

## Theory of Diffusion and Equilibrium Position of Interstitial Impurities in the Diamond Lattice

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A theory is developed for diffusion of interstitial impurities in the diamond lattice. For ionized impurities the theory is based on a model in which the interaction of the ion with the host atoms is given by an attractive potential produced by the polarization of the host atoms, and a repulsive potential due to overlap of nonbonding electrons. The interaction energy is calculated at two interstitial positions of symmetry, and the activation energy for diffusion is taken as the difference between the two. Good agreement with experiment is found for lithium, copper, and silver. The theory predicts an optimum impurity size for diffusion, and thus explains the great diffusivity of copper. It also claims that the interstitial position of lithium and copper is not one of tetrahedral symmetry.

### I. INTRODUCTION

AN impurity is considered to be interstitial, purely so or in equilibrium with a substitutional form, if its diffusion constant is several orders of magnitude greater than the diffusion constant of impurities which are definitely substitutional. As an example, the diffusion constants of substitutional group III and V impurities in germanium range from  $10^{-13}$  to  $10^{-10}$  cm<sup>2</sup>/sec at around 850°C.<sup>1</sup> An interstitial impurity like lithium, on the other hand, has a diffusion constant of about  $10^{-5}$  at that temperature.<sup>1</sup> The theory of diffusion for interstitial impurities which has occasionally been applied to semiconductors<sup>2</sup> is the theory developed by Wert and Zener.<sup>3</sup> This theory was developed to explain diffusion of interstitial atoms in metals. Since metals have close-packed crystal lattices, it is not surprising that Wert and Zener assumed that the activation energy for diffusion is expended essentially in the elastic distortion of the lattice, as the impurity moves from an equilibrium position over a saddle point to another equilibrium position. In their theory the authors do not attempt to calculate this energy; they show, however, how to estimate the entropy for diffusion on the basis of this mechanism, by proving that strain increases the entropy of the lattice.<sup>4</sup>

We have developed a theory of diffusion for interstitial impurities in crystals with the diamond lattice which differs from that of Wert and Zener in two important respects: (a) We believe that lattice distortion contributes only a small fraction to the activation energy for diffusion in such crystals. Typically, the contribution may be of the order of 10%, depending on the size of the impurity. (b) We actually attempt to calculate the activation energy for diffusion by estimating the interaction energy of the impurity with the host atoms at an equilibrium site and a saddle point. We are able to do these calculations since we are dealing with

valence crystals in which the atoms are covalently bonded with their neighbors, and hence have essentially closed electron shells. The impurity will, of course, disturb the bonding but we assume that it does not disrupt it.

The fact that we are dealing with a very open lattice means that the repulsion energy between the impurity and the host atoms need not be the main contribution to the activation energy for diffusion. A lithium ion, for example, has a radius<sup>5</sup> of 0.60 Å compared to a nearest-neighbor distance of 2.25 Å in germanium at the smaller of the two interstitial sites [Fig. 1(b)]. Nevertheless, it

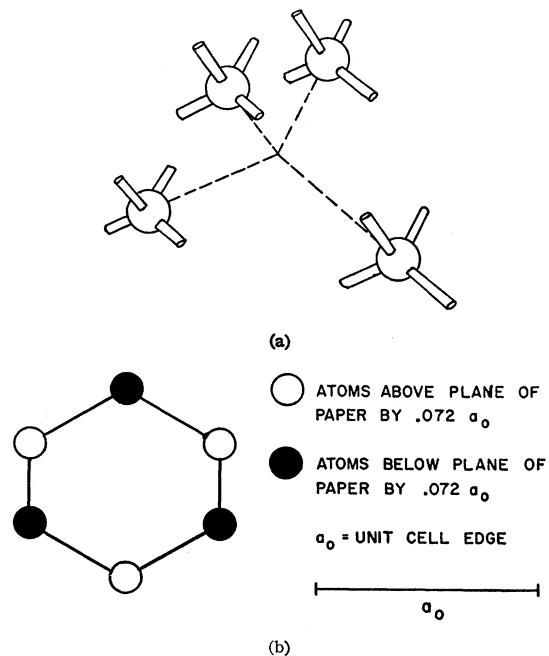


FIG. 1. Interstitial sites in the diamond lattice. (a) Tetrahedral site (*T* site)—nearest neighbors at  $0.433 a_0$ ; next-nearest neighbors at  $0.500 a_0$ . (b) Hexagonal site (*H* site)—nearest neighbors at  $0.415 a_0$ ; next-nearest neighbors at  $0.649 a_0$ ; plane of paper normal to  $[111]$  direction.

<sup>1</sup> H. Reiss and C. S. Fuller, *Semiconductor*, edited by N. B. Hannay (Reinhold Publishing Corporation, New York, 1959), Chap. VI.

<sup>2</sup> See for example: J. N. Hobstetter, *Progress in Metal Physics* (Interscience Publishers, Inc., New York, 1958), Vol. 7, p. 1.

<sup>3</sup> C. A. Wert and C. Zener, *Phys. Rev.* **76**, 1169 (1949).

<sup>4</sup> C. Zener, *Acta. Cryst.* **2**, 163 (1949).

<sup>5</sup> O. K. Rice, *Electronic Structure and Chemical Bonding* (McGraw Hill Book Company, Inc., New York, 1940), Chap. XIV.

is found that lithium has an appreciable energy of diffusion.<sup>1</sup> Furthermore, the larger copper ion diffuses even faster than lithium.<sup>1</sup> The size of the impurity can therefore not be the only factor in determining the ease of diffusion. We have therefore devoted our main effort to an attempt to calculate the electrostatic interaction energy of the impurity and the host atoms, and we find that it makes a major contribution to the activation energy for diffusion.

In this paper we shall mainly develop a theory for the important case of diffusion by an ionized interstitial impurity. (A theory of diffusion of substitutional impurities in the diamond lattice has been given by Swalin.<sup>6</sup>) Most interstitial impurities probably exist in this state in germanium, silicon, and similar substances. The only interstitial impurities which are likely to exist to any appreciable extent in the same form as in vacuum are hydrogen, helium, and perhaps neon, as has previously been discussed by the author.<sup>7</sup> In Sec. VI we will give a qualitative discussion of the diffusion of such impurities. With the exception of certain transition elements, other interstitials are known to carry a positive charge, as evidenced by the effect of an electric field on their diffusion. This effect has been observed for lithium by Fuller and Severiens<sup>8</sup>; for copper in germanium by the same authors, and in silicon by Gallagher<sup>9</sup>; for silver in germanium by Kosenko *et al.*<sup>10</sup> and in silicon by Boltaks *et al.*<sup>11</sup>; for gold in silicon by Boltaks *et al.*<sup>12</sup>

In the case of transition elements new effects can occur as a result of the possibility of transferring electrons to the partially filled *d* shell. Ludwig and Woodbury, by studying electron spin resonance,<sup>13</sup> have observed some of these elements not only in electrically neutral form but even as negatively charged ions. The theory developed here is based on estimating the interaction of an ion with the host atoms at different interstitial sites. To include the transition elements it would be necessary to calculate the magnitude of the splitting of *d* levels by the crystal field at various sites, and this calculation is beyond the scope of this paper.

