

## Mechanism of Impurity Conduction in Semiconductors

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A new possible mechanism of impurity conduction in semiconductors at low temperatures is proposed. The conductivity is thought of as due to the carrier jumps over the Coulomb potential wall from the occupied impurity centers to the empty ones. The activation energy of conductivity and, in the case of strong carrier-phonon interaction, the conductivity itself is calculated and compared with Fritzsche's experimental data for the so-called " $\epsilon_2$  anomaly" in *p*- and *n*-type germanium.

IN 1955 Fritzsche<sup>1</sup> observed a new low-temperature anomaly in the temperature dependence of conductivity and Hall coefficient in *p*-type germanium at temperatures between 3° and 10°K. The impurity (Ga) concentrations ranged from  $2.1 \times 10^{16}$  to  $7.3 \times 10^{16}$  cm<sup>-3</sup> and compensation *K* was about 10%. At temperatures above 10°K a normal extrinsic conduction occurred; at temperatures lower than 3°K the impurity conduction with activation energy  $\epsilon_3$  about  $1 \times 10^{-3}$  ev was observed. This latter impurity conduction was investigated by many authors<sup>2-5</sup> and was explained as the result of tunneling of carriers from the ground states of occupied impurity centers to the ground states of unoccupied ones. Such unoccupied majority centers are always present because of compensation.

As in the extrinsic and the " $\epsilon_3$  range," so also in the range of the new anomaly the conductivity depends exponentially on  $1/T$ . But the important feature is a strong dependence of the activation energy  $\epsilon_2$  on the concentration of majority impurities. The activation energy decreases with increasing impurity concentration, changing from  $4.04 \times 10^{-3}$  to  $0.93 \times 10^{-3}$  ev in the impurity concentration range specified above.

The same anomaly occurs also in *n*-type germanium with impurity (Sb) concentrations from  $2.4 \times 10^{16}$  to  $5.5 \times 10^{16}$  cm<sup>-3</sup> and compensation of the order of a few percent.<sup>6</sup> As for the *p* type, the anomaly was observed in the temperature range from 3° to 10°K; in the given range of impurity concentration  $\epsilon_2$  decreases from  $5.3 \times 10^{-3}$  to  $1.6 \times 10^{-3}$  ev.

James and Anderson<sup>7</sup> proposed for the interpretation of the " $\epsilon_2$  anomaly" a tunneling mechanism of conduction along chains formed by the most closely spaced impurities. It is not clear, however, how one in this way can obtain the large values of the activation energy  $\epsilon_2$  which were observed experimentally.

It is also difficult to interpret quantitatively the " $\epsilon_2$  anomaly" conduction as resulting from carrier jumps from the occupied impurity centers to the

empty ones through a certain quantized excited state. The system formed by two impurity ions and one carrier is analogous to the  $H_2^+$  ion. In this ion<sup>8</sup> the energy gap between very closely spaced states  $1s\sigma_g$ ,  $2p\sigma_u$ , and other excited states is almost constant and about one-half the isolated center ionization energy  $E_a$ , if the distance between the ions is in the range from four to seven effective Bohr radii. This range of distances corresponds to the observed range of impurity concentrations in germanium. Because the ionization energy of Ga in Ge is  $1.08 \times 10^{-2}$  ev,<sup>9</sup> and of Sb in Ge is  $9.8 \times 10^{-3}$  ev,<sup>10</sup> it apparently seems impossible in this way to obtain the right value and concentration dependence of  $\epsilon_2$ . As is well known,<sup>11,9</sup> the shallow impurity centers in *p*-type Ge do not behave strictly as hydrogenlike atoms, but the deviations in the energy gaps from the simple hydrogenlike model do not exceed 25%. They cannot give any substantial improvement. A similar situation occurs in the case of *n*-type Ge,<sup>12,10</sup> with only the distinction that the Sb center in Ge possesses an excited state very close to the ground state; the energy gap between them is of the order of  $10^{-4}$  ev.<sup>13</sup> This is one order of magnitude smaller than the observed value of  $\epsilon_2$ .

