

## Relaxation and Activation Energies for an Interstitial Neutral Defect in an Alkali Halide Lattice\*

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A method has been developed for calculating the relaxation energy for an interstitial neutral defect in an alkali halide lattice by expanding the electrostatic, polarization, and dipole-dipole energy contributions to second order in terms of the displacements of the ions from their regular positions. The repulsive energy contributions involving the defect atom are treated exactly, whereas the repulsive contributions involving the regular ions themselves are also expanded to second order. This method has been applied to the case of an interstitial chlorine atom in NaCl for positions where the defect atom is at the center of a cube of ions and at the center of a square of ions; the difference when related to the same standard configuration gives an activation energy of approximately 0.5 eV for the migration of a neutral interstitial chlorine atom in NaCl.

### I. INTRODUCTION

**R**ADIATION damage studies<sup>1</sup> and color center studies<sup>2</sup> have focused considerable interest on the nature of defects in crystals. In the alkali halides Seitz,<sup>3</sup> Varley,<sup>4</sup> and St. James<sup>5</sup> have proposed models for the *V* centers, assuming them to be either single or paired vacancies, and Känzig *et al.*<sup>6</sup> have shown strong experimental evidence for the presence of molecular ions, for example Cl<sub>2</sub><sup>-</sup>, in which a neutral chlorine atom and a chlorine ion are joined by an attractive force. The presence of neutral atoms in the alkali halides was made understandable<sup>4</sup> by a mechanism in which ionizing radiation would strip several electrons from an anion, the neighboring ions then forcing it into an interstitial position where it would pick up electrons until it became neutral. The present method of calculation was developed to investigate the distortions around such a neutral atom and its activation energy for migration. The neutral atom is assumed to be close to a position of

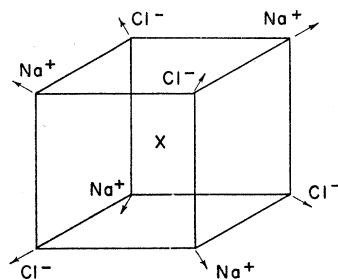


FIG. 1. Neutral interstitial atom (X) at the center of a cube of ions. The arrows indicate that on relaxation the ions will move outwards.

symmetry, either at the center of a cube of ions or at the center of a square of ions as shown in Figs. 1 and 2, and removed somewhat from the vacancy originally associated with the displacements. No special attractive part to the potential between the defect atom and its neighbors is assumed. The presence of attractive forces would tend to favor the production of a molecular ion; in this calculation we wish to find the stable positions under the influence of the crystal forces alone.

Various methods have been developed for the calculation of relaxation energies, i.e., energies associated with ions displaced from their normal lattice positions. Mott and Littleton<sup>7</sup> treated the relaxation around the vacancy in alkali halides and assumed a polarizable medium past the first shell of neighbors. In this case the defect possesses a net charge and the electric fields so produced are relatively large, making necessary special consideration for the polarization terms. Kurosawa *et al.*<sup>8</sup> have studied the polarization contributions in some detail, paying special attention to overlap. Several recent models of the polarization have been developed by Lundquist,<sup>9</sup> following the work of Löwdin<sup>10</sup> on wave functions in ionic crystals, and by Woods *et al.*<sup>11</sup> based on a phenomenological method. For the neutral defects considered here the simple point-ion model of polarization effects should be appropriate since the main energies will be repulsive in nature. Tosi and Fumi<sup>12</sup> and Guccione *et al.*<sup>13</sup> have been concerned with the influence

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<sup>1</sup> See, e.g., G. J. Dienes and G. H. Vineyard, *Radiation Effects in Solids* (Interscience Publishers, Inc., New York, 1957).

<sup>2</sup> See, e.g., F. Seitz, *Revs. Modern Phys.* **18**, 384 (1946).

<sup>3</sup> F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954).

<sup>4</sup> J. H. O. Varley, *J. Nuclear Energy* **1**, 130 (1954); *Nature* **174**, 886 (1954).

<sup>5</sup> D. St. James, *J. Phys. Radium* **17**, 907 (1956); **18**, 260 (1957).

<sup>6</sup> W. Känzig, *Phys. Rev.* **99**, 1890 (1955); T. Castner and W. Känzig, *J. Phys. Chem. Solids* **3**, 178 (1957); T. O. Woodruff and W. Känzig, *ibid.* **5**, 268 (1958); W. Känzig and T. O. Woodruff, *ibid.* **9**, 70 (1959).

<sup>7</sup> N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.* **34**, 485 (1938).

<sup>8</sup> J. Kurosawa, *J. Phys. Soc. Japan* **13**, 153 (1958), J. Yamashita and J. Kurosawa, *ibid.* **10**, 610 (1955).

<sup>9</sup> S. O. Lundquist, *Arkiv Fysik* **12**, 263 (1957).

<sup>10</sup> P. Löwdin, *Phys. Rev.* **99**, 1474, 1490, 1509 (1955); *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 1.

<sup>11</sup> A. D. B. Woods, W. Cochran, and B. N. Brockhouse, *Phys. Rev.* **119**, 980 (1960).

<sup>12</sup> F. G. Fumi and M. P. Tosi, *Discussions Faraday Soc.* **23**, 92 (1957), *Nuovo cimento* **2**, 95 (1950).

<sup>13</sup> R. Guccione, M. P. Tosi, and M. Asdente, *J. Phys. Chem. Solids* **10**, 162 (1959).

of different repulsive interactions on the migration energies in the alkali halides. Both the Born-Mayer exponential form and an inverse twelfth power in the distance have been used. The Born-Mayer exponential form is used in this work. In the calculations presented here the crystal is not considered to be a polarizable continuum, but as in other work on neutral defects, for example the divacancy calculation of Dienes,<sup>14</sup> the contributions from each individual ion are summed. Since the neutral atom is a "large" defect, particular attention was given to the repulsive energies, and, as the calculations show, they mainly determine the relaxed positions of the ions surrounding the defect.

Thus, the calculations to be described represent an investigation of the distortion around a neutral defect in alkali halides and of the activation energy for migration of such a defect within the framework of classical crystal forces. In Sec. II the notation and some general formulas are described; in Secs. III-VI the expressions are developed for the various energy terms; Secs. VII-VIII contain the energy calculations for the two configurations of the neutral atom depicted in Figs. 1 and 2; the activation energy is discussed in Sec. IX; and in Sec. X a brief discussion is given of the limitations and possible improvements of the present method of calculation.

