explanation may not be the only one that can be chosen to account for the stimulation and quenching with infrared radiation of conductivity and light in (ZnCd)S phosphors. Since it explains, with a minimum number of assumptions, the basic experimental results, and fits into the general band picture for these phosphors, it seems a reasonable starting point in a quantitative theory of the electronic transitions in such phosphors.

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Electrical Properties of *p*-Type Indium Antimonide at Low Temperatures*

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The electrical resistivity ρ, Hall coefficient R, and transverse magnetoresistive ratio $\Delta\rho/\rho$ of *p*-type single crystals of indium antimonide have been measured between 370°K and 1.5°K. Low-temperature anomalies similar to those observed by Hung on germanium have been found, a steep maximum in the $\log R$ *versus* $1/T$ curve and a change of slope of the $\log\rho$ *versus* $1/T$ curve. Contrary to the case with germanium, the magnetoresistive ratio of InSb does not vanish in the lowest temperature range, but it changes its sign from positive to negative as the sample is cooled to a temperature somewhat lower than that at which the Hall coefficient reaches its maximum value. Negative values of the magnetoresistive ratio cannot be explained by the usual theory of semiconductors. At the present time it also is not clear how Hung's model of impurity band conduction can account for negative values of the magnetoresistive ratio.

INTRODUCTION

At temperatures above 78°K indium antimonide behaves like a conventional semiconductor, as previous measurements[1,2] of the Hall coefficient and the resistivity have shown.

Several materials, however, which show the normal behavior of semiconductors at higher temperatures exhibit anomalous electrical properties at low temperatures which cannot be explained by the usual semiconductor theory. Germanium, for instance, shows large deviations from the normal behavior in the range below 50°K, as Hung[3] discovered in 1950. The Hall coefficient of germanium does not increase indefinitely as the temperature is lowered, but reaches a maximum value and decreases thereafter by orders of magnitude. In the $\log\rho$ *vs* $1/T$ curve, one can distinguish a larger slope in the higher temperature range, before the Hall maximum is reached, and a much smaller slope at still lower temperatures.

Anomalies similar to those discovered by Hung on Ge have been found by Busch and Labhart[4] on SiC. Also, TiO_2 seems to show the same abnormal behavior at low temperatures, as recent measurements in this laboratory indicate.

As an explanation for the anomalous behavior of germanium at low temperatures, Hung[5] suggested that a small but finite conduction takes place in the impurity band, in addition to conduction in the ordinary conduction band.

A detailed theory of conduction in impurity bands has not yet been worked out. In any theoretical discussion, however, the explanation of the formation of a conducting impurity band with impurity concentrations as low as 10^{15}/cc is rather difficult. It would be of interest, therefore, to investigate whether other materials also exhibit anomalies at low temperatures and how they differ from those in germanium. This might throw some light on the conduction properties of impurity bands or even suggest a different explanation for the anomalies. For this reason, an investigation of the electrical properties of indium antimonide at very low temperatures has been undertaken.

This paper reports the measurements of electrical resistivity, Hall coefficient, and magnetoresistive ratio on several *p*-type single crystals of indium antimonide down to 2°K.[6]

EXPERIMENTAL PROCEDURE

A. Preparation of Samples

The samples used were prepared by Miss L. Roth of this laboratory. The indium obtained from the Indium

* Supported by U. S. Signal Corps.
[1] H. Welker, Z. Naturforsch. **7a**, 744 (1952) and **8a**, 248 (1953), Physica **20**, 893 (1954), also Scientia Electr. **1**, 2 (1954); H. Weiss, Z. Naturforsch. **8a**, 463 (1953); R. G. Breckenridge, Phys. Rev. **90**, 488 (1953); M. Tanenbaum and J. P. Maita, Phys. Rev. **91**, 1009 (1953); Cunnel, Saker, and Edmond, Proc. Phys. Soc. (London) **B66**, 1115 (1953); O. Madelung and H. Weiss, Z. Naturforsch. **9a**, 527 (1954).
[2] Breckenridge, Blunt, Hosler, Frederikse, Becker, and Oshinsky, Phys. Rev. **96**, 571 (1954).
[3] C. S. Hung and J. R. Gliessman, Phys. Rev. **79**, 726 (1950) and **96**, 1226 (1954); see also H. Fritzsche and K. Lark-Horovitz, Physica **20**, 834 (1954).
[4] G. Busch and H. Labhart, Helv. Phys. Acta **19**, 463 (1946).
[5] C. S. Hung, Phys. Rev. **79**, 727 (1950).
[6] Some low-temperature measurements on InSb have also been made by the Oxford group, without giving the details reported here. See J. Hatton and B. V. Rollin, Proc. Phys. Soc. (London) **A67**, 385 (1954).

