11 300	7.2×10^{-4}	8
R(110)									
etched	2500	5700	21	3200	2.2×10^{-3}	7	33 000	7.2×10^{-4}	24
sand blasted	2800	...	...	2900	1.9×10^{-3}	5.5	5 700	4.2×10^{-4}	2.4
S(100)									
etched	1030	5800	40	5820	3.7×10^{-3}	21.6	64 700	7.4×10^{-4}	48
T(110)									
etched	1110	5670	>65	4500	3.8×10^{-3}	16.0	38 000	11.5×10^{-4}	44
sand blasted	1110	...	...	5800	3.0×10^{-3}	18.0	29 000	3.4×10^{-4}	10
U									
etched	15 800	8380	>100	7×10^{5}	3.9×10^{-5}	27	$>2.5\times10^{5}$	$>2.25\times10^{-5}$	>6
sand blasted	16 000	...	...	36 000	9.9×10^{-5}	3.6	...	3.8×10^{-5}	...

accepted; so far, no experiments have yielded a value for the effective mass of this band.

The present investigation of the magnetoresistance and the Hall effect was primarily undertaken in order to obtain further information concerning the valence band structure. Our results favor a model which places the maximum of the band at (or extremely close to) the center of the zone. The field dependence of the Hall effect can be explained by the assumption of two kinds of holes.

Measurements of the galvanomagnetic effects were extended down to 1.7°K. The negative magnetoresistance observed by other workers[7,18] was confirmed. The temperature dependence of the conductivity and Hall effect suggests conduction *via* impurities at very low temperatures.[7,19,20] The nature of this conduction mechanism is, however, not sufficiently well understood to explain the magnitude of the Hall effect and the magnetoresistance at liquid helium temperatures.

EXPERIMENTAL

The sample preparation as well as the apparatus used for the measurement of galvanomagnetic effects have been described in a previous paper on n-type InSb.[21] Several specimens were submitted to different surface treatments in order to study possible surface effects at low temperatures. Measurements were made with the ordinary 6-probe method [current leads at the end of the specimen; 2 sets of Hall probes each located about one quarter away from the ends of the sample; the (magneto) resistivity was measured between two Hall probes on one side face of the specimen].

MAGNETORESISTANCE AND HALL EFFECT AT 78°K

The magnetoresistive effect has been measured on ten different samples. Three of these specimens showed a considerable impurity gradient and will therefore not be discussed. The characteristics of the other seven samples are presented in Table I. Curves of $\Delta\rho/\rho_0$ *vs* H on a log log scale are shown for samples R, Q, and U in Figs. 2, 3, and 4. The magnetoresistance is proportional to H^2 at low magnetic fields and starts to deviate from this behavior above 1000 oersted. In all cases the longitudinal effect is more than an order of magnitude smaller than the transverse effect; values for the ratio of the two effects are given in Table I. From these results one can conclude that the valence band is approximately isotropic.[22,23]

It is still possible to reconcile our results with the theoretical picture of the valence bands as derived by Kane and others[8,9] (Fig. 1). This requires, however, that the energy surfaces at the maxima of the band are very nearly spherical, and this is likely only when the maxima are very close to the center of the zone.

Let us now consider the magnitude and magnetic field dependence of the magnetoresistance and the Hall coefficient. If the simple model is applicable (i.e., isotropic, one-carrier model, scattering by acoustical lattice waves) the magnetoresistive effect is given by

$$\Delta\rho/\rho_0=0.38\times10^{-16}\mu_L{}^2H^2.$$

In case of mixed scattering the factor 0.38 decreases to a minimum of 0.012 for small contributions of ion-scattering, while it increases by an order of magnitude when collisions with ionized impurities become predominant.[24] An accurate calculation for our samples is

