Galvanomagnetic Effects in *n*-Ge in the Impurity Conduction Range*

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Measurements of the magnetoresistance and magnetic field dependence of the Hall coefficient of several samples of *n*-type germanium in the impurity conduction range have been made employing magnetic field strengths up to 28 kgauss. The magnitude and the crystalline anisotropy of the magnetoresistance are interpreted in terms of the changes in the donor wave functions which are produced by the magnetic field. The field dependence of the Hall coefficient is interpreted as a magnetoresistance effect of the conduction band.

I. INTRODUCTION

THE electrical conductivity and Hall constant of a typical specimen of *n*-type germanium are shown as a function of temperature in Fig. 1. There are two temperature ranges in which the phenomena are qualitatively different. The explanation of this observation was originally given by Hung.[1] The essential features are as follows:

The conductivity tensor of an isotropic material in a magnetic field (in direction 3) has the form

$$\boldsymbol{\sigma}=\begin{bmatrix}\sigma_{11} & \sigma_{12} & 0\\ -\sigma_{12} & \sigma_{11} & 0\\ 0 & 0 & \sigma_{33}\end{bmatrix}. \tag{I.1}$$

This tensor can be regarded as the sum of two contributions. One contribution is that of the electrons in the conduction band. The other contribution is that of electrons which have "frozen out" of the conduction band into states associated with the donor impurities. For the range of impurity concentrations in our samples the latter electrons are responsible for "impurity conduction" which involves jumping of electrons from neutral to ionized donors.[2] The number of electrons in the conduction band decreases and the number of electrons in donor states increases as the temperature is lowered. The difference between the high-temperature and low-temperature regions in Fig. 1 is that in the high-temperature region the contribution of the conduction band to σ_{11} and σ_{33} dominates, whereas in the low-temperature region the contribution of impurity conduction to σ_{11} and σ_{33} dominates. For this reason the low-temperature region is referred to as the impurity conduction region. The only significant contribution to σ_{12} in either region is that of the conduction band.

We shall denote the contribution of impurity conduction to $\boldsymbol{\sigma}$ by $\mathbf{s}$ and the contribution of the conduction band by $\mathbf{S}$. Thus, in the impurity conduction region, $\boldsymbol{\sigma}$ has the form

$$\boldsymbol{\sigma}=\begin{bmatrix}s_{11} & S_{12} & 0\\ -S_{12} & s_{11} & 0\\ 0 & 0 & s_{33}\end{bmatrix}. \tag{I.2}$$

The order of magnitude of S_{12} is the same as or less than that of S_{11}, and, therefore, $S_{12}\ll s_{11}$ in the impurity conduction region. Thus the resistivity tensor, the reciprocal of $\boldsymbol{\sigma}$ has the form

$$\boldsymbol{\rho}=\begin{bmatrix}s_{11}^{-1} & -S_{12}/s_{11}^{2} & 0\\ S_{12}/s_{11}^{2} & s_{11}^{-1} & 0\\ 0 & 0 & s_{33}^{-1}\end{bmatrix} \tag{I.3}$$

and the Hall constant has the value

$$R_H=S_{12}/Hs_{11}^{2}. \tag{I.4}$$

The tensor $\mathbf{s}$ in the absence of a magnetic field has been intensively studied elsewhere.[3,4] Here we shall describe our investigation of the magnetic field de-

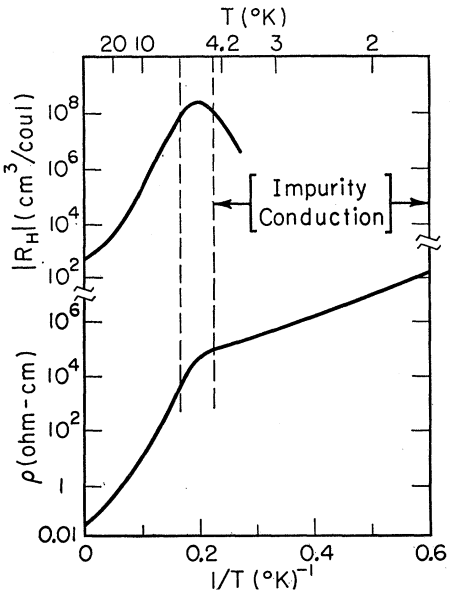

FIG. 1. Low-temperature electrical properties of a sample of *n*-type germanium with a donor concentration of about 10^{16} cm^{-3}. (after Fritzsche[3]).