Corporation of America and the antimony obtained from Bradley Mining Company were zone heated separately in a hydrogen atmosphere until they were spectroscopically pure. The metals were then melted together and zone heated sixteen times in a hydrogen atmosphere. No impurities were added to the melt intentionally. Single crystals of indium antimonide were grown by the Czochralski method at a rate of 2 inches per hour in a hydrogen flow of about two liters per minute. Single crystals weighing up to 130 grams have been obtained. One crystal was annealed at 375°C in a vacuum of about 10^{-6} mm Hg for 77 hours.

The top parts of the crystals usually have a smaller conductivity than the bottom parts. This makes it possible to cut samples with different conductivity from the same ingot. The samples were cut to a size of about 10 mm×4 mm×1 mm with their large areas transverse to the concentration gradient in order to minimize the error due to such a gradient inside the sample. The sample surfaces were then ground with No. 600 carborundum.

Measurements of the resistivity along the length of the samples at 300°K and 78°K showed the samples to be homogeneous.

TABLE I. Properties of samples of p-type InSb on which measurements were made.

InSb Sample	R (78°K) cm³ coulomb⁻¹	ρ (78°K) ohm-cm	R_{ex}/ρ (2.5°K) cm² volt⁻¹ sec⁻¹	N_A $m^*=m_0/6$ cm⁻³	N_D $m^*=m_0/6$ cm⁻³	Crystal orientation of current flow I	Crystal orientation of mag. field H
a[a]	7300	1.23	0.6	1.6×10^{16}	1.5×10^{16}	(110)	(112)
b[a]	6300	1.23	0.8	1.8×10^{16}	1.6×10^{16}	(110)	(112)
c	1200	0.19	5.9	1.6×10^{16}	6.8×10^{15}	(110)	(112)
d	200	0.072	120			(110)	(100)
e	76	0.065	180			polycrystalline	

[a] Sample a is annealed at 375°C, whereas sample b is not.

Teflon insulated 0.0003-in. copper wires were attached to the sides of the sample with Cerroseal-35 solder to serve as current and potential leads in the usual arrangement for Hall and resistivity measurements.

B. Apparatus

The cryostat and the electrical measuring circuit are identical with those used and described before.[3] The cryostat allows one to take measurements at any temperature between 1.3°K and 300°K. Care was taken that no light or room temperature radiation could reach the sample during the measurements at low temperatures.

All voltages were measured with the conventional compensating method using a type K-2 potentiometer and a Leeds and Northrup high-sensitivity galvanometer.

EXPERIMENTAL RESULTS

The samples on which measurements were made are listed in Table I. The samples a, b, c, and d are single crystals. The polycrystalline sample e is included for comparison with the other samples in the lowest temperature region. The samples a and b are identical but for the fact that b was measured before and a after it was annealed for 77 hours at 375°C.

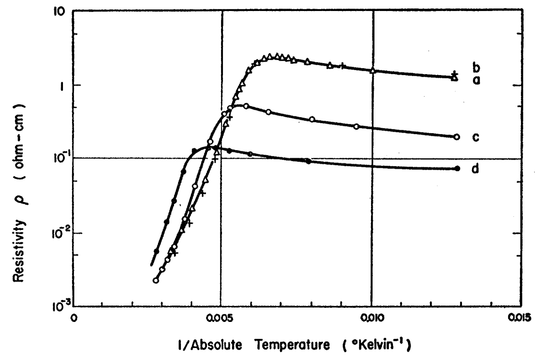

FIG. 1. Resistivity of p-type indium antimonide as a function of $1/T$ between 78°K and 370°K.