[18] J. Hatton and B. V. Rollin, Proc. Phys. Soc. (London) **A67**, 385 (1954).
[19] C. S. Hung and J. R. Gleissman, Phys. Rev. **96**, 1226 (1954).
[20] H. Fritzsche, Phys. Rev. **99**, 406 (1955).
[21] H. P. R. Frederikse and W. R. Hosler, Phys. Rev. **108**, 1136 (1957), preceding paper.
[22] B. Abeles and S. Meiboom, Phys. Rev. **95**, 31 (1954).
[23] M. Shibuya, Phys. Rev. **95**, 1385 (1954).
[24] V. A. Johnson and W. J. Whitesell, Phys. Rev. **89**, 941 (1953); J. Appel, Z. Naturforsch. **9a**, 167 (1954); R. K. Willardson and A. C. Beer, Bull. Am. Phys. Soc. Ser. II, **2**, 142 (1957); J. H. Becker, Bull. Am. Phys. Soc. Ser. II, **1**, 57 (1957).

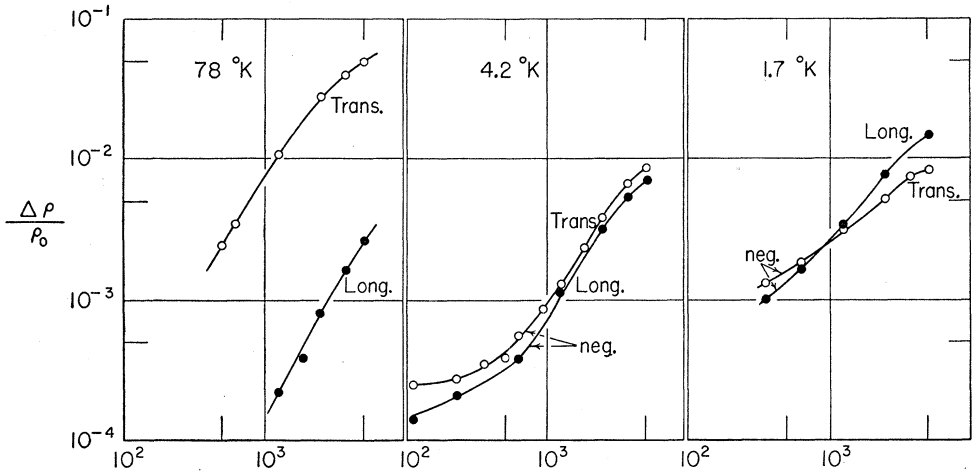

FIG. 2. Magnetoresistance of p-type InSb as a function of magnetic field (sample Q).

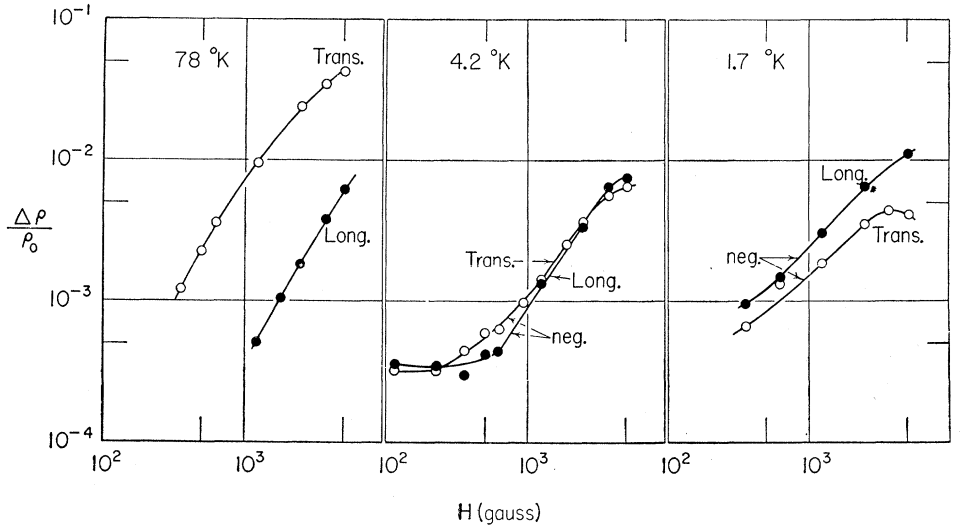

FIG. 3. Magnetoresistance of p-type InSb as a function of magnetic field (sample R).

