crystals (Figs. 4–6) one weak absorption band is observed in each case. The frequency of this band, which is called ν_3 in Table I, is close to both $\nu_1(TO)+\nu_{LO}$ and $3\nu_1$. After subtracting out the background absorption, the strength of this band is approximately an order of magnitude less than the two phonon combination band at ν_2. Exact agreement is not expected between the values of $3\nu_1$ (or $\nu_1+\nu_{LO}$) and ν_3 since ν_1 is the *TO* frequency at zero wave vector which may differ considerably from the *TO* frequency in other parts of Brillouin zone. The question may be raised as to why the $2\nu_1$ was not observed for any of these materials. The frequency of this band places it beyond the spectral range of the transmission measurements, and it occurs very close to the minimum in the reflectivity curves. Assuming the strength of this band to be the same as that of the ν_2 band, calculations showed that it would be very difficult to observe in the reflectivity.

As previously indicated, several sharp emission lines of Sm^{++} in CaF_2, SrF_2, and BaF_2 were followed by a group of lines which were considered to be the result of interactions with the host lattice. One of the two strongest satellite lines in SrF_2 and BaF_2 is separated from the sharp electronic (magnetic dipole) transition by 216 and 186 cm^{-1}, respectively. These values agree very well with the measured *TO* frequencies of 217 cm^{-1} and 184 cm^{-1}, indicating that the fluorescence occurs to a vibrational level above the terminal electronic state. In SrF_2, a weak satellite line with a separation of ≈ 90 cm^{-1} is observed and a relation to the $\nu_{ac}=99$ cm^{-1} discussed above is likely. The fluorescence of Sm^{++} in CaF_2 is quite different from that in SrF_2 and BaF_2. The major emission line of Sm^{++} in CaF_2(14 118 cm^{-1}) corresponds to an electric dipole transition involving a lattice vibration. The vibrational structure following this intense line has several distinct maxima. One of these maxima is separated from the main fluorescent line by 250 cm^{-1} (at 77°K), which is close to the observed *TO* frequency of 257 cm^{-1}. Therefore, vibrational levels occur for Sm^{++} in all three fluorides which can be identified with the *TO* mode of vibration of the host lattice.

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Weak-Field Magnetoresistance of Impurity Conduction in *n*-Type Germanium*

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The coefficients B, C, and D of the weak-field magnetoresistance in n-type germanium are calculated in the phonon-induced hopping region at low temperatures. The shrinking of each donor wave function by a magnetic field decreases the transition probability of electrons from a donor site to an unoccupied one and gives rise to a magnetoresistive effect. The phase difference produced by the field between two neighboring donor wave functions contributes to the magnetoresistance to the same order of magnitude as the effect of the shrinking. The results show some characteristic properties of B, C, and D different from those of electrons in the conduction band: (1) The absolute magnitude of the coefficients is larger for specimens with smaller carrier mobility; (2) the magnitude is much larger than that expected from the usual transport theory of conduction electrons; (3) the isotropic part of the coefficients B is the largest; and (4) the coefficient D, which represents the anisotropy of the electronic motion, is the smallest among the three coefficients. These properties are in qualitative agreement with recent experiments in a slightly higher impurity concentration range in n-type germanium.

I. INTRODUCTION

THE theory of weak-field magnetoresistance was developed for conduction electrons in n-type germanium by Abeles and Meiboom[1] and Shibuya.[2] By introducing a many-valley model with an anisotropic effective mass in each valley, verified by cyclotron resonance experiments,[3] they could explain the large anisotropy of the magnetoresistance in n-type germanium.

A phenomenological relation[4] between the electric field $\mathbf{E}$ and the electric current $\mathbf{J}$ in a weak magnetic field $\mathbf{H}$,

$$\mathbf{E}=\rho_0[\mathbf{J}+A\mathbf{J}\times\mathbf{H}+BH^2\mathbf{J}+C\mathbf{H}(\mathbf{J}\cdot\mathbf{H})+D\mathbf{M}\mathbf{J}], \quad (1.1)$$

holds generally in cubic crystals such as germanium, where ρ_0 is the resistivity in zero magnetic field and

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† On leave of absence from the Electrotechnical Laboratory, Nagatacho, Tokyo, Japan, where this work was begun.
[1] B. Abeles and S. Meiboom, Phys. Rev. **95**, 31 (1954).
[2] M. Shibuya, Phys. Rev. **95**, 1385 (1954).
[3] G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. **98**, 368 (1955).
[4] F. Seitz, Phys. Rev. **79**, 372 (1950).

the tensor $\mathbf{M}$ is given by

$$\mathbf{M}=\begin{pmatrix} H_1^2 & 0 & 0 \\ 0 & H_2^2 & 0 \\ 0 & 0 & H_3^2 \end{pmatrix}, \tag{1.2}$$

when the coordinate axes coincide with the cubic axes of crystals. Since the relation (1.1) can be derived from the thermodynamics of irreversible processes and the crystal symmetry, its form holds beyond the limits of applicability of the theory of the galvanomagnetic effects based on the band theory of electrons. Therefore, we may use (1.1) in impurity conduction.