## II. NOTATION AND GENERAL FORMULAS

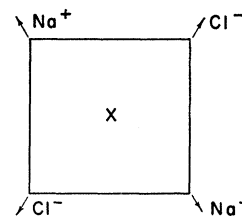
Some of the regular ions of the crystal will be displaced from their normal positions by interaction with the defect. Capital letters, such as  $N, M$ , will be used to refer to these movable ions. The fixed ions will be referred to by Greek letters as  $\alpha, \beta$ . Small letters as  $i, j$  will be used to refer to all the ions of the crystal. The notation for physical parameters is the following:  $\mathbf{r}_i$  = position vector of ion at its normal position,  $\mathbf{r}'_i$  = position vector of ion at its relaxed position,  $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$  = vector joining two ions in their normal positions,  $\mathbf{r}'_{ij} = \mathbf{r}'_i - \mathbf{r}'_j$  = vector joining two ions in their relaxed positions,  $r_{ij}, r'_{ij}$  = distances between ions,  $e_i$  = ionic charge, and  $\alpha_i$  = polarizability. The coordinate system used is illustrated in Fig. 3. In the current study, the position of the neutral defect will be either  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  for the cube-center position or  $(\frac{1}{2}, \frac{1}{2}, 0)$  for the square-center position with the unit of distance being  $r_0$ , the anion-cation separation.

The expressions for the various energies involve, in general, summations over all the ions in the crystal in their relaxed positions. It is convenient to separate this into a sum over the movable ions in their relaxed positions plus a sum over the fixed ions,

$$\sum_i f(\mathbf{r}'_i) = \sum_N f(\mathbf{r}'_N) + \sum_\alpha f(\mathbf{r}_\alpha). \quad (1)$$

where  $f(\mathbf{r}_i)$  is some function of the coordinate vector

FIG. 2. Neutral interstitial atom (X) at the center of a square of ions, with arrows indicating the relaxation of the surrounding ions.



of ion  $i$ . The sum over  $\alpha$  may be rewritten to give

$$\sum_i f(\mathbf{r}'_i) = \sum_N [f(\mathbf{r}'_N) - f(\mathbf{r}_N)] + \sum_k f(\mathbf{r}_k). \quad (2)$$

In this way a sum over all the ions in their relaxed positions has been separated into two sums; one over the movable ions only, and the other over all the ions of the crystal in their regular positions. The procedure is then to expand the sum over the movable ions by Taylor's series up to second order in  $\mathbf{r}'_N - \mathbf{r}_N \equiv \Delta \mathbf{r}_N$ . Some of these sums are available in the literature, others vanish because of symmetry; the others that are needed are computed. The electrostatic energy terms do not involve the neutral defect atom, and are a double sum over all the ions. Similarly, the polarization energy terms that do not involve the defect atom are a triple sum while the dipole-dipole terms are a quadruple sum. The repulsive energy terms that do not involve the additional atom are treated by the expansion method but the terms involving the additional atom will be calculated exactly.

Expanding the first summation in Eq. (2) by Taylor's series to terms of second order gives

$$f(\mathbf{r}'_N) - f(\mathbf{r}_N) = \nabla_N f(\mathbf{r}_N) \cdot \Delta \mathbf{r}_N + \frac{1}{2} \Delta \mathbf{r}_N \cdot \nabla_N \nabla_N f(\mathbf{r}_N) \cdot \Delta \mathbf{r}_N, \quad (3)$$

where  $\nabla_N$  is the gradient with respect to the variables  $x_N, y_N, z_N$  and the dots represent the scalar product of the vectors involved. Summing over all the ions (fixed and movable) gives

$$\sum_i f(\mathbf{r}'_i) = \sum_N [\nabla_N f(\mathbf{r}_N) \cdot \Delta \mathbf{r}_N + \frac{1}{2} \Delta \mathbf{r}_N \cdot \nabla_N \nabla_N f(\mathbf{r}_N) \cdot \Delta \mathbf{r}_N] + \sum_k f(\mathbf{r}_k). \quad (4)$$

Equation (4) refers to functions involving one variable  $\mathbf{r}_i$ . This expression can be extended to a function of several variables by iteration of the procedure to obtain

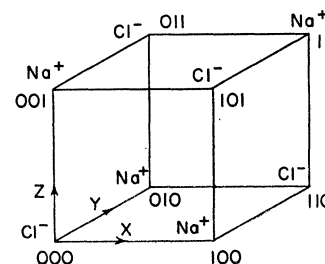


FIG. 3. The coordinate system used in describing the crystal.

<sup>14</sup> G. J. Dienes, J. Chem. Phys. 16, 620 (1948).

the general expression<sup>15</sup>

$$\begin{aligned} & \sum_{ij \dots n} [f(\mathbf{r}'_i, \mathbf{r}'_j, \dots, \mathbf{r}'_n) - f(\mathbf{r}_i, \mathbf{r}_j, \dots, \mathbf{r}_n)] \\ &= \sum_N \{ \sum_{j \dots n} \nabla_N [f(\mathbf{r}_N, \mathbf{r}_j, \dots, \mathbf{r}_n) + f(\mathbf{r}_j, \mathbf{r}_N, \dots, \mathbf{r}_n) + \dots + f(\mathbf{r}_j, \dots, \mathbf{r}_N)] \} \cdot \Delta \mathbf{r}_N \\ &+ \frac{1}{2} \sum_N \Delta \mathbf{r}_N \cdot \{ \sum_{j \dots n} \nabla_N \nabla_N [f(\mathbf{r}_N, \mathbf{r}_j, \dots, \mathbf{r}_n) + \dots + f(\mathbf{r}_j, \dots, \mathbf{r}_N)] \} \cdot \Delta \mathbf{r}_N \\ &+ \sum_{ML} \Delta \mathbf{r}_M \cdot \{ \sum_{i \dots n} \nabla_M \nabla_L [f(\mathbf{r}_M, \mathbf{r}_L, \mathbf{r}_i, \dots, \mathbf{r}_n) + f(\mathbf{r}_M, \mathbf{r}_i, \mathbf{r}_L, \dots, \mathbf{r}_n) + \dots + f(\mathbf{r}_i, \dots, \mathbf{r}_M, \mathbf{r}_L)] \} \cdot \Delta \mathbf{r}_L. \quad (5) \end{aligned}$$

It is to be noted that in Eq. (5) the number of functions for each of the first two terms on the right-hand side is  $n$ , while the number of functions that will appear in the third term will be the number of pairs chosen from  $n$  quantities or  $n(n-1)/2$ .