The question arises as to whether the two-center model is correct. Is the " $\epsilon_2$  conduction" the conduction in an excited impurity band formed by interacting excited states of impurity centers? The carrier can be excited to such a band from the ground state of the center by phonons. Koshino<sup>14</sup> interpreted in this way one pair of the curves of  $\rho$  vs  $1/T$  and  $R$  vs  $1/T$  given in the work of Fritzsche.<sup>1</sup> This result cannot, however, be regarded as of great importance, because the agreement with experimental data was obtained by an arbitrary choice of the values of as many as nine parameters. In this interpretation  $\epsilon_2$  corresponds to the energy gap between the ground state of the impurity

<sup>1</sup> H. Fritzsche, Phys. Rev. **99**, 406 (1955).

<sup>2</sup> V. H. Fritzsche, and M. Cuevas, Phys. Rev. **119**, 1238 (1960).

<sup>3</sup> P. Csavinsky, Phys. Rev. **119**, 1605 (1960).

<sup>4</sup> Y. Toyozawa, Progr. Theoret. Phys. **23**, 378, 380 (1960).

<sup>5</sup> A. Miller, and E. Abrahams, Phys. Rev. **120**, 745 (1960).

<sup>6</sup> H. Fritzsche, J. Phys. Chem. Solids **6**, 69 (1958).

<sup>7</sup> H. M. James, and P. W. Anderson, in "Report on the second symposium on the physics of semiconductors" [J. Phys. Chem. Solids **2**, 76 (1957)].

<sup>8</sup> D. R. Bates, K. Ledsham, and A. L. Steward, Phil. Trans. Roy. Soc. London **A246**, 215 (1953).

<sup>9</sup> P. Fisher and H. Y. Fan, Phys. Rev. Letters **2**, 456 (1959).

<sup>10</sup> H. Y. Fan and P. Fisher, J. Phys. Chem. Solids **8**, 270 (1959).

<sup>11</sup> D. Schechter, Carnegie Institute of Technology, thesis, 1958 (unpublished).

<sup>12</sup> W. Kohn, Solid-State Physics, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1957) Vol. 5, p. 257.

<sup>13</sup> E. M. Conwell, Phys. Rev. **99**, 1195 (1955); H. Fritzsche, Phys. Rev. **115**, 336 (1959).

<sup>14</sup> S. Koshino, J. Phys. Soc. Japan **11**, 608 (1956).

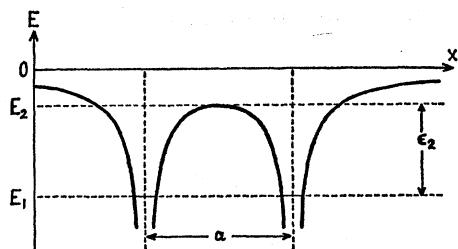


FIG. 1. The potential energy of the carrier in the field of two impurity ions. The zero level is at the bottom (top) of the conduction (valence) band.

center and the bottom of the excited impurity band, and not to half this energy, because due to compensation the impurity centers are partially ionized, and so at the low temperatures the Fermi level is situated very near the ground state. However, as follows from the theoretical considerations of Baltensperger,<sup>15</sup> this energy gap is, independent of impurity concentration, never smaller than  $0.6 E_a$ , which is in disagreement with the observed values of  $\epsilon_2$ . If one takes into account the statistical distribution of the positions of the impurities in the crystal,<sup>16</sup> then the bottom and the top of the impurity band disappear. The density of states of this band has "tails" to lower and higher energies. However, it seems unlikely that this statistical effect is large enough to explain the right value of  $\epsilon_2$  in this way.

Because of all these difficulties, it may be worthwhile to consider another possible mechanism of conduction. The carrier can jump over the Coulomb potential wall from the occupied impurity center to the empty one, but not through an eigenstate of the two-center potential. The possibility of such a conduction arises from the fact that, due to the carrier-phonon interaction, the wave functions of the carriers partially lose their coherence, the energies of the carriers becoming different from the energy eigenvalues of the two-center potential.

In the following we shall first calculate the activation energy  $\epsilon_2$  in the proposed mechanism and then estimate the value of the conductivity in the case of strong carrier-phonon interaction. We assume throughout that compensation is small ( $K \ll 1$ ).