For the later discussion we clarify the physical meanings of the coefficients A, B, C, and D in (1.1), which is most easily illustrated by the simple case of Maxwell-Boltzmann distribution of electrons in a conduction band with spherical energy surfaces and constant mean free path.[4] The coefficient A is proportional to the Hall coefficient, which is not considered in this paper.[5] The coefficient B represents the isotropic part and determines the transverse magnetoresistance in this case. The coefficient C is negative in sign and contributes to the magnetoresistance only as combined with the B and D terms. The relation $C=-B$, which holds in the present case, means zero longitudinal magnetoresistance. The coefficient D becomes zero in this case, since it represents an anisotropy of the electronic motion.

According to the theory of Abeles and Meiboom[1] and Shibuya,[2] the characteristic properties of B, C, and D in n-type germanium can be summarized as follows.

[A.I] The coefficients B, C, D are proportional to the square of the mobility of electrons. This property does not depend on the band structure of n-type germanium, but is common to electrons represented by nonlocalized wave functions in the usual energy bands. In other words, this is deeply related to the curvature of electron orbits by the Lorentz force.

[A.II] The relation $C=-B$ holds under the assumption of acoustic phonon scattering of electrons.

[A.III] The relation $D\cong 2B$ holds. This strong anisotropy results from the strong anisotropy of the effective mass of electrons in the conduction band, which consists of the four spheroidal energy surfaces with axes in the [111] directions.

Most of the electrons are in the conduction band at room and liquid nitrogen temperatures and show a behavior following approximately the properties [A.I]–[A.III].[6]

At liquid helium and lower temperatures, however, electrons are frozen into the donor impurity levels (at lower impurity concentrations, $N_D\lesssim 10^{16}$ cm^{-3}) or into the so-called impurity band (at higher concentrations, $N_D\gtrsim 10^{17}$ cm^{-3}), to which the usual transport theory cannot be applied. The situation at the lower concentrations is particularly different from that in the conduction band. Electrons in the donor levels can be represented by localized wave functions with different potential energies, induced by compensating acceptor impurities. In an applied electric field, electrons can hop to nearby vacant sites by the emission or absorption of phonons to conserve the energies. Many experimental and theoretical papers[7,8] have been published on the transport properties associated with such phonon-induced hopping in zero magnetic field. The agreement of the theory with the experiment seems to be satisfactory apart from certain unsolved problems. It is therefore desirable to study in detail the effect of the magnetic field on the hopping process, using the same model that has been successful in zero magnetic field.

Some interesting papers have already been published on this subject. The effect of a strong magnetic field on an isolated donor wave function was theoretically studied by Yafet, Keyes, and Adams,[9] who showed that the hydrogen-like wave function shrinks more or less in all directions in a sufficiently strong magnetic field. Sladek and Keyes[10–12] measured the strong-field magnetoresistance of n-type indium antimonide and germanium at low temperatures and interpreted their results phenomenologically in terms of the shrinking of the donor wave functions. Miller and Abrahams[13,14] discussed the weak-field magnetoresistance using a hydrogen model of the donor wave function, but they did not give detailed consideration to the magnetoresistance coefficients B, C, and D.

Recently, Yamanouchi and Sasaki[15] have measured the weak-field magnetoresistance at intermediate concentrations between the hopping (or nonmetallic) and the impurity band (or metallic) regions and found remarkable differences of the properties of B, C, and D from those of electrons in the conduction band. Even though the experiments[16] are confined at present to the intermediate range, where the conduction mechanism has not been satisfactorily understood, one can infer from their results the characteristic properties of B, C, and D in the hopping region as follows.

[B.I] The absolute magnitude of the coefficients is larger for specimens with smaller carrier mobility.

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[5] T. Holstein, Phys. Rev. **124**, 1329 (1961).

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

[7] N. F. Mott and W. D. Twose, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1961), Vol. 10, p. 107; see this review article for a comprehensive list of references.

[8] Recently, the two-phonon process was discussed by J. Mycielski [Phys. Rev. **125**, 46 (1962)].

[9] Y. Yafet, R. W. Keyes, and E. N. Adams, J. Phys. Chem. Solids **1**, 137 (1956).

[10] R. W. Keyes and R. J. Sladek, J. Phys. Chem. Solids **1**, 143 (1956).

[11] R. J. Sladek, J. Phys. Chem. Solids **5**, 157 (1958).

[12] R. J. Sladek and R. W. Keyes, Phys. Rev. **122**, 437 (1961).

[13] A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).

[14] A. Miller, thesis, Rutgers University, 1960 (unpublished).

[15] C. Yamanouchi and W. Sasaki (private communication).

[16] C. Yamanouchi and W. Sasaki are now performing the experiment in the hopping region (private communication).

[B.II] The magnitude of the coefficients is much larger than that expected from the usual transport theory of conduction electrons. The properties [B.I] and [B.II] are also expected from the experiments of Sladek and Keyes[12] in a strong magnetic field.

[B.III] The coefficient B is larger than C.

[B.IV] The coefficient D is the smallest among B, C, and D.

It is the purpose of this paper to derive the properties [B.I]–[B.IV] using the currently accepted model of the hopping process.

In Sec. II we discuss the various conceivable effects of a magnetic field on impurity conduction and outline a simple model for magnetoresistance in the hopping region. The effect of the shrinking of the donor wave function is calculated in Sec. III. In Sec. IV we calculate the effect of the phase difference between neighboring donor wave functions produced by the magnetic field. Section V is devoted to discussion of the results.