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[1] C. S. Hung, Phys. Rev. **79**, 727 (1950).

[2] E. M. Conwell, Phys. Rev. **103**, 51 (1956); N. F. Mott, Can. J. Phys. **34**, 1356 (1956).

[3] H. Fritzsche, Phys. Rev. **99**, 406 (1955).

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

TABLE I. Characteristics of the Ge samples. The resistivity and Hall coefficient values are for room temperature.

Sample	Donor	Plane	Length	ρ_0 (ohm cm)	$-R_H$(5 kgauss) (coul^{-1} cc)
2*A*	Sb	(111)	110	0.120	349
2*Z*	Sb	(1$\bar{1}$1)	110	0.151	434
3*X*	Sb	(100)	001	0.245	801
14–4	As	(110)	1$\bar{1}$0	0.068	177
14–4	As	(110)	001	0.0837	202
15–10	As	(110)	001	0.145	443

pendence of ρ. After a short summary of the experimental details in Sec. II, we shall present and discuss in Sec. III our measurements of the magnetoresistance in the impurity conduction region, which are, effectively, measurements of s_{11} and s_{33}. Section IV will be devoted to our measurements of the field dependence of the Hall constant, from which we find S_{12} as a function of magnetic field. The fact that germanium is a cubic crystal rather than an isotropic solid introduces some additional complications into the interpretation of the galvanomagnetic effects. The additional complicating features, however, afford additional opportunities for the comparison of models with experiment.

II. EXPERIMENTAL DETAILS

The samples were cut with a cavitron from lapped slices of single crystal Ge doped with either Sb or As and are characterized in Table I. Donor concentrations, N_D, were deduced from the tabulated Hall coefficients by means of the relation $N_D=-0.92/R_Hec$, where e is the electronic charge and c is the velocity of light. When possible the compensation of a sample was deduced from the activation energy for impurity conduction.[5] In these cases it was between about 5% and 10%.

The length-to-width ratios of the samples were about seven in all but two cases for which they were about six and ten. There were six side arms of 0.3 mm width on each sample for attaching potential leads. The outer arms were located more than a sample width away from the ends. Each sample was etched for a few minutes with an H_2O_2+HF+H_2O etch before the current and potential leads of No. 36 and No. 40 copper wire were attached with InSn solder and then re-etched after the leads had been attached.

For the electrical measurements the samples were immersed in liquid helium, hydrogen, or nitrogen (or He gas for the room temperature measurements) contained in a metal Dewar flask with a small diameter appendix suspended between the poles of an Arthur D. Little electromagnet. The magnetic field was measured and monitored with a Rawson rotating coil fluxmeter. Sample temperature was determined from the vapor pressure of the liquid bath. Sample current and potentials were measured with a vibrating reed electrometer (Applied Physics Corporation, model 30S) or with a potentiometer (Leeds and Northrup, type K-3)—galvanometer system.

III. MAGNETORESISTANCE

For all the germanium samples listed in Table I we have found magnetoresistance effects in the impurity conduction region which are of the same order of magnitude as those observed when the current is carried by electrons in the conduction band. The mechanism involved must be entirely different, however, since the mobility of electrons responsible for impurity conduction is many orders of magnitude less than that of electrons in the conduction band.[3] The crystalline anisotropy of the impurity conduction magnetoresistance is quite different from that of the conduction band. The difference is illustrated in Fig. 2, in which the transverse magnetoresistance with the current along a twofold axis of the crystal is plotted as a function of magnetic field orientation for two temperatures in the impurity conduction region and for one temperature in the conduction band region. Longitudinal magnetoresistance is also present in both regions.

