lines as they are, they could also be associated with some centers of different symmetry. Lines with 15- and 49-cm^{-1} separations might also be due to phonon difference frequencies as Sugano[12] suggested. Also, there was no compelling reason to associate any of these lines we observed at 4°K with transitions between exchange-coupled ion-pair states.

CONCLUDING REMARKS

On the basis of the spectroscopic evidence we suggest that coupling by phonons is the predominant factor accounting for the usually observed band widths of Mn absorptions in ZnS and for the band width and non-

Gaussian distribution of the Mn emission in ZnS. Since we recently observed similarly structured emission of Mn-activated CdS and structure in the absorption bands of ZnSe:Mn, it is probably safe to state that the process described is not restricted to the ZnS host lattice but might apply to divalent manganese as a luminescence and absorption center in general.

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[12] S. Sugano (private communication).

Impurity Conduction in the Intermediate Concentration Region*

Hisashi Nishimura†

The Catholic University of America, Washington, D. C.

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The impurity conduction in semiconductors in the intermediate impurity concentration region is investigated theoretically by using the data available on antimony-doped germanium with small compensations. The origin of the activation energy ϵ_2 which characterizes the resistivity in a certain temperature range is discussed on the basis of the D^--band model, which is provided by the formation of a band as a result of the interaction between the states of negatively charged donors, the D^- states. The hydrogenic model is employed for the donor ground state, and we assume that the wave function describing the behavior of an electron in the weakly bound D^- state is of an exponential type. By using the tight-binding approximation, it is shown that the interaction between these states leads to the formation of the D^- band. Thus, the energy gap from the donor ground state, which is assumed to be localized, to the bottom of the D^- band is related to the observed activation energy ϵ_2. The numerical estimations are in qualitative agreement with the observed values.

I. INTRODUCTION

THE impurity conduction which is observed in semiconductors containing impurities at low temperatures has been recognized as having three different types of mechanism corresponding to the concentrations of impurities, i.e., low-, intermediate-, and high-concentration regions,[1,2] respectively.

At low concentrations, the effect of electron correlation dominates the electrical conduction.[2,3] The electrons (in what follows, the terminology is applicable to n-type samples) are localized at impurity sites and the

electrical conduction takes place through the hopping processes of electrons from occupied to unoccupied sites with the aid of phonons, if there are any neighboring vacant sites as a result of compensation.[2,4]

At high concentrations, the interaction between impurities which are distributed at random is so strong that the so-called impurity band is formed.[5,6] The electrons behave like a degenerate Fermi gas in the band and the transport properties are metallic in nature.[3] The main cause of scattering is the random distribution of impurities itself and therefore the resistivity is independent of temperature.[7]

At intermediate concentrations, $0.6 \sim 1 \times 10^{17}$ cm^{-3} in the case of Sb-doped Ge, the electrical conductivity is

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[1] H. Fritzsche, J. Phys. Chem. Solids 6, 69 (1958); H. Fritzsche and M. Cuevas, Phys. Rev. 119, 1238 (1960).

[2] N. F. Mott and W. D. Twose, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1961), Vol. 10, p. 107.

[3] N. F. Mott, Can. J. Phys. 34, 1356 (1956); Phil. Mag. 6, 287 (1961).

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[4] T. Kasuya and S. Koide, J. Phys. Soc. Japan 13, 1287 (1958); A. Miller and E. Abrahams, Phys. Rev. 120, 745 (1960).

[5] H. M. James and A. S. Ginzbarg, J. Phys. Chem. 57, 840 (1953).

[6] M. Lax and J. G. Phillips, Phys. Rev. 110, 41 (1958).

[7] T. Matsubara and Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) 26, 739 (1961).

well represented by

$$\sigma = \sigma_0 \exp(-\epsilon_2/k_B T), \qquad (1.1)$$

in a certain temperature range. In this region of concentration the Hall effect is appreciable, although the Hall concentration decreases rapidly with decreasing impurity concentration.[8] Magnetoresistance experiments[8,9] and piezoresistance experiments[10] show that the activation energy ϵ_2 depends remarkably on the overlap of the donor wave functions. These features are attributed to neither hopping nor metallic types of conduction.