All samples were found to be p-type. In order to show that these samples of indium antimonide behave completely normally at higher temperatures and in agreement with the results of other investigators, the temperature dependences of their resistivity and Hall coefficients between 370°K and 78°K are shown in Figs. 1 and 2, respectively.

For these measurements the low-magnetic-field approximation was used for the Hall coefficient. Resistivity and Hall coefficient are independent of the current for electric fields between a hundred microvolts/cm and a hundred millivolts/cm. No breakdown measurements have been performed with higher electric fields.

A. Hall Measurements

The Hall coefficient was measured with magnetic fields between 450 and 900 gauss. Since it was found that R is independent of the magnetic field strength up to fields of about 1000 gauss, above which R begins to decrease with increasing field strength, the values of R reported here follow the low-field approximation. A

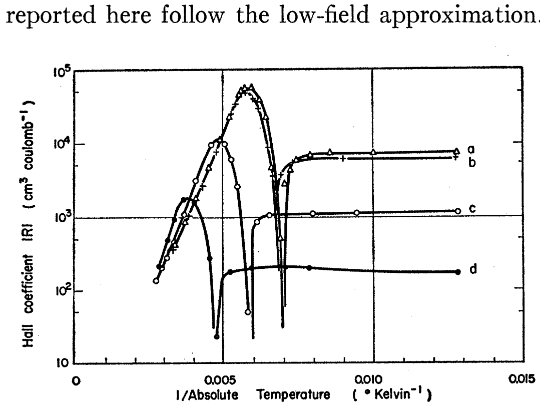

FIG. 2. Hall coefficient of p-type indium antimonide as a function of $1/T$ between 78°K and 370°K.

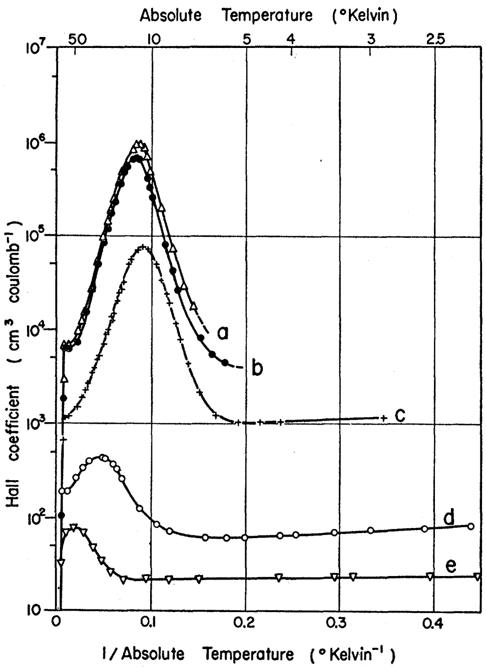

FIG. 3. Hall coefficient of p-type InSb as a function of $1/T$. Note the small slopes of the Hall curves of the samples c and d at temperatures below 5°K. These slopes are much smaller than those of the corresponding resistivity curves in the same temperature range.

larger field of 3500 gauss was used only in the lowest temperature range where the Hall coefficient becomes very small. Electric fields between a few millivolts/cm and several hundred millivolts have been used. In this range the Hall coefficient is independent of the current through the sample.

Figure 3 shows how the Hall coefficient of indium antimonide containing various amounts of impurities depends on temperature between 78°K and 2°K. The main features of these curves can be summarized as follows:

(a) The Hall coefficient reaches a maximum value with decreasing temperature and then drops rapidly as the temperature is lowered, down to a value which is of the same order of magnitude as the Hall coefficient at exhaustion. (b) If plotted logarithmically against $1/T$ the Hall curves are approximately symmetric with respect to the temperature at which the Hall coefficient has its maximum value. (c) The Hall maximum decreases in magnitude and shifts to higher temperatures with increasing impurity concentration.

The concentrations of acceptors N_A and of donors N_D in the samples a, b, and c have been obtained from the analysis of the temperature dependence of their hole concentrations.[7] The effective mass of the holes was assumed to be $m^* = m_0/6$. This is the only known value so far. It was calculated[2] using the product of hole and electron concentrations in the intrinsic range, the ratio of electron to hole mobility at room temperature and the temperature dependence of the intrinsic energy gap as determined optically.