We attribute the impurity conduction magnetoresistance to the effect of the magnetic field on the wave function of an electron bound to an impurity atom. Impurity conduction is a result of overlapping of wave functions centered on nearby impurity atoms.[2] A magnetic field decreases the spatial extent of a bound electronic wave function, thus decreasing the

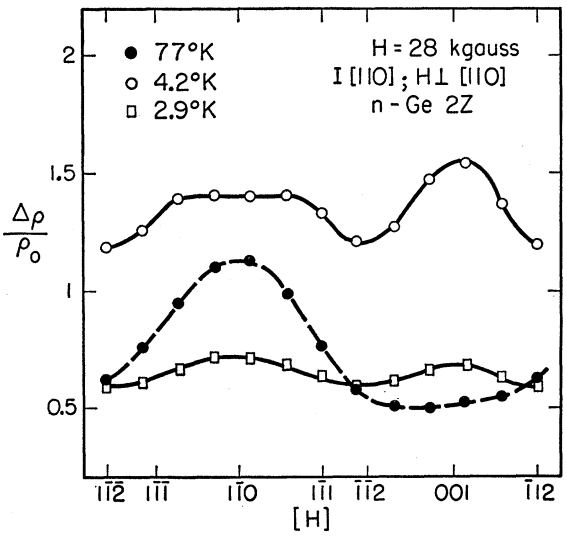

FIG. 2. Transverse magnetoresistance of sample 2*Z* (1.3×10^{16} Sb donors/cm^3) in the conduction band region (77°K) and impurity conduction region (4.2°K and 2.9°K).

[5] A. Miller, thesis, Rutgers University, 1960 (unpublished); A. Miller and E. Abrahams, Bull. Am. Phys. Soc. **5**, 159 (1960); Phys. Rev. **120**, 745 (1960).

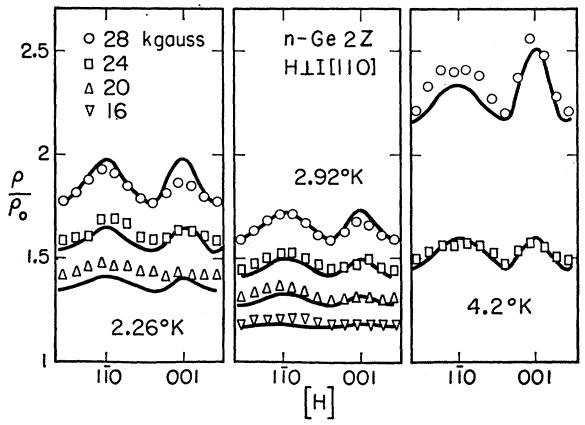

FIG. 3. Fit of the transverse magnetoresistance of sample $2Z$ to the model described by Eqs. (III.1)–(III.3).

overlap between neighboring wave functions.[6,7] This decrease of overlap produces an increase in resistance, as observed.

We have previously studied related effects in InSb.[6–8] The theory of the effect of a magnetic field on the bound wave functions is much more complicated in the case of germanium than in the case of InSb, however, because of the anisotropic effective mass in germanium. We have not formulated the theory for the anisotropic case, but have interpreted our results on the basis of a phenomenological model which is suggested by simple physical arguments, and also by the theories of Kasuya and Koide[9] and of Miller and Abrahams[5] for zero magnetic field. The principal features of this model are:

(1) The impurity conduction is the sum of conductivity contributions from each of the four valleys with axes $a^{(i)}$:

$$\mathbf{s}=\sum_{i=1}^{4}\mathbf{s}^{(i)}. \qquad \text{(III.1)}$$

(2) The $a^{(i)}a^{(i)}$ component of $\mathbf{s}^{(i)}$ vanishes and the other two diagonal components of $\boldsymbol{\sigma}^{(i)}$ are equal, even in a magnetic field. Thus $\mathbf{s}^{(i)}$ has the form

$$\mathbf{s}^{(i)}=f^{(i)}(H)(1-a^{(i)}a^{(i)}). \qquad \text{(III.2)}$$

The vanishing of the $a^{(i)}a^{(i)}$ component of $\mathbf{s}^{(i)}$ is a result of the large effective mass and consequent small spatial extent of the bound wave function in the $a^{(i)}$ direction, and has been verified experimentally by Fritzsche.[10] The equality of the other two components of $\mathbf{s}^{(i)}$ in a magnetic field is not a necessary assumption,

TABLE II. The values of α and β [Eq. (III.3)] used to calculate the curves of Fig. 3.