Since Fritzsche summarized the proposed mechanisms for the origin of ϵ_2, various models have been considered.[1,2,8] Among these models, the D^--band model seems to be the most preferred one. The band is considered to arise from resonance between the states of the negatively charged donors, the D^- ions. Mott pointed out that the simultaneous occupation of any site by two electrons in the limit of low concentration, that is, the formation of an isolated D^- ion, requires an activation energy which is equal to the ionization energy less the electron affinity of an isolated neutral impurity. This activation energy is lowered by the resonance energy as a result of interaction between the D^- states. The energy gap from the donor ground state to the bottom of D^- band thus formed may be related to the observed activation energy ϵ_2. The excess electrons are partly excited to the D^- band and partly localized at the donor ground states. The behavior of electrons in the D^- band may predominate in a certain range of temperature. The recent analysis of experiments on galvanomagnetic effects[8] has given a support to a model of the D^- band which is formed from the D^- states having antiparallel spin configuration in the D^- ion.

However, no theoretical investigation has been presented which successfully describes the origin of ϵ_2 and the conduction mechanism in the intermediate concentration region. It is the purpose of the present paper to discuss the formation of the D^- band and the origin of ϵ_2 by using the analogy between the D^- ion and the negatively charged hydrogen atom, and to discuss the conduction mechanism in the intermediate impurity concentration region on the basis of the D^--band model.

We consider the n-type germanium doped with antimony throughout this paper. In Sec. II, a discussion about the D^- state is given. The D^- state will be assumed to be the state of an electron in the D^- ion which is meaningful at considerably large radial distances where the resonance with the state of neighboring D^- ion is effective, and assumed to have the energy equal to the difference in energy of the ground states of the

D^- ion and of the neutral donor which approximates the state of the other electron. In Sec. III, we discuss the D^- band which is formed by the resonance between the D^- states. The optical model[6] of the random lattice is used and is expected to give a fairly good approximation because the wave function of the D^- state is extended considerably. Accordingly, the summation over the sites of neutral donor (neutral cores of the D^- ion) will be replaced by an integral over the volume of the system. Thus, the low-energy levels may be described approximately with the wave numbers. On the other hand, the ground states of donors are assumed to be localized. Considering the cases of small compensation, we shall neglect the random fluctuation at impurity sites due to the Coulomb field of the ionized acceptors, so that the ground states of neutral donors are of the same energy. The number of electrons in the D^- band, which is small compared to the number of donors at low temperatures, is expressed as a function of temperature in terms of the energy gap between the bottom of D^- band and the localized ground state. The electrical conductivity is discussed in Sec. IV. The main contribution to the conductivity comes from the D^--band electrons which are scattered by various causes. The temperature dependence of the conductivity may be dominated by the temperature dependence of the number of electrons in the D^- band, and then one-half of the energy gap will correspond to the observed activation energy ϵ_2. In Sec. V, some numerical estimates and comparison with experiments are given. Section VI is devoted to some discussions and remarks.

II. THE D^- STATE

The hydrogenic model is assumed to be valid for the ground state of the neutral donor atom.[11] Then it is convenient to introduce the following units:

1. Unit of mass $= m$, which is the effective mass of the donor electron,
2. unit of length $= a = \hbar^2 \kappa / me^2 = a_H (\kappa m_0 / m)$, $a_H = \hbar^2/m_0 e^2$ being the radius of first Bohr orbit of hydrogen atom, m_0 the free electron mass, and κ the static dielectric constant,
3. unit of energy $= me^4/\hbar^2\kappa^2$, which is twice the ionization potential of neutral donor.

With the use of the atomic-type units defined above, the Schrödinger equation for the donor state occupied by two electrons, that is, the state of the negatively charged donor, the D^- ion, is written as

$$\Delta_1\Psi + \Delta_2\Psi + 2(E + (1/r_1) + (1/r_2) - (1/r_{12}))\Psi = 0, \quad (2.1)$$

where r_1 and r_2 are the respective distances of the two electrons from the donor center and r_{12} is the distance between them. Equation (2.1) is of the same form as the Schrödinger equation for the negatively charged hydro-

[8] C. Yamanouchi and W. Sasaki, J. Phys. Soc. Japan 17, 1664 (1962); C. Yamanouchi, ibid. 18, 1775 (1963).
[9] G. Sadasiv, Phys. Rev. 128, 1131 (1962).
[10] H. Fritzsche, Phys. Rev. 125, 1552, 1560 (1962); K. Sugiyama and A. Kobayashi, J. Phys. Soc. Japan 18, 163 (1963).