II. MODEL FOR MAGNETORESISTANCE

There are various conceivable effects of a magnetic field on impurity conduction, and it is instructive to enumerate these to clarify the difference between metallic and nonmetallic conduction. At higher impurity concentrations, electrons are represented by nonlocalized wave functions in the impurity band, and the effect of a magnetic field is somewhat similar to that on the conduction electrons. (1) The Lorentz force causes a curvature of electron orbits and gives rise to a magnetoresistive effect. (2) If there is some kind of localized spin ordering[17,18] among the scattering centers for electrons carrying the current, the application of a magnetic field may decrease the scattering rate and lead to a negative magnetoresistance. (3) The structure of the impurity band may be more or less sensitive to the impurity concentration, i.e., to the overlapping of donor wave functions so that a magnetic field changes the band structure by shrinking the donor wave function.

On the other hand, there are four different effects of a magnetic field at lower concentrations. (1) Shrinking of the donor wave function by the magnetic field decreases the overlapping of two neighboring wave functions and gives rise to the magnetoresistance. (2) The phase difference between two neighboring wave functions also gives a magnetoresistive effect. (3) A magnetic-field-induced change of the contributions from four valleys to the ground-state wave function is expected in n-type germanium because of the different magnetic energies of valley minima[19] and the anisotropic g factors of the donor electrons.[20] (4) If one takes into account the excited impurity levels such as the triplet states of 1s-like levels,[21] a magnetic-field-induced change in the electron population and therefore a change of the resistivity is expected. When we consider the *weak*-field magnetoresistance at *very low* temperatures, effects (3) and (4) are of higher order and are neglected in this paper.

We accept the well-known model of the hopping process in zero magnetic field, which has been developed by Kasuya and Koide,[22] Miller and Abrahams,[13,14] Twose,[7,23] and Yamashita and Kurosawa.[24] We consider n-type germanium with N_D donors and N_A acceptors which compensate the N_A donors and have negative charge. At sufficiently low impurity concentrations, the potential energy difference due to the nearby ionized impurities between two donor sites is larger than the resonance or transfer energy. Then the electron is localized on one donor site and can hop into the nearby vacant site only by the emission or absorption of a phonon. The transition probability of the electron from a neutral donor (i) to the ionized donor site (j) is proportional to the square of the resonance energy[13] W:

$$W=L-SJ, \tag{2.1}$$

$$\begin{aligned} L&\equiv(\Psi_i,(-e^2/\kappa r_j)\Psi_j),\\ S&\equiv(\Psi_i,\Psi_j),\\ J&\equiv(\Psi_i,(-e^2/\kappa r_j)\Psi_i), \end{aligned} \tag{2.2}$$

where κ is the dielectric constant of the host crystal, r_j is the distance from the donor site (j) to the position of the electron. The ground-state wave function[21] of the donor (i) is written as

$$\Psi_i(\mathbf{r})=\sum_{p=1}^{4}\tfrac{1}{2}F_p(\mathbf{r})\phi_p(\mathbf{r}), \tag{2.3}$$

where $\phi_p(\mathbf{r})$ is the Bloch function for the pth conduction-band minimum and $F_p(\mathbf{r})$ is the envelope function

$$F_p(\mathbf{r})=(\pi a^2 b)^{-\frac{1}{2}}\exp\{-[x^2+y^2)/a^2+z^2/b^2]^{\frac{1}{2}}\}, \tag{2.4}$$

when we choose the z along the pth valley axis. We now assume for simplicity that the conductivity is proportional to a weighted angular average of the square of W, without carrying out the complicated

[17] The idea of the existence of a localized spin ordering in the impurity band was proposed by Y. Toyozawa (private communication) to interpret the negative magnetoresistance found by H. Fritzsche and K. Lark-Horovitz [Phys. Rev. **99**, 400 (1955)]; W. Sasaki and Y. Kanai [J. Phys. Soc. Japan **11**, 894 (1956)]; W. Sasaki, C. Yamanouchi, and G. M. Hatoyama [*Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Science, Prague, 1961), p. 159].

[18] A similar effect in the magnetoresistance in dilute alloy was discussed by K. Yosida [Phys. Rev. **107**, 396 (1957)].

[19] A similar effect in the piezoresistance was discussed by P. J. Price [Phys. Rev. **104**, 1223 (1956)] and H. Fritzsche [*ibid.* **119**, 1899 (1960); **125**, 1552, 1560 (1962)].

[20] See, for instance, H. Hasegawa, Phys. Rev. **118**, 1523 (1960); and L. M. Roth, *ibid.* **118**, 1534 (1960).

[21] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 257.

[22] T. Kasuya and S. Koide, J. Phys. Soc. Japan **13**, 1287 (1958).

[23] W. D. Twose, thesis, University of Cambridge, 1959 (unpublished).

[24] J. Yamashita and T. Kurosawa, J. Phys. Soc. Japan **15**, 802 (1960).

statistical calculation over the random distribution of impurities.[25] The changes in Ψ_i and Ψ_j, i.e., in W give rise to the magnetoresistance.

We must calculate the change in W for three independent arrangements of **J**, **E**, and **H** to determine the three coefficients B, C, and D in (1.1). The coordinate system used in our calculation is shown in Fig. 1, where (1,2,3) are the cubic axes of the crystal and (X,Y,Z) are in the [111], [11$\bar{2}$] and [$\bar{1}$10] directions, respectively. We choose the current always in the Z direction and specify three cases as follows.

$$\begin{aligned} &\text{Case I:} && \mathbf{H}=(H,0,0),\\ &\text{Case II:} && \mathbf{H}=(0,H,0),\\ &\text{Case III:} && \mathbf{H}=(0,0,H), \end{aligned} \tag{2.5}$$

in the (X,Y,Z) coordinate system. From the relation (1.1), one obtains

$$\begin{aligned} (\rho-\rho_0)/\rho_0&=(B+\tfrac{1}{3}D)H^2, && \text{(Case I)}\\ &=(B+\tfrac{1}{6}D)H^2, && \text{(Case II)}\\ &=(B+C+\tfrac{1}{2}D)H^2, && \text{(Case III)} \end{aligned} \tag{2.6}$$

where ρ is the resistivity in the magnetic field.