#### ACTIVATION ENERGY OF CONDUCTIVITY

From Fig. 1 we can see the idea of obtaining the activation energy of conductivity  $\epsilon_2$  in the proposed mechanism. The solid line shows the potential energy of the carrier in the electrostatic field of two impurity ions separated by a distance  $a$ . The energy of the carrier in the ground state of the impurity center, taking into account the interaction with the ionized center, is

$$E_1 = -E_a - (e^2/\mathcal{E}a). \quad (1)$$

Here  $E_a$  is the ionization energy of an isolated impurity

center,  $e$  is the elementary charge, and  $\mathcal{E}$  is the dielectric constant. The energy of the top of the potential wall is

$$E_2 = -4e^2/\mathcal{E}a. \quad (2)$$

The activation energy of conductivity  $\epsilon_2$  equals  $E_2 - E_1$ , so

$$\epsilon_2 = E_a - (3e^2/\mathcal{E}a). \quad (3)$$

For simplicity we assume in the following that the majority impurity centers form in the crystal an "impurity sublattice." This assumption gives reasonable results in the theory of the " $\epsilon_3$  anomaly."<sup>3</sup> We are interested only in the jumps to the nearest neighbors in this sublattice, because, as follows from formula (3),  $\epsilon_2$  rises with rising  $a$  and the jumps over larger distances will be much more improbable at low temperatures. For any type of sublattice we have

$$1/a = SN^{\frac{1}{3}}, \quad (4)$$

where  $S$  is a parameter depending on the type of sublattice, but never far from unity:  $S=0.89$  for the face-centered cubic and the hexagonal closed-packed sublattices;  $S=0.92$  for the body-centered cubic sublattice;  $S=1.00$  for the simple cubic sublattice;  $S=1.15$  for the diamond-type sublattice.  $N$  is the concentration of the majority impurities, and  $a$  denotes now the distance between the nearest neighbors in the impurity sublattice.

From formulas (3) and (4) we obtain

$$\epsilon_2 = E_a - (3e^2/\mathcal{E})SN^{\frac{1}{3}}. \quad (5)$$

Thus we are led to expect that on the  $\epsilon_2$  vs  $N^{\frac{1}{3}}$  plot the experimental points lie on a straight line and that the coefficient  $S$  determined from the slope of this line and from formula (5) is close to unity.

In Fig. 2 we have the experimental points obtained by Fritzsche<sup>1,6</sup> and the ionization energies of Ga and Sb in germanium.<sup>9,10</sup> For  $p$ -type Ge these points lie well on a straight line. From the slope of this line, taking  $\mathcal{E}=16.0$ ,<sup>17</sup> we have

$$S=0.88. \quad (6)$$

For  $n$ -type Ge the points lie also on a straight line with a larger slope, but the line does not coincide with the point given by the ionization energy of Sb in Ge. Perhaps the values of  $\epsilon_2$  for  $n$ -type Ge were measured with much less accuracy than for  $p$ -type; the straight lines on the  $\rho$  vs  $1/T$  plots are much shorter here than in the case of the  $p$  type.

In the preceding considerations we neglected the effect of the Coulomb field of the compensating impurities. These impurities, being all ionized, attract the "empty states" of the majority centers. The empty states are then partially bound to the compensating centers; such states do not contribute to the conduction. However, the binding energy is small and for  $K \ll 1$ ,

<sup>15</sup> W. Baltensperger, Phil. Mag. 44, 1355 (1953).

<sup>16</sup> P. Aigrain, Physica 20, 978 (1954).

<sup>17</sup> F. A. D'Altroy, and H. Y. Fan, Phys. Rev. 103, 1671 (1956).

and in the temperature range considered, most of the empty states are not bound.<sup>18</sup> We are justified in neglecting this effect.

We would like to point out that formula (5) holds not only for the shallow but also for the deep impurity states and is independent of the band structure. The only assumption concerning the bulk material is the isotropy of the dielectric constant.

#### CONDUCTIVITY IN THE CASE OF STRONG CARRIER-PHONON INTERACTION

If in the proposed mechanism the carrier jumps from the neutral impurity center to the ionized one, it must first be excited to an energy higher than the top of the potential wall and second diffuse to the empty center. Whether the first or the second process limits the conductivity depends on the value of the carrier-phonon interaction. No other interaction can play a role in the carrier's scattering on its way between the two centers. We now discuss the case of strong carrier-phonon interaction, in which diffusion is the limiting factor. The probability of excitation of the carrier is so high that the volume density of carriers in the neutral center is given by the density at thermal equilibrium in the deformed band. In the empty center the density is zero. Of course by "density of carriers" we mean the probability of finding the carrier in a unit volume. We shall consider the diffusion current from the neutral center to the ionized one and obtain first the jumping frequency and then the electric conductivity.