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

gen atom. The ground-state energy E and the wave function $\Psi(r_1,r_2)$ of Eq. (2.1) have been well investigated by Bethe and others.[12] According to their results, the best value of the ground-state energy E (in rydbergs) is

$$E = -1.05545(m/m_0)(1/\kappa^2) \text{ Ry.} \quad (2.2)$$

The observed value of the ionization energy, $-E_1 = m/(m_0\kappa^2)$ Ry, of the neutral donor is 9.6×10^{-3} eV for Sb.[13] Using this value, we have

$$E = -10.1323\times10^{-3} \text{ eV.} \quad (2.3)$$

The ionization potential J of the D^- ion, that is, the electron affinity, is the difference in energy of the ground states of the neutral donor and of the negatively charged donor:

$$J = E_1 - E = 0.53\times10^{-3} \text{ eV.} \quad (2.4)$$

Thus, the activation energy required to make an isolated D^- ion from neutral donors is

$$\epsilon = -E_1 - J = 9.07\times10^{-3} \text{ eV.} \quad (2.5)$$

According to the variational method,[12] the ground-state wave function of Eq. (2.1) has the form, in the first approximation,

$$\Psi = e^{-(1-\sigma)(r_1+r_2)}, \quad (2.6)$$

where the screening constant σ is $\frac{5}{16}$. Although the higher order approximations are also of interest, they are not of tractable form for the present problem. The zero-order wave function (2.6) has a simple form which is the product of two hydrogen-like ground-state wave functions with a constant screening factor, and is convenient for the practical problem which does not require very high accuracy. Nevertheless, it is a very crude approximation and gives no binding at all. In reality, the effective screening is not constant, but varies as a function of radial distance. It has been shown that the hydrogenic charge distribution obtained from Eq. (2.6) is too small both at very small and at very large radial distances.[12] Therefore, we cannot employ the screening constant in Eq. (2.6), because we are concerned mainly with large radial distances.

The wave function for the D^- ion can be written in the form

$$\Psi(r_1,r_2) = \sum_{nlm} \phi_{nlm}(r_1)u_{nlm}(r_2), \quad (2.7)$$

where u_{nlm} are the orthonormalized hydrogen-like wave functions and satisfy the equation

$$\Delta u_{nlm} + 2(E_n + (1/r))u_{nlm} = 0. \quad (2.8)$$

From Eqs. (2.1) and (2.7), we obtain

$$\left[-\Delta_1 - \frac{2}{r_1} + 2\int u_{nlm}^*(r_2)\frac{1}{r_{12}}u_{nlm}(r_2)dr_2\right]\phi_{nlm}(r_1)$$
$$= 2(E-E_n)\phi_{nlm}(r_1). \quad (2.9)$$

[12] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), p. 146 ff; E. A. Hylleraas and J. Midtdal, Phys. Rev. **103**, 829 (1956).
[13] J. A. Burton, Physica **20**, 845 (1954).

With the use of the expansion by the Legendre polynomials for $r_1 > r_2$:

$$r_{12}^{-1} = r_1^{-1}\sum_{n=0}^{\infty}(r_2/r_1)^n P_n(\cos\theta), \quad (2.10)$$

θ being the angle between the vectors r_1 and r_2, we can see the state of affairs in which the values of r_1 are very large compared with the radial distances for which $u_{nlm}(r_2)$ is appreciable. In the approximation that the terms of higher order than that of $n=0$ are neglected in Eq. (2.10), that is, in the case of $r_1\gg r_2$, Eq. (2.9) becomes

$$[\Delta_1 + 2(E-E_n)]\phi_{nlm}(r_1) = 0. \quad (2.11)$$

Since the wave function must be bounded at infinity, the radial part of ϕ must be proportional to $\exp[-\sqrt{2}(E_n-E)^{1/2}r_1]$ asymptotically. Thus, the term of $n=1$ in Eq. (2.11) will predominate at sufficiently large distances. Therefore, for the spherically symmetric ground state of D^- ion, we have asymptotically

$$\phi_{100}(r) = a_1\exp[-\sqrt{2}(E_1-E)^{1/2}r]$$
$$= a_1\exp(-0.235r), \quad (2.12)$$

where a_1 is an unknown constant. Equation (2.12) seems to well exhibit the behavior of the ground state Ψ of D^- ion at very large radial distances. The exponent in Eq. (2.12) is much smaller than that in Eq. (2.6) and the correct wave function has a much longer tail.[12]

