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Galvanomagnetic Effects in a Semiconductor with Two Sets of Spheroidal Energy Surfaces

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The conductivity, Hall coefficient, and low-field magnetoresistance are calculated for a semiconductor with conduction in two sets of spheroids, one set oriented along [100] directions, the other along [111] directions in reciprocal lattice space. These calculations are used in an analysis of experimental data on alloys of twelve to seventeen percent silicon in germanium. A good fit to the data is obtained assuming such a conduction band, with the shape of the [111] spheroids similar to that found in germanium and the shape of the [100] spheroids like those in silicon. Some interband scattering is introduced to give the observed mobility variation with composition. The calculated energy separations of the [111] and the [100] minima depend strongly on the scattering assumed.

I. INTRODUCTION

A PHENOMENOLOGICAL theory of the galvanomagnetic effects in semiconductors having spheroidal energy surfaces has been discussed by a number of authors.[1–4] The treatments have been applied in particular to the two cases: (a) six spheroids with axes along the [100] directions in reciprocal lattice space, (b) four or eight spheroids with major axes along the [111] directions in reciprocal lattice space. Case (a) describes the conduction band in silicon[5,6] and case (b) describes the germanium conduction band.[5,6] It is of interest to consider a semiconductor with a conduction band made up (considering possible occupied states) of a set of type (a) and a set of type (b), with minima separated in energy by

$$\Delta\mathcal{E}=\mathcal{E}_{100}^{0}-\mathcal{E}_{111}^{0}. \tag{1}$$

The alloy system germanium-silicon contains possible examples of a semiconductor with conduction occurring in these two sets.[6,7] Figure 1 is a plot of the optical band gap of the germanium-silicon alloys as a function of composition, taken from Johnson and Christian's letter.[7] These data can be fitted by one line from 0 to 15 percent silicon content and another line of different slope from 15 to 100 percent silicon. To explain[6] these results, it is first assumed that in germanium the [100] states are about 0.18 ev above the [111] states. As silicon is added to form the alloys, both sets of states move away from the valence band, but the [100] move less rapidly than the [111]. At about 15 percent silicon content, the two sets are at the same energy. For alloys with greater than 15 percent silicon, conduction is mainly in the [100] states. The break in slope in the optical band gap curve is caused by a transition from a semiconductor with conduction in the [111] minima to one in which conduction occurs in [100] minima. An alloy of about 15 percent silicon would then be an example of a semiconductor with conduction occurring in two different states or bands.

We shall calculate the galvanomagnetic effects of such a semiconductor and then apply these results to measurements made on germanium-silicon alloys of 12–16 percent silicon content.

II. CALCULATIONS

In treating the transport processes, the following assumptions are made.

(a) The conduction band consists of six [100]-oriented spheroids and four [111]-oriented spheroids, each of which is represented by an equation of the form

$$\mathcal{E}=\mathcal{E}^{0}+\frac{P_1^2+P_2^2}{2m^t}+\frac{P_3^2}{2m^l}. \tag{2}$$

$\mathcal{E}^0$ is the energy difference between the bottom of the spheroid and the top of the valence band, and the coordinates are taken along and perpendicular to the spheroid axis. There are two sets of effective masses, one (m^l) along the axis and one (m^t) perpendicular to it, for each class of spheroid.

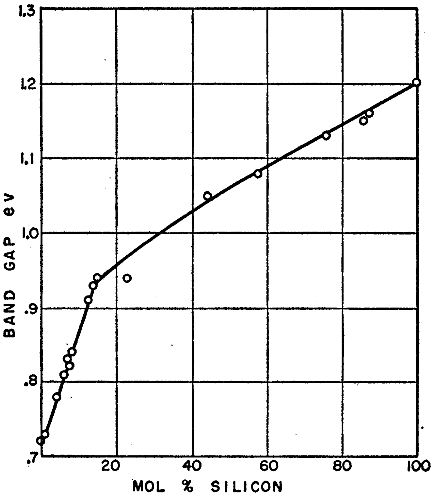

FIG. 1. Optical energy band gap for the germanium-silicon alloys as function of silicon content.