### III. ELECTROSTATIC ENERGY TERMS

The electrostatic energy for all the ions in their relaxed or movable positions is

$$\sum_{ij(i \neq j)} \frac{1}{2} (e_i e_j / r_{ij}'),$$

so that  $f(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{2} (e_i e_j / r_{ij}')$  in Eq. (5). Equation (5) reduces to a double sum in which many terms vanish by

symmetry. The final result is

$$\Delta E_s = A_s \sum_{NL(N \neq L)} \Delta \mathbf{r}_N \cdot \left\{ \frac{\epsilon_N \epsilon_L}{r_{NL}^5} [r_{NL}^2 \mathbf{I} - 3 \mathbf{r}_{NL} \mathbf{r}_{NL}] \right\} \cdot \Delta \mathbf{r}_L, \quad (6)$$

where  $\Delta E_s$  = difference in electrostatic energy in ev,  $\epsilon_N = e_N / |e_N|$  (and similarly for  $\epsilon_L$ ),  $A_s = \frac{1}{2} (e^2 / r_0)$  (= 2.56 ev for NaCl),  $r_0$  = internuclear separation, and  $\mathbf{I}$  = unit dyadic.

One can examine the electrostatic potential in the rigid lattice at a position  $(x, y, z)$  near the ion site  $(0, 0, 0)$ , with the ion at  $(0, 0, 0)$  missing, by making use of the following expression<sup>16</sup>:

$$\begin{aligned} \frac{r_0 V}{e} = & - \sum_{H_i} \frac{\exp[-\frac{1}{4}\pi \sum (2H_i - 1)^2] \{ 8 \cos[\pi x(2H_1 - 1)] \cos[\pi y(2H_2 - 1)] \cos[\pi z(2H_3 - 1)] \}}{\frac{1}{4}\pi \sum (2H_i - 1)^2} \\ & + \frac{\Phi([\pi(x^2 + y^2 + z^2)]^{\frac{1}{2}})}{(x^2 + y^2 + z^2)^{\frac{1}{2}}} \sum_n \frac{G(\pi^{\frac{1}{2}}[(n_1 - x)^2 + (n_2 - y)^2 + (n_3 - z)^2]^{\frac{1}{2}})}{[(n_1 - x)^2 + (n_2 - y)^2 + (n_3 - z)^2]^{\frac{1}{2}}} (-1)^{n_1 + n_2 + n_3}, \quad (7) \end{aligned}$$

where the  $H_i$ 's take on all positive integer values, the function  $\Phi$  is given by

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-x^2) dx,$$

the values of  $n_1$ ,  $n_2$ , and  $n_3$  being all positive integers except the combination 0, 0, 0, this being the meaning of the prime on the  $S_n$ , and finally

$$G(x) = 1 - \Phi(x).$$

Expansion of Eq. (7) to fourth order in  $x, y, z$  gives

$$\begin{aligned} r_0 V / e = & 1.7473 + 3.7(x^4 + y^4 + z^4) \\ & - 10.8(x^2 y^2 + x^2 z^2 + y^2 z^2). \quad (8) \end{aligned}$$

<sup>15</sup> A detailed discussion of Eq. (5) and of several other equations in this paper is given in the Appendix which has been deposited as Document No. 6822 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints or \$1.25 for 35 mm microfilms. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

From this expansion the electric field at  $(x, y, z)$  involves terms of third order and the gradient of the electric field terms of second order. Both terms vanish when the ion is at its lattice position. By taking the gradient of Eq. (7) or Eq. (8) the electric field may be conveniently calculated. It would be needed when the additional atom is at any position other than a symmetrical one, as for example when it is allowed to be placed along the diagonals of the basic cube or square. By using Laplace's equation  $\nabla^2 V = 0$  we see that the coefficients of the  $x^4$  and  $x^2 y^2$  are related by  $3.7 \cong 10.8/3$  and also that the  $x^2$  term must vanish.

### IV. POLARIZATION ENERGY TERMS

#### (a) Terms Not Involving the Additional Atom

The polarization energy of a polarizable ion, made up of the energy of formation of a dipole and the energy of interaction between the dipole and the electric field is

$$-\frac{1}{2} \alpha E^2,$$

where  $\alpha$  is the polarizability and  $\mathbf{E}$  the electric field at

<sup>16</sup> P. P. Ewald, Ann. Physik 64, 253 (1921).

the ion's position. In the undisturbed lattice this term vanishes since the electric field is zero at the ion's position. However, with relaxation around a defect this term can be important. As the type of defect considered here is neutral the regular ions and the defect may be considered separately. For the regular ions the energy becomes

$$\sum_i (-\frac{1}{2}\alpha_i E_i^2),$$

where  $\mathbf{E}_i$  is the electric field at the position of ion  $i$ . When the ions are in their relaxed positions this electric

field is a sum over the contribution from each ion so that the energy becomes

$$\sum_{\substack{ijk \\ (i \neq j, i \neq k)}} \left( -\frac{1}{2} \alpha_i \frac{e_j \mathbf{r}_{ij}'}{r_{ij}'^3} \cdot \frac{e_k \mathbf{r}_{ik}'}{r_{ik}'^3} \right). \quad (9)$$

We note that the restrictions on the ions do not disallow  $j=k$ . Equation (5) then involves a triple sum. After considerable reduction the expression for this polarization energy term becomes

$$\Delta E_p = \sum_{NL} \Delta \mathbf{r}_N \cdot \left[ \left( -\frac{1}{2} \epsilon_N \epsilon_L \right) \sum_i \alpha_i \left( \frac{-3 \mathbf{r}_{iL} \mathbf{r}_{iL}}{r_{iL}^5 r_{iN}^3} - \frac{3 \mathbf{r}_{iN} \mathbf{r}_{iN}}{r_{iN}^5 r_{iL}^3} + \frac{\mathbf{I}}{r_{iN}^3 r_{iL}^3} + \frac{9(\mathbf{r}_{iN} \cdot \mathbf{r}_{iL}) \mathbf{r}_{iN} \mathbf{r}_{iL}}{r_{iL}^5 r_{iN}^5} \right) \right] \cdot \Delta \mathbf{r}_L. \quad (10)$$