Now we assume that the second electron is approximately in the hydrogen-like ground state $u_{100} = \pi^{-1/2}e^{-r}$ and look for the spherically symmetric solution ϕ. This approximation may be fairly good for large radial distances due to the discussion in the above paragraph. Then we have

$$\int u_{100}(r_2)\frac{1}{r_{12}}u_{100}(r_2)dr_2 = -\left(1+\frac{1}{r_1}\right)e^{-2r_1} + \frac{1}{r_1}. \quad (2.13)$$

Thus, from Eqs. (2.9) and (2.13), we obtain the one-electron wave equation:

$$\left[-\tfrac{1}{2}\Delta_1 - \left(1+\frac{1}{r_1}\right)e^{-2r_1}\right]\phi(r_1) = (E-E_1)\phi(r_1), \quad (2.14)$$

which is considered to describe approximately the behavior of the electron in the D^- ion at large radial distances. However, it is difficult to obtain the lowest-state solution of Eq. (2.14) which gives a bound state. It is considered by using the parallelism with the negatively charged hydrogen ion that the D^- ion possesses no other bound state than that given by Eq. (2.3). Therefore, we assume that the D^- state is as follows: The energy is $E-E_1$, where E and E_1 are the energies of the ground states of the negatively charged donor and of the neutral donor, respectively; the wave function describing the state of the electron is of an exponential form $(\alpha^3/\pi)^{1/2}\exp(-\alpha r)$, the other electron in the D^-

ion being approximated by the ground state of the neutral donor; the potential $-(1+1/r)\exp(-2r)$ is exerted to the first electron by the neutral core of the D^- ion. Then, the parameter α in the model wave function may be considered to be adjustable when we discuss the D^- band in the following sections.

The true wave function of the D^- state would never be written as such a simplified exponential function with a single constant screening factor. It should be noted here that the simplified wave function assumed above would not give any negative eigenvalue $E-E_1$ in Eq. (2.14). However, the zero-order wave function and the form of the wave function at sufficiently large radial distances are of this type. We shall therefore proceed to the next step by assuming this simplified form for the wave function.

III. THE D^- BAND

It is considered that the D^- band is formed by the interaction between the D^- states. If n electrons (per unit volume of the system) are excited to the D^- band, then n ionized donors are thereby formed. These ionized donors give rise to the random fluctuation of the energies of D^- states. However, the number of ionized donors is small at low temperatures and we neglect the fluctuation of potential because it is considered to be small compared with the resonance energy between the D^- states. Considering the cases of small compensation, we also neglect the potential fluctuation due to the presence of ionized acceptors and donors. However, the effect of ionized impurities probably should be taken into account when calculating the electron mobility.

We make use of the tight binding approximation. Then the Hamiltonian for electrons in the D^- band can be written, by neglecting the terms of three-site centers, as

$$\mathcal{H}=\sum_{n\neq l}\sum U_{nl}a_n{}^*a_n+\sum_{m\neq n}\sum V_{mn}a_m{}^*a_n, \quad (3.1)$$

where U_{nl} is the energy of electron in the nth D^- state in the potential field from the lth neutral donor and is written as

$$U_{nl}=U(|\mathbf{R}_n-\mathbf{R}_l|)=\int\phi_n(\mathbf{r})v(|\mathbf{r}-\mathbf{R}_l|)\phi_n(\mathbf{r})dV, \quad (3.2)$$

$v(|\mathbf{r}-\mathbf{R}_l|)$ being the potential due to the lth neutral donor, and V_{mn} is the energy integral for the transfer of an electron from the nth to the mth D^- states and is written as

$$V_{mn}=V(|\mathbf{R}_m-\mathbf{R}_n|)$$

$$=\int\phi_m(\mathbf{r})v(|\mathbf{r}-\mathbf{R}_m|)\phi_n(\mathbf{r})dV, \quad (3.3)$$

and $a_m{}^*$ and a_m are the creation and annihilation operators of the electron in the mth D^- state, and the energy

$E-E_1$ of an isolated D^- state is taken as the origin of energy. The integrals are taken over the volume of the system, V.