T (°K)	α (10^{-9} gauss^{-2})	β (10^{-9} gauss^{-2})
2.26	0.39	0.82
2.92	0.31	0.67
4.2	0.29	1.53

but is adequate to fit the experimental results, as will be discussed below.

(3) The effect of a magnetic field on the wave function of a bound state derived from a particular valley is largest when the magnetic field is parallel to the valley axis $a^{(i)}$. Obviously, many functions $f^{(i)}(H)$ which possess this property exist. Our attempts to choose a simple form which can be used to fit the data shows that a reasonably adequate two-parameter function is

$$f^{(i)}(H)=f^{(i)}(0)\exp[-H^2(\alpha+\beta/\cos\theta/)], \qquad \text{(III.3)}$$

where θ is the angle between the magnetic field and the valley axis.

We have used Eqs. (III.1)–(III.3) to fit magnetoresistance measurements on several samples. We shall summarize certain important features of the results here:

(1) Our model can give an almost quantitative accounting of the crystalline anisotropy. This is shown in Fig. 3, which compares the transverse magnetoresistance of a specimen with length in a [110] direction with values calculated from Eqs. (III.1)–(III.3). The values of α and β used are given in Table II. These values also give a good fit to the longitudinal magnetoresistance.

(2) Equations (III.1)–(III.3) predict that in a sample with length in the [001] direction the magnetoresistance is the same for H in the [001] direction (longitudinal) and H in the [010] direction (transverse). This prediction is a direct consequence of our assump-

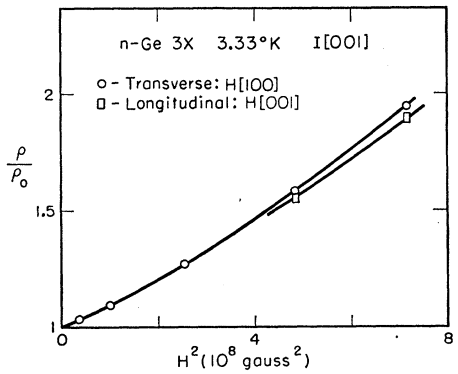

FIG. 4. A comparison of transverse and longitudinal magnetoresistance when H is in a [100]-type direction in sample $3X$ (7.8×10^{15} Sb atoms/cc).

[6] Y. Yafet, R. W. Keyes, and E. N. Adams, J. Phys. Chem. Solids **1**, 137 (1956).
[7] R. W. Keyes and R. J. Sladek, J. Phys. Chem. Solids **1**, 143 (1956).
[8] R. J. Sladek, J. Phys. Chem. Solids **5**, 154 (1958).
[9] T. Kasuya and S. Koide, J. Phys. Soc. Japan **13**, 1287 (1958).
[10] H. Fritzsche, Phys. Rev. **119**, 1899 (1960).

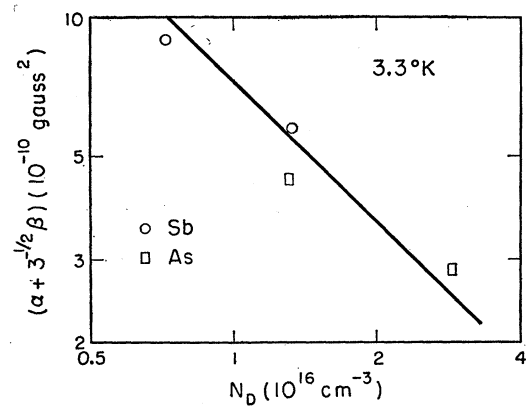

FIG. 5. The magnetoresistance coefficient at 3.3°K for H in a [001] direction [see Eq. (III.3)] as a function of N_D. The line represents the relationship $(\alpha+3^{-\frac{1}{2}}\beta)=(K/32mc^2)N_D^{-1}$.