III. SHRINKING OF DONOR WAVE FUNCTION

According to the Kohn-Luttinger theory,[21] the effective mass equation for $F_p(\mathbf{r})$ in a magnetic field is given by

$$\left\{\frac{1}{2m_t^*}\left(\frac{\hbar}{i}\frac{\partial}{\partial z}-\frac{e}{c}A_z\right)^2+\frac{1}{2m_t^*}\left[\left(\frac{\hbar}{i}\frac{\partial}{\partial x}-\frac{e}{c}A_x\right)^2+\left(\frac{\hbar}{i}\frac{\partial}{\partial y}-\frac{e}{c}A_y\right)^2\right]-\frac{e^2}{\kappa r}\right\}F_p(\mathbf{r})=EF_p(\mathbf{r}), \tag{3.1}$$

when the z axis is chosen along the pth valley axis, where m_l^*, m_t^* are the longitudinal and transverse effective masses, respectively, and **A** is the vector potential. In general, the effect of the magnetic field in an arbitrary direction on the shape of the ground-state wave function is very complicated and gives rise to a deviation from the spheroidal shape of (2.4). Fortunately, the strong anisotropy of the effective mass of the conduction band, $m_l^*\cong 20m_t^*$ in n-type germanium, permits us to neglect the first term of the magnetic perturbation in (3.1) and therefore to consider the shrinking of only the transverse spatial extent by the magnetic field. A similar approximation was made in the phenomenological analysis of the strong-field magnetoresistance by Sladek and Keyes.[12] We expect such an approximation to lead to an upper limit to the value of the anisotropy D.

In the case of a spherical energy surface, the effective-mass equation reduces to

$$\left(-\frac{\hbar^2}{2m^*}\nabla^2-\frac{e^2}{\kappa r}-\frac{eH}{2m^*c}l+\frac{e^2H^2}{8m^*c^2}r^2\sin^2\Theta\right)F_p(\mathbf{r})=EF_p(\mathbf{r}), \tag{3.2}$$

when one chooses the symmetric gauge

$$\mathbf{A}=\tfrac{1}{2}H(-y,x,0), \tag{3.3}$$

where l is the z component of the angular momentum and Θ is the angle between the position vector **r** and the magnetic field direction. The linear Zeeman term has no effect in this case, since l remains a good quantum number for the perturbed wave function. In the case of a spheroidal energy surface, however, the linear Zeeman term may have some effects except in the special case where **H** is parallel to the valley axis. Our assumption mentioned above corresponds just to the consideration of such a special case and excludes automatically the effect of the linear Zeeman term.

The effect of the quadratic Zeeman term on the hydrogen-like wave function has been discussed by Csavinszky[26] using an ordinary perturbation method and by Miller[14,27] using a variational method. Both

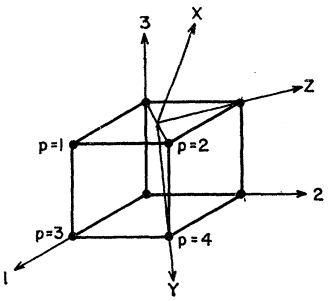

FIG. 1. The coordinate systems used in Sec. II and the designation of valleys. (1,2,3) are the cubic axes of the crystal and (X,Y,Z) are in the [111], [11$\bar{2}$], and [$\bar{1}$10] directions.

[25] We do not take the average of $|W|^2$ over the radial distribution of impurities in this paper, since the reliable average method has not been given at present (see, for instance, reference 7, p. 150).

[26] P. Csavinszky, Phys. Rev. **119**, 1605 (1960). Csavinszky calculated the shrinking effect on the hydrogenlike 1s function by an ordinary perturbation method, where the perturbation of the quadratic Zeeman term mixes the 2s, 3s, 3d_z, 4s, $\cdots$ states into the ground state. He limited the calculation to the mixing of the 2s function. Our calculation on the same model shows that the mixing of the excited states has a slow covergency, e.g., if

$$\Psi=\Psi_{1s}+\alpha\Psi_{2s}+\beta\Psi_{3s}+\cdots,$$

then

$$\alpha=0.662(\kappa a^3H^2/m^*c^2),\quad \beta=0.206(\kappa a^3H^2/m^*c^2),\cdots.$$

More seriously, the change of the resonance energy diverges at the large separation of two donor sites, since the change of W due to the mixing of the 2s, 3s, 4s, $\cdots$ functions is roughly proportional to $\exp(-R/2a)$, $\exp(-R/3a)$, $\exp(-R/4a)$, $\cdots$. This may be physically self-evident because the states with higher energies have the larger wave-function tails at large distances. The same difficulty of an ordinary perturbation theory and a modified perturbation scheme have been already discussed by many authors [see, for instance, M. H. Cohen, D. A. Goodings and V. Heine, Proc. Phys. Soc. (London) **73**, 811 (1959)].