As has been discussed in the preceding section, one can write the wave function $\phi_n(\mathbf{r})$ of the D^- state and the potential energy $v(|\mathbf{r}-\mathbf{R}_m|)$ of the electron resulting from the mth neutral donor as

$$\phi_n(\mathbf{r})=\phi(|\mathbf{r}-\mathbf{R}_n|)=[(\alpha/a)^3/\pi]^{1/2}e^{-\alpha|\mathbf{r}-\mathbf{R}_n|/a}, \quad (3.4)$$

and

$$v(|\mathbf{r}-\mathbf{R}_m|)$$
$$=-(e^2/\kappa a)(1+(a/|\mathbf{r}-\mathbf{R}_m|))e^{-2|\mathbf{r}-\mathbf{R}_m|/a}, \quad (3.5)$$

where we have returned to the usual units. Then, from Eqs. (3.2) and (3.3), we obtain

$$U_{nl}=-V_0\left\{\frac{2\alpha^3(2-\alpha^2)}{(1-\alpha)^2(1+\alpha)^2}+\frac{2\alpha^4(\alpha^2-3)}{(1-\alpha)^3(1+\alpha)^3}\frac{a}{R_{nl}}\right.$$
$$+\left[\frac{2\alpha^4}{(1-\alpha)^2(1+\alpha)^2}-\frac{2a^4(\alpha^2-3)}{(1-\alpha)^3(1+\alpha)^3}\frac{a}{R_{nl}}\right]$$
$$\left.\times e^{-2(1-\alpha)R_{nl}/a}\right\}e^{-2\alpha R_{nl}/a}, \quad (3.6)$$

and

$$V_{mn}=-V_0\left\{\frac{\alpha^3(4+3\alpha)}{(1+\alpha)^2}-\frac{\alpha^4(3+2\alpha)}{(1+\alpha)^3}\frac{a}{R_{mn}}\right.$$
$$+\left[\frac{\alpha^4}{(1+\alpha)^2}+\frac{\alpha^4(3+2\alpha)}{(1+\alpha)^3}\frac{a}{R_{mn}}\right]e^{-2R_{mn}/a}\right\}e^{-\alpha R_{mn}/a}, \quad (3.7)$$

where $R_{mn}=|\mathbf{R}_m-\mathbf{R}_n|$ and V_0 is the ionization potential of neutral donor

$$V_0=e^2/2\kappa a. \quad (3.8)$$

Now we consider the diagonalization of the Hamiltonian (3.1) by the unitary transformation

$$a_m{}^*=\sum_k c_k{}^*(\mathbf{k}|m), \quad (3.9)$$

$$\sum_m(\mathbf{k}|m)(m|\mathbf{k}')=\delta_{kk'}, \quad (3.10)$$

and

$$\sum_{n,l}{}'(\mathbf{k}|n)U_{nl}(n|\mathbf{k}')+\sum_{m,n}{}'(\mathbf{k}|m)V_{mn}(n|\mathbf{k}')$$
$$=E(\mathbf{k})\delta_{kk'}, \quad (3.11)$$

where $\sum'$ means that the terms of $n=l$ are excluded in the summation. Then Eq. (3.1) is transformed to

$$\mathcal{H}=\sum_k F(\mathbf{k})c_k{}^*c_k. \quad (3.12)$$

We see that diagonalization of Eq. (3.1) can be approximated by using the transformation function

$$(n|\mathbf{k})=(NV)^{-1/2}\exp(i\mathbf{k}\cdot\mathbf{R}_n), \quad (3.13)$$

where N is the number density of neutral donors. It should be noted that $\mathbf{R}_n$ are distributed at random.

Then Eq. (3.10) holds under the approximation that R_m is regarded as a continuous variable and the summation is replaced by an integral using the periodic boundary condition for convenience. Thus we obtain

$$\sum_{n,l}'(\mathbf{k}|n)U_{nl}(n|\mathbf{k}')+\sum_{m,n}'(\mathbf{k}|m)V_{mn}(n|\mathbf{k}')$$

$$= (NV)^{-1}\sum_{n,l}' U_{nl}e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_n}$$

$$+ (NV)^{-1}\sum_{m,n}' V_{mn}e^{-i(\mathbf{k}\cdot\mathbf{R}_m-\mathbf{k}'\cdot\mathbf{R}_n)}$$

$$= \delta_{\mathbf{kk}'}N\left(\int d\mathbf{R}_{nl}U_{nl}+\int d\mathbf{R}_{mn}V_{mn}e^{-i\mathbf{k}\cdot\mathbf{R}_{mn}}\right), \quad (3.14)$$

where the summations over the D^- states have been approximated by the integrals. This is essentially the optical model,[6] which is considered to be valid because the wave function of the D^- state is considerably extended and we are concerned only with small wave numbers k.