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[1] B. Abeles and S. Meiboom, Phys. Rev. 95, 31 (1954).
[2] M. Shibuya, Phys. Rev. 95, 1385 (1954).
[3] C. Herring, Bell System Tech. J. 34, 237 (1955).
[4] C. Herring and E. Vogt (to be published).
[5] Dresselhaus, Kip, and Kittel, Phys. Rev. 98, 368 (1955).
[6] F. Herman, Phys. Rev. 95, 847 (1954).
[7] E. R. Johnson and S. M. Christian, Phys. Rev. 95, 560 (1954)

(b) The scattering of the carriers in each spheroid may be represented by a relaxation time τ, and this relaxation time is a function of the energy only. Scattering by longitudinal acoustical waves is of this form.[8] Intervalley lattice scattering and neutral impurity scattering also should yield such a relaxation time.[3] Scattering by ionized impurities and by some of the acoustical modes may be poorly described by such a relaxation time. For these cases, Herring and Vogt[4] have introduced three relaxation times for the principal ellipsoidal directions. The result of such a treatment for the galvanomagnetic effects is to weight the reciprocal effective mass by the relaxation time for that direction. An analysis which assumes one $\tau(\mathcal{E})$ may then incorporate such a relaxation time anisotropy into the calculated energy surface anisotropy.

(c) The conductivity is the sum of the contributions from each spheroid. The two sets differ in their contributions because of different shapes and orientation, different relaxation times, and because of different distances from the Fermi energy.

(d) The calculations are carried out in the limit of "weak" magnetic fields, i.e., terms in H^3 and higher in the series expansion of the distribution function are neglected.

Use is made of the treatment given by Abeles and Meiboom[1] for the simpler cases of [111] and of [100] spheroids alone. Where the treatment is identical, their results are referred to.

The electric current density in the presence of electric and magnetic fields is

$$\mathbf{I}=\frac{e}{4\pi^3\hbar^3}\int \operatorname{grad}_k\mathcal{E}\frac{\partial f_0}{\partial \mathcal{E}}\phi dV, \tag{3}$$

where ϕ is a function[9] of the electric field $\mathbf{E}$, magnetic field $\mathbf{H}$, the energy $\mathcal{E}$ and the shape of the energy surfaces, and the scattering relaxation time τ. Here f_0 is the electron distribution function in the absence of fields.

The current contribution from each spheroid is

$$i_i=\sigma_{ik}E_k+\sigma_{ikl}E_kH_l+\sigma_{iklm}E_kH_lH_m, \tag{4}$$

where the σ's are integrals over momentum space. The summation convention is used throughout. When $\tau=\tau(\mathcal{E})$, and the momentum coordinates are chosen along and perpendicular to the principal axis of the energy spheroid, the σ's are

$$\begin{aligned}&\sigma_{11}=\sigma_{22}=uKF_1,\\&\sigma_{33}=uF_1,\end{aligned} \tag{5a}$$

$$\begin{aligned}&\sigma_{123}=-\sigma_{213}=-uvK^2F_2,\\&\sigma_{231}=\sigma_{312}=-\sigma_{132}=-\sigma_{321}=uvKF_2,\end{aligned} \tag{5b}$$

$$\begin{aligned}&\sigma_{1122}=\sigma_{2211}=-uvK^2F_3,\\&\sigma_{1133}=\sigma_{2233}=-uv^2K^3F_3,\\&\sigma_{3311}=\sigma_{3322}=-uv^2KF_3,\\&\sigma_{ijij}=uv^2KF_3.\end{aligned} \tag{5c}$$

The other components of the σ tensor are zero. Here[10]

$$u=\frac{4ne^2}{3\pi^{\frac{1}{2}}m^l}(kT)^{-5/2}, \tag{6}$$

$$v=\frac{e}{c}(m^l)^{-1}, \tag{7}$$

$$K=m^l/m^t, \tag{8}$$

$$F_\alpha=\int[\tau(\mathcal{E})]^\alpha\mathcal{E}^{\frac{3}{2}}\exp(-\mathcal{E}/kT)d\mathcal{E}, \tag{9}$$

and n is the density of carriers in this spheroid:

$$n=2\left(\frac{2\pi kT}{h^2}\right)^{\frac{3}{2}}m^t(m^l)^{\frac{1}{2}}\exp(-\mathcal{E}_F/kT). \tag{10}$$