The conductivity obtained on this way is expected to be equal to the observed one in cases in which the carrier-phonon interaction is strong, and to be larger than the experimental values if this interaction is weak. In other words, if the proposed mechanism determines the conduction, our calculated conductivity must be not smaller than the observed one.

We want first to obtain the density of carriers in the neutral center at thermal equilibrium. We assume that the strong carrier-phonon interaction is weak enough to permit the treatment of the ground state of the carrier at the impurity center as a stationary quantized state. We are interested in the density at such a distance from the ion, at which the field of the ion can be treated as a Coulomb field; very close to the ion there are deviations depending on the nature of the impurity. We do not take into account the density of the carrier in the ground state. Let us introduce the coordinate system  $x, y, z$  in such a way that the ion of the neutral center has the coordinates  $(-\frac{1}{2}a, 0, 0)$  and the ionized one  $(\frac{1}{2}a, 0, 0)$ . We denote by  $q$  the electric charge of the carrier ( $|q|=e$ ) and by  $\varphi$  the potential resulting from the two centers,

$$\varphi = -\frac{q}{\epsilon} \left\{ \left[ \left( x + \frac{1}{2}a \right)^2 + y^2 + z^2 \right]^{-\frac{1}{2}} + \left[ \left( x - \frac{1}{2}a \right)^2 + y^2 + z^2 \right]^{-\frac{1}{2}} \right\}. \quad (7)$$

<sup>18</sup> S. H. Koenig, and G. R. Gunther-Mohr, J. Phys. Chem. Solids 2, 268 (1957), Appendix by P. J. Price.

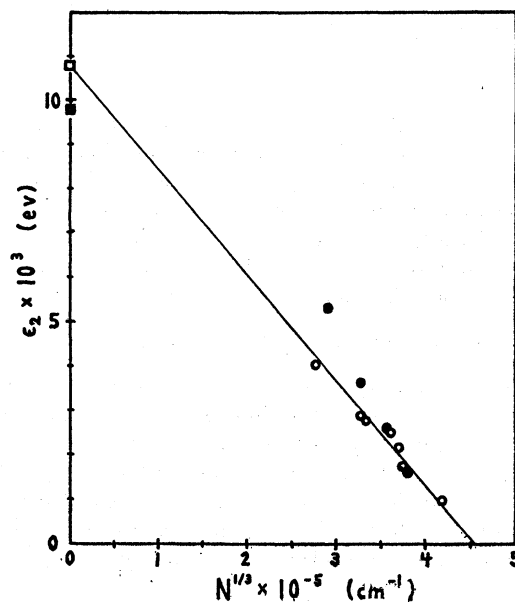


FIG. 2. The dependence of the activation energy of conductivity on concentration of the majority impurities. The empty circles and square are for  $p$ -Ge,<sup>1,9</sup> the full ones for  $n$ -Ge.<sup>6,10</sup>

By  $n_{rr}$  we denote the density of carriers at thermal equilibrium. If, as was assumed, the carrier-phonon interaction is strong, then the excited quantized states of the two-center potential disappear and the well-known formula holds:

$$n_{rr} = (1/\sqrt{2\pi}) (m^* kT/\pi)^{\frac{1}{2}} f. \quad (8)$$

Here  $m^*$  is the density-of-states effective mass of the carrier and  $f$  is the occupation probability of the states at the bottom (top) of the deformed conduction (valence) band, i.e., of the states of energy  $q\varphi$ .