## II. INTERACTION ENERGY OF AN ION WITH THE HOST LATTICE

### A. Diffusion Path

The interaction energy of an ionized interstitial impurity with the atoms of the host crystal will consist

primarily of two components: (a) an attractive potential produced by the interaction of the ion with the dipoles it has induced in the host atoms, and (b) a repulsive potential characteristic of the interaction of atoms or molecules with closed shells.<sup>14</sup> We shall neglect the contributions of the attractive van der Waals potential, which is an order of magnitude smaller than the induced dipole-ion interaction energy, or polarization energy, which we shall calculate. It will be seen below, that the polarization energy is of the order of 5 eV while the van der Waals energy is of the order of a few tenths of an eV.<sup>7</sup> Furthermore, the existence of an attractive van der Waals potential will not affect the conclusions which will be reached.

If it were not for the existence of polarization energy, the impurity would choose sites of symmetry with respect to the surrounding host atoms; at those sites it will be farthest away from any one of them, and hence the repulsive energy will be a minimum. In the diamond lattice there will be two such sites, as illustrated in Fig. 1. One site, which we shall call tetrahedral, is characterized by four nearest neighbors at a distance of  $0.433 a_0$  from the center, and six next-nearest neighbors at a distance of  $0.500 a_0$ ;  $a_0$  is the unit-cell edge length. The center of the hexagonal site is at a distance of  $0.415 a_0$  from six nearest neighbors, and  $0.649 a_0$  from eight next-nearest neighbors. It is clear that consideration of nearest neighbors only makes the hexagonal site one of greater repulsive energy for the impurity than the tetrahedral site. When next-nearest neighbors are considered [Eq. (7)] the difference is somewhat reduced. On the other hand, calculations of the polarization energy  $U_{\text{pol}}$ , at the two sites [see Sec. II(B)] show that  $U_{\text{pol}}$  is greater, i.e., more negative, at the hexagonal site than at the tetrahedral site. From the point of view of lowering its electrostatic energy, the ion thus prefers the hexagonal site.

The diffusion path will then be given by: hexagonal-tetrahedral-hexagonal, or tetrahedral-hexagonal-tetrahedral, depending on which of the two sites is a position of lower energy. If the atom were to continue in this direction it would encounter a host atom, and thus be repelled. As a result it will have to branch off into another [111] direction, and in this manner it will diffuse through the crystal in zig-zag fashion. It is clear that the main conclusions of this paper can be reached already at this point: For a very small ion, for which the repulsive energy at the center of the two "cavities" is small, the hexagonal site will be the equilibrium site, and the tetrahedral site the saddle point; the activation energy for diffusion will then be given mainly by the difference in polarization energy at the two positions. For a very large ion, the repulsive energy will dominate the picture, and the tetrahedral site will be the equilibrium position; the energy of activation for diffusion will

<sup>6</sup> R. A. Swalin, *J. Phys. Chem. Solids* **18**, 290 (1961).

<sup>7</sup> K. Weiser, *J. Phys. Chem. Solids* **17**, 149 (1960).

<sup>8</sup> C. S. Fuller and J. C. Severiens, *Phys. Rev.* **96**, 21 (1954).

<sup>9</sup> C. J. Gallagher, *J. Phys. and Chem. Solids* **3**, 82 (1957).

<sup>10</sup> V. E. Kosenko, E. G. Miselynk, and L. A. Khamenko, *Fiz. Tverdogo Tela U.S.S.R. Sbornik (Supplement) I*, 100 (1959).

<sup>11</sup> B. I. Boltaks and H. Shih-Yin, *Fiz. Tverdogo Tela* **2**, 2677 (1960); [translation: *Soviet Phys.—Solid State* **2**, 2389 (1961)].

<sup>12</sup> B. I. Boltaks, G. S. Kulikov, and R. Sh. Malkovich, *Fiz. Tverdogo Tela* **2**, 2395 (1960); [translation: *Soviet Phys.—Solid State* **2**, 2134 (1961)].

<sup>13</sup> G. W. Ludwig and H. H. Woodbury, *Phys. Rev. Letters* **5**, 98 (1960).

<sup>14</sup> See for example: M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Chap. I.

then be given mainly by the difference in repulsive energy at the two sites. The intriguing possibility may then arise that for an ion of intermediate size the difference in polarization energy can just balance the difference in repulsive energy so that the activation energy for diffusion vanishes.

A correction to this simple picture arises from the fact that in the presence of the electrostatic attraction between the ion and the dipoles it has induced in the surrounding host atoms, the ion will not remain at the center of either cavity since this will not be a position of stable equilibrium. In the Appendix this displacement will be considered, and it will be seen that it does not alter the conclusions drawn above which are based on a model in which the ion is at the center of the cavity.

Another approximation of the model is that the lattice is rigid, which cannot be entirely correct: On the one hand, the electrostatic attraction of the ionic charge will tend to pull the lattice toward it; on the other hand, the repulsive forces will push the host atoms away from the impurity. In the Appendix we examine the importance of this effect and conclude that it is relatively unimportant.

In parts A and B of this section we shall estimate the electrostatic energy and the repulsive energy, respectively, at the centers of the hexagonal and tetrahedral positions. The difference between the sum of these energies at the two sites should equal the activation energy for diffusion, except for the corrections considered in Appendices A and B. It is assumed that the potential energy curve along a [111] direction is monotonic between the centers of the two sites. If a hump exists, then the activation energy calculated by our theory (aside from the inevitable simplifications involved in the treatment) must be a lower limit for the true activation energy along this path.

## B. Polarization Energy in the Diamond Lattice

The polarization energy of a charged ion in a dielectric medium is the energy released when the ion is placed into the medium. The physical origin of this release in energy lies in the decrease in the electric field in the medium surrounding the ion compared to its value in free space.<sup>15</sup> An atomistic approach to the polarization of a lattice by a charge was first developed by Mott and Littleton,<sup>16</sup> in an attempt to estimate the energy of formation of a lattice vacancy in an alkali halide. With minor modifications, introduced by Rittner, Hutner, and du Pré<sup>17</sup> their method will be employed here.

The polarization of an atom at a given distance from the charge will be calculated on the basis of the following model: (1) The dipole  $\mathbf{u}$  induced on an atom varies

linearly with the field  $\mathbf{E}$ . The constant of proportionality, the polarizability  $\alpha$ , is thus taken to be independent of the polarization of other atoms, particularly those of its neighbors. (2) The polarizability is taken to be isotropic. (3) The direction of the dipoles is along the radius vector from the charge. (4) The field at the center of an atom is the vector sum of the field which originates at the charge and the fields which are produced by all the other dipoles induced on the atoms of the crystal. (5) The field produced by a dipole  $\mathbf{u}_j$  at  $\mathbf{r}_j$  from the origin (the charge site) at a point  $\mathbf{r}_i$ , is given in the point dipole approximation as:

$$\mathbf{E}_i = \nabla_i [\mathbf{u}_j \nabla_i (1/r')], \quad (1)$$

where  $\mathbf{r}'$  is the radius vector from  $\mathbf{r}_j$  to  $\mathbf{r}_i$ . The subscript  $i$  on the  $\nabla$ 's indicates that the differentiation is to be carried out at  $\mathbf{r}_i$ . With this model it is now possible to calculate the dipoles on the atoms in the lattice. Since the dipole on any one atom depends on the dipoles on all the other atoms, the exact solution of the problem involves  $N$  simultaneous equations in the  $N$  atoms of the lattice. Mott and Littleton chose a set of atoms surrounding the charge and arranged them into spherical shells around the charge. The induced dipoles in a given shell were presumed to be equal, and it was then only necessary to find the dipoles on any one atom of a shell. The problem was now solved in the  $n$ th order approximation by treating the dipoles on the first  $n$  shells as unknown. The dipoles on atoms beyond the  $n$ th shell were approximated by their macroscopic value, and their contribution to the field on atoms of the first  $n$  shells was taken into account. Rittner *et al.*<sup>17</sup> decided to drop the contributions of dipoles beyond the  $n$ th shell to the field. Besides making the computations for any order of approximation simpler, the method can be justified by the following argument: If the crystal beyond the  $n$ th shell is considered as a continuum, the field produced by the induced charges on the surface of the spherical cavity carved out by the  $n$  shells, will in general be equal to zero. In the  $n$ th order approximation, the following set of equations is therefore to be solved:

$$\begin{aligned} \mu_1 &= \alpha(e/r_1^2 + E_{11}\mu_1 + E_{12}\mu_2 + E_{13}\mu_3 \cdots + E_{1n}\mu_n), \\ \mu_2 &= \alpha(e/r_2^2 + E_{21}\mu_1 + E_{22}\mu_2 + E_{23}\mu_3 \cdots + E_{2n}\mu_n), \\ \mu_3 &= \alpha(e/r_3^2 + E_{31}\mu_1 + E_{32}\mu_2 + E_{33}\mu_3 \cdots + E_{3n}\mu_n), \\ &\quad \dots \\ \mu_n &= \alpha(e/r_n^2 + E_{n1}\mu_1 + E_{n2}\mu_2 + E_{n3}\mu_3 \cdots + E_{nn}\mu_n). \end{aligned} \quad (2)$$

In this equation,  $\mu_1, \mu_2, \dots, \mu_n$  are the dipoles on atoms of the first, second,  $\dots$  and  $n$ th shell, and  $r_1, r_2, \dots, r_n$  are the respective distances of these shells from the charge. The vector symbol has been omitted from the dipoles since, according to assumption (3), all dipoles are directed along the radius vector from the charge. A matrix element  $E_{ij}$ , when multiplied by  $\mu_j$ , is the electric field in the radial direction produced at an atom of shell  $i$  by the dipoles in shell  $j$ .  $E_{ii}\mu_i$  refers to the field at an atom of shell  $i$  by the other dipoles in the same shell  $i$ .

<sup>15</sup> C. J. F. Bottcher, *Theory of Electric Polarization* (Elsevier Publishing Company, Inc., New York, 1952), Chap. V.

<sup>16</sup> N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.* **34**, 485 (1938).

<sup>17</sup> E. S. Rittner, R. A. Hutner, and F. K. du Pré, *J. Chem. Phys.* **17**, 198 (1949).

The elements  $E_{ij}$  or  $E_{ii}$  are of course given by carrying out the differentiation indicated in Eq. (1) at a point  $(x_0, y_0, z_0)$  of shell  $i$ .

$$E_{ij} = \sum_{G_j} \frac{1}{R_j r'^5} S_{ij}, \quad (3)$$

$$[-x_j(r'^2 - 3\xi^2) + y_j(3\xi\eta) + z_j(3\xi\rho)]x_0/R_i$$

$$S_{ij} = +[x_j(3\xi\eta) - y_j(r'^2 - 3\eta^2) + z_j(3\eta\rho)]y_0/R_i$$

$$+ [x_j(3\xi\rho) + y_j(3\eta\rho) - z_j(r'^2 - 3\rho^2)]z_0/R_i.$$

The summation is to be carried out over all  $G_j$  lattice points  $(x_j, y_j, z_j)$  in shell  $j$ . For  $E_{ii}$  the summation omits the contribution of the point  $x_0, y_0, z_0$  at which the fields  $E_{ii}$  is to be computed. In Eq. (3),  $R_j$  is the radius of the  $j$ th shell;  $x_0, y_0,$  and  $z_0$  is an arbitrary lattice point of the  $i$ th shell since by definition a shell is chosen so that all atoms in it experience the same field from all the dipoles in the lattice. The Greek symbols  $\xi, \eta, \rho$  are the components of the distance from a lattice point  $x_j, y_j, z_j$  of the  $j$ th shell to the reference point  $x_0, y_0, z_0$  of the  $i$ th shell;  $r'$  is the distance between these points:  $\xi = x_j - x_0, \eta = y_j - y_0, \rho = z_j - z_0, r' = r_j - r_0$ . The polarizability  $\alpha$  which enters these equations can be obtained from the Lorentz-Lorenz equation which relates the dielectric constant  $K$  and the atomic polarizability:

$$(K-1)/(K+2) = \frac{4}{3}\pi\alpha/v, \quad (4)$$

where  $v$  is the volume occupied by each atom. The derivation of this relation<sup>18</sup> is based on precisely the same assumptions which are employed in the method of Mott and Littleton. It should be emphasized that although the host atoms are considered as discrete entities they are not considered as free atoms. Their polarizability is determined not only by their properties

as free atoms but by their interaction with the lattice as a whole.<sup>19</sup>

Having solved Eq. (2) for the  $\mu$ 's, the potential  $\phi$  produced by them at the charge site can then be computed from

$$\phi = -\sum_i^n \sum_{G_j} \frac{\mu_j}{R_j^2} - \frac{q}{R_{n+1}} \left(1 - \frac{1}{K}\right). \quad (5)$$

$G_j$  is the number of atoms in the  $j$ th shell of radius  $R_j$ ,  $n$  is the order of approximation, and the  $\mu$ 's are the values found for the  $n$ th order approximation. The second term on the right is the contribution to the potential from dipoles beyond the  $n$ th shell if this region is treated as a continuum.<sup>20</sup> The polarization energy is equal to  $\frac{1}{2}q^2\phi$ .

The calculations were carried out for the two interstitial positions in the diamond lattice shown in Fig. 1. An initial set of atoms was chosen around each origin, and arranged into shells of atoms equidistant from it. A maximum radius of  $1.5 a_0$  was chosen for the set of points, which totaled 112 for the hexagonal case and 108 for the tetrahedral case. The matrix elements  $E_{ii}$  and  $E_{ij}$  of Eq. (3) were then computed with the help of an IBM 7090 computer. To insure that all atoms of a given shell are geometrically equivalent, the quantities  $E_{ij}$  were obtained for all points of a shell. In most cases it was found that it did not matter which shell point was taken as representative of a given shell but for some shells it was found necessary to split them into two subshells; each subshell contained atoms which gave the same  $E_{ij}$  with respect to all shells  $j$ . After the computation of the  $E_{ij}$ , Eq. (3) could be solved using the value for  $\alpha$  derived from Eq. (4). An  $n$ th order solution for the  $\mu$ 's yields an  $n$ th order approximation for  $\mu_1$ , an  $(n-1)$ st order approximation for  $\mu_2 \dots$ , and a first-order approximation for  $\mu_n$ . As seen in Fig. 2, the convergence one obtains with successive orders of approximation for the solution of the  $\mu$ 's is very satisfactory for the hexagonal case but not quite as satisfactory for the tetrahedral case. In the latter case a difficulty arose when the approximation was increased from third to fourth order. The fourth shell had to be split, as explained above, and the  $E_{ij}$  value for one of the split shells turned out to be very large. As a result, serious loss of convergence occurred which did not disappear even when a fourteenth-order approximation was used. To obtain convergence it was necessary to average the  $E_{ij}$ 's involving the fourth shell. In the case of the hexagonal site where such shell splitting was also necessary it made very little difference whether the  $E_{ij}$ 's were averaged as just described, or whether the  $\mu$ 's of the subshells were averaged.