The contributions from each of the six [100] spheroids and the four [111] spheroids are summed to give the total current in the i-direction.

$$I_i=\sum\nolimits_{ik}E_k+\sum\nolimits_{ikl}E_kH_l+\sum\nolimits_{iklm}E_kH_lH_m, \tag{11}$$

$$\begin{aligned}\sum\nolimits_{ik}=\{&(4/3)u_{111}(2K_{111}+1)F_1^{(111)}\\&+2u_{100}(2K_{100}+1)F_1^{(100)}\}\delta_{ik},\end{aligned} \tag{12a}$$

$$\begin{aligned}\sum\nolimits_{ikl}=\{&-(4/3)u_{111}v_{111}K_{111}(K_{111}+2)F_2^{(111)}\\&-2u_{100}v_{100}K_{100}(K_{100}+2)F_2^{(100)}\}\epsilon_{ikl},\end{aligned} \tag{12b}$$

$$\begin{aligned}\sum\nolimits_{iklm}&=-(8/9)u_{111}v_{111}^2K_{111}(K_{111}-1)^2F_3^{(111)}\\&\qquad\qquad i=k=l=m\\&=-(4/9)u_{111}v_{111}^2K_{111}(2K_{111}^2+5K_{111}+2)F_3^{(111)}\\&\quad-2u_{100}v_{100}^2K_{100}(K_{100}^2+K_{100}+1)F_3^{(100)}\\&\qquad\qquad i=k\neq l=m\\&=(4/9)u_{111}v_{111}^2K_{111}(K_{111}^2+7K_{111}+1)F_3^{(111)}\\&\quad+6u_{100}v_{100}^2K_{100}^2F_3^{(100)}\qquad i=l\neq k=m\\&=(4/9)u_{111}v_{111}^2K_{111}(K_{111}-1)^2F_3^{(111)}\\&\qquad\qquad i=m\neq k=l.\end{aligned} \tag{12c}$$

To calculate the Hall constant R_0 and the magnetoresistance coefficients, Eq. (11) is inverted to give the electric field as a function of the current and the magnetic field. For cubic crystals the magnetoresistance

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[8] J. M. Radcliffe, Proc. Phys. Soc. (London) **A68**, 675 (1955).

[9] H. Jones and C. Zener, Proc. Roy. Soc. (London) **A145**, 268 (1934).

[10] If $\tau=\Lambda\mathcal{E}^p$, $F_\alpha=\Lambda^\alpha(kT)^{\alpha p+5/2}\Gamma(\alpha p+5/2)$.

can be represented by the expression[11]

$$\frac{\Delta\rho}{\rho H^2}=b+c\frac{(\mathbf{I}\cdot\mathbf{H})^2}{I^2H^2}+d\frac{I_1^2H_1^2+I_2^2H_2^2+I_3^2H_3^2}{I^2H^2}. \tag{13}$$

Substituting into Eqs. (12) the expressions for the functions u and v, and taking the reciprocal resistivity tensor, we have the relations

$$\sigma_0=\frac{16\sqrt{2}\pi e^2}{3h^3kT}s\exp(-\mathcal{E}_F^{(111)}/kT), \tag{14a}$$

$$R_0=\frac{3h^3kT}{16\sqrt{2}\pi ec}\frac{t}{s^2}\exp(\mathcal{E}_F^{(111)}/kT), \tag{14b}$$