It is to be noted that the double sums over all of the ions of the lattice have disappeared through symmetry, leaving a single sum over  $i$ , with the restriction that  $i$  should not equal either  $L$  or  $N$ . Once these sums are calculated then a double sum over the movable ion remains. The sums over  $i$  must be computed for each different pair of ions  $L, N$  and there is a pair of sums for each case, one over the anions, with polarizability

$\alpha_-$  and one over the cations, with polarizability  $\alpha_+$ . However, it is again possible to reduce considerably, by symmetry, the number of sums necessary, e.g., for similar length vectors joining  $L$  and  $N$  the results are related. Letting  $e_N = \epsilon_N |e|$ ,  $\alpha_+ = \alpha_+' \times 10^{-24}$ ;  $e_L = \epsilon_L |e|$ ,  $\alpha_- = \alpha_-' \times 10^{-24}$ , expressing distances in terms of the anion-cation distance  $r_0$ , and expressing the energy in ev, one obtains from Eq. (10)

$$\Delta E_p = A_p \sum_{NL} \Delta \mathbf{r}_N \cdot \left\{ (\epsilon_N \epsilon_L) \left[ \sum_{i+} \alpha_+' \left( \frac{-3 \mathbf{r}_{iL} \mathbf{r}_{iL}}{r_{iL}^5 r_{iN}^3} - \frac{3 \mathbf{r}_{iN} \mathbf{r}_{iN}}{r_{iN}^5 r_{iL}^3} + \frac{\mathbf{I}}{r_{iN}^3 r_{iL}^3} + \frac{9(\mathbf{r}_{iN} \cdot \mathbf{r}_{iL}) \mathbf{r}_{iN} \mathbf{r}_{iL}}{r_{iL}^5 r_{iN}^5} \right) \right. \right. \\ \left. \left. + \sum_{i-} \alpha_-' \left( -\frac{3 \mathbf{r}_{iL} \mathbf{r}_{iL}}{r_{iL}^5 r_{iN}^3} - \frac{3 \mathbf{r}_{iN} \mathbf{r}_{iN}}{r_{iN}^5 r_{iL}^3} + \frac{\mathbf{I}}{r_{iN}^3 r_{iL}^3} + \frac{9(\mathbf{r}_{iN} \cdot \mathbf{r}_{iL}) \mathbf{r}_{iN} \mathbf{r}_{iL}}{r_{iL}^5 r_{iN}^5} \right) \right] \right\} \cdot \Delta \mathbf{r}_L, \quad (11)$$

where

$$A_p = \left( -\frac{1}{2} \frac{e^2}{r_0^4} \times 10^{-24} \right).$$

For sodium chloride  $A_p = (-0.115)$  ev. To simplify the summations one of the ions  $L$  or  $N$  can always be taken as the ion at the origin, and as we are summing the components of a tensor, by examining the symmetries of  $L$  and  $N$  many of the components can be seen to be related. In addition many summations vanish through symmetry. Furthermore, by writing  $\mathbf{r}_{iL}$  as  $\mathbf{r}_i - \mathbf{r}_L$ , some summations already obtained in connection with previous expressions can be used.

### (b) Terms Involving the Additional Atom

If the interstitial is placed at the cube-center or square-center position, then the electric field on it is zero in the rigid lattice. However, because of relaxation an electric field may act on it if the relaxation is not symmetrical about the interstitial. Also, if the additional atom is slightly off its central position, then an electric field is present even in the undistorted lattice. If  $\mathbf{r}_v$  and  $\mathbf{r}_v'$  refer to the additional atom, then the polariza-

tion energy is given by

$$-\frac{1}{2} \alpha_v \sum_{jk} \frac{e_j \mathbf{r}_{vj}'}{r_{vj}'^3} \cdot \frac{e_k \mathbf{r}_{vk}'}{r_{vk}'^3}.$$

Expressing the above term as

$$\sum_v \left( \sum_{jk} f(\mathbf{r}_v', \mathbf{r}_j', \mathbf{r}_k') \right),$$

and using Eq. (5) for the double summation and Eq. (3) for the terms with index  $v$ , one obtains

$$\Delta E_{PA} = 2 \sum_M \Delta \mathbf{r}_v \cdot \left[ \sum_l \nabla_v \nabla_M f(\mathbf{r}_v, \mathbf{r}_M, \mathbf{r}_l) \right] \cdot \Delta \mathbf{r}_M \\ + \left[ \sum_{jk} \nabla_v f(\mathbf{r}_v, \mathbf{r}_j, \mathbf{r}_k) \right] \cdot \Delta \mathbf{r}_v \\ + \frac{1}{2} \Delta \mathbf{r}_v \cdot \left[ \sum_{jk} \nabla_v \nabla_v f(\mathbf{r}_v, \mathbf{r}_j, \mathbf{r}_k) \right] \cdot \Delta \mathbf{r}_v, \quad (12)$$

with the  $f$  function as indicated above. We note once again the appearance of double sums over all the ions of the lattice. However, carrying out the differentiation and making use of the fact that the additional atom is originally in a symmetrical position, these sums vanish.

The single sum also vanishes in this case by symmetry considerations, so that there is no additional polarization energy, to the order considered here, for the additional atom. The reason for this can be understood by considering expansions of the electric field in a crystal in the neighborhood of the cube-center or square-center position. As in Eq. (8) the terms in  $x^2$ , etc. will vanish. With this term vanishing, only the repulsive interactions of the additional atom need be considered and the electrical energies can be computed independently of the type of neutral atom present. Since the expansions are in terms of the distance of a relaxed ion from its normal position, this restriction must apply to the additional atom as well, so that in this approximation cases cannot be treated where the interstitial is placed at arbitrary large distances from the symmetry positions. Such cases can, however, be treated by expanding about the new position of the interstitial and possibly also about a new position for a nearby displaced ion which may have been moved a large distance from a lattice position.

#### V. DIPOLE-DIPOLE ENERGY TERMS

Since the interstitial is not polarized in the configurations considered here, only the regular ions of the lattice enter into the dipole-dipole energy calculations.