Because of carrier-carrier interaction it is impossible to have two or more carriers at one center; the states of the neutral center are occupied alternatively by one carrier only. This yields

$$f_I/f_{II} = \exp[(E_{II} - E_I)/kT], \quad (9)$$

where  $f_{I,II}$  and  $E_{I,II}$  are, respectively, the occupation probabilities and energies for the states I and II. Let us take for the state I the state at the bottom (top) of the deformed band; then  $f_I = f$  and  $E_I = q\varphi$ . For the state II we take one of the ground states in the neutral center; then at low temperatures we have  $f_{II} \cong 1/\gamma$ , where  $\gamma$  is the degeneracy of the ground energy level, and  $E_{II} = E_1$  [see formula (1)]. Hence

$$f = \frac{1}{\gamma} \exp \left[ - \left( E_a + \frac{e^2}{\epsilon a} + q\varphi \right) / kT \right]. \quad (10)$$

We put

$$n_{r0} = \frac{1}{\sqrt{2\pi}} \left( \frac{m^* kT}{\pi} \right)^{\frac{1}{2}} \exp \left[ - \left( E_a + \frac{e^2}{\epsilon a} \right) / kT \right]. \quad (11)$$

From the formulas (8), (10), and (11) we obtain finally

$$n_{rr} = n_{r0} \exp(-q\varphi/kT). \quad (12)$$

Now we shall write the diffusion equation for the carrier. We assume that the carrier's diffusion coefficient  $D$  and mobility  $\mu$  in the band, both limited by the carrier-phonon interaction only, are isotropic. We denote by  $\mathbf{J}$  the density of the probability current of the carrier and by  $n_r$  the density of carriers. Using the Einstein formula for  $D$ , we have, for positive  $q$ :

$$\mathbf{J} = -(kT\mu/e) \text{grad} n_r - \mu n_r \text{grad} \varphi. \quad (13)$$

Now we impose the boundary conditions: On a surface surrounding the ion of the neutral center [i.e., the point  $(-\frac{1}{2}a, 0, 0)$ ] and not very close to it we put  $n_r = n_{rr}$ , and on an analogous surface surrounding the ion of the ionized center [i.e., the point  $(\frac{1}{2}a, 0, 0)$ ] we put  $n_r = 0$ . Outside of these surfaces  $\text{div} \mathbf{J} = 0$ ; using formula (13) and  $\Delta\varphi = 0$ , we obtain

$$\Delta n_r + (q/kT) \text{grad} \varphi \text{grad} n_r = 0. \quad (14)$$

Let us define a new function  $\chi$  by the equation

$$n_r = n_{r0} \chi \exp(-q\varphi/kT). \quad (15)$$

This yields instead of (14)

$$\Delta \chi - (q/kT) \text{grad} \varphi \text{grad} \chi = 0. \quad (16)$$

Using (12) we now express the boundary conditions in terms of  $\chi$ . On the surface surrounding the point  $(-\frac{1}{2}a, 0, 0)$ ,  $\chi = 1$ ; and on the surface surrounding the point  $(\frac{1}{2}a, 0, 0)$ ,  $\chi = 0$ .

We now focus our attention on the vicinity of the point  $(0, 0, 0)$ . There the potential energy of the carrier has smaller value than in any point on the  $x=0$  plane. Thus most current flows here. If we neglect the terms of third and higher orders in the coordinates, then  $\varphi$  in the vicinity of the point  $(0, 0, 0)$  is given by the formula

$$\varphi \cong -(4q/\mathcal{E}a) + (8q/\mathcal{E}a^3)(y^2 + z^2 - 2x^2). \quad (17)$$

With  $\varphi$  of the shape (17), Eq. (16) has a solution

$$\chi = -\frac{4e}{(\pi \mathcal{E} a^3 kT)^{1/2}} \int_{-\infty}^x \exp(-16e^2 t^2 / \mathcal{E} a^3 kT) dt + 1. \quad (18)$$

To a good approximation at low temperatures our boundary conditions are fulfilled by this function, because for  $x \rightarrow -\infty$  we have  $\chi \rightarrow 1$ , and for  $x \rightarrow +\infty$  we have  $\chi \rightarrow 0$ .