$$\begin{aligned} b=&R_0^2\sigma_0^2\{(s/t^2)[(4/9)(m_{111}^l)^{-\frac{3}{2}}\\ &\times(2K_{111}^2+5K_{111}+2)F_3^{(111)}\\ &+2(m_{100}^l)^{-\frac{3}{2}}(K_{100}^2+K_{100}+1)DF_3^{(100)}]-1\},\\ c=&R_0^2\sigma_0^2\{1-(s/t^2)[(4/9)(m_{111}^l)^{-\frac{3}{2}}\\ &\times(2K_{111}^2+5K_{111}+2)F_3^{(111)}\\ &+6(m_{100}^l)^{-\frac{3}{2}}K_{100}F_3^{(100)}D]\},\\ d=&R_0^2\sigma_0^2(s/t^2)[(8/9)(m_{111}^l)^{-\frac{3}{2}}(K_{111}-1)^2F_3^{(111)}\\ &-2(m_{100}^l)^{-\frac{3}{2}}(K_{100}-1)^2F_3^{(100)}D], \end{aligned} \tag{14c}$$

where

$$s=\frac{4}{3}(m_{111}^l)^{\frac{1}{2}}\frac{2K_{111}+1}{K_{111}}F_1^{(111)}+2(m_{100}^l)^{\frac{1}{2}}\frac{2K_{100}+1}{K_{100}}F_1^{(100)}D,$$

$$t=(4/3)(m_{111}^l)^{-\frac{1}{2}}(K_{111}+2)F_2^{(111)}+2(m_{100}^l)^{-\frac{1}{2}}(K_{100}+2)F_2^{(100)}D,$$

$$D=\exp[-(\mathcal{E}_{100}^0-\mathcal{E}_{111}^0)/kT].$$

The magnetoresistance is then a function of the Hall mobility $R_0\sigma_0$, the scattering, the longitudinal, and transverse effective masses of each set of valleys, and the energy separation of the two sets. All of these cannot be determined from the measured values of R_0, σ_0, b, c, and d.

In the cases where there are six [100] valleys or four [111] valleys alone, the following symmetry conditions hold:

$$\left.\begin{aligned} b+c=0\\ d>0 \end{aligned}\right\} \text{[111]-oriented,} \tag{15}$$

$$\left.\begin{aligned} b+c+d=0\\ d<0 \end{aligned}\right\} \text{[100]-oriented.} \tag{16}$$

When the two sets contribute to conduction, neither of these relations holds. Instead there are relations among the constants b, c, and d which involve the shape of the valleys, their energy separation and the relaxation times.

A and B are defined by the equations

$$b+c=A(b+c+d), \tag{17}$$

$$b+(R_0\sigma_0)^2=B(b+c+d), \tag{18}$$

where

$$A=\frac{9}{4}\left(\frac{m_{111}^l}{m_{100}^l}\right)^{\frac{3}{2}}\frac{(K_{100}-1)^2}{(K_{111}-1)^2}\frac{F_3^{(100)}}{F_3^{(111)}}\exp(-\Delta\mathcal{E}/kT), \tag{19}$$

$$B=\frac{2K_{111}^2+5K_{111}+2}{2(K_{111}-1)^2}+\frac{9}{4}\frac{K_{100}^2+K_{100}+1}{(K_{111}-1)^2}\times\left(\frac{m_{111}^l}{m_{100}^l}\right)^{\frac{3}{2}}\frac{F_3^{(100)}}{F_3^{(111)}}\exp(-\Delta\mathcal{E}/kT). \tag{20}$$

If the shape of the valleys, i.e., the effective masses, and the ratio of relaxation time integrals are known, Eqs. (19) and (20) may be used to give independent estimates of the energy separation. A comparison of the results should serve as a check on the theory.

The energy, longitudinal effective masses and scattering may be eliminated from Eqs. (19) and (20):

$$B=\frac{2K_{111}^2+5K_{111}+2}{2(K_{111}-1)^2}+\frac{K_{100}^2+K_{100}+1}{(K_{100}-1)^2}\cdot A. \tag{21}$$

A is a quantity which is zero for [111] conduction alone and becomes very large for predominant [100] conduction. B has the same behavior, with a finite value for [111] conduction, which increases as the [100] states begin to contribute. This Eq. (21) is analogous to the symmetry conditions (15) and (16). It provides a condition which is satisfied if there are two sets of valleys of [100] and [111] orientation contributing to the conduction. It does not depend on the number of