Because of the large number of assumptions involved in the calculation, the effective mass is uncertain to a large degree.[8] The concentrations of acceptors N_A and of donors N_D listed in Table I can, therefore, be used only for qualitative comparison of the samples.

This comparison yields the following results. The samples a and b which, due to their large Hall coefficients at exhaustion, were thought to be the purest samples obtained actually contain large concentrations of both acceptors and donors which compensate each other. Sample c is the purest sample, although it also contains a large number of compensated impurities.

Evidence for this is found also in the measurements of resistivity and magnetoresistive ratio as will be shown later.

B. Resistivity Measurements

The log resistivity *versus* $1/T$ curves are shown in Fig. 4. The log resistivity *versus* $1/T$ curves have large slopes at temperatures above the Hall maximum and much smaller slopes at temperatures below the Hall maximum. The resistivity can be described approxi-

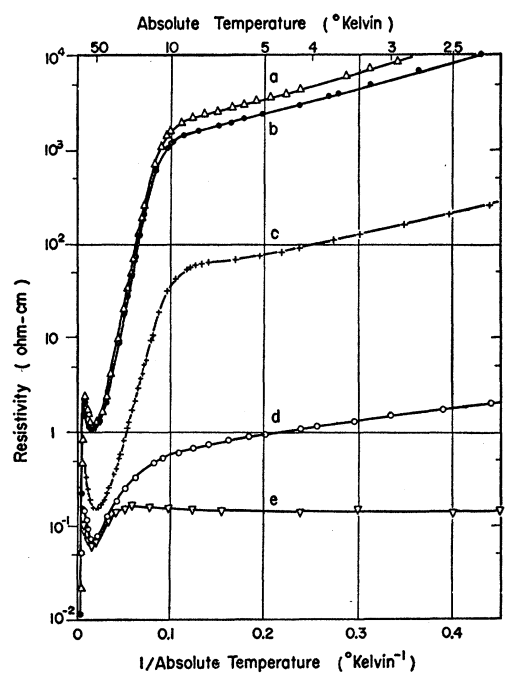

FIG. 4. Resistivity of p-type InSb as a function of $1/T$. The $\log\rho$ *versus* $1/T$ curves are straight lines from about 5°K down to 1.5°K, which is the lowest temperature at which measurements have been performed.

[7] H. Fritzsche, Ph.D. thesis, Purdue University, 1954 (to be published).

[8] We are indebted to C. Kittel for letting us see a manuscript on cyclotron resonance in InSb [Dresselhaus, Kip, Kittel, and Wagoner, Phys. Rev. 98, 556 (1955)], which suggests tentatively one effective mass value for holes in InSb as $m^* = 0.18m_0$.

mately by an equation

$$1/\rho = C_1 e^{-\epsilon_1/kT} + C_2 e^{-\epsilon_2/kT}, \quad (1)$$

with $\epsilon_1 \approx 8\times10^{-3}$ ev and $\epsilon_2 \approx 4.5\times10^{-4}$ ev, where the C_i may depend slightly on temperature.

The first exponential term of this equation is due to the temperature dependence of the hole concentration in the valence band, as can be seen from the exponential increase of R with increasing $1/T$ before the Hall maximum is reached. The second term, however, cannot be explained as being due to excitation of electrons from the valence band into lower-lying acceptor levels, as the completely different behavior of the Hall coefficient in the lowest temperature range shows. The measurement of the resistivity has been extended down to temperatures of about 1.5°K. The resistivity of the samples continues to increase as described by Eq. (1), and no further change has been observed.

The logarithm of the Hall mobility R/ρ of these samples is plotted against $\log T$ in Fig. 5. The Hall mobility passes through a maximum at a higher temperature than that at which the Hall coefficient reaches its maximum value. At lower temperatures R/ρ decreases, first slowly, and then very rapidly at temperatures below that at which the Hall maximum occurs. This last part is certainly not proportional to any drift mobility because the Hall coefficient ceases to be proportional to the reciprocal of the carrier concentration as long as it decreases with decreasing temperature.