The dipole-dipole interaction energy of two polarizable ions of polarizabilities  $\alpha_1$  and  $\alpha_2$  and separation  $\mathbf{r}_{21}$  is given by

$$V_{d-d} = \alpha_1 \alpha_2 \left( \frac{\mathbf{E}_1 \cdot \mathbf{E}_2}{r_{21}^3} - \frac{3(\mathbf{r}_{21} \cdot \mathbf{E}_1)(\mathbf{r}_{21} \cdot \mathbf{E}_2)}{r_{21}^5} \right),$$

where  $\mathbf{E}_1$  is the electric field at the ion 1 caused by the ion at 2 and  $\mathbf{E}_2$  is the electric field at ion 2 caused by the ion at 1. For all the regular ions in the lattice in

arbitrary relaxed positions, this energy is

$$V_{d-d} = \sum_{ij (i \neq j)} \frac{1}{2} \alpha_i \alpha_j \left( \frac{\mathbf{E}_i'(k') \cdot \mathbf{E}_j'(l')}{r_{ij}{}^3} - \frac{3[\mathbf{r}_{ij}' \cdot \mathbf{E}_i'(k')][\mathbf{r}_{ij}' \cdot \mathbf{E}_j'(l')]}{r_{ij}{}^5} \right), \quad (13)$$

where  $\mathbf{E}_i'(k')$  represents the electric field at ion  $i$  in its relaxed position caused by all the other ions in their relaxed positions, with a similar definition for  $\mathbf{E}_j'(l')$ . Using

$$\mathbf{E}_i'(k') = \sum_{k (k \neq i)} \frac{e_k \mathbf{r}_{ik}'}{r_{ik}{}^3}$$

in Eq. (13), one obtains for the dipole-dipole interaction energy,  $\Delta E_D$ , the quadruple sum

$$\begin{aligned} \Delta E_D &= \sum_{ijkl} f(\mathbf{r}_i', \mathbf{r}_j', \mathbf{r}_k', \mathbf{r}_l') \\ &= \sum_{\substack{ijkl \\ (i \neq j, k \neq i, l \neq j)}} \frac{1}{2} \alpha_i \alpha_j \left[ \frac{e_k \mathbf{r}_{ik}' \cdot e_l \mathbf{r}_{jl}'}{r_{ik}{}^3 r_{jl}{}^3 r_{ij}{}^3} - \frac{3(\mathbf{r}_{ij}' \cdot e_k \mathbf{r}_{ik}')(\mathbf{r}_{ij}' \cdot e_l \mathbf{r}_{jl}')}{r_{ik}{}^3 r_{jl}{}^3 r_{ij}{}^5} \right]. \quad (14) \end{aligned}$$

Equation (5) is then applied, and in order to convert to eV we let  $\alpha_i = \alpha_i' \times 10^{-24}$ ,  $e_k = \epsilon_k |e|$  and  $A_p = \frac{1}{2}(e^2/r_0^7) \times [10^{-24}]^2$ , which is 0.0050 eV for the case of sodium chloride. The calculation of the complete expression for  $\Delta E_D$  in terms of the  $\Delta \mathbf{r}_N$  is straightforward but tedious. The triple sums over all ions and several of the double sums vanish because of symmetry. The terms remaining give

$$\begin{aligned} \Delta E_D &= A_p \sum_{MN} \Delta \mathbf{r}_N \cdot \epsilon_N \epsilon_M \left[ \sum_{\substack{ql \\ (q \neq l, q \neq M, l \neq N)}} \alpha_q' \alpha_l' \left( \frac{1}{r_{ql}{}^3 r_{qM}{}^3 r_{lN}{}^3} - \frac{3\mathbf{r}_{lN} \mathbf{r}_{lN}}{r_{ql}{}^3 r_{qM}{}^3 r_{lN}{}^5} - \frac{3\mathbf{r}_{qM} \mathbf{r}_{qM}}{r_{ql}{}^3 r_{qM}{}^5 r_{lN}{}^3} - \frac{3\mathbf{r}_{ql} \mathbf{r}_{ql}}{r_{ql}{}^5 r_{qM}{}^3 r_{lN}{}^3} \right) \right. \\ &\quad \left. + \frac{9(\mathbf{r}_{qM} \cdot \mathbf{r}_{lN}) \mathbf{r}_{lN} \mathbf{r}_{qM}}{r_{ql}{}^3 r_{qM}{}^5 r_{lN}{}^5} + \frac{9(\mathbf{r}_{ql} \cdot \mathbf{r}_{lN}) \mathbf{r}_{lN} \mathbf{r}_{ql}}{r_{qM}{}^3 r_{lN}{}^5 r_{ql}{}^5} + \frac{9(\mathbf{r}_{ql} \cdot \mathbf{r}_{qM}) \mathbf{r}_{ql} \mathbf{r}_{qM}}{r_{qM}{}^5 r_{lN}{}^3 r_{ql}{}^3} - \frac{27(\mathbf{r}_{ql} \cdot \mathbf{r}_{qM})(\mathbf{r}_{ql} \cdot \mathbf{r}_{lN}) \mathbf{r}_{lN} \mathbf{r}_{qM}}{r_{qM}{}^5 r_{lN}{}^5 r_{ql}{}^5} \right] \cdot \Delta \mathbf{r}_M. \quad (15) \end{aligned}$$

The reason for so many of the other terms vanishing is connected once again with the fact that the expansion of the electric field in the neighborhood of an ion is strongly convergent. Equation (15) contains a set of rather formidable double sums over all ions of the lattice, except for the particular restrictions, and these sums have to be evaluated for each pair of movable ions that are chosen. However the terms for pairs of ions connected by similar length vectors are simply related to each other. Since the dipole-dipole energy is inversely proportional to  $r^7$ , the terms decrease rapidly as a function of distance. Thus only a few of the terms are large enough to consider and in the applications

made in Secs. VII and VIII this term was estimated from the first terms of the series and treated as a correction to the main energy terms. It is to be noted that because of the appearance of the factors  $\alpha_q' \alpha_l'$  inside the summations it is necessary to separate the sum into four parts as follows

$$\begin{aligned} \sum_{q,l} \alpha_q' \alpha_l' \left( \right) &= \sum_{+,+} \alpha_+ \alpha_+ \left( \right) + \sum_{+,-} \alpha_+ \alpha_- \left( \right) \\ &\quad + \sum_{-,+} \alpha_- \alpha_+ \left( \right) + \sum_{-,-} \alpha_- \alpha_- \left( \right), \end{aligned}$$

where the +’s and -’s refer to a summation over cations and anions, respectively. One of the ions, say  $M$ , may be chosen as the (0,0,0) ion to simplify the expressions and, in order to take all cases into account, has to be considered alternately as a cation and as an anion in order to include all possible symmetry cases. One useful approximation in evaluating sums is to consider only cases where  $M$  and  $N$  are not more than two units apart, and to place a similar restriction on  $q$  and  $l$ ,  $q$  and  $M$ , and  $l$  and  $N$ . In other calculations of relaxation energy in the literature, these dipole-dipole and polarization terms had been approximated by the introduction of a polarizable medium. Certainly such a concept should apply far from the defect, but it is to be noted that the larger terms in the sum come from ions which are relatively close by.