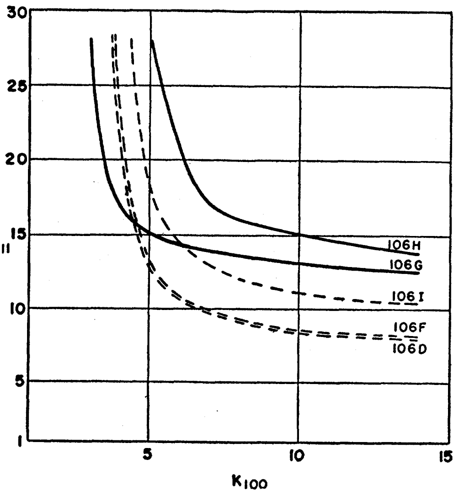

FIG. 2. Ratio K_{111} of longitudinal to transverse effective masses for [111] spheroids as function of K_{100} for [100] spheroids.

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[11] G. L. Pearson and H. Suhl, Phys. Rev. 83, 768 (1951).

valleys, nor on the form of energy dependence of the scattering. However, this condition depends quantitatively on the shape of the valleys. If this condition holds or is assumed to hold, some information on the shape of the valleys may be deduced. Equation (21) may be written in the form:

$$B=C_1(K_{111})+AC_2(K_{100}).$$

Both C_1 and C_2 are positive and greater than or equal to unity for all values of K. The measured quantities A and B may be used to calculate K_{111} as a function of K_{100} from Eq. (21). Such a curve has vertical and horizontal asymptotes, so that the possible values of K_{111} and K_{100} are limited in range (see Fig. 2). Since C_1 and C_2 have the same values for $1/K$ as for K, the prolate and oblate spheroids cannot be distinguished.

III. COMPARISON WITH EXPERIMENT

We apply this treatment to measurements[12] on n-type germanium-silicon alloys. Table I lists the pertinent data. Observations were made at 290°K.

Crystal 106T, with some six to seven percent silicon dissolved at random in the lattice, has a magnetoresistance effect which fits the [111]-spheroid model very well. This is also true for other crystals with less than eight percent silicon, reported in reference 12. The measured data for crystals in the range ten to seventeen percent silicon deviate from what is expected from a one-band model. This is shown in the last two columns of Table I, where the values of A and B are listed. A differs appreciably from zero for the crystals with more than ten percent silicon.

We first explore the question of whether the data are fitted by the model assumed. If Eq. (21) is applied to the above data, a plot of K_{111} as a function of K_{100} is obtained for each crystal. These curves are shown in Fig. 2. There is an experimental error which is not shown, large enough so that the curves may be considered to overlap considerably. These curves should contain a set of K's which correspond to the physical situation in the alloys, if the symmetry condition (21) is valid. The ratio K_{111} appears to vary little from its value of about 12 in going from germanium to an eight percent alloy.[12] As well, the effective masses in the [100] minima are probably changed only a small amount in going from silicon to germanium, since it is expected that the interacting states do not change their relative positions appreciably. Some recent observations[13] on an alloy of twenty-five percent silicon obey the [100] symmetry conditions, with $K_{100}\approx 5.5$. All the curves of Fig. 2 are consistent with the set of values $K_{111}=13.5$, $K_{100}=5.5$. Thus the symmetry condition (21) is satisfied for these crystals by effective mass ratios in good agreement with those given by the magnetoresistance data[12] in germanium and silicon and expected to apply in this alloy region.

TABLE I. Galvanomagnetic measurements on Ge-Si alloys.

Crystal	Percent Si	ρ_0 (ohm-cm)	$R_0\sigma_0$ (cm²/v-sec)	b	c (10^6 cm⁴/v²-sec²)	d	A	B
Ge	0	5–7	4250	8.6	−8.0	18.0	0.03	1.43
106T	6–7	1.5	2330	2.3	−2.3	5.4	0.01	1.42
106H	12–13	6.2	840	0.55	−0.46	0.70	0.14	1.57
106G	∼14	8.3	580	0.29	−0.18	0.25	0.31	1.77
106I	∼14	10.2	495	0.20	−0.11	0.13	0.39	2.07
106D	∼16	9.2	540	0.21	−0.11	0.12	0.45	2.27
106F	∼17	9.4	510	0.17	−0.09	0.10	0.45	2.31