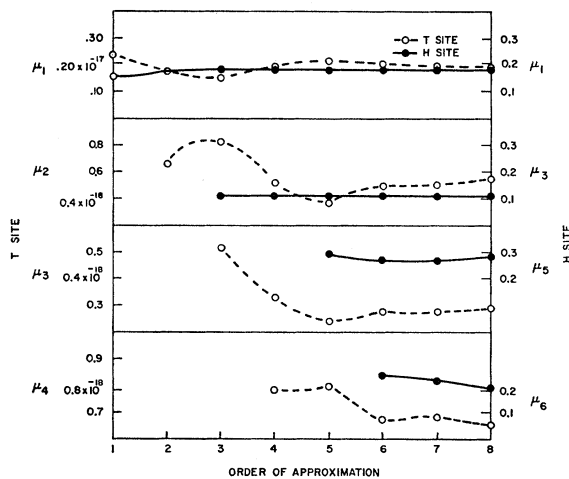


Fig. 2. Dipole moments  $\mu_j$  on various shells  $j$  vs order of approximation. Left scale—tetrahedral site; right scale—hexagonal site.

<sup>18</sup> See for example: C. Kittel, *Introduction to Solid-State Physics* (J. Wiley & Sons, Inc., New York, 1956), 2nd ed., Chap. VII.

<sup>19</sup> W. Cochran, Proc. Roy. Soc. (London) **A253**, 260 (1959).

<sup>20</sup> N. F. Mott and R. W. Guernsey, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1948), 2nd ed., Chap. II.

TABLE I. Repulsive energy contribution to the energy of diffusion for various impurities in germanium and silicon according to Eq. (8).

Impurity	Ionic radius <sup>a</sup> (Å)	$\Delta U_{\text{rep}}^{\text{diff}}$ (ev)	
		Ge	Si
Lithium	0.60	0.18	0.23
Copper	0.96	0.54	0.69
Sodium	0.96	0.53	0.68
Silver	1.26	1.35	1.70
Gold	1.36	1.83	2.30

<sup>a</sup> See reference 5.

Figure 3 shows the convergence for the polarization energy as a function of the order of approximation. It is seen that very satisfactory convergence was obtained for both cases. In fact, it seems hardly necessary to have carried out the calculations beyond the third-order approximation.

From the point of view of understanding diffusion by an interstitial ion, the important result is that the polarization energy at the hexagonal site is greater by about 0.75 ev (see Fig. 3) than at the tetrahedral site. While the results shown in Figs. 2 and 3 are for silicon, the calculations give essentially the same results for germanium.

### C. Repulsive Energy

To estimate the repulsive energy  $U_{\text{rep}}$  between the ion and the surrounding host atoms, we have used the Born-Mayer equation, which has been successful in the theory of the cohesive energy of ionic crystals<sup>14</sup>:

$$U_{\text{rep}} = A \exp(r_L + r_I - r) / \rho. \quad (6)$$

In Eq. (6),  $A$  is merely a scalar factor (0.63, if  $U_{\text{rep}}$  is to be expressed in electron volts),  $r_L$  is the effective radius of a host atom,  $r_I$  the ionic radius of the impurity, and  $r$  the distance between them. The constant  $\rho$  determines how rapidly the repulsion falls off with distance. The repulsive energy of the ion at the center of the tetrahedral and of the hexagonal cavities is thus given by

$$U_{\text{rep}} = 4A \exp(r_L + r_I - r_T) / \rho + 6A \exp(r_L + r_I - 1.15r_T) / \rho, \quad \text{tetrahedral site,} \quad (7a)$$

$$U_{\text{rep}} = 6A \exp(r_L + r_I - r_H) / \rho + 8A \exp(r_L + r_I - 1.56r_H) / \rho, \quad \text{hexagonal site,} \quad (7b)$$

where interaction with nearest and next-nearest neighbors has been included. In Eqs. (7a) and (7b),  $r_T$  and  $r_H$  are the distances from the center of each "cavity" to the nearest host atom for the tetrahedral and hexagonal case, respectively.

To estimate the magnitude of the repulsive energy it is necessary to assign values to the constants  $\rho$  and  $r_L$ . For ionic crystals a value of  $\rho = 0.33 \times 10^{-8}$  cm has been found to be an average for many ion-pairs.<sup>14</sup> It does not

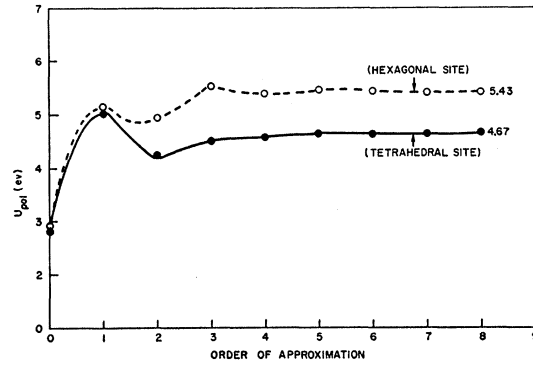


FIG. 3. Polarization energy (silicon) vs order of approximation (interstitial charges).

seem unreasonable to choose the same value for  $\rho$  in the case dealt with here: the repulsion between an ion and a host atom with a filled valence shell by virtue of being covalently bonded to other host atoms. In both cases the repulsion arises from the Pauli exclusion principle, and hence one might expect it to fall off similarly with distance. As for the other parameter, the effective host-atom radius  $r_L$ , there is experimental reason to choose it as the covalent radius of a host atom, or one-half the interatomic distance. The experimental reason is that pairing experiments between lithium and acceptors in germanium and silicon<sup>21</sup> show that the distance of closest approach is given by the sum of the lithium ionic radius and the covalent radius of the acceptor. We shall therefore take  $r_L$  equal to 1.22 Å for germanium and 1.17 Å for silicon.<sup>22</sup>

With these values for the parameters appearing in Eq. (7), we estimate that the contribution of next nearest neighbors is equal to about 50% of that of the nearest neighbors in the tetrahedral case, and about 2% in the case of the hexagonal site. The difference in repulsive energy between the two sites is equal to

$$U_{\text{rep}}^H - U_{\text{rep}}^T = \Delta U_{\text{rep}} \text{ (ev)} = 0.030 \exp(r_I / \rho) \quad \text{for Ge,} \quad (8) \\ = 0.038 \exp(r_I / \rho) \quad \text{for Si.}$$

The important conclusion for the understanding of diffusion is that from the point of view of lowering the repulsive energy, the ion prefers the tetrahedral site. Values for the repulsive energy contribution to the energy for diffusion for various ions in germanium are given in Table I.