$$\Delta E_R = \sum_{NL (N \neq L)} \Delta \mathbf{r}_N \cdot \left\{ \frac{A_{NL} R e^{-Rr_{NL}}}{2R_{NL}^3} [r_{NL}^2 \mathbf{I} - (1 + Rr_{NL}) \mathbf{r}_{NL} \mathbf{r}_{NL}] \right\} \cdot \Delta \mathbf{r}_L$$

$$+ \sum_N \Delta \mathbf{r}_N \left\{ \sum_{i \neq N} \frac{A_{Ni} R e^{-Rr_{Ni}}}{2r_{Ni}^3} [-r_{Ni}^2 \mathbf{I} + (1 + Rr_{Ni}) \mathbf{r}_{Ni} \mathbf{r}_{Ni}] \right\} \cdot \Delta \mathbf{r}_N. \quad (16)$$

Equation (16) contains a sum over all the ions of the crystal which converges quickly because of the exponential part. Since  $A_{Ni}$  will be chosen differently for the different pairs of ions four sums are necessary in order to have results good for an arbitrary alkali halide, if  $R$  is chosen the same for each. These sums will be variations on the expression

$$A_{N+} \sum_{+} \frac{e^{-Rr_{N+}}}{2r_{N+}^3} [-r_{N+}^2 \mathbf{I} + (1 + Rr_{N+}) \mathbf{r}_{N+} \mathbf{r}_{N+}], \quad (17)$$

where + represents the cations, by replacing + with - for anions and considering  $N$  as either an anion or a cation. In this sum  $N$  can be considered as the (0,0,0) ion whence from symmetry the off-diagonal terms are zero and the  $\mathbf{r}_{N+} \mathbf{r}_{N+}$  ones can be replaced by  $\frac{1}{3} r_{N+}^2 \mathbf{I}$ , so that Eq. (17) reduces to

$$A_{N+} \sum_{+} \frac{e^{-Rr_{N+}}}{3} \left\{ -\frac{1}{r_{N+}} + \frac{R}{2} \right\} \mathbf{I},$$

with similar expressions for the other terms. These summations can be easily evaluated on choosing a value for  $R$ . For  $R=8.14$ ,

$$\sum_{\text{odd}} \exp(-8.14r_i)/r_i = 0.001753,$$

$$\sum_{\text{even}} \exp(-8.14r_i)/r_i = 0.000085,$$

$$\sum_{\text{odd}} \exp(-8.14r_i) = 0.001756,$$

$$\sum_{\text{even}} \exp(-8.14r_i) = 0.000121,$$

## VI. REPULSIVE ENERGY TERMS

### (a) Terms Not Involving the Additional Atom

The exponential form,

$$A_{ij} e^{-Rr_{ij}}$$

was chosen for the repulsive energy between ions  $i$  and  $j$ , where  $A_{ij}$  has different values for different pairs of ions, and  $R$  is a constant which will be chosen the same for the different pairs but may be varied to see its importance. The method of choosing these constants will be presented in the next section; in this section expressions are derived for the repulsive energy for the various ions in the lattice. For all of the regular ions in the lattice in their relaxed positions, the repulsive energy is

$$\sum_{i,j (i \neq j)} \frac{1}{2} A_{ij} e^{-Rr_{ij}}.$$

Application of Eq. (5) gives

where “odd” refers to ions that can be reached from the origin by an odd number of steps and “even” to those that are reached by an even number of steps.

### (b) Terms Involving the Additional Atom

The expansion method is used for ions further away than the first shell. Representing the interaction constant by  $A_{vN}$  between the additional atom and ion  $N$ , and using the same  $R$  as before, this energy difference,  $\Delta E_{RA}$ , is, from Eq. (3)

$$\Delta E_{RA} = \Delta \mathbf{r}_v \cdot \left[ \sum_l (-\frac{1}{2} A_{vl} R) \left( \frac{\exp(-Rr_{vl})}{r_{vl}} \right) \right. \\ \left. \times \left( \mathbf{I} - \frac{(1 + Rr_{vl}) \mathbf{r}_{vl} \mathbf{r}_{vl}}{r_{vl}^2} \right) \right] \cdot \Delta \mathbf{r}_v. \quad (18)$$

Here  $l$  stands for those ions which are further away than the first shell and the  $\Delta \mathbf{r}_v$  is the displacement of the additional atom from its symmetrical position. This term can be further reduced by symmetry in the manner of Eq. (17).

For the nearest neighbors exact expressions will be used (in the sense that expansions are not employed) for the energy difference on relaxation. This energy  $\Delta E_{RS}$  is given by

$$\Delta E_{RS} = \sum_N A_{vN} (e^{-Rr_{vN'}} - e^{-Rr_{vN}}), \quad (19)$$

where the  $N$  ions are restricted to the first shell and will usually be considered to be among the movable

ions. Provision has been made here in the  $r_{vN}'$  term for the cases where the additional atom will be considered near its symmetrical position. In order to bring the  $\Delta\mathbf{r}_N$ 's into this expression we use

$$\mathbf{r}_{vN}' = \mathbf{r}_{vN} - \Delta\mathbf{r}_N + \Delta\mathbf{r}_v,$$

but treat the additional parts exactly.

All of the terms have now been derived, giving for the total energy of relaxation  $\Delta E$

$$\Delta E = \Delta E_S + \Delta E_P + \Delta E_D + \Delta E_R + \Delta E_{RA} + \Delta E_{RS}, \quad (20)$$

with  $\Delta E_S$  from Eq. (16),  $\Delta E_P$  from Eq. (11),  $\Delta E_D$  from Eq. (15),  $\Delta E_R$  from Eq. (16),  $\Delta E_{RA}$  from Eq. (18), and  $\Delta E_{RS}$  from Eq. (19).  $\Delta E$  is a function of the  $\Delta\mathbf{r}_N$  and  $\Delta\mathbf{r}_v$ . The equilibrium energy, for small  $\Delta\mathbf{r}_N$ 's and  $\Delta\mathbf{r}_v$ , may be obtained from the equations

$$\partial\Delta E/\partial(\Delta\mathbf{r}_N)_x = 0, \quad (21)$$

where  $x$  stands for the  $x$ ,  $y$ , or  $z$  component of  $\Delta\mathbf{r}_N$  and  $N$  takes on all values of the movable ions as well as the additional atom. In general Eq. (21) will be difficult to solve, especially when the additional atom takes on an unsymmetrical position, and the usual procedure will be to pick various values for the  $\Delta\mathbf{r}_N$ 's and, by examining Eq. (20), to find what choices will make it a minimum. It will be noticed that with the exception of  $\Delta E_{RS}$  all the terms have the form

$$\sum_{N,M} \Delta\mathbf{r}_N \cdot \mathbf{B}_{NM} \cdot \Delta\mathbf{r}_M,$$

where  $\mathbf{B}_{NM}$  is a tensor and  $N$  can equal  $M$ , taking care of the special cases where  $N=M$  by choosing  $\mathbf{B}_{NN}=0$ .