[27] Solving Eq. (3.2) by the variational method with the effective Bohr radius a as a parameter, Miller[14] obtained the shrinking effect as

$$a=a_0[1-\tfrac{1}{2}(\kappa a_0^3/m^*c^2)H^2].$$

If we use this in a change of the transverse effective Bohr radius, we obtain

$$B=-C=D=\tfrac{1}{3}(a_0/R)^2\kappa R^3/m_t^*c^2,$$

which is smaller than (3.23) by a factor $\sim 20(a_0/R)^2$. This is

treatments, however, are not designed to give information of the wave function at large distances from the donor nucleus. We therefore apply another perturbation method to the problem, which was developed by Dargarno and Lewis,[28] and Schwartz.[29] According to their theory, the perturbed wave function can be expressed as

$$\Psi=\Psi_0[1+F-(\Psi_0,F\Psi_0)], \tag{3.4}$$

where the function F is given as the solution of an inhomogeneous differential equation

$$\Psi_0\nabla^2F+2(\nabla F)\cdot(\nabla\Psi_0) = (2m^*/\hbar^2)[\mathcal{H}'-(\Psi_0,\mathcal{H}'\Psi_0)]\Psi_0. \tag{3.5}$$

Here $\mathcal{H}'$ is the perturbation Hamiltonian, i.e.,

$$\mathcal{H}'=\frac{e^2H^2}{8m^*c^2}r^2\sin^2\Theta \tag{3.6}$$

in the present problem, and hence

$$(\Psi_0,\mathcal{H}'\Psi_0)=e^2H^2a^2/4m^*c^2. \tag{3.7}$$

Equation (3.5) has the solution

$$F=-\frac{1}{24}\frac{\kappa H^2}{m^*c^2}[r^3\sin^2\Theta+\tfrac{5}{2}r^2a(1-\tfrac{3}{5}\cos^2\Theta)]. \tag{3.8a}$$

We neglect the terms of order (a/r) compared with unity and use the approximate solution

$$F\cong-\frac{1}{24}\frac{\kappa H^2}{m^*c^2}r^3\sin^2\Theta, \quad (r\gg a,\ \sin^2\Theta\sim1). \tag{3.8b}$$

If we again neglect the term $(\Psi_0,F\Psi_0)\sim(a/r)^3F$ in (3.4), we obtain

$$\Psi\cong\Psi_0\left(1-\frac{1}{24}\frac{\kappa H^2}{m^*c^2}r^3\sin^2\Theta\right) \tag{3.9}$$

at large distances from a nucleus. It is to be noted that the perturbation expansion of (3.9) is invalidated near the radius r_c at which the magnetic energy becomes equal to the Coulomb energy, i.e.,

$$e^2/\kappa r_c=e^2H^2r_c^2\sin^2\Theta/8m^*c^2. \tag{3.10}$$

We now proceed to estimate a change in the resonance energy for one pair of donors in the plane perpendicular to the magnetic field. If we use elliptic coordinates[30] (μ,ν,φ) and put $\sin^2\Theta=1$ for simplicity, we obtain

$$\begin{aligned}L&=-\frac{e^2R^2}{2\kappa a^3}\int_1^\infty d\mu\int_{-1}^1 d\nu\ (\mu-\nu)e^{-R\mu/a}\\&\qquad\times[1-\tfrac{1}{4}R^3\lambda(\mu^3+3\mu\nu^2)],\\S&=\frac{R^3}{4a^3}\int_1^\infty d\mu\int_{-1}^1 d\nu\ (\mu^2-\nu^2)e^{-R\mu/a}\\&\qquad\times[1-\tfrac{1}{4}R^3\lambda(\mu^3+3\mu\nu^2)],\\J&=-\frac{e^2R^2}{2\kappa a^3}\int_1^\infty d\mu\int_{-1}^1 d\nu\ e^{-R(\mu+\nu)/a}(\mu+\nu)\\&\qquad\times[1-\tfrac{1}{4}R^3\lambda(\mu+\nu)^3],\end{aligned} \tag{3.11}$$

R being the donor separation and

$$\lambda\equiv\kappa H^2/24m^*c^2. \tag{3.12}$$

The integration of (3.11) gives the results

$$\begin{aligned}L&\cong-(e^2R/\kappa a^2)e^{-R/a}(1-R^3\lambda/2),\\S&\cong(R^2/3a^2)e^{-R/a}(1-2R^3\lambda/5),\end{aligned} \tag{3.13}$$

while $J\cong-e^2/\kappa R$ remains unchanged. Therefore, the square of the resonance energy becomes

$$|W|^2\cong(2e^2/3\kappa a^2)^2R^2e^{-2R/a}(1-1.1R^3\lambda). \tag{3.14}$$

We now assume that an expression similar to (3.14) can be used in the change of the resonance energy for our complicated wave functions, since as will be seen later the main contributions to $|W_p|^2$ come from pairs in the plane perpendicular to the valley axis, i.e., to the *effective* magnetic field in our approximation. Thus, the effect of the magnetic field to $|W_p|^2$ is given by a factor

$$1-\frac{11}{240}\frac{\kappa R^3}{m_t^*c^2}H^2\cos^2\varphi_p, \tag{3.15}$$

where φ_p is the angle between the magnetic field and the pth valley axis directions. The various assumptions such as (3.15) made in this section are good to within a numerical factor of order unity.