Before concluding this section on the repulsive interaction energy it should be pointed out that Eq. (7) can only be a lower limit for the repulsive energy for a very large ion. When  $(r_L + r_I)$  exceeds  $r_T$  or  $r_H$ , either expansion of the lattice or compression of the ion or both

<sup>21</sup> See for example: H. Reiss, C. S. Fuller, and F. J. Morin, Bell System Tech. J. **35**, 535 (1956).

<sup>22</sup> See reference 18, Chap. I.

must take place. In other words, we would then have to add the Wert-Zener theory to the one developed here. For this reason, it is probable that the repulsive energy for gold is somewhat higher than is estimated here.

### III. PRE-EXPONENTIAL FACTOR OF THE DIFFUSION CONSTANT. ENTROPY OF DIFFUSION

Following Wert and Zener<sup>3</sup> we write the pre-exponential factor in the diffusion expression

$$D = D_0 \exp(-\Delta U^{\text{diff}}/RT)$$

as

$$D_0 = \frac{1}{6} g l (\Delta U^{\text{diff}}/2m)^{\frac{1}{2}} \exp(\Delta S^{\text{diff}}/R). \quad (9)$$

No specific model is involved in this equation, except that it is assumed that the diffusing atom oscillates in its equilibrium position, in the direction toward the saddle point, with a frequency equal to  $(\Delta U^{\text{diff}}/2l^2m)^{\frac{1}{2}}$ . In Eq. (9),  $g$  is the number of saddle points surrounding the equilibrium site;  $l$  is the distance between equilibrium sites;  $\Delta U^{\text{diff}}$  is the activation energy for diffusion, and  $R$  is the gas constant.  $\Delta S^{\text{diff}}$  is the entropy of diffusion.

Since the entropy of a solid is determined by its vibrations,<sup>23</sup> the entropy of diffusion will be given by the difference in vibrations with the ion in the saddle point and in its equilibrium site. A solution to this problem seems only remotely possible but an estimate of the magnitude of the entropy of diffusion can be gained by treating the lattice as a continuum of given dielectric constant. This approach is similar to the one taken by Wert and Zener<sup>3</sup> in their theory of interstitial diffusion in metals, in which the host lattice was treated as an elastic continuum. In the continuum expression for the polarization energy, the ion is considered to be embedded in a cavity of radius  $R_c$  carved out of the dielectric. The polarization energy is then equal to<sup>15,20</sup>

$$U_{\text{pol}} = -(q^2/2R_c)(1-1/K). \quad (10)$$

The right side of Eq. (10) represents the energy liberated when the space beyond  $R_c$  is filled with a dielectric medium with permittivity  $K$ . It can be shown, that the entropy associated with this process is given by<sup>15</sup>

$$S_{\text{pol}} = \int_{R_c}^{\infty} \frac{E^2}{8\pi} \frac{dK}{dT} dV, \quad (11a)$$

where  $E$  is the electric field in the dielectric, and  $dV$  is a volume element. Setting  $E$  equal to  $q/Kr^2$ ,  $dV$  equal to  $4\pi r^2 dr$ , and integrating Eq. (11a) yields

$$S_{\text{pol}} = \frac{q^2}{2R_c K} \frac{d \ln K}{dT}. \quad (11b)$$

The contribution to the entropy of diffusion, which is due to polarization, is then equal to the difference in

the entropy of polarization at the hexagonal site and the tetrahedral site:

$$\Delta S_{\text{pol}} = \frac{q^2}{2K} \frac{d \ln K}{dT} \left( \frac{1}{R_c^H} - \frac{1}{R_c^T} \right) \approx \frac{\Delta U_{\text{pol}}}{K} \frac{d \ln K}{dT}. \quad (12)$$

In our calculations for the interaction energy, and hence the activation energy for diffusion, we have assumed so far that the atoms retain their normal positions. In Appendix B we attempt to show that this approximation is quite good in that only a small portion of the interaction energy goes into distortional energy of the lattice. Hence we shall neglect that part of the entropy of diffusion which according to the Wert-Zener theory comes from the distortion of the lattice. We assume, therefore, that Eq. (12) represents the major part of the total entropy of diffusion. Using values for  $\Delta U_{\text{pol}}$  calculated in Sec. II(B) and experimental values for<sup>24</sup>  $K$  and<sup>25</sup>  $d \ln K/dT$  for germanium and silicon, we obtain an entropy of diffusion of  $6.6 \times 10^{-6}$  ev/deg for the former and  $5.1 \times 10^{-6}$  ev/deg for the latter. Even near the melting points of the elements the correction  $T\Delta S$  to  $\Delta U_{\text{pol}}$  is thus of the order of only about 0.01 ev.

Having estimated  $\Delta S^{\text{diff}}$ , we obtain the following values for  $D_0$ :

$$\begin{aligned} D_0 &= 0.22 a_0 (\Delta U^{\text{diff}}/m)^{\frac{1}{2}}, && \text{tetrahedral equilibrium site} \\ &= 0.11 a_0 (\Delta U^{\text{diff}}/m)^{\frac{1}{2}}, && \text{hexagonal equilibrium site.} \end{aligned} \quad (13)$$

The difference between the two sites arises from the fact that  $g$  equals two for the hexagonal site and four for the tetrahedral site. In calculating  $D_0$  from Eq. (9) we have set  $l$  equal to  $\frac{3}{4}a_0$ .

### IV. COMPARISON OF THEORY WITH EXPERIMENT

Using the value of 0.75 ev for  $\Delta U_{\text{pol}}$  found in Sec. II(B) and the values for  $\Delta U_{\text{rep}}$  listed for various impurities in Table I, it is possible to calculate the activation energy for diffusion as the difference between the two. The total energy is of course the absolute value of this difference. Depending on whether the repulsive energy is greater or smaller than 0.75 ev, the equilibrium site will be tetrahedral or hexagonal. The proper value for  $D_0$  from Eq. (13) can then be chosen, and the diffusion constant can be computed.

In comparing theory and experimental data it is best to treat lithium separately from other elements. In the first place, lithium has been studied extensively, and its diffusivity is well known over a wide range of temperature. In the second place, since it exists only in interstitial form, the complication of isolating interstitial diffusion from total diffusion does not exist. The diffusion of lithium in germanium and silicon has been

<sup>23</sup> See for example: R. C. Tolman, *Statistical Mechanics* (Oxford University Press, New York, 1938), Chap. XIV.

<sup>24</sup> E. M. Conwell, Proc. Inst. Radio Engrs. **40**, 1327 (1952).

<sup>25</sup> M. Cardona, W. Paul, and H. Brooks, J. Phys. Chem. Solids **8**, 204 (1959).

TABLE II. Comparison of theoretical and experimental results<sup>a</sup> for  $D_0$  and  $\Delta U^{\text{diff}}$  for lithium in germanium and silicon.