Since we have, for an infinitely large volume of system,

$$\int e^{-pR}e^{-i\mathbf{k}\cdot\mathbf{R}}d\mathbf{R}=\frac{8\pi p}{(p^2+k^2)^2}, \quad (3.15)$$

$$\int \frac{e^{-pR}}{R}e^{-i\mathbf{k}\cdot\mathbf{R}}d\mathbf{R}=\frac{4\pi}{p^2+k^2}, \quad (3.16)$$

we obtain, from Eqs. (3.6), (3.7), (3.11), and (3.14),

$$E(k)=-4\pi a^3NV_0\left\{1+\left[\frac{2(4+3\alpha)}{(1+\alpha)^2(1+k^2a^2/\alpha^2)}-\frac{\alpha^2(3+2\alpha)}{(1+\alpha)^3}\right]\frac{1}{(1+k^2a^2/\alpha^2)}\right.$$

$$\left.+\left[\frac{2\alpha^4}{(1+\alpha)^2(2+\alpha)(1+k^2a^2/(2+\alpha)^2)}+\frac{\alpha^4(3+2\alpha)}{(1+\alpha)^3}\right]\frac{1}{(2+\alpha)^2(1+k^2a^2/(2+\alpha)^2)}\right\}. \quad (3.17)$$

For small wave numbers, the energy spectrum of the D^- band can be written as

$$E(k)=E_0+\lambda k^2, \quad (3.18)$$

where

$$E_0=-4\pi a^3NV_0\left[1+\frac{16(4+\alpha)}{(2+\alpha)^3}\right], \quad (3.19)$$

$$\lambda=64\pi a^5NV_0\frac{3\alpha^3+22\alpha^2+40\alpha+32}{\alpha^2(2+\alpha)^5}. \quad (3.20)$$

If the origin of energy is taken at the bottom of conduction band, Eq. (3.18) is rewritten as

$$E_k\equiv E(k)=E_m+\lambda k^2, \quad (3.21)$$

$$E_m=E-E_1+E_0. \quad (3.22)$$

Thus we have seen that the D^- band is formed through the interaction between the D^- states and that the D^- band lies with the energy gap $-(E_1-E_m)$ above the ground state of donor which is assumed to be localized. We can consider that the excess electrons are partly excited to the D^- band and partly localized at the ground states of donors.

By neglecting the number of acceptors, the Fermi energy ζ is determined by the relation[14]

$$N_D=\frac{N_D}{\frac{1}{2}e^{(E_1-\zeta)/k_BT}+1}+\int_{E_m}^{\infty}\frac{2D(E_k)}{e^{(E_k-\zeta)/k_BT}+1}dE_k, \quad (3.23)$$

where N_D is the number density of donors and the effect of electron spin has been taken into account. The state density of D^- band $D(E_k)$ is given by

$$D(E_k)=(1/8\pi^3)4\pi k^2dk/dE_k. \quad (3.24)$$

In the case of $n\ll N_D$ at low temperatures, with which we are concerned, we obtain

$$\zeta=(E_m+E_1)/2+(k_BT/2)\log[2N_D(\pi\lambda/k_BT)^{3/2}]. \quad (3.25)$$

Thus we have the number of D^--band electrons per unit volume at thermal equilibrium

$$n=(1/2\sqrt{2})N_D^{1/2}(k_BT/\pi\lambda)^{3/4}e^{-(E_m-E_1)/2k_BT}. \quad (3.26)$$

IV. ELECTRICAL CONDUCTIVITY

In this section we do not evaluate the electrical conductivity, but discuss only its temperature dependence. We neglect the contribution from the electrons in the donor ground states to the conductivity. Then the conductivity is given only by the contribution of the D^--band electrons. According to the theory of electric conduction in which the collision time τ is assumed, the conductivity is expressed as

$$\sigma=(ne^2/m^*)\langle\tau\rangle, \quad (4.1)$$

where m^* is the effective mass of the D^--band electron

$$m^*=\hbar^2(\partial^2 E_k/\partial k^2)^{-1}=\hbar^2/2\lambda, \quad (4.2)$$

and the average is taken as

$$\langle\tau\rangle=\frac{\displaystyle\int \tau k_x^2 e^{-E_k/k_BT}D(E_k)dE_k}{\displaystyle\int k_x^2 e^{-E_k/k_BT}D(E_k)dE_k}. \quad (4.3)$$

[14] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Oxford, 1953), p. 115.