The resonance energy in zero magnetic field[13] is calculated using (2.1) to (2.4):

$$|W|^2=\left(\frac{e^2}{6\kappa a^2}\right)^2\sum_{p=1}^{4}R_p^2\exp\left(\frac{-2R_p}{a}\right), \tag{3.16}$$

where

$$\begin{aligned}R_p&\equiv a\{(x_{ij}^2+y_{ij}^2)/a^2+z_{ij}^2/b^2\}^{1/2}\\&=R(1+\alpha\cos^2\theta_p)^{1/2}.\end{aligned} \tag{3.17}$$

Here, $\alpha=(a^2/b^2-1)\cong20$ in arsenic- or antimony-doped germanium, θ_p is the angle between the pth valley axis and the direction of the donor pair (i)–(j). One can see from (3.16) the separate contribution of four valleys to $|W|^2$.

We take the angular average as follows. First, we assume the vacant sites (j) are distributed with equal probability around the occupied site (i), on a sphere

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because the shrinking of the Bohr radius is determined by the magnetic perturbation near the donor nucleus and hence it underestimates the perturbation at large distances.

[28] A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. (London) **A233**, 70 (1956).

[29] C. Schwartz, Ann. Phys. (New York) **6**, 156 (1959).

[30] See, for instance, H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), p. 367.

TABLE I. The weighted angular average of $|W|^2$ in (3.16).

Valley No., p	1, 3	2, 4
$\langle R_p^2 e^{-2R_p/a}\rangle_{\rm av}/R^2e^{-2R/a}$	$(a\pi/144\alpha R)^{\frac{1}{2}}$	$(a\pi/16\alpha R)^{\frac{1}{2}}$

with the radius of the average donor separation R. Secondly, the weight of the pair contributing to the current is taken into account by multiplying by the square of the direction cosine of the angle between the pair and the current direction.[11] Thirdly, the average is taken over the hemisphere in the current direction. On account of the large anisotropy ($\alpha\gg1$) in the exponential term of (3.16) the main contribution to $|W|^2$ comes from the pairs with $\theta_p\cong\pi/2$. From a simple geometrical calculation we obtain the weighted average of $R_p^2\exp(-2R_p/a)$ for each valley in Table I (see also Fig. 1 for the designation of valleys). Thus, we can write

$$\langle|W|^2\rangle_{\rm av}=\left(\frac{e^2}{6\kappa a^2}\right)^2\left(\frac{\pi b^2}{16Ra}\right)^{1/2}R^2\sum_{p=1}^{4}\beta_p\exp\left(\frac{-2R}{a}\right),\quad(3.18)$$

where

$$\beta_p=\begin{cases}1/3 & \text{for } p=1,3\\ 1 & \text{for } p=2,4.\end{cases}\quad(3.19)$$

The square of the resonance energy in the magnetic field is obtained by inserting the factor (3.15) into (3.18),

$$\langle|W|^2\rangle_{\rm av}=\langle|W_0|^2\rangle_{\rm av}\times\left\{1-\frac{11}{640}\frac{\kappa R^3}{m_t{}^*c^2}H^2\sum_{p=1}^{4}\beta_p\cos^2\varphi_p\right\},\quad(3.20)$$

$$\langle|W_0|^2\rangle_{\rm av}\equiv\frac{8}{3}\left(\frac{e^2}{6\kappa a^2}\right)^2\left(\frac{\pi b^2}{16Ra}\right)^{1/2}R^2\exp\left(\frac{-2R}{a}\right),\quad(3.21)$$

where the values of $\cos^2\varphi_p$ of each valley for three cases of the magnetic field are given in Table II. Using the relation in our simple model,

$$\frac{\rho-\rho_0}{\rho_0}=\frac{\langle|W_0|^2\rangle_{\rm av}}{\langle|W|^2\rangle_{\rm av}}-1,\quad(3.22)$$

and comparing with (2.6), we obtain

$$B=-C=D=(11/720)(\kappa R^3/m_t{}^*c^2).\quad(3.23)$$

We conjecture that the anisotropy term D is the smallest among the three terms because of an overestimation of the mass anisotropy in our approximation.

IV. EFFECT OF PHASE DIFFERENCE BETWEEN TWO DONOR WAVE FUNCTIONS

When we consider one donor wave function in a magnetic field, the origin of the vector potential $\mathbf{A}$ can be chosen arbitrarily, usually at the position of the donor nucleus [see (3.3)]. In the two-donor problem we must fix the origin at a point, for example at the donor site (i), then the wave function for the site (j) is altered by a phase factor[5,14,31]

$$\exp\left[\frac{ieH}{2c\hbar}(x_{ij}'y'-y_{ij}'x')\right],\quad(4.1)$$

when the coordinate system is so chosen as the z axis is in the direction of the magnetic field. The phase factor (4.1) does not change the physical properties of the donor (j), but affects quantities relating to two-donor wave functions such as the resonance energy. This effect on the magnetoresistance was discussed first by Miller[14] using the hydrogen model of donor impurities. In this section a somewhat detailed calculation will be carried out in n-type germanium to determine the magnetoresistance coefficients B, C, and D.

When the line between two donor atoms is in the magnetic field direction, there is no effect of the phase difference because $x_{ij}=y_{ij}=0$. On the other hand, when the pair direction is perpendicular to the field direction, the phase difference leads to a magnetoresistive effect. This effect may be interpreted in semiclassical terms as follows. As an electron moves from a site (i) to the site (j), its *orbit* is curved by the magnetic field in the plane perpendicular to the field direction; usually this effect is represented by the Lorentz force in band conduction. Such an effect may remain in the quantum transition in the present problem and disturb the ease of the transition. In a weak magnetic field this effect contributes to the magnetoresistance separately from the shrinking of the wave functions, i.e., the magnetoresistance is given by the sum of the two effects.