We shall write now the  $x$  component of the density of current on the plane  $x=0$ . The formulas (13), (15), (11), (17), and (18) yield

$$J_z(x=0) = \frac{2k^2 T^2 \mu}{\pi^2 \gamma \hbar^3} \left( \frac{2m^{*3}}{\mathcal{E} a^3} \right)^{1/2} \exp\left(\frac{-\epsilon_2}{kT}\right) \times \exp\left[-8e^2 \left(\frac{y^2 + z^2}{\mathcal{E} a^3 kT}\right)\right], \quad (19)$$

where  $\epsilon_2$  is given by the formula (3). Integrating  $J_z(x=0)$  over the  $x=0$  plane, we obtain the total current flow from the neutral center to the ionized one, i.e., the jumping frequency  $W$ :

$$W = \frac{(2m^{*3} \mathcal{E} a^3)^{1/2} k^2 T^2 \mu}{4\pi e^2 \hbar^3 \gamma} \exp\left(\frac{-\epsilon_2}{kT}\right). \quad (20)$$

A simple reasoning gives the diffusion coefficient  $D_2$  for the empty states of impurities as

$$D_2 = Pa^2 W / 6, \quad (21)$$

where  $a$  is the distance between the nearest neighbors and  $P$  is the number of the nearest neighbors in the assumed "impurity sublattice." Using the Einstein formula for the electric conductivity  $\sigma_2$  given by the proposed mechanism, we obtain

$$\sigma_2 = e^2 Pa^2 W n / 6kT. \quad (22)$$

Here  $n$  is the concentration of the ionized majority centers, not bound to the compensating impurities. In our temperature range and for  $K \ll 1$  we can put  $n \cong KN$ .<sup>18</sup> The formulas (22), (20), and (4) yield

$$\sigma_2 = \frac{(2\mathcal{E} m^{*3})^{1/2} PK k^2 T^2 \mu}{24\pi \hbar^3 \gamma S^{7/2} N^{1/6}} \exp\left(\frac{-\epsilon_2}{kT}\right). \quad (23)$$

Here  $\epsilon_2$  is given by the formula (5).

Thus we have the conductivity with the activation energy  $\epsilon_2$ . The coefficient before the exponential function, denoted  $C_2$  by Fritzsche,<sup>1</sup> depends weakly on  $N$  and  $T$ , because the dependence of  $\mu$  on  $T$  is between  $T^{-1.5}$  to  $T^{-2.5}$ . The formula (23) holds for shallow as well as deep univalent impurity states and is independent of the band structure.

We shall compare now the coefficient  $C_2$  given by the formula (23) with the values obtained by Fritzsche.<sup>1,6</sup> Using the subscript  $h$  for  $p$ -type Ge and  $e$  for  $n$ -type Ge, we take  $\mathcal{E} = 16.0$ ,<sup>17</sup>  $m_h^*/m_0 = 0.36$ ,<sup>19</sup>  $m_e^*/m_0 = 0.55$ ,<sup>19</sup>  $\gamma_h = 4$ ,<sup>11</sup>  $\gamma_e = 2$ ,<sup>13</sup>  $S_{h,e} = 0.88$  [from formula (6)]; for  $n$ -Ge a rather arbitrary value),  $P_{h,e} = 12$  (as for the close-packed structures, because  $S_{h,e}$  has a value similar to that characteristic for these structures),  $\mu_h = 9.1 \times 10^8 T^{-2.3} \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$  (an empirical formula for the phonon-limited mobility obtained with this coefficient by Prince<sup>20</sup> for the temperature region above 200°K),  $\mu_e = 3.5 \times 10^7 T^{-1.6} \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$  (Prince's<sup>20</sup> formula obtained for the temperature region above 220°K). The typical experimental conditions are  $N_{h,e} = 4.5 \times 10^{16} \text{ cm}^{-3}$ ,<sup>1,6</sup>  $K_h = 0.1$ ,<sup>1</sup>  $K_e = 0.03$  (an approximate value from reference 6),  $T = 5^\circ \text{K}$ .<sup>1,6</sup>

<sup>19</sup> H. Brooks, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, New York, 1955), Vol. 7, p. 85.

<sup>20</sup> M. B. Prince, *Phys. Rev.* **92**, 681 (1953).