TABLE II. Functions of the energy separation of the valleys.[a]

Sample	A	$\left(\frac{F_3^{(100)}}{F_3^{(111)}}D\right)_A$	B	$\left(\frac{F_3^{(100)}}{F_3^{(111)}}D\right)_B$	$\left(\frac{F_3^{(100)}}{F_3^{(111)}}D\right)_{\text{Av}}$
106T (6–7% Si)	0.01	0.016	1.42	0.028	0.022
106H (12–13%)	0.14	0.231	1.57	0.163	0.197
106G (∼14%)	0.31	0.511	1.77	0.345	0.428
106I (∼14%)	0.39	0.643	2.07	0.618	0.631
106D (∼16%)	0.45	0.742	2.27	0.799	0.771
106F (∼17%)	0.45	0.742	2.31	0.835	0.789

[a] $D=\exp(-\Delta\mathcal{E}/kT)$.

The application of Eqs. (19) and (20) to the data should yield the energy separation of the valleys, provided we know the effective masses and the relaxation times. The symmetry condition is satisfied by $K_{111}=13.5$ and $K_{100}=5.5$. If in addition the longitudinal effective masses are assumed to have the cyclotron resonance values,[5] i.e., $(m_{111}^l/m_{100}^l)=1.63$, the scattering integrals and the energy separation are left as unknown quantities. Table II lists the products $[F_3^{(100)}/F_3^{(111)}]\exp(-\Delta\mathcal{E}/kT)$ calculated from A and B, and the average value for each crystal.

In order to estimate the energy separation, some assumptions about the scattering need to be introduced. As a first simple trial, the relaxation times are assumed to have the form $\tau=\Lambda\mathcal{E}^p$, where Λ and p may be different for each type of valley and may vary with composition. We examine the behavior of τ as a function of composition outside the competition region (approximately ten to twenty percent), and extend this dependence into this region. In silicon and germanium, the magnetoresistance data may be used to give values of F_3F_1/F_2^2 which, under the above assumptions, is a function of p alone. This function is 1.17 in germanium and 1.16 in silicon, for the resistivities noted in reference 12. These values correspond to $p=-0.42$ or -0.43. The alloys of low composition have data consistent with a decreased value for p, in the range -0.36 to -0.39, depending on impurity content. Crystal 106T, with about the same impurity concentration as the other 106 crystals, yields $p=-0.39$, and this was used in fitting the data.

The Hall mobility is proportional to F_2/F_1 and this may be used to calculate Λ. If Λ_{100} and Λ_{111} are assumed

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[12] M. Glicksman, Phys. Rev. **100**, 1146 (1955). The compositions listed are based on recent spectrographic analyses.

[13] S. M. Christian and M. Glicksman (unpublished).

TABLE III. Energy separation of the valleys.

	With no interband scattering		Interband scattering		
Sample	$\Delta \mathcal{E}/kT$	$R_0\sigma_0$ (cm²/v-sec)	$\Delta \mathcal{E}/kT$	$R_0\sigma_0$ (cm²/v-sec)	$(R\sigma)_{\text{obs}}$ (cm²/v-sec)
106*T* (6–7% Si)	2	2100			2330
106*H* (12–13% Si)	−0.6	1120	0.9	785	840
106*G* (~14% Si)	−1.4	870	0.6	640	580
106*I* (~14% Si)	−1.7	800	0.35	570	495
106*D* (~16% Si)	−1.9	715	0.25	515	540
106*F* (~17% Si)	−2.0	685	0.2	490	510

independent of the separation of the two sets of minima, the strong decrease in mobility in the twelve to seventeen percent silicon composition region is not in accord with that deduced from the magnetoresistance observations. The magnetoresistance data in the competition region are a combination of [111] and [100] contributions. However, the mobility has about the value expected for [100] conduction alone, estimated from the observations in the range up to ten percent and at twenty-five percent silicon content.[13] If a scattering mechanism is introduced which appreciably lowers the mobilities of the valleys, these conditions can be simultaneously satisfied. Such a mechanism may be the enhanced scattering (and reduced mobility) of electrons in the [111] valleys into the [100] valleys, and the reverse, i.e., a type of intervalley scattering[3] which is interband scattering.[14] Since this should introduce no appreciable asymmetry into τ, the magnetoresistance conditions will not be strongly affected. However, the expected mobility would be reduced with respect to that found outside the competition region.