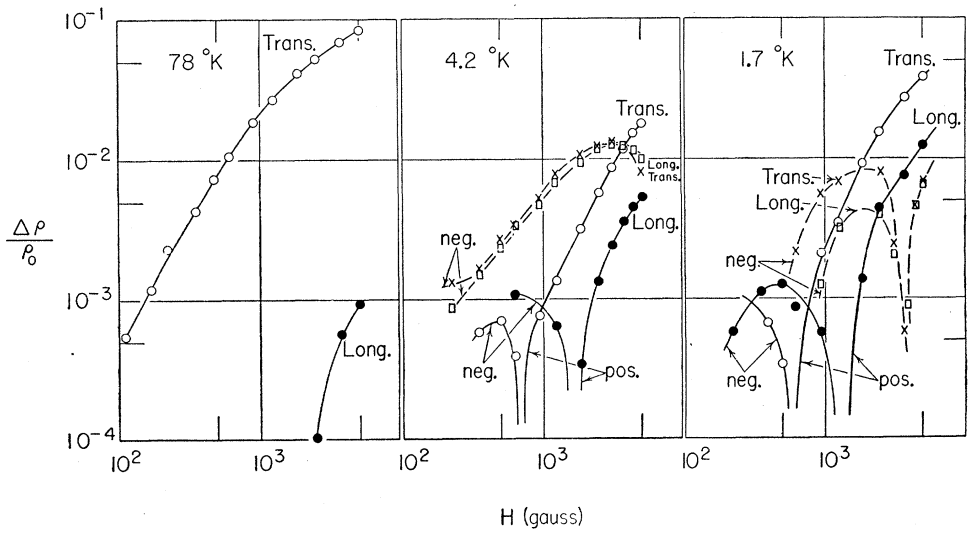

FIG. 4. Magnetoresistance of p-type InSb as a function of magnetic field (sample U) (full-drawn lines: etched surfaces; dashed lines: sand-blasted surfaces).

difficult to make, because the absolute value of the mobility μ_L (due to lattice scattering only) is not known. A reasonable estimate shows, however, that the calculated values of the total mobility are 6 to 10 times larger than the $R\sigma$-values given in Table I. Such a discrepancy could be explained if we assume that a small number of "fast" holes contributes to the conduction.[25]

Other evidence for a two-carrier model comes from the dependence of $\Delta\rho/\rho_0$ and R_H on the magnetic field. The magnetoresistance as a function of magnetic field begins to deviate from the H^2 behavior at 1000 oersted. Considering that $\mu H \approx 5\times10^6$ at this field strength, one would not expect this deviation unless two kinds of holes are present. The Hall coefficient has not yet reached its saturation value at 5000 oersted (see Fig. 5). We see, however, that $r=R_0/R_\infty$ is certainly larger than 1.5. Such values can be reached if both lattice waves and ionized impurities contribute to the scattering mechanism.[26] It would, however, require $\rho_I/(\rho_I+\rho_L)=0.9$ to make $r=1.5$, which seems to be unreasonably high for the samples studied. On the other hand, a small number of fast holes taking part in the conduction increases r appreciably. A model which assumes ellipsoidal energy surfaces would yield values of R_0/R_∞ smaller than $3\pi/8$.[22,23]

Our conclusion is that the top of the valence band of InSb consists of two bands with different effective masses. The upper band is approximately spherical and the maxima either coincide at the center of the zone or are very close to it.

ELECTRICAL CONDUCTION AT LOW TEMPERATURES

On the basis of the above valence band model one expects p-type InSb to behave similarly to p-type germanium in the low temperature range.

The breakdown effect[27] originally observed in Ge has also been found in p-type InSb.[28] A sharp increase of the current occurs when the electric field strength across the InSb sample reaches a value of 47 volts/cm. We have also observed this effect at a slightly lower critical field. The experiments reported on below are all performed with electric fields of less than 1 volt/cm in order to avoid breakdown effects. Even at the lowest voltages the behavior is not strictly ohmic, but the deviations from Ohm's law are of the order of a few percent or less.