The collision time is considered to consist of the contributions from several types of scattering mechanism. First, the main cause of scattering is inherent in the D^- band itself which is formed from a random array of neutral donors, and we denote its contribution as τ_r. Its energy dependence may be not sensitive for small wave numbers and this will give rise to a nearly temperature-independent contribution to the conductivity. In addition, we might have to take account of the effects of the exchange of the electron with a bound electron and of the polarization of a neutral donor. Second, the other causes of scattering are the presence of ionized impurities, which consist of the ionized acceptors (negative) and donors (positive), and the lattice vibrations. The collision time τ_i due to the ionized impurity scattering may be estimated by the Brooks and Herring formula.[15] The contribution of τ_i to τ may, however, be considered to be much smaller than that of τ_r in the case of small compensations and small number of ionized donors. The contribution of the lattice vibrations τ_l to τ would be quite small at sufficiently low temperatures. Although the collision time can be written as

$$(1/\tau) = (1/\tau_r) + (1/\tau_i) + (1/\tau_l), \qquad (4.4)$$

it may therefore be considered that $\langle \tau \rangle$ consists of a main term which is nearly independent of temperature and of small temperature-dependent corrections. Thus the temperature dependence of electrical conductivity is mainly represented by that of the number of D^--band electrons given by Eq. (3.26). From Eqs. (3.26) and (4.1), the conductivity is written as

$$\sigma = \sigma_0 e^{-(E_m - E_1)/2k_B T}, \qquad (4.5)$$

$$\sigma_0 = \frac{e^2 N_D^{1/2} \lambda^{1/4} (k_B T)^{3/4} \langle \tau \rangle}{2^{1/2} \pi^{3/4} \hbar^2}. \qquad (4.6)$$

We can therefore consider that one half of the energy gap from the donor ground state to the bottom of D^- band corresponds to the observed activation energy ϵ_2.

V. COMPARISON WITH EXPERIMENTS

As has been stated in Sec. I, the electrical resistivity is well characterized experimentally by the activation energy ϵ_2. In the preceding sections, we have discussed how this activation energy originated, on the basis of the hydrogenic model of donor states. Now we carry out the numerical estimation and compare it with experiments.

The radius of the electron orbit of the donor ground state is determined as $a = 47 \times 10^{-8}$ cm, by using the observed ionization energy of the neutral donor 9.6×10^{-3} eV, the dielectric constant $\kappa = 16$, and the value of the first Bohr radius of hydrogen atom. From Eqs. (2.5) and (3.22), the quantity corresponding to

[15] H. Brooks, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1956), Vol. 7, p. 87.

TABLE I. Activation energy in the impurity conduction of Sb-doped Ge in the intermediate concentration region.

N_D 10^{16} cm^{-3}	K %	N 10^{16} cm^{-3}	Calculated $\frac{1}{2}(E_m - E_1)$ 10^{-3} eV	Measured[a] ϵ_2 10^{-3} eV
10.3	7.2	9.56	0.302	0.106 y
8.5	10	7.65	1.15	0.38 y
7.7	3	7.47	1.23	0.37 y
6.9	5	6.55	1.63	0.69 s
7.7	26	5.7	2.01	1.00 y
5.9	5	5.6	2.06	1.25 s
5.5	5	5.22	2.22	1.6 f
6.0	20	4.8	2.41	1.15 y
4.5	5	4.27	2.64	2.5 f
3.5	5	3.32	3.07	3.6 f

[a] The measured values marked by f, s, and y in the column are employed from the experiments by Fritzsche, Sadasiv, and Yamanouchi, respectively.

the observed activation energy is written as

$$\tfrac{1}{2}(E_m - E_1) = \tfrac{1}{2}(\epsilon + E_0), \qquad (5.1)$$

where ϵ and E_0 are given in Eqs. (2.5) and (3.19). In Eq. (3.19) the number density of neutral donors is given by

$$N = N_D - K N_D, \qquad (5.2)$$

where K is the degree of compensation.

We have assumed in Sec. II that the wave function of the D^- state is represented by an exponential function with constant screening factor α. As has been discussed, the zero-order wave function and the form of the wave function at sufficiently large radial distances are of exponential types with the respective screening constants, though the true wave function would never be written by an exponential function with a single constant screening factor. In order to determine the value of α to be employed, we have to consider over what part of the range of radial distances the resonance energy contributes most effectively. If we measure the average separation between impurities by the radius r_s of sphere which approximates the average volume $(4\pi/3)r_s^3 = 1/N_D$ surrounding each impurity atom, the intermediate concentration region corresponds mainly to the values $r_s/a = 3 \sim 4$, while the range of wave function extends to $r/a \approx 0.235^{-1}$ as has been shown in Eq. (2.12). We can therefore consider that the main contribution to the resonance energy comes from a range of considerably larger radial distances than a. Here we tentatively employ the value $\alpha = 0.235$ in order to estimate the value of E_0 in Eq. (3.19). The comparison with experiments is shown in Table I.