tion that $\mathbf{s}^{(i)}$ is isotropic in the plane perpendicular to $a^{(i)}$, even in an arbitrarily oriented magnetic field. An example of data which afford a test of this prediction is given in Fig. 4. We find that for the two cases in question the value of $\Delta\rho/\rho$ differs in fact by only 5%, the transverse magnetoresistance being larger. This figure, 5%, represents approximately the magnetoconductivity anisotropy in the plane perpendicular to $a^{(i)}$ when the angle between H and $a^{(i)}$ is arc $\cos(3^{-\frac{1}{2}})\approx 55°$.

(3) The magnitude of the magnetoresistance effect is reasonable according to our model. The effect of the magnetic field on the bound wave function will be cut off the wave function rather sharply outside of the radius at which the magnetic energy in the Hamiltonian[6] becomes equal to Coulombic energy. This condition defines a critical radius r_c, given by

$$e^2/Kr_c=e^2H^2r_c^2/8m_tc^2, \qquad \text{(III.4)}$$

where e=electronic charge, K=dielectric constant, m_t=effective mass transverse to valley axis, H=magnetic field, and c=velocity of light. Equation (III.4) applies to the case of a magnetic field parallel to the valley axis and r measured from the impurity in the plane perpendicular to the valley axis. We expect that the magnetoresistance effect will be large when the magnetic field has reduced r_c to one half the average distance between donors, $N_D^{-\frac{1}{3}}/2$. This occurs at $H=3.5\times10^4$ gauss in our sample 2A. In fact, we see from Fig. 3 that the resistance is increased by a factor of 1.5 to 2.5 by fields of 2.8×10^4 gauss, in good accord with our arguments.

(4) The reasoning of the preceding paragraph also leads us to a semiquantitative prediction of the dependence of the magnetoresistance effect on N_D. We expect that the magnetoresistance will be a function of $r_c/(N_D^{-\frac{1}{3}}/2)$ or of

$$8r_c^3N_D=64m_tc^2N_D/KH^2. \qquad \text{(III.5)}$$

In terms of the functional description of Eq. (III.3), this means that α and β are proportional to $(K/64m_tc^2N_D)$. We show the values of $\alpha+3^{-\frac{1}{2}}\beta$, the magnetoresistance coefficient for H in a [001] direction, as a function of N_D for three different donor concentrations in Fig. 5. It is seen that the coefficient is approximately proportional to N_D^{-1}, as expected. The coefficient of proportionality is $(K/32m_tc^2)$, of the order of magnitude which we expect.

There are certain features of the results which we do not understand. The most important of these is the temperature dependence of the magnetoresistance, which is apparent in Fig. 3, and is not predicted by our model. Another is the form of $f^{(i)}(H)$, Eq. (III.3), for which we have provided no basis in theory. We feel that the interpretation of these features must await further development of the theory of impurity conduction in a magnetic field and that measurements of the type which we report here will acquire greatly enhanced significance when such interpretations become available.

Recently other authors[5,11] have presented estimates of the effect of a magnetic field on the donor wave functions. We believe that these estimates are not as useful for the interpretation of magnetoresistance as the point of view we have presented here. The reasons are as follows. First, the methods used are not designed to give information about the shape of the wave function at large distances (several effective Bohr radii) from the donor atom. Even in our most heavily doped sample the distance between donor centers is about seven Bohr radii, so that overlap of the wave functions at large distances is the determining factor in impurity conduction. Second, the mass anisotropy must be very important in any quantitative theory of the effect of a magnetic field on the donor wave functions. Such a theory would be quite complicated, since in general, the presence of the magnetic field destroys the rotational symmetry of the Hamiltonian of the donor in germanium.