In a weak magnetic field, (4.1) can be expanded as

$$1+\frac{ieH}{2c\hbar}(x_{ij}'y'-y_{ij}'x')-\frac{1}{2}\left(\frac{eH}{2c\hbar}\right)^2(x_{ij}'y'-y_{ij}'x')^2+\cdots,\quad(4.2)$$

where the linear term of H vanishes in the course of the calculation of W. Thus, we must include the quadratic term in the integrand of L and S in (2.2), while

TABLE II. The values of $\cos^2\varphi_p$ in (3.20) for three cases.

Case	(I)	(II)	(III)
$\cos^2\varphi_1$	1/9	2/9	2/3
$\cos^2\varphi_2$	1	0	0
$\cos^2\varphi_3$	1/9	2/9	2/3
$\cos^2\varphi_4$	1/9	8/9	0

[31] E. Kemble, *The Fundamental Principles of Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1937), p. 29.

$J\cong(-e/\kappa R)$ is not changed by the phase factor. Using Eulerian angles (ψ,ϕ,ω), we obtain the phase factor in the coordinate system in which the z axis is in the pair direction,

$$1-\frac{1}{2}\left(\frac{eH}{2c\hbar}\right)^2 R^2\sin^2\omega(x\cos\phi+y\sin\phi)^2, \qquad (4.3)$$

where ϕ can be arbitrarily chosen, for example $\phi=0$. Now, making use of elliptic coordinates[30] (μ,ν,φ) we obtain for one pair of donors,

$$L=-\frac{e^2}{\kappa\pi a^3}\sum_{p=1}^{4}\frac{1}{4}e^{-i\mathbf{p}\cdot\mathbf{R}}\times\int_0^{2\pi}d\varphi\int_1^{\infty}d\mu\int_{-1}^{1}d\nu\,\frac{R_p^2}{4}(\mu-\nu)e^{-R_p\mu/a}\times[1-\tfrac{1}{8}(kR_p)^2(\mu^2-1)(1-\nu^2)\cos^2\varphi],$$

$$S=\frac{1}{\pi a^3}\sum_{p=1}^{4}\frac{1}{4}e^{-i\mathbf{p}\cdot\mathbf{R}}\times\int_0^{2\pi}d\varphi\int_1^{\infty}d\mu\int_{-1}^{1}d\nu\,\frac{R_p^3}{8}(\mu^2-\nu^2)e^{-R_p\mu/a}\times[1-\tfrac{1}{8}(kR_p)^2(\mu^2-1)(1-\nu^2)\cos^2\varphi], \qquad (4.4)$$

where $\mathbf{p}$ is the wave number vector of the Bloch function at the pth minimum of the conduction band. In (4.4) we put, for brevity,

$$k\equiv(eRH/2c\hbar)\sin\omega, \qquad (4.5)$$

where ω is the angle between the pair line and the magnetic field direction (see Fig. 2). The integration of (4.4) is simple and gives the results

$$L=-\frac{e^2}{4\kappa a^2}\sum_{p=1}^{4}e^{-i\mathbf{p}\cdot\mathbf{R}}e^{-R_p/a}\times\left[R_p+a-\frac{a^3k^2}{4}\left(1+\frac{R_p}{a}+\frac{R_p^2}{3a^2}\right)\right],$$

$$S=\tfrac{1}{4}\sum_{p=1}^{4}e^{-i\mathbf{p}\cdot\mathbf{R}}e^{-R_p/a}\times\left[1+\frac{R_p}{a}+\frac{R_p^2}{3a^2}-\frac{a^2k^2}{2}\left(1+\frac{R_p}{a}+\frac{2R_p^2}{5a^2}+\frac{R_p^3}{15a^3}\right)\right]. \qquad (4.6)$$

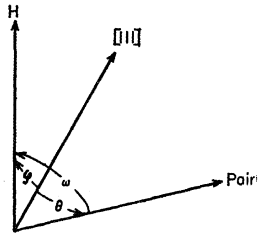

FIG. 2. The angles used in the calculation of the resonance energy The main contribution to the resonance energy comes from the pairs with $\theta\cong\pi/2$.

Thus, we obtain for the square of the resonance energy

$$|W|^2\cong|W_0|^2-\frac{3a}{20}\left(\frac{e^2}{6\kappa a^2}\right)^2\left(\frac{eRH}{2c\hbar}\right)^2\sum_{p=1}^{4}(\sin^2\omega)R_p^3\times\exp(-2R_p/a), \qquad (4.7)$$

where $|W_0|^2$ is given by (3.16).

The weighted angular average of the last sum of (4.7) can be performed in the same way as in Sec. III, using some geometrical considerations. The results are given in Table III. Using (2.6), (3.22), (4.7), and Table III we obtain the magnetoresistance coefficients,

$$B=\frac{9\epsilon}{320}\frac{\kappa R^3}{m_t^*c^2}, \qquad -C=\tfrac{2}{3}B, \quad D=\tfrac{1}{3}B, \qquad (4.8)$$

where ϵ is defined by the relation

$$(ea^2/\hbar c)^2=\epsilon(\kappa a^3/m_t^*c^2). \qquad (4.9)$$

$\epsilon\cong0.67$ for Sb-doped and $\cong0.56$ for As-doped germanium if we take $a(\mathrm{Sb})=69.3$ Å and $a(\mathrm{As})=58.1$ Å, respectively.