From formula (23) we have

$$C_{2h} = 1.0 \times 10^8 \text{ ohm}^{-1} \text{ cm}^{-1}, \quad (24)$$

$$C_{2e} = 1.4 \times 10^2 \text{ ohm}^{-1} \text{ cm}^{-1}. \quad (25)$$

The experimental values of  $C_{2h}$  obtained by Fritzsche<sup>1</sup> for *p*-type germanium are, independently of  $N$ , about  $4.2 \text{ ohm}^{-1} \text{ cm}^{-1}$ . For *n*-type germanium the plot in the paper<sup>6</sup> gives (for the sample “-20”)  $C_{2e} \cong 6 \text{ ohm}^{-1} \text{ cm}^{-1}$ . Thus in both cases the theoretical values are too high. Certainly the extensive extrapolation consisting of the use of the formulas for  $\mu$  at low temperatures results in large errors in the theoretical values. However, the fact that the experimental values of  $C_2$  are much smaller than those given by formula (23) assures, on one hand, the fulfillment of the necessary conditions for the possibility of the proposed mechanism, and, on the other hand, is consistent with the weak carrier-phonon

interaction in germanium. This weak interaction yields the high mobilities observed. Therefore the limiting process for the conduction is the excitation of carriers from the ground states to the energies higher than  $\epsilon_2$ . This process requires a separate consideration.

Formula (23) can have an immediate application, and not only that of giving the upper limit of the conductivity in the case of semiconductor with strong carrier-phonon interaction. Unfortunately, up to the present time, we have no experimental results on any such material.

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### Electric Field Gradients in Point-Ion and Uniform-Background Lattices\*

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The lattice contribution to the field gradient in ionic crystals and metals is a quantity which has a well-defined value. However, for an actual evaluation, the field gradient is usually broken up into a number of conditionally convergent series with poor convergence. Rapidly convergent expressions for these series, and consequently, for the field gradient can be obtained by applying the method of *plane-wise summation*. This method is applied to the field gradient in ionic crystals with tetragonal and hexagonal symmetry and to the field gradient in tetragonal and hexagonal close-packed metal structures. As an example, an expression for the field gradient at the position of the anion is derived for ionic crystals with the  $\text{CdI}_2$  structure. This expression is numerically evaluated for  $\text{CoBr}_2$ ,  $\text{FeBr}_2$ ,  $\text{MgBr}_2$ ,  $\text{MnBr}_2$ ,  $\text{CaI}_2$ ,  $\text{CdI}_2$ ,  $\text{CoI}_2$ ,  $\text{FeI}_2$ ,  $\text{GeI}_2$ ,  $\text{MgI}_2$ , and  $\text{MnI}_2$ . Rather extensive numerical results are also presented for both close-packed metal structures, including values for the field gradient in Li, Be, Zn, In, and Rh.

#### I. INTRODUCTION

IN the theory of nuclear quadrupole resonance, one is interested in the total electric-field gradient (FG) at the position of the nucleus. The FG may be considered to consist of two contributions,  $\text{FG}_{\text{cell}}$  and  $\text{FG}_{\text{lattice}}$ .  $\text{FG}_e$  is due to the electrons inside the central cell surrounding the nucleus, and  $\text{FG}_l$  is due to all the electrons and nuclei making up the rest of the lattice. Evaluation of  $\text{FG}_e$  requires a detailed knowledge of the electronic wave functions inside the central cell, but for an evaluation of  $\text{FG}_l$  of comparable accuracy, a precise knowledge of the electronic wave functions is much less essential. As a first approximation, the crystal may be considered as an electrostatic assembly of point charges (the ion cores), which, in the case of metals, are embedded in a uniform sea of negative

charge (the conduction electrons). Such models have been used for the evaluation of  $\text{FG}_l$  in ionic crystals<sup>1</sup> as well as in metals.<sup>2,3</sup> The advantage of such a model is that the evaluation of  $\text{FG}_l$  is reduced to a purely electrostatic problem, namely, to that of the evaluation of lattice sums of the type

$$S = \sum_{\lambda}' \frac{2P_2(\cos\theta_{\lambda})}{r_{\lambda}^3} \quad (1)$$

(notation explained in Sec. II). In this paper, we will restrict ourselves exclusively to this problem.

At this point, we would like to remark that, although the expression for  $\text{FG}_l$  contains lattice sums like (1) which are conditionally convergent (i.e., their values

<sup>1</sup> R. Bersohn, J. Chem. Phys. **29**, 326 (1958).

<sup>2</sup> M. Pomerantz and T. P. Das, Phys. Rev. **119**, 70 (1960).

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<sup>3</sup> W. W. Simmons, thesis, University of Illinois, 1960 (unpublished); W. W. Simmons and C. P. Slichter, Phys. Rev. **121**, 1580 (1961).