Measurements have been made on five p-type samples (etched surfaces). Characteristic values of the conductivity σ, the Hall coefficient R, and the Hall mobility $R\sigma$ are listed in Table I. The magnetoresistance of samples Q, R and U as a function of magnetic field strength is shown in Figs. 2, 3, and 4 for two temperatures in the liquid helium range. Little difference is observed between similar specimens with different orientations, $Q(100)$ and $R(110)$. The more impure samples show a negative magnetoresistive effect for all fields up to 5000 gauss in agreement with earlier observations of other workers.[18,19] The quadratic dependence on H is satisfied only in a small field range at 4.2°K.

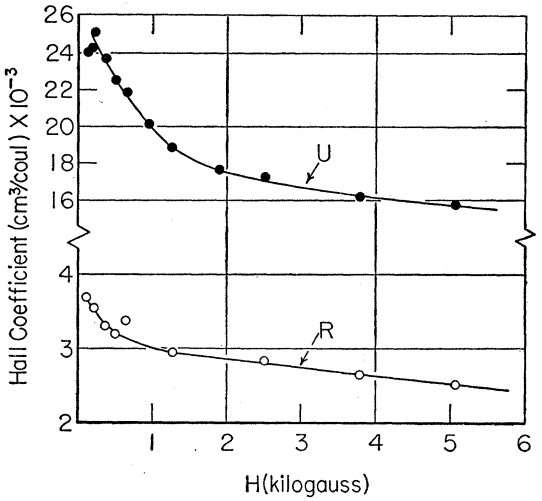

FIG. 5. Hall coefficient as a function of magnetic field at 78°K.

Sample U shows a quite different behavior. In this case the negative effect is limited to low magnetic field values, while a positive effect is observed at higher fields. The value of the longitudinal magnetoresistance is considerably different from the transverse effect. Samples T and S are in some respect similar to specimen U; the transverse effect shows also a reversal to positive values, but only at 1.7°K.

The temperature dependence (1.7–300°K) of the Hall effect and conductivity was investigated on three samples; curves covering the range 4.2–300°K are shown in Figs. 6 and 7 for two of these samples. This

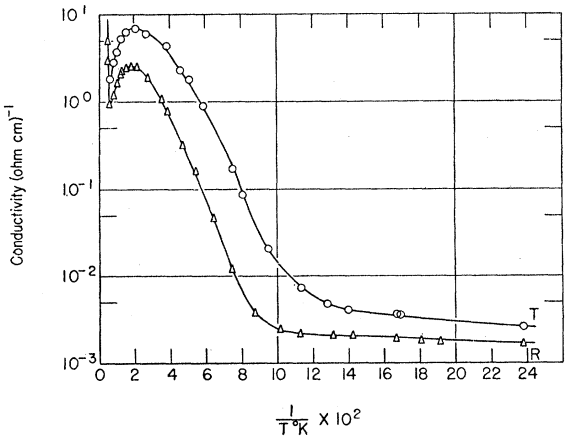

FIG. 6. Conductivity of 2 p-type samples as a function of inverse temperature.

[25] Willardson, Harman, and Beer, Phys. Rev. **96**, 1512 (1954).
[26] V. A. Johnson and K. Lark-Horovitz, Phys. Rev. **82**, 977 (1951).
[27] Sclar, Burstein, Turner, and Davisson, Phys. Rev. **91**, 215 (1954).
[28] R. Bray, Phys. Rev. **100**, 1262 (1955).