TABLE III. The weighted angular average of $(\sin^2\omega)R_p^3\times\exp(-2R_p/a)$ in (4.7). The unit is $(1/72)(\pi a/4\alpha R)^{\frac{1}{2}}R^3\times\exp(-2R/a)$.

Valley No. \ Case	(I)	(II)	(III)
1	8	7	9
2	36	27	9
3	8	7	9
4	28	35	9

V. DISCUSSION

Comparison of (3.23) with (4.8) shows that the two effects, the shrinking of each donor wave function and the phase difference between two neighboring donors, contribute the same order of magnitude to the magnetoresistance. This fact suggests the importance of the phase-factor effect even in the strong-field magnetoresistance, which has been interpreted so far by the shrinking effect. A simple theory is given for the strong-field case in a subsequent paper.[32]

The characteristic properties of the magnetoresistance coefficients will be illustrated by plotting them vs the donor concentration N_D and the carrier mobility μ. The concentration dependence of the coefficients for the two effects are shown in Fig. 3 for arsenic-doped germanium, where B_s, $|C|_s$, D_s represent the components due to the shrinking effect and B_p, $|C|_p$, D_p are due to the phase-factor effect. We see that B, $|C|$, D are proportional to $1/N_D$. Moreover, B_p, $|C|_p$, D_p

[32] N. Mikoshiba, Phys. Rev. 127, 1962 (1962).

have an impurity species dependence through the difference of a, i.e., the magnetoresistance coefficients are large for the impurity having large a and small impurity ionization energy. In Fig. 4 the mobility dependence of the coefficients is shown, using a simple assumption that the mobility is proportional to $\langle|W_0|^2\rangle_{\rm av}$ of (3.21), i.e.,

$$\mu=\gamma(R/a)^{3/2}\exp(-2R/a), \tag{5.1}$$

γ being a factor independent of R. From Fig. 4 one can see a remarkable difference from the μ^2 dependence of the coefficients in conduction electrons.

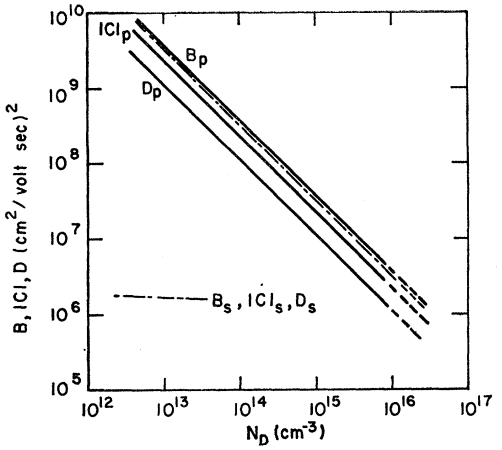

FIG. 3. The concentration dependences of B_p, $|C|_p$, D_p due to the phase-factor effect and of B_s, $|C|_s$, D_s due to the shrinking effect. We take for As-doped germanium the values $\kappa=16$, $m_t^*/m_0=0.0813$ (m_0; free-electron mass), a(As)$=58.1$ Å and $N_D=R^{-3}$.

Generally speaking, the shrinking effect in hopping conduction corresponds to the magnetic-field-induced change in the band structure or the change in the effective mass in band conduction. Such an effect is usually very small compared to that of the Lorentz force which corresponds to the phase-factor effect in hopping conduction. A remarkable difference in the mobility dependence of magnetoresistance can be interpreted as follows. Electrons in the conduction band experience the Lorentz force over the length of the mean free path. Therefore, electrons with large

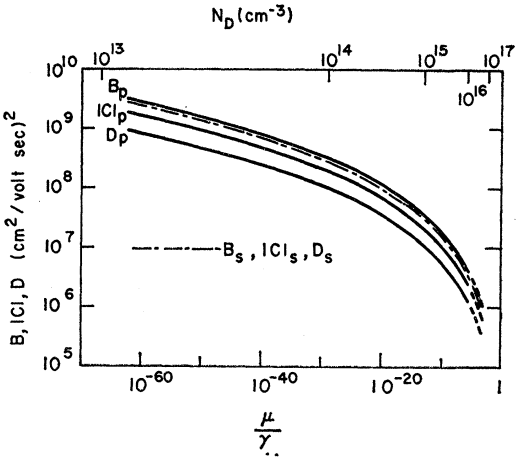

FIG. 4. The mobility dependences of B_p, $|C|_p$, D_p due to the phase-factor effect and of B_s, $|C|_s$, D_s due to the shrinking effect for As-doped germanium. We assume $\mu=\gamma(R/a)^{3/2}\exp(-2R/a)$, γ being a factor independent of R.

mean free path or mobility suffer strongly the magnetic field effect and show a large magnetoresistance. In the hopping process the mean average distance between donors corresponds to the mean free path in the conduction band, concerning the effect of the magnetic field. In contrast to the conduction electrons, the mobility is not proportional to such characteristic ("memory") distance and is very small in this case. This difference leads to the different mobility dependence and also extraordinarily large magnetoresistance.

Since there are no experiment in the hopping region at present, a quantitative comparison of theory with experiment is impossible. However, the formulas [B.I]–[B.IV] mentioned in the Introduction are displayed qualitatively by our simple model.

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