A proper choice for the energy dependence of the scattering under such conditions should involve a good number of parameters (in a phenomenological approach) as has been discussed by Herring.[3] The utility of a detailed analysis is limited, since there are insufficient types of data to determine these parameters. We choose arbitrarily to represent the scattering relaxation times by the expression

$$\tau = \Lambda(\Delta\mathcal{E})\mathcal{E}^p,$$

where

$$\frac{1}{\Lambda} = \frac{1}{\Lambda'} + \alpha \exp[-\beta(\Delta\mathcal{E}/kT)^2]. \tag{22}$$

Such a choice is made for simplicity, and the analysis is carried out to show the possibility of fitting both the magnetoresistance and mobility data by introducing a scattering time which has a minimum when the two bands are close together.

Λ' is fitted to the data at low alloy compositions, where the interband scattering should be small. It depends quite strongly on alloy composition, since the Hall mobility decreases rapidly with increasing silicon content. The scattering of charge carriers by the randomly positioned atomic potentials in the disordered alloy has been treated by Nordheim[15] for the case of a metal, and his approach may be simply extended to a semiconductor. Brooks[16] has considered the semiconductor problem, but treated the random array in terms of energy band fluctuations. He has calculated a scattering time and mobility for this mechanism for an alloy of silicon in germanium. In either case, it is found that the appropriate scattering time is proportional to $\{x(1-x)\}^{-1}$, where x is the fraction of silicon atoms present. The alloy scattering relaxation time has the same energy dependence as the thermal scattering time. Brooks predicted that this contribution to the scattering would equal that due to the thermal vibrations for an alloy of about eight percent silicon in germanium. Some preliminary measurements on the temperature dependende of the mobility made by the author give approximately the expected temperature dependence for this mechanism and equality with the thermal scattering at about nine percent silicon in germanium. In accordance with these observations, Λ_{111}' is taken as

$$\Lambda_{111}' = \frac{0.082}{0.082 + x(1-x)} \Lambda_{111}^0,$$

where Λ_{111}^0 is the value at $x=0$. Arbitrarily Λ_{100}' is assumed to have the same functional behavior.[13] The values of the Λ's for $x=0$ are chosen to fit the Hall mobilities in germanium and silicon, with a small adjustment in value to account for the impurity concentration in crystals 106. This fit requires $\Lambda_{100}^0/\Lambda_{111}^0 = 0.48$.

The interband term in Λ has two adjustable parameters, α and β, which give the strength of the scattering and the sharpness of its dependence on the energy separation. Since the current flow from the [111] minima into the [100] minima should equal the reverse current, β will be the same for the [111] and [100] valleys, and the ratio $\alpha_{111}/\alpha_{100}$ is determined.

In Table III are listed the results of this analysis. The second and third columns give values for $\Delta\mathcal{E}/kT$ and $R_0\sigma_0$ calculated with $\alpha=0$; the next two columns give similar calculations with $\alpha_{111}\Lambda_{111}^0 = 0.6$, $\beta = 0.7$. In the last column are listed the experimental values of $R_0\sigma_0$. The calculated values for no interband scattering are about fifty percent larger than the observed values in the competition region. However, the introduction of considerable interband scattering gives good agreement.

The calculated energy separation $\Delta\mathcal{E}$ is very sensitive to the amount of interband scattering present, in this simple approximation of the scattering. The values quoted in the table may be considered only as representative of the small separation in the above crystals. The mobility calculated for interband scattering shows

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[14] H. Brooks and W. Paul, Bull. Am. Phys. Soc. Ser. II, **1**, 48 (1956).

[15] L. Nordheim, Ann. Physik **9**, 607 and 641 (1931).