The Hall mobility of sample c is much larger than that of the samples a and b despite the fact that sample c has a smaller Hall coefficient at exhaustion. This can be understood because the samples a and b contain a larger concentration of compensated impurities which act as additional ionized scattering centers. In other words, in samples a and b the concentration of ionized impurity centers $N_I = 2N_D + n$ is larger, although the concentration of electrons at exhaustion $n_{\text{exh}} = N_A - N_D$ is smaller, than in sample c.

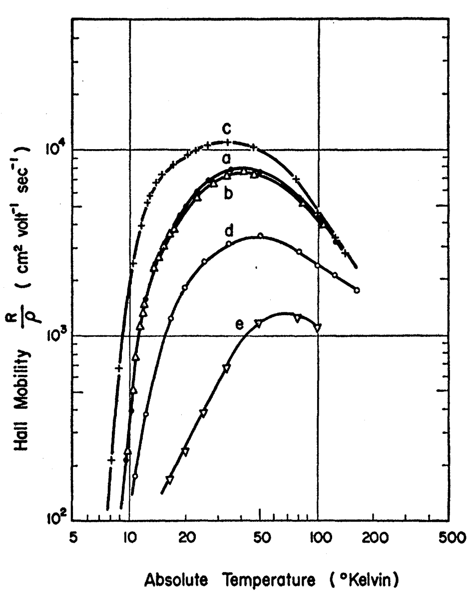

FIG. 5. The temperature dependence of the Hall mobility R/ρ. The Hall mobility of sample c is larger than those of samples a and b indicating the smaller impurity content of sample c.

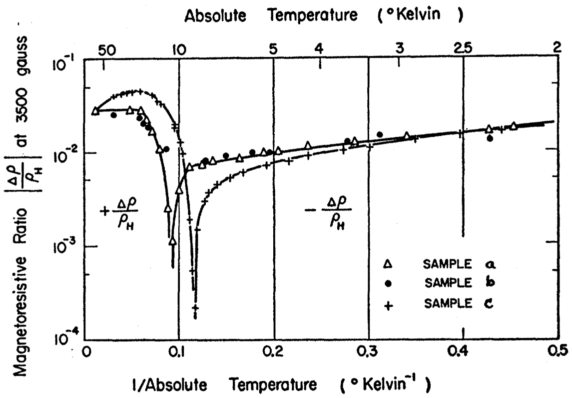

FIG. 6. The absolute value of the transverse magnetoresistive effect, as measured with a magnetic field of 3500 gauss, as a function of $1/T$. The temperature at which the magnetoresistive ratio changes from positive to negative values depends on the impurity content of the InSb samples. It is somewhat lower than the temperature of the Hall maximum.

All resistivity curves have a finite slope in the lowest temperature range which, however, is larger than the slope of their corresponding Hall curve.

The measurements on the polycrystalline sample e are included in these graphs because they show one characteristic which is found to be not only a property of indium antimonide but also of germanium. In the lowest temperature range, the resistivity and Hall curves of polycrystalline samples, plotted logarithmically against $1/T$, always have a much smaller slope than those of single crystals.

C. Magnetoresistive Ratio

The transverse magnetoresistive effect of the three samples a, b, and c was measured as a function of temperature using a field of 3500 gauss. For each measurement of the resistivity in the presence of the transverse magnetic field, four readings were taken with opposite directions of sample current and opposite directions of magnetic field to eliminate thermal emf's and pick-up in the circuit and to see whether the magnetoresistive ratio is an even function of the magnetic field strength. This was found to be the case within the limits of accuracy of the measurements.

In Fig. 6 are shown the magnetoresistive ratio *versus* $1/T$ curves for the samples a, b, and c. At about the temperature of the Hall maximum the magnetoresistive ratio drops sharply as the temperature is lowered, reverses its sign, and then remains negative down to the lowest temperature investigated, which is about 2°K. At temperatures below the reversal, the absolute magnitude of the magnetoresistive ratio first increases