Equation (21) can also be used in a process of successive approximations by minimizing with respect to some of the  $\Delta\mathbf{r}_N$ 's first, and then, with these values fixed, minimizing again with respect to the other  $\Delta\mathbf{r}_N$ 's.

## VII. RELAXATION ABOUT THE CUBE-CENTER POSITION

As a first example, the general method is applied in this section to the case of a neutral chlorine atom situated at the center of a cube of ions in sodium chloride and the relaxation energy is computed with the chlorine atom considered fixed and only the first shell of  $\text{Cl}^-$  and  $\text{Na}^+$  ions movable. A symmetrical relaxation diagonally outward is assumed; the  $\text{Cl}^-$  ion (0,0,0) moves with  $\Delta\mathbf{r} = (-p, -p, -p)$  and the  $\text{Na}^+$  ion at (1,1,1) with  $\Delta\mathbf{r} = (q, q, q)$ , where  $p$  and  $q$  are the rectangular components of motion with the nearest-neighbor distances as unity. Equation (21) is applied to this two-parameter problem to solve for the  $p$  and  $q$  and hence for  $\Delta E$ . Two cases are treated, first without and then with the dipole-dipole correction term included.

The constants used in the repulsive interaction are obtained from the Born-Mayer form of interaction  $\Phi(r)$

between two ions,

$$\Phi(r) = C_{12}b \exp[(r_1 + r_2 - r)/\rho],$$

where  $r$  is the distance between the ions;  $r_1$  and  $r_2$  are the radii of the ions;  $\rho$  has an average value of  $0.345 \times 10^{-8}$  cm;  $C_{12} = 1 + Z_1/N_1 + Z_2/N_2$ , where  $Z_1$ ,  $Z_2$  and  $N_1$ ,  $N_2$  are the charges and number of outer electrons respectively for the two ions; and  $b$  is a constant for each alkali halide, being  $2.19 \times 10^{-13}$  erg for NaCl. For  $r_1$  and  $r_2$  the Goldschmidt radii are used: 1.81 Å for  $\text{Cl}^-$  and 0.98 Å for  $\text{Na}^+$ . The same form and the same  $b$  and  $\rho$  are used for the interactions involving the  $\text{Cl}^0$  atom. After comparing with the  $\text{Cl}^-$  radius and by calculating the average radius from the outer  $P$ -wave function for  $\text{Cl}^0$ ,

$$r_{\text{av}} = \int_0^\infty r P^2 dr / \int_0^\infty P^2 dr,$$

where  $P$  represents the wave function, we chose 1.56 Å for the  $\text{Cl}^0$  radius. The wave functions that were used<sup>17</sup> involved exchange. For NaCl,  $R$  is 8.14 and  $A_{ij}$  (in eV) has the following values for the different interactions:

$$\begin{aligned} \text{Cl}^- - \text{Cl}^-, & 3850; \quad \text{Cl}^- - \text{Cl}^0, & 2190; \quad \text{Cl}^- - \text{Na}^+, & 466; \\ \text{Na}^+ - \text{Cl}^0, & 252; \quad \text{Na}^+ - \text{Na}^+, & 52. \end{aligned}$$

To obtain a more accurate interaction energy between  $\text{Cl}^0$  and  $\text{Cl}^-$  is not an easy task. The Born-Mayer results do not strictly apply to neutral atoms. A calculation according to the Hartree method is exceedingly complicated, although possible, for example by the methods of Löwdin.<sup>10</sup> Recently the Thomas-Fermi method has been used by Abrahamson *et al.*<sup>18</sup> to obtain interaction potentials between neutral atoms for small separation. This method can be applied to the interaction between an atom and an ion but its results will not be very accurate in the region of separations used here. The repulsive potential is the least accurate of the various energy expressions and the effect on the activation energies of changing the parameters in the potential will be noted.

The polarizabilities of  $\text{Na}^+$  and  $\text{Cl}^-$  were taken from

TABLE I. Energy contributions in terms of coefficients of  $p$  and  $q$  for the cube-center case, in eV.

Term	$p^2$	$q^2$	$pq$
$\Delta E_S$	54.4	54.4	-266.4
$\Delta E_P$	-35.8	-104.0	64.6
$\Delta E_R$	165.3	82.8	134.4
Total	183.9	33.2	-67.4

<sup>17</sup> D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957). S. F. Boys and V. E. Price, *Phil. Trans. Roy. Soc. (London)* **A246**, 451 (1954).

<sup>18</sup> A. A. Abrahamson, R. D. Hatcher, and G. H. Vineyard, *Phys. Rev.* **121**, 159 (1961).

the work of Tessman *et al.*<sup>19</sup> as

$$\alpha_+ = 0.41 \times 10^{-24} \text{ cm}^3, \quad \alpha_- = 2.96 \times 10^{-24} \text{ cm}^3.$$

The polarizability of  $\text{Cl}^0$  was not needed in these calculations. For later work, where the  $\text{Cl}^0$  will be considered in a position relatively distant from a symmetrical position, it is necessary to know its polarizability and for this purpose a rough value of about half of that for  $\text{Cl}_2$  may be used,  $2.25 \times 10^{-24} \text{ cm}^3$ .