IV. HALL EFFECT

A large decrease in the magnitude of the Hall constant, R_H, with increasing magnetic field in the impurity conduction region has been observed previously in p-type germanium at low magnetic fields.[3] As in the conduction band region, this has been ascribed to there being holes of two different masses.[3] No such decrease in $|R_H|$ has hitherto been reported in n-type Ge and, of course, none is expected from the above cause since there is only one type of conduction band electrons. However, we have found that a large decrease in $|R_H|$ occurs in Sb-doped germanium[12] at higher

[11] P. Csavinszky, Phys. Rev. **119**, 1605 (1960).

[12] We have not yet been able to determine whether such an effect occurs in As-doped Ge because the higher resistivity of this type of material coupled with the limited accuracy of our potential measurements at liquid helium temperatures did not permit deduction of the Hall effect component of the voltage across the Hall arms in As-doped samples.

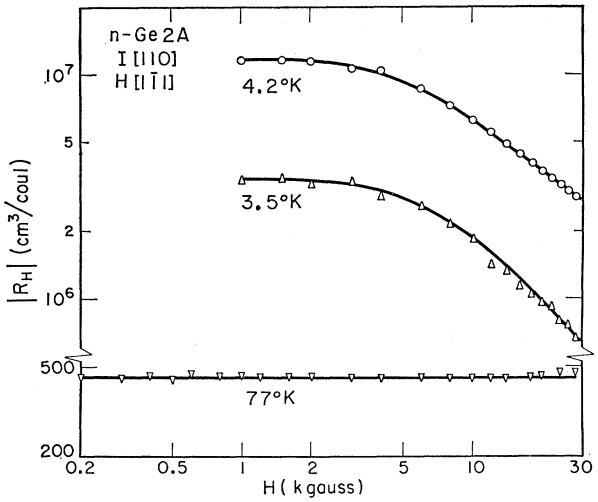

FIG. 6. Magnetic field dependence of the Hall coefficient of sample 2A (1.7×10^{16} Sb donors/cm^3) in the conduction band region (77°K) and in the impurity conduction region (4.2°K and 3.5°K).

magnetic fields in the impurity conduction region but not in the conduction band region. Representative data are shown in Fig. 6, in which we compare our measurements of $|R_H|$ at 77°K with those at 4.2°K and 3.5°K. It is seen that at 77°K the Hall constant is practically independent of field strength, but that at the lower temperatures it decreases rapidly with increasing magnetic field for fields above 3000 gauss.

The field dependence of the Hall constant can be understood as follows: In a magnetic field the current in the conduction band is acted on by the Lorentz force. Even though the contribution of the conduction band to the total conduction current may be negligible, it carries the transverse Hall current. The question as to whether there is a Lorentz current associated with impurity conduction, which has not been satisfactorily resolved as yet, is not relevant here, as a Lorentz current of normal magnitude, i.e., about $(\mu_i H/c)$ times the impurity conduction current, would be completely negligible under the conditions of our measurements because of the small value of the impurity mobility, μ_i. The compensating transverse current due to the Hall electric field is due to impurity conduction, however. The resistance to each of these currents is increased by the magnetoresistance effects as the magnetic field is increased. Since, in our sample, the conduction band magnetoresistance is larger than the impurity conduction magnetoresistance, the net result of the magnetoresistance effects is a decrease of the Hall constant. Equally striking effects cannot occur when both the Lorentz current and the compensating conduction current are carried by the conduction band, because then the magnetoresistance effect must be very nearly the same for both currents.

A quantitative interpretation of the Hall effect data on the basis of the foregoing model is somewhat beclouded by the fact that the usual theory of the transport properties of the electrons in the conduction band is based on the assumption $\hbar/\tau \ll kT$,[13] whereas in a typical sample of germanium used for impurity conduction studies $\hbar/\tau = kT$ for $T \approx 20$°K. Nevertheless, we know of no experiments which demonstrate the incorrectness of the usual transport theory at very low temperatures. In fact, the use of this usual theory appears to provide very reasonable semiquantitative interpretations of various low-temperature transport properties, for example, the phenomenon of impurity band conduction and the results which we have presented in Fig. 6. For this reason we will present the quantitative interpretation of our data in terms of the usual theory in this section. It must be borne in mind, however, that subsequent developments in the study of transport phenomena in the region $T < \hbar/\tau k$ may alter the quantitative interpretation of our results.