[16] H. Brooks (private communication).

a shallow minimum in its variation with $\Delta\mathcal{E}$ (or composition) in the competition region.

IV. CONCLUSIONS

The room temperature magnetoresistance data for the germanium-silicon alloys can be explained by a conduction band of [111] spheroids for alloys with less than ten percent silicon in germanium. However, the data for alloys of ten to seventeen percent silicon show a different anisotropy, not in accord with the assumption of one set of spheroids. These data are fitted satisfactorily by a conduction band made up of two sets of spheroids, with an energy separation varying with composition—one set having four [111]-oriented spheroids, the other having six [100]-oriented spheroids. This is in agreement with the alloy band structure suggested by Herman[6] to explain the variation with composition of the optical band gap.[7]

This analysis does not yield unique values for the effective masses of the spheroids. However, the effective masses which fit the data for germanium and silicon satisfy the magnetoresistance symmetry condition for the ten to seventeen percent silicon alloys.

An analysis of the data to yield the energy separation of the two bands as a function of composition depends sensitively on the scattering behavior in the alloys. If the scattering in each band is assumed independent of the other, the observed Hall mobility in the competition region is only about two-thirds that expected from an analysis of the magnetoresistance. The mobilities can be correlated with the magnetoresistance if some interband scattering is assumed. Such scattering lowers the band mobilities but leaves the magnetoresistance symmetry conditions unchanged.

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Electron and Nuclear Spin Resonance and Magnetic Susceptibility Experiments on Dilute Alloys of Mn in Cu*

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Dilute alloys of Mn in Cu are expected to show marked effects of the exchange interaction between the $3d^5$ ion core electrons of the Mn atoms and the $4s$ conduction electrons of the crystal. The simple model leads to the prediction of indirect exchange ferromagnetism; electronic Knight shift of the electron spin resonance line; nuclear Knight shift of the copper nuclear resonance; electron spin relaxation by the coupling with the conduction electrons; and a contribution to the electrical resistivity by the Elliott-Schmitt mechanism. The observed width of the electron spin resonance line suggests that the *sd* exchange interaction may be of the order of 0.2 of the interaction in the free ion. The dilute alloys appear to be antiferromagnetic, but with a ferromagnetic interaction also present which is rather stronger than calculated on the indirect exchange model. An unexpected experimental result is that the nuclear Knight shift is unaffected by the presence of Mn, suggesting that the conduction electron magnetization by the *sd* coupling is less than 1/50 of what might be expected.

IT occurred to us that it might be profitable to study by electron spin resonance methods the electronic properties of metallic alloys. We were particularly interested in observing the effect on the conduction electrons of the host metal when a low concentration of a second component is added. For several reasons it was decided to emphasize at the beginning the study of dilute solutions of manganese in copper: (a) The conduction band of copper is believed to have a simple structure, containing $4s$ electrons with an approximately isotropic effective mass nearly equal to the free electron mass. (b) The presence of paramagnetic solute ions permits the application to the problem of powerful magnetic methods, including susceptibility determination; line width, intensity, and position in electron and nuclear spin resonance; and neutron diffraction.[1] (c) It was anticipated that a ferromagnetic coupling between Mn ions might result from an indirect exchange coupling[2] via the conduction electrons. (d) There was some

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[1] Neutron diffraction studies of the Cu–Mn system are being carried out at the Argonne National Laboratory under the direction of Dr. S. Sidhu, to whom we are indebted for interest and cooperation.

[2] The idea is based on the observed exchange energy difference $^5S-^7S=9473$ cm^{-1} of the $3d^54s$ configuration of free Mn$^+$. A Mn^{++} ion is viewed as magnetizing the $4s$ conduction electrons, which in turn magnetize other Mn^{++} ions by the same interaction. Similar mechanisms have been proposed by H. Fröhlich and F. R. N. Nabarro, Proc. Roy. Soc. (London) **A175**, 382 (1940); C. Zener, Phys. Rev. **81**, 440 (1951); see also M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954). The application to the Cu–Mn problem was suggested independently by J. Fisher (unpublished).