	$D_0$ (calc)	$D_0$ (exp)	$\Delta U^{\text{diff}}$ (calc)	$\Delta U^{\text{diff}}$ (exp)
	(cm <sup>2</sup> /sec)		(ev)	
Li in Ge	$1.7 \times 10^{-3}$	$2.5 \times 10^{-3}$	0.57	0.51
Li in Si	$1.6 \times 10^{-3}$	$2.3 \times 10^{-3}$	0.53	0.66

<sup>a</sup> See reference 1.

studied by means of the  $p$ - $n$  junction method with and without electric field by Fuller and Ditzenger,<sup>26</sup> by Fuller and Severiens,<sup>8</sup> and by an out-diffusion method by Pell.<sup>27</sup> At low temperatures the diffusion constants have been obtained from ion-pairing experiments by Maita<sup>28</sup> as well as by the ion-drift method developed by Pell.<sup>29</sup> Agreement between the various methods is quite remarkable.<sup>1</sup> In Table II we compare the experimental results with those derived here theoretically. It should be emphasized that according to our theory the equilibrium site for lithium is the hexagonal site, and the saddle-point position is the tetrahedral site. As shown in the Appendix, however, appreciable displacement from the center is likely to occur.

In general, the agreement of theory and experiment is quite satisfactory. Somewhat disturbing is the failure of the theory to predict any marked difference in the activation energy for diffusion for germanium and silicon. Since the theory predicts the same value for  $\Delta U_{\text{po1}}$  and a slightly larger value for  $\Delta U_{\text{rep}}$  for silicon, it predicts a lower activation energy for diffusion for silicon than for germanium, contrary to experimental data. The author is unable to offer an explanation for this discrepancy.

Other elements which can exist in substitutional as well as interstitial form, such as copper, silver, or gold, appear to diffuse by the so-called dissociative mechanism. This mechanism, first suggested by Frank and Turnbull<sup>30</sup> to explain the diffusion of copper into

 TABLE III. Calculated values for  $D_0$  and<sup>a</sup>  $\Delta U^{\text{diff}}$  for sodium, copper, silver, and Gold in germanium and silicon.

	Ionic radius (A)	Germanium		Silicon	
		$D_0$ (cm <sup>2</sup> /sec)	$\Delta U^{\text{diff}}$ (ev)	$D_0$ (cm <sup>2</sup> /sec)	$\Delta U^{\text{diff}}$ (ev)
Sodium	0.95	$4 \times 10^{-4}$	0.22	$2 \times 10^{-4}$	0.07
Copper	0.96	$3 \times 10^{-4}$	0.21	$2 \times 10^{-4}$	0.06
Silver	1.26	$9 \times 10^{-4}$	0.60	$11 \times 10^{-4}$	1.05
Gold	1.37	$9 \times 10^{-4}$	1.08	$10 \times 10^{-4}$	1.55

<sup>a</sup>  $\Delta U^{\text{diff}} = |\Delta U_{\text{po1}} - \Delta U_{\text{rep}}| = |0.75 - \Delta U_{\text{rep}}|$ , where  $\Delta U_{\text{rep}}$  is taken from Table I. The theory predicts that the equilibrium site for copper and sodium is the hexagonal site, and the tetrahedral site is the saddle point. For the other elements the situation is reversed. It is of interest that no experimental data are available for sodium.

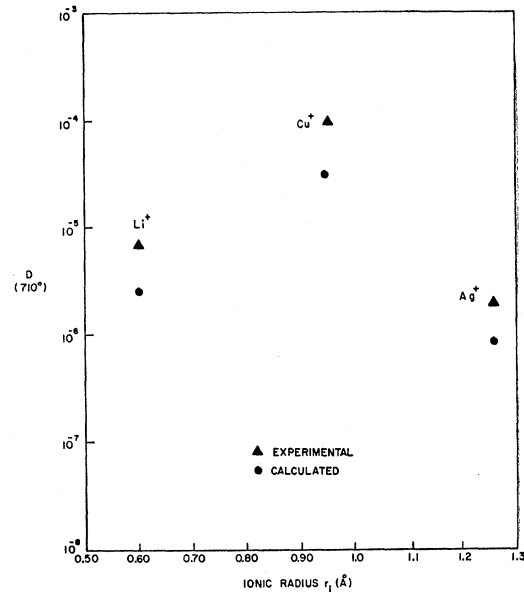
<sup>26</sup> C. S. Fuller and J. A. Dietzenberger, J. Appl. Phys. **28**, 40 (1957).

<sup>27</sup> E. M. Pell, Phys. Rev. **119**, 1014 (1960).

<sup>28</sup> J. P. Maita, J. Phys. Chem. Solids **4**, 68 (1958).

<sup>29</sup> E. M. Pell, Phys. Rev. **119**, 1222 (1960).

<sup>30</sup> F. C. Frank and D. Turnbull, Phys. Rev. **104**, 617 (1956).


 FIG. 4. Calculated and experimental values for the diffusion constants of  $\text{Li}^+$ ,  $\text{Cu}^+$ , and  $\text{Ag}^+$  in germanium.

germanium, explains the dependence of the diffusivity on the dislocation content of the crystals. The proposal that copper exists both in interstitial and in substitutional form was first made by van der Maesen and Brenkman,<sup>31</sup> and the dependence of the diffusivity on dislocation content was first observed by Fuller and Ditzenger.<sup>26</sup> When dissociative diffusion takes place the effective diffusion constant is not equal to the diffusion constant of the interstitial species alone.<sup>1</sup> In dislocation-free material, however, it is possible to isolate the diffusion of the interstitial species. Working with such material, Tweet has studied the diffusion of copper into germanium,<sup>32</sup> and Wei has recently studied that of silver into germanium.<sup>33</sup> Tweet found too much scatter in the data to allow him to calculate an activation energy for diffusion, but states that it is certainly less than 0.5 ev. Wei measured diffusion at only one temperature, namely 710°C. In Fig. 4 we plot the calculated and the experimental values of the diffusion constants at that temperature against the ionic radius of the impurity for lithium, copper, and silver in germanium. The agreement with experiment is quite satisfactory, and the graph clearly brings out the idea of an optimum size for the diffusing ion. In Table III we also present the values for  $D_0$  and  $\Delta U^{\text{diff}}$  calculated with our theory. It is hoped that future experiments with diffusion into dislocation free crystals will be used to check these values. It is worthwhile to point out that the theory predicts an even larger diffusion constant for copper in silicon than in germanium.

<sup>31</sup> F. van der Maesen and J. A. Brenkman, J. Electrochem. Soc. **102**, 229 (1955).

<sup>32</sup> A. G. Tweet, J. Appl. Phys. **30**, 202 (1959).

<sup>33</sup> L. Y. Wei, J. Phys. Chem. Solids **18**, 162 (1961).

Diffusion studies of copper, silver, and gold in germanium and silicon without regard to the role of dislocations in the diffusion process have been fairly extensive.<sup>34</sup> It is felt that there is no point in comparing the experimental data with our theory since neither agreement nor disagreement would be convincing in view of the fact that the measured diffusion constants will not, in general, reflect the diffusion constant of the interstitial species alone. Agreement of theory with these experimental data is generally within one or two orders of magnitude.