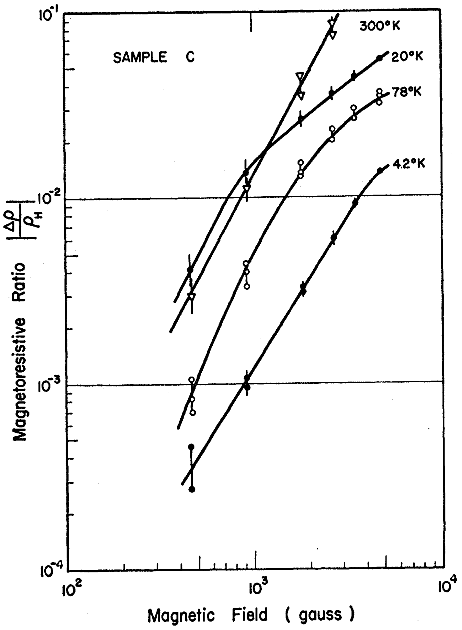

FIG. 7. The transverse magnetoresistive ratio of sample c as a function of magnetic field strength at various temperatures. $\Delta\rho/\rho_H$ is negative at 4.2°K and positive at 20°K, 78°K, and 300°K.

quickly, then slower with decreasing temperature, and is still rising at about 2°K. In the lowest temperature range the slopes of the $\log(\Delta\rho/\rho_H)$ *versus* $1/T$ curves seem to be comparable with those of the log resistivity *versus* $1/T$ curves.

Between 78°K and 20°K, the magnetoresistive ratio of samples a and b is smaller than that of sample c indicating a smaller mobility in agreement with the assumption that samples a and b contain a larger concentration of compensated ionized impurities than sample c does.

The magnetic field dependence of the magnetoresistive ratio is shown in Fig. 7 for one sample measured at 300°K, 78°K, 20°K, and 4.2°K. At 300°K and 78°K the curves start with a slope of about two at low fields and then bend over as the field strength is increased. At the lower temperatures the quadratic field dependence either does not exist or is limited to smaller fields than those with which measurements could be made. For these temperatures a linear plot of the magnetoresistive ratio *versus* field strength seems to be appropriate. Such a plot is shown in Fig. 8 for samples a, b, and c at 4.2°K. At fields larger than about 1000 gauss, the magnetoresistive ratio increases linearly with increasing field strength. The slopes of these curves are the same for all the samples despite their different values at a particular field.

A linear variation of $\Delta\rho/\rho_H$ with fields between 3500 and 800 gauss, with no indication of saturation, has been observed before[9] for p-type material at temperatures above 80°K.

[9] Harman, Willardson, and Beer, Phys. Rev. **93**, 912 (1954).

DISCUSSION

The experimental results show clearly that at low temperatures the electrical properties of indium antimonide deviate strongly from those of a normal semiconductor. The kind of anomalies observed in the temperature dependence of the Hall coefficient and resistivity are identical with those found in germanium: the maximum of the Hall curve, the small slope of the resistivity curve in the lowest temperature range and the strong dependence of these effects on the concentration of impurities. This last factor has always been the strongest argument in favor of Hung's model of impurity band conduction, because on the basis of this model one expects a rapid decrease of the mobility in the impurity band with increasing separation between the impurity atoms.

The simplest model which assumes additional conduction in an impurity band is that of Hung.[5] The impurity band of his model is formed by the interaction between the ground states of the impurities.

Assuming that at low temperatures practically all charge carriers, which at exhaustion are in the conduction band, contribute to the conduction in the impurity band, Hung defines an impurity band mobility by[10]

$$\mu_i(T)=R_{\text{ex}}/\rho(T), \tag{2}$$

for all temperatures low enough so that conduction in the ordinary conduction band can be neglected. For impurity concentrations less than about 10^{16} atoms/cc, the impurity band mobility is found to be many orders of magnitude smaller than the ordinary conduction band mobility. From this, one would expect that the magnetoresistive ratio is vanishingly small at low temperatures where conduction in the impurity band predominates. This has actually been found experimentally on germanium samples.

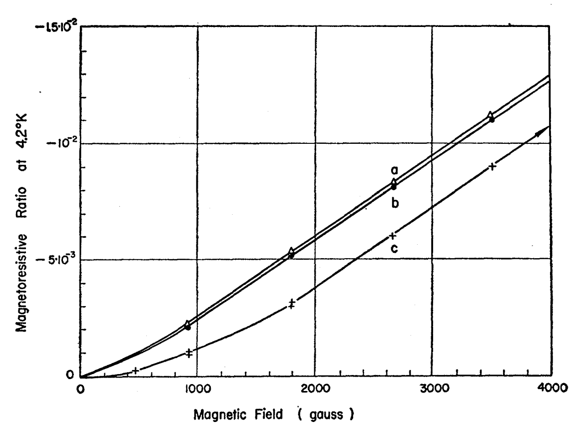

FIG. 8. The transverse magnetoresistive ratio at 4.2°K plotted linearly against magnetic field strength. $\Delta\rho/\rho_H$ is a linear function of the magnetic field between 2000 gauss and 4600 gauss which is the largest field with which measurements have been performed.