The theory of magnetoresistance[14] shows that for an isotropic conduction band S_{12} has the value

$$S_{12}=\frac{ne^2\omega}{m}\frac{1}{\langle E\rangle}\left\langle\frac{E\tau^2}{1+\omega^2\tau^2}\right\rangle. \tag{IV.1}$$

Here n is the concentration of electrons in the conduction band, τ is the momentum relaxation time of the electrons, and $\omega = eH/mc$. The angular brackets $\langle\ \rangle$ are Boltzmann averages as defined by Herring.[15] In the low-field limit, S_{12} can be expanded in the form

$$\frac{S_{12}}{H}=\frac{ne}{c}\mu_H\mu_c\left(1-\frac{H^2U^2}{c^2}\right), \tag{IV.2}$$

where

$$U^2=\frac{\langle E\tau^4\rangle\langle E\rangle}{\langle E\tau^2\rangle^2}\mu_H\mu_c \tag{IV.3}$$

and U has the dimensions of a mobility. μ_H and μ_c are the Hall and conductivity mobilities as usually defined. The theory can be extended to the case of a multivalley conduction band, following the ordinary magnetoresistance theory.[15,16] This extension shows that Eq. (IV.2) is also valid in the multivalley case, provided that the definition of U^2 in Eq. (IV.3) is modified to

$$U^2=\frac{\langle E\tau^4\rangle\langle E\rangle}{\langle E\tau^2\rangle^2}\Gamma\mu_H\mu_c, \tag{IV.4}$$

where Γ is a factor which depends on K, the anisotropy of the mobility tensor of a valley ($K=\mu_\perp/\mu_\parallel$), and on the crystallographic orientation of the current and the magnetic field.

It is apparent that Eqs. (IV.2) and (IV.4) are a

[13] C. Herring, International Conference on Semiconductor Physics, Prague, 1960 (unpublished).
[14] A. H. Wilson, *Theory of Metals* (Cambridge University Press, New York, 1953).
[15] C. Herring, Bell System Tech. J. **34**, 237 (1955).
[16] B. Abeles and S. Meiboom, Phys. Rev. **95**, 31 (1954); M. Shibuya, Phys. Rev. **95**, 1385 (1954).

TABLE III. The parameters of Eq. (IV.2) for sample 2A.

T (°K)	$(S_{12}/H)_0$ (gauss ohm cm)$^{-1}$	U^2 (cm^4/v^2 sec^2)	μ (cm^2/v sec)	$\log_{10} n$
4.18	1.13×10^{-10}	1.16×10^{8}	3810	9.70
3.82	1.68×10^{-11}	1.00×10^{8}	3540	8.92
3.54	3.7×10^{-12}	9.4×10^{7}	3420	8.29
3.22	7.0×10^{-13}	...	...	7.75

very useful pair of relationships, since S_{12} can be determined from measurements of the resistivity tensor by using Eq. (I.3) and the mobility and the carrier concentration of the conduction band in the impurity conduction region can then be deduced from (IV.2) and (IV.4). The principal uncertainty in carrying out this program comes from defective knowledge of the first two factors in Eq. (IV.4). These factors are known to much better than an order of magnitude, however, and are not expected to be strongly temperature dependent, so that the uncertainty in their value does not seriously affect the usefulness of the method.