## V. DISCUSSION

It is first of all worthwhile to point out that the theory developed here is applicable with only minor modifications to any element or compound which crystallizes in the diamond or zincblende lattice. One interesting difference between these two lattices is the fact that there are two types of tetrahedral sites in the latter, one in which the four nearest neighbors are atoms *A* and the six next-nearest neighbors atoms *B*, and the other site in which the situation is reversed. There may thus be a preferred diffusion path in which one type of tetrahedral site is preferred over the other. This effect would, of course, show up most markedly in compounds in which the two constituent atoms differ markedly in size and polarizability; it would be interesting to study the diffusion of a given impurity such as lithium in a large number of compounds. In general, however, one might expect that the results obtained in this paper for germanium and silicon are valid for the compounds as well, making the hexagonal site the one favored for the reason of lowering the electrostatic energy, and the tetrahedral site the one with a lower repulsive energy. Hence, one would expect an optimum ion size for diffusion, and in particular one would expect copper to have a high diffusivity. Recent results by Fuller and Wolfstirn on Li in GaAs<sup>35</sup> and by Hall and Racette on copper in GaAs,<sup>36</sup> confirm that copper diffuses more rapidly than Lithium.

The idea of an optimum diffusion size for an interstitial impurity should also be applicable to such elements as hydrogen or helium. In this case, the attractive potential will be given by a van der Waals potential which falls off as the sixth power of distance.<sup>7</sup> We have estimated the van der Waals interaction energy of such an impurity with the host atoms out to eight shells

surrounding each site, and we find that in this case too the hexagonal site is favored. If, however, the repulsive energy is greater than the attractive energy, the tetrahedral site will be favored. Again, therefore, an atom or molecule of just the right size may diffuse with almost no activation energy. Since diffusion studies for neutral impurities have been limited to hydrogen and helium<sup>37</sup> not enough experimental evidence exists to test his hypothesis.

It is unfortunate that it is difficult to test separately the various approximations and parameters which have been employed in developing the theory presented here. The good agreement between theory and experiment is, of course, very gratifying, but it is always possible that a cancellation of the errors introduced by the various approximations and assumptions is responsible for it. To test the theory more rigorously, it is first of all desirable that diffusion studies in dislocation-free crystals be carried out with a larger number of elements and over a wider temperature range. Diffusion experiments carried out under hydrostatic pressure would also provide a valuable check on the theory. Such experiments may be difficult to do at high temperatures, but since ion-pairing permits a study of diffusion at very low temperatures such experiments are quite feasible.

In any case, it is hoped that the theory developed here, besides explaining such puzzling facts about interstitial diffusion as the great diffusivity of copper, will serve as a useful guide to the planning and interpretation of future experiments.

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## APPENDIX A. DISPLACEMENT OF THE ION FROM THE CENTER OF THE CAVITY

The theory developed in the body of the text assumes that the ion remains at the center of either the tetrahedral or the hexagonal cavity. Since a charge cannot be in a position of stable equilibrium with respect to electrostatic forces only, the ion may move away from the center of the cavity toward the host atoms until the opposing repulsive force becomes equal to the force of electrostatic origin which tends to displace it from the center. The effect will be most pronounced for a small ion like lithium and will decrease in importance for the larger ions. One may obtain an idea of the magnitude of the displacement and the correction it introduces to the energies calculated in the following manner:

<sup>34</sup> W. C. Dunlap, *Phys. Rev.* **97**, 614 (1955); J. D. Struthers, *J. Appl. Phys.* **27**, 1560 (1956); A. A. Bugay, V. E. Kosenko, and E. G. Miselyuk, *Zhur. Tekh. Fiz.* **27**, 1671 (1957); B. I. Boltaks and I. I. Sozinov, *ibid.* **28**, 679 (1958) [translation: *Soviet Phys.—Tech. Phys.* **2**, 1553 (1958)]; see reference 11; B. I. Boltaks, G. S. Kulikov, and R. Sh. Malkovich, *Fiz. Tverdogo Tela* **2**, 181 (1960) [translation: *Soviet Phys.—Solid State* **2**, 2134 (1961)].

<sup>35</sup> C. S. Fuller and K. B. Wolfstirn, *J. Appl. Phys.* (to be published).

<sup>36</sup> R. N. Hall and J. H. Racette, *Bull. Am. Phys. Soc.* **7**, 234 (1962).

<sup>37</sup> A. Van Wieringen and N. Warmoltz, *Physica* **22**, 849 (1956); R. C. Frank and J. E. Thomas, *J. Phys. Chem. Solids* **16**, 144 (1960).



If the charge is not at the center of a cavity of a dielectric, the continuum expression for the polarization energy is expressed in spherical harmonics,<sup>15</sup>

$$-U_{\text{pol}} = \frac{q^2}{2R_c} \left(1 - \frac{1}{K}\right) \times \left[1 + \frac{2}{3} \frac{\partial^2}{R_c^2} + \text{higher powers in } (\partial/R)\right], \quad (\text{A1})$$

where  $\partial$  is the displacement of the charge from the center of the cavity of radius  $R_c$ . It is clear that Eq. (10) is the leading term of this expansion. The total energy with the ion displaced from the center of a tetrahedral cavity will then be given to second order by

$$U^{\text{tot}} = -U_{\text{pol}}^0 \left[1 + \frac{2}{3} (\partial^2/R_c^2) + \dots\right] + \frac{1}{4} U_{\text{rep}}^0 (e^{\partial/\rho} + 3e^{-\partial/\rho}), \quad (\text{A2})$$

where the superscripts 0 indicate the value of the two energies with the ion at the center of the cavity. For the sake of simplicity we have chosen as the direction of displacement the direction toward one of the nearest host atoms. Each host atom with its associated next nearest neighbors contributed one quarter of the repulsive energy at the center. The factor  $g$  ( $g = \cos 71^\circ = 0.33$ ) in the exponent of the last term arises from the geometry of the tetrahedral site since  $\partial \cos 71^\circ$  is the projection of  $\partial$  in the direction toward one of the other three atoms. We differentiate Eq. (16) with respect  $\partial$  and set the derivative equal to zero:

$$-\frac{dU}{d\partial} = U_{\text{pol}}^0 \frac{4}{3} \frac{\partial}{R_c^2} - \frac{U_{\text{rep}}}{4\rho} (e^{\partial/\rho} - e^{-\partial/\rho}) = 0.$$

The resulting transcendental equation can be solved graphically for  $\partial_{\text{eq}}$ , the equilibrium displacement from the center; a value of  $\partial_{\text{eq}} = 0.41 \text{ \AA}$  was obtained for lithium in germanium. The change in total energy is then given by:

$$\begin{aligned} \Delta U^{\text{tot}} &= -U_{\text{pol}}^0 \frac{2}{3} (\partial_{\text{eq}}/R_c)^2 \\ &\quad + \frac{1}{4} U_{\text{rep}}^0 [(e^{\partial_{\text{eq}}/\rho} - 1) + 3(e^{-\partial_{\text{eq}}/\rho} - 1)] \\ &= -0.25 + 0.18 = -0.07 \text{ ev.} \end{aligned}$$

A similar calculation was carried out for the hexagonal case. Since the method of calculating the change in energy is similar to the one shown above the details of the calculation will not be given here. The resulting lowering in energy is 0.12 ev. The over-all change in the energy of diffusion is thus 0.05 ev in going from a hexagonal site to a tetrahedral site. The correction is undoubtedly less than the accuracy of our calculation and can be neglected. For larger ions than lithium the correction becomes even smaller.