[10] R_{ex} is the value of the Hall coefficient in the exhaustion range.

The magnetoresistive ratio of p-type indium antimonide samples, however, exhibits a completely different behavior. As the temperature is lowered, the magnetoresistive ratio reverses its sign from positive to negative values shortly after the Hall maximum is reached and remains negative in the whole temperature range in which the anomalous conduction predominates.

The strong relation between the anomalies observed in the resistivity, Hall coefficient, and magnetoresistive ratio becomes evident in Fig. 9, in which the results measured on one sample are plotted on the same temperature scale.

A negative magnetoresistive ratio cannot be explained by the usual theory which calculates the effect of a magnetic field on the motion of the charge carriers. That one has to deal with a different process in the case of negative magnetoresistive ratios is also indicated by the linear magnetic field dependence in contrast to the quadratic field dependence of the ordinary magnetoresistive ratio.

It is difficult to estimate how far the splitting of the electronic energy levels in the impurity band due to a magnetic field affects the conduction in the impurity band or how the model of impurity band conduction can account for a negative magnetoresistive ratio, because no detailed theory has been worked out yet.

The definition (2) of the impurity band mobility implies many crude assumptions, as was pointed out in the discussion of behavior of germanium.[7] However, it still might be a useful parameter for describing the conduction process at low temperatures. For this reason, the values of μ_i as calculated from the resistivity of the indium antimonide samples at 2.5°K are listed in Table I.

Comparing the μ_i value of sample a with that of sample c, which has the same concentration of acceptor levels, one finds that the impurity band mobility is not only determined by the concentration of impurities which form the impurity band, but it depends also on the concentration of carriers occupying the band. This one has to expect, since the mobility of Eq. (2) is actually an average mobility involving many carriers which occupy states with different effective masses.

The higher values of μ_i of these indium antimonide samples as compared to those of p-type germanium of similar acceptor concentrations might also be explained as being partly due to this fact. The samples of indium antimonide contain a large concentration of compensated impurities and therefore a smaller carrier concentration in the impurity band at low temperatures than the germanium samples of equal acceptor concentration do.

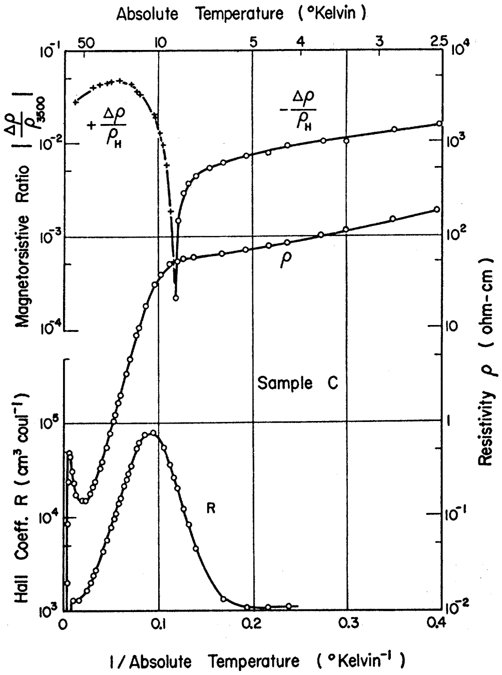

FIG. 9. Hall coefficient, resistivity, and magnetoresistive ratio of sample c plotted logarithmically against $1/T$. All three quantities deviate from their normal behavior in the same temperature range, indicating that one and the same process gives rise to these anomalies.

The measurements on indium antimonide show that the low-temperature anomalies are not restricted to germanium but seem to be a more general property of semiconductors. The negative value of the magnetoresistive ratio in the lowest temperature range, however, constitutes an additional problem.

ACKNOWLEDGMENTS

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