We shall illustrate the use of Eqs. (IV.2) and (IV.4) by analyzing data from our sample 2A, on which we have obtained the required measurements of S_{12} at several temperatures. This sample was cut so that the current was in the [110] direction, and Hall measurements were made with the magnetic field in the [$\bar{1}$11] direction. The data at 4.2°K and 3.5°K have been shown in Fig. 6. As an aid in deciding what value of Γ and of $\langle E\tau^4\rangle\langle E\rangle/\langle E\tau^2\rangle^2$ to use in analyzing these data we present Fig. 7, which shows Γ as a function of K for the particular orientation of our sample and values of the relaxation time factor calculated with the assumption $\tau\sim E^p$. We believe that $\Gamma=2$ and $\langle E\tau^4\rangle\langle E\rangle/\langle E\tau^2\rangle^2=4$ are reasonable values. Furthermore, it can be concluded from Fig. 6 that $\mu_H\approx\mu_c$ at 77°K. Therefore we set $(\mu_H\mu_c)^{\frac{1}{2}}=\mu$, the "mobility," in Eqs. (IV.2) and (IV.4), and have, in particular, for (IV.4), $U^2=8\mu^2$.

Our results for sample 2A are collected in Table III. They are plotted in Fig. 8 together with values of μ and n which were found in the usual way in the liquid hydrogen and liquid nitrogen ranges. It is seen that

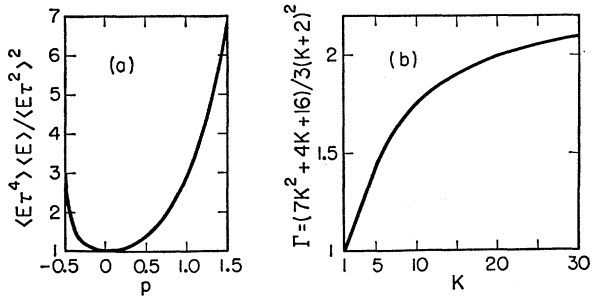

FIG. 7. The factors which enter into Eq. (IV.4). (a) $\langle E\tau^4\rangle\langle E\rangle/\langle E\tau^2\rangle^2$ calculated with the assumption $\tau\sim E^p$; (b) the factor Γ as a function of K for a germanium sample with current in the [1$\bar{1}$0] direction and magnetic field in the [111] direction.

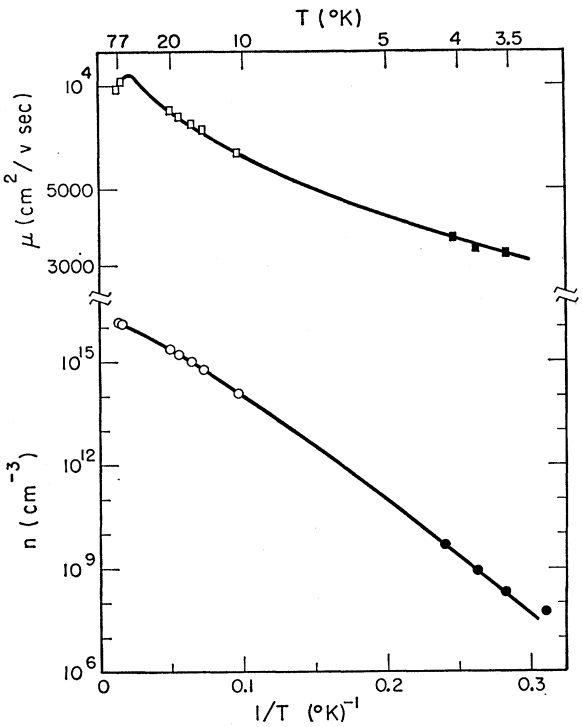

FIG. 8. Mobility and concentration of conduction band electrons in sample 2A in the impurity conduction region (full points) and in the conduction band region (open points).

the results derived by our method in the liquid helium range are a natural extension of those obtained at the higher temperatures.

Many applications of this technique for studying the properties of the conduction band at very low temperatures immediately come to mind. For example: (a) the extension of the range of T^{-1} over which n can be found should increase the accuracy with which the thermal ionization energies of impurities can be determined; (b) values of τ determined by other means, such as cyclotron resonance, can be compared with those determined by a transport experiment; (c) a careful study of U^2 as a function of the crystallographic orientations of the current and the magnetic field may allow K to be deduced in the impurity conduction region. The actual value of the technique is limited, however, by the difficulty of making Hall effect measurements on very high resistivity samples, a difficulty which increases with decreasing temperature and with decreasing impurity concentration.

ACKNOWLEDGMENTS

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