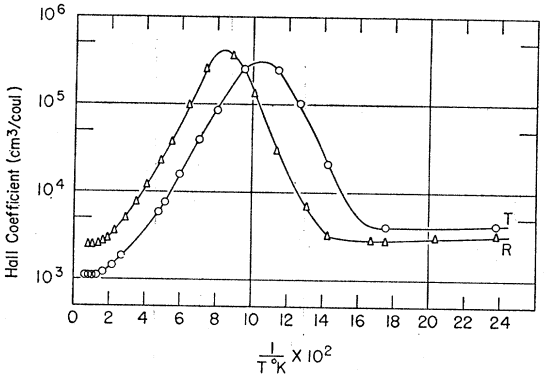

FIG. 7. Hall coefficient of 2 p-type samples as a function of inverse temperature.

behavior suggests a gradual condensation of holes into the impurity band with decreasing temperature.[7,19] The activation energy in the temperature range 50–10°K is 7×10^{-3} to 9×10^{-3} ev for all samples. The slope of the conductivity in the helium range, as calculated from the values at 4.2 and 1.7°K, varies from sample to sample. Specimen S shows a slope corresponding to 4.5×10^{-4} ev; Q, R, and T give a value of 3×10^{-4} ev, while both ρ and R_H of sample U stay practically constant in this range.

In order to investigate the influence of surface treatment, several samples were remeasured after the surfaces were sandblasted. The results with respect to magnetoresistive effects are shown in Fig. 4; data on Hall coefficient and conductivity are listed in Table I. One sees that the surface treatment has little influence on the behavior of the impure samples R and T down to 4.2°K. Larger differences are observed at 1.7°K. Sample U, however, shows spectacular differences in ρ, R and $\Delta\rho/\rho_0$ after sandblasting. The most significant change is the field dependence of the magnetoresistance; $\Delta\rho/\rho_0$ is now negative over the whole range at 4.2°K, and reverts to positive values at much higher field strengths when the temperature is 1.7°K.

As yet no consistent model has been developed which is able to explain the present results and those of other workers. It may be useful, however, to give a few comments on the above data.

The two major questions concerning the conduction mechanism of semiconductors (such as Ge and p-type InSb) at very low temperatures are the following: (1) Can the theory of impurity (band) conduction explain a finite conductivity? (2) To what extent does surface conduction play a role? As far as the first question is concerned, a finite conductivity in pure samples seems to be impossible as long as only one type of impurity (n or p) is present. Recently several workers[29] have emphasized the importance of compensation, i.e., the simultaneous presence of acceptors and donors. Such a compensation would explain the possibility of conduction even when the impurity concentration is too small to give rise to an impurity band. The acceptors (or donors) can then be divided into two groups: ionized sites and neutral sites. Carriers are therefore able to jump from a neutral to an ionized impurity atom. If this is the case, the conductivity will be determined by the number of minority impurities.

We have calculated the degree of compensation for the samples Q-U using the Brooks-Herring formula[30] for the mobility due to ion scattering at 78°K. The numbers of acceptors and donors present in each sample are given in Table II. Although these figures are very inaccurate, it is clear that all our samples are strongly compensated. However, comparing these numbers with the values of the conductivity at 4.2 and 1.7°K, no obvious correlation seems to exist. Even more puzzling is the fact that $\sigma_{1.7}$ is about the same for all samples (except sample U).

Another feature which is difficult to explain is the behavior of the Hall coefficient in the helium range. On the basis of Hung and Gliessman's model of impurity band conduction,[19] one expects at helium temperatures a value of the Hall coefficient equal to the extrinsic value at 78°K. Such a rule is often not obeyed experimentally. It seems especially hard to understand how the Hall coefficient at very low temperatures can be orders of magnitude higher than in the exhaustion range. A possible explanation could be constructed if one assumes that two mechanisms involving carriers with widely different mobilities contribute to the conduction. Let the concentrations of the two types of carriers be n_1 and n_2 and their mobilities μ_1 and μ_2; then the Hall coefficient is given by[23]

$$R=\frac{r}{en_1}\frac{1+(n_2/n_1)(\mu_2/\mu_1)^2}{[1+(n_2/n_1)(\mu_2/\mu_1)]^2}.$$