## APPENDIX B. DISTORTION OF THE LATTICE SURROUNDING THE ION

The question arises as to how serious the approximation is of treating the lattice as stationary. The electrostatic forces will tend to pull the host atoms toward the ion, while the repulsive forces will tend to repel the lattice atoms. The displacement will stop when the forces tending to displace the lattice atoms are balanced by elastic restoring forces. Let us first consider the inward displacement of the lattice as a result of the electrostatic attraction. From Eq. (10) we see that the polarization energy is inversely proportional to the effective cavity radius  $R_c$ . Equation (10) treats the lattice as a continuum with a dielectric constant  $K$ . We shall call  $R_c$  the "dielectric" cavity radius to distinguish it from the "physical" cavity radius  $R_0$ , which we identify with the distance to the nearest neighbors. The dielectric cavity radius is obtained by inserting the value for the polarization energy calculated in Sec. II(B) into Eq. (10). For the tetrahedral site the value of  $0.26a_0$  is obtained, and for the hexagonal site a value of  $0.22a_0$ . These distances are approximately one half the "physical" cavity radius. We now regard the lattice as an elastic as well as a dielectric continuum, and we assume that, as the lattice contracts, the change in dielectric radius is approximately equal to the change in "physical" radius. The total energy will then be given by

$$U_{\text{pol}} = \frac{q^2}{2(R_c - \Delta R)} \left(1 - \frac{1}{K}\right) + 8\pi G R_0 (\Delta R)^2. \quad (\text{B1})$$

The second term on the right side of Eq. (B1) is the energy needed to expand a cavity of radius  $R_0$  by an amount  $\Delta R$  in an infinite elastic medium of shear modulus  $G$ .<sup>4,38</sup> We differentiate Eq. (B1) with respect to  $\Delta R$ , set the derivative equal to zero, and solve for  $\Delta R$ . For the tetrahedral site we find  $R \approx 0.1 \text{ \AA}$ . Substituting this value into Eq. (B1) we find that the polarization energy is increased by about 0.50 ev at the expense of about 0.25 ev of strain energy. Thus, since the polarization energy is about 5 ev, only about 5% of the total energy goes into distortional energy.

Similarly, to estimate the expansion of the lattice in order to reduce the Born-Mayer repulsive potential, we may write the total energy as

$$U_{\text{tot}} = U_{\text{rep}}^0 e^{-\Delta R/\rho} + 8\pi G R_0 (\Delta R)^2, \quad (\text{B2})$$

where it is understood that  $U_{\text{rep}}^0$  is the repulsive energy calculated by means of Eq. (8), i.e. with the impurity at the cavity center. We again differentiate with respect to  $\Delta R$ , set the derivative equal to zero, and solve for  $\Delta R$ . Using the rather high value of 1.5 ev for  $U_{\text{rep}}^0$  (see Table I), we find  $\Delta R$  approximately equal to  $0.08 \text{ \AA}$ . Substituting this value into Eq. (B2), we find that the Born-Mayer repulsive energy has been reduced by about 0.30 ev, at the expense of about 0.16 ev of elastic strain energy. In this case, approximately 10% of the

<sup>38</sup> K. Weiser, J. Phys. Chem. Solids 7, 118 (1958).

energy goes into lattice distortion. It must be remembered that the actual lattice expansion will be less because of the opposing tendency toward contraction due to the electrostatic attraction considered above.

We conclude that the contribution of lattice distortion to the energy of diffusion in the diamond lattice should be negligible (of the order of a few percent), except for much larger impurities than the ones considered here.

## Treatment of Ionized Impurity Scattering in Degenerate Semiconductors. Application of the Variational Technique in the Partial-Wave Method

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Using the partial-wave method, ionized impurity scattering in degenerate semiconductors is discussed. It is shown that the scattering process is adequately described by considering only the zeroth-order phase shift. By making use of Kohn's variational principle this quantity is determined analytically and an analytical formula is derived for the resistivity due to ionized impurity scattering alone.

### I. INTRODUCTION

IONIZED impurity scattering is an important factor in determining the charge transport in semiconductors. Theoretical treatments<sup>1</sup> of the scattering process make use either of the Born approximation<sup>2</sup> or of the more exact partial-wave method.<sup>3</sup> The latter approach has been used by Blatt<sup>4</sup> for discussing ionized impurity scattering in nondegenerate semiconductors. Unfortunately, the form of his scattering potential did not permit the derivation of analytical formulas for the phase shifts of the partial waves.

The present paper considers ionized impurity scattering in degenerate semiconductors. It is shown that in this case the scattering process is adequately described by considering only the zeroth-order phase shift. By making use of Kohn's variational principle<sup>5</sup> this quantity is determined analytically. As an example, the scattering of electrons by donor ions is discussed and an analytical formula is derived for the resistivity due to ionized impurity scattering alone. The scattering potential used is of the same form as that of Blatt,<sup>4</sup> namely a screened Coulombic potential.<sup>6</sup> It is assumed that in an elastic scattering act only one donor ion participates. As in Blatt's work, anisotropies in the electronic effective mass are ignored and a scalar effective mass is used.

<sup>1</sup> The subject is reviewed by F. J. Blatt, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 343 ff; H. Brooks, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1955), Vol. VII, p. 156 ff; W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), p. 258 ff.

<sup>2</sup> L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., p. 161 ff.

<sup>3</sup> See reference 2, p. 103 ff.

<sup>4</sup> F. J. Blatt, *J. Phys. Chem. Solids* **1**, 262 (1957).

<sup>5</sup> W. Kohn, *Phys. Rev.* **74**, 1763 (1948).

<sup>6</sup> R. B. Dingle, *Phil. Mag.* **46**, 831 (1955).

### II. CALCULATIONS

#### 1. Calculation of the Total Scattering Cross Section

In the partial-wave method<sup>3</sup> the total scattering cross section for elastic scattering of a particle by spherically symmetric potentials is given by

$$Q' = 2\pi \int_0^\pi \sigma(\vartheta) \sin\vartheta d\vartheta, \quad (1)$$

where

$$\sigma(\vartheta) = \frac{1}{k^2} \left| \sum_{l=0}^{\infty} (2l+1) e^{i\eta_l} \sin\eta_l P_l(\cos\vartheta) \right|^2 \quad (2)$$

is the differential scattering cross section. If a weighting factor is introduced for large-angle scattering, then Eq. (1) becomes,<sup>7</sup>

$$Q = 2\pi \int_0^\pi (1 - \cos\vartheta) \sigma(\vartheta) \sin\vartheta d\vartheta. \quad (3)$$

Using Eq. (2) one finds from Eq. (3) that

$$Q = \sum_{l=0}^{\infty} Q_l = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (l+1) \sin^2(\eta_l - \eta_{l+1}), \quad (4)$$

where  $\eta_l$  is the phase shift of the  $l$ th partial wave and  $k$  is the wave number of the scattered particle. Assuming a radius  $R$  beyond which the scattering potential is "negligible," the summation for practical computations extends<sup>3</sup> from  $l=0$  to a maximum  $l$  of the order of  $kR$ . In what follows it is assumed that the electron's energy is such that  $kR \gtrsim 1$ . In this case Eq. (4) reduces to

$$Q_0 = (4\pi/k^2) \sin^2(\eta_0 - \eta_1). \quad (5)$$

<sup>7</sup> K. Huang, *Proc. Phys. Soc. (London)* **60**, 161 (1948).