The experimental data of Fritzsche,[1] Sadasiv,[9] and Yamanouchi[8] are used. In accordance with the aim of the present paper, which is concerned with small compensations, the degrees of compensation in these data are of the order of 10% or less except for two samples in Yamanouchi's. We have taken K equal to 0.05 in the cases of Fritzsche and Sadasiv. In view of the simple character of the theory developed, the agreement between theoretical and experimental values is satisfactory.

However, the discrepancy becomes larger with increasing impurity concentration, though the agreement is better at lower concentrations. The calculated values decrease linearly with the increase in the number density of neutral donors, while the observed values decrease more rapidly with increasing impurity concentration. This complicated dependence of activation energy on the impurity concentration might be attributed in part to the screening effects of electrostatic interaction, which may have an influence upon the bottom of D^- band, E_m, and in part, at the higher concentrations of impurity, to the interaction between the donor ground states which causes the formation of the so-called impurity band and would give rise to a reduction of the energy gap. These effects would tend to decrease the activation energy still more rapidly.

VI. DISCUSSION

We have discussed the impurity conduction in the intermediate impurity concentration region on the basis of a D^--band model which has been provided by the formation of a band as a result of the interaction between the states of negatively charged donors, the D^- states. We assumed a simplified form of the wave function describing the behavior of an electron in the weakly bound D^- state. On the other hand, the donor ground states have been considered to be localized and of approximately the same energy in the cases of small compensation. Then it has been considered that the excess electrons are localized partly in the donor ground states and excited partly to the D^- band, and that the behavior of electrons in the D^- band predominates in a certain temperature range because of their much larger mobility as compared to that of electrons in the donor ground states, though the number of electrons in the D^- band is very small at sufficiently low temperatures. Thus, the observed activation energy ϵ_2 has been related to the energy gap between the bottom of D^- band and the donor ground state.

The numerical estimation given in the previous section is a tentative one. One can improve it by using a more realistic wave function for the D^- state instead of the simplified wave function used in this paper. We did not evaluate the electrical conductivity. The scattering mechanism is considered to be mainly due to the random distribution of impurity sites itself. In order to make quantitative calculations of the structure of the D^- band and the electrical conductivity, it may be imperative to take account seriously of the random lattice properties by employing another approach[7] to the problem.

A remark should be made about $\rho_0 = \sigma_0^{-1}$ and ϵ_2 in Eq. (1.1). The experiments[8] show the marked dependences of ρ_0 and ϵ_2 upon the impurity concentrations which are much stronger than that obtained in the present paper, though we cannot argue about ρ_0 because of the lack of evaluation for the collision time $\langle \tau \rangle$. As has been discussed in the previous section which was concerned with a calculation of ϵ_2, these dependences may be attributed partly to the screening effects which also have influence upon the curvature of the D^- band, λ, and the collision time, τ, directly and indirectly through the number of D^--band electrons.

In a higher range of concentration, the interaction between donor ground states may be appreciable and these states will tend to form a band. One can see from the discussion in the previous section that the bottom of D^- band is lowered with increasing impurity concentration more rapidly than Eq. (3.19) indicates. Thus, both bands may merge into one another above a certain critical concentration of impurity and the activation energy ϵ_2 will disappear. Then it turns out that we would have the metallic type of conduction, and we would be able to estimate roughly the concentration at which the transition to the metallic conduction occurs, by using Eqs. (3.19) and (5.1). Mott has suggested that a sharp transition from a nonmetallic to a metallic state must occur for a crystalline array of atoms at a certain critical distance between them, and that the transition in the impurity conduction is also of this type, the sharpness being lost because of disordered arrangement.[3] It may be mentioned that in the impurity conduction the transition point should correspond to the concentration where the activation energy ϵ_2 disappears. However, we cannot argue here whether the transition is as sharp as a discontinuous one or not in the impurity conduction, because it is considered to depend on the many-body effects essentially.

In the present paper, we did not discuss the effects of magnetic field at all, nor take into account the spin configuration in the D^- ion. The experiments show that the activation energy ϵ_2 increases proportionally to the square of magnetic field strength while the preexponential factor ρ_0 decreases little. These effects may be explained by virtue of the shrinkage effect of the wave function in a magnetic field as well as the spin configuration. These problems will be discussed in a separate paper.