In the exhaustion range n_1 is the number of free carriers and μ_1 is very large (of the order of many thousands cm²/volt-sec). If the second kind of carrier has a much smaller concentration and a much smaller mobility, the Hall coefficient will hardly differ from r/en_1. At low temperatures, however, μ_1 represents the very small mobility of the n_1 bound carriers. Now the condition may be such that $n_1>n_2$, but $\mu_2\gg\mu_1$. Hence the Hall coefficient may be considerably higher than the extrinsic value at 78°K. In this case ($R\sigma$) is a function of n_1, n_2, μ_1, and μ_2. The source of the second type of carrier is not known. We want to mention, however, the possibility that these carriers are associated with surface states or with a space-charge layer at the

[29] N. Mott, Can. J. Phys. 34, 1356 (1956); H. M. James [Semiconductor Conference at National Bureau of Standards, Washington, D. C., October 1956; a short report of this conference by F. Herman appeared in J. Phys. Chem of Solids 2, 72 (1957)]; S. H. Koenig and G. R. Gunther-Mohr (private communication).

[30] H. Brooks, in *Advances in Electronics and Electron Physics* (Academic Press, Inc., New York, 1955), Vol. 7, p. 158.

surface caused by adsorbed oxygen.[31] The main argument for the existence of surface carriers is the fact that the number would be determined by the surface area and therefore be constant. Their influence would be dominant only in the purest samples. In such specimens the conductivity and Hall coefficient would be constant (as observed in Sample U). The two mechanisms are competing processes in more impure samples; hence the temperature dependence of the impurity conduction would be observed.

The result, which is most difficult to explain, is the negative magnetoresistance. Mackintosh[32] and Stevens[33] have tried to account for a negative magnetoresistive effect by considering the influence of the magnetic field on the impurity levels. The application of a magnetic field splits the impurity states, causing a displacement of the energy levels by $\pm\frac{1}{2}g\beta H$,[34] with respect to their original position. As a result the electrons will be redistributed over the states of the conduction and impurity bands and the magnetoresistance is primarily due to a change in the number of electrons (holes) in the conduction (valence) band. These authors, however, did not take into account the fact that in p-type InSb the activation energy is 0.007 ev (they use 0.0005 ev), and therefore only a negligible number of carriers is left in the main crystal band at 4.2°K. Moreover, the splitting is small compared with kT.

A study of the expression for the magnetoresistance, when two types of carriers contribute to the conduction, shows that the result will always be positive even in the case where several scattering mechanisms are present.[35] It is, however, possible to obtain negative values of $\Delta\rho/\rho_0$ in very thin layers under certain conditions, as has been shown by Sondheimer.[36] Although the behavior of sample U seems to indicate that the solution might lie in this direction, one meets great difficulties when this idea is applied to the other samples (Q, R, T, and S). Experiment shows that for these specimens surface treatment has no influence on the Hall effect and conductivity and only a small effect on the magnetoresistance.

Neither Hung and Gliessman's theory of impurity band conduction, nor the model based on jumping between ionized and neutral sites, has been able to give a satisfactory explanation of a negative magnetoresistive effect.

The low-temperature behavior of p-type InSb (as well as of other semiconductors) is not yet fully understood and probably requires considerably more experimental and theoretical study.

TABLE II. Donor and acceptor concentrations of p-type samples.

	N_A-N_D	N_A	N_D
Q, R	3×10^{15}	1.2×10^{16}	9.0×10^{15}
S, T	7×10^{15}	1.55×10^{16}	8.5×10^{15}
U	5×10^{14}	3.75×10^{15}	3.25×10^{15}

ACKNOWLEDGMENTS

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[31] Frederikse, Hosler, and Roberts, Phys. Rev. **103**, 67 (1956).
[32] I. M. Mackintosh, Proc. Phys. Soc. (London) **B69**, 403 (1956).
[33] K. W. H. Stevens, Proc. Phys. Soc. (London) **B69**, 406 (1956).
[34] g = spectroscopic splitting factor and β = Bohr magneton.
[35] R. G. Chambers, Proc. Phys. Soc. (London) **A65**, 903 (1952).
[36] E. H. Sondheimer, in *Advances in Physics* (Taylor and Francis, Ltd., London, 1952), Vol. 1, p. 1.