With the constants chosen as above the various energy expressions of Eq. (20) were evaluated and expressed as functions of the parameters  $p$  and  $q$ . The results (after the evaluation of a considerable number of sums) are given in Table I. The contribution from  $\Delta E_{RS}$  is

$$\Delta E_{RS} = 7.60 \exp(-14.10p) - 7.60 + 0.88 \exp(-14.10q) - 0.88,$$

so that

$$\Delta E = 7.60 \exp(-14.10p) + 0.88 \exp(-14.10q) - 8.48 + 183.9p^2 + 33.2q^2 - 67.4pq,$$

and Eqs. (21) become

$$\begin{aligned} \partial \Delta E / \partial p &= -107.2 \exp(-14.10p) + 367.8p - 67.4q = 0, \\ \partial \Delta E / \partial q &= -12.3 \exp(-14.10q) + 66.4q - 67.4p = 0. \end{aligned} \quad (22)$$

Solving the second of Eqs. (22) for  $p$  and substituting in the first of Eqs. (22) yields an equation in  $q$  which can be solved by numerical methods to give  $q = 0.125$  and  $p = 0.097$ , i.e., both of the order of a 10% relaxation along each of the axes. This is small enough that the expansion methods remain valid. These values of  $p$  and  $q$  yield for  $\Delta E$  the value  $-4.97 \text{ ev}$ .

There are several interesting consequences of these results. Table II shows the contributions to the energy difference due to the terms separately, and in the last column the results that would be obtained by considering only the four  $\text{Cl}^-$  ions as the movable ions (a separate calculation which gave  $p = 0.086$ ). It is clearly necessary to include the  $\text{Na}^+$  ions, especially because of the large difference in the electrostatic and repulsive terms. It is also noted that each of the terms

TABLE II. Contributions to the relaxation energy in the cube-center position for the  $p, q$  and  $p$  cases, in ev.

Term	$p, q$	$p$
$\Delta E_S$	-1.87	0.40
$\Delta E_P$	-1.19	-0.26
$\Delta E_R$	4.48	1.22
$\Delta E_{RS}$	-6.39	-5.36
Total	-4.97	-4.00

<sup>19</sup> J. Tessman, A. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

TABLE III. Energy contributions in terms of coefficients of  $p$  and  $q$  for the square-center case, in ev.

Term	$p^2$	$q^2$	$pq$
$\Delta E_S$	7.2	7.2	-61.4
$\Delta E_P$	-8.0	-23.4	8.1
$\Delta E_R$	49.8	27.4	40.4
Total	49.0	11.2	-12.9

is important although the repulsive terms dominate. As would be expected, by considering only  $\Delta E_S$ ,  $\Delta E_P$ , and  $\Delta E_R$  the equilibrium values are obtained with  $p = q = 0$  and this is a solution for stable equilibrium, i.e., essentially the additional atom has been removed.

An estimate of the dipole-dipole terms gives  $-18.4 pq$ , which, although considerably smaller than any of the other  $pq$  terms affects the sum proportionately more, by changing it from  $-67.4 pq$  to  $-85.8 pq$ . Carrying through the calculation as before for  $p, q$ , and  $\Delta E$  yields

$$p = 0.104, \quad q = 0.158, \quad \Delta E = -5.23,$$

i.e., a difference of 0.26 ev in the relaxation energy results.

#### VIII. RELAXATION ABOUT THE SQUARE-CENTER POSITION

With the  $\text{Cl}^0$  atom fixed at the center of a square of ions, a relaxation calculation was carried out with the two nearest  $\text{Cl}^-$  ions and the two nearest  $\text{Na}^+$  ions as movable ions. Table III gives the results of the computation in terms of  $p$  and  $q$ , the  $x$  and  $y$  displacement outwards for  $\text{Cl}^-$  and  $\text{Na}^+$ , respectively ( $z$  displacement is zero since the relaxation is confined to a plane).

The contribution from  $\Delta E_{RS}$  is

$$\Delta E_{RS} = 13.87 \exp(-11.51p) - 13.87 + 1.60 \exp(-11.51q) - 1.60,$$

so that

$$\Delta E = 13.87 \exp(-11.51p) + 1.60 \exp(-11.51q) - 15.47 + 49.0p^2 + 11.2q^2 - 12.9pq,$$

and Eqs. (21) become

$$\begin{aligned} \partial \Delta E / \partial p &= -159.6 \exp(-11.51p) + 98.0p - 12.9q = 0, \\ \partial \Delta E / \partial q &= -18.4 \exp(-11.51q) + 22.4q - 12.9p = 0. \end{aligned} \quad (23)$$

Solving these equations gives

$$p = 0.196, \quad q = 0.199, \quad \Delta E = -12.04 \text{ ev}.$$

A calculation was also made in which only the two nearest  $\text{Cl}^-$  ions were allowed to move symmetrically outward. This yielded  $p = 0.191$  and  $\Delta E = -10.54 \text{ ev}$ , a difference of 1.50 ev with respect to the previous case; it is clearly necessary to include the  $\text{Na}^+$  ions. In the square-center situation it is to be noted that the values of  $p$  and  $q$  are almost the same, so that a calculation in which the same outward displacement for  $\text{Na}^+$  as for



TABLE IV. Contributions to the relaxation energy in the square-center position for the  $p,q$  and  $p$  cases, in ev.

Term	$p,q$	$p$
$\Delta E_S$	-1.82	0.26
$\Delta E_P$	-0.92	-0.29
$\Delta E_R$	4.58	1.82
$\Delta E_{RS}$	-13.88	-12.33
Total	-12.04	-10.54

$\text{Cl}^-$  was chosen would yield a good value. Table IV shows the contributions made by the respective terms in the  $p,q$  case and the  $p$  case. The repulsive terms dominate even more than before because of the closeness of the ions to the additional atom.

The dipole-dipole terms were here calculated to be  $-3.9 pq$ , to give for the corrected values

$$p=0.200, \quad q=0.215, \quad \Delta E=-12.19 \text{ ev.}$$

In this case an energy difference of only 0.15 ev results, whereas in the cube-center case the change due to the dipole-dipole terms was 0.26 ev.

### IX. ACTIVATION ENERGY

To calculate the activation energy between the cube-center and square-center positions it is necessary to refer both computations to a standard configuration, which was chosen as the regular lattice configuration without the additional atom. The energy differences are then easily calculated as the repulsive energy of interaction of the additional atom with the nearby ions in their regular positions. The results are 8.48 ev for the cube configuration and 16.00 ev for the square. The results of the activation energy calculation are summarized in Table V. The cube-center configuration, as expected, turns out to possess less energy than the square-center one, the difference, or activation energy, being 0.45 ev, which is rather small in comparison with the various contributing terms. If the dipole-dipole corrections are included, the activation energy becomes 0.56 ev.

Mott and Littleton<sup>7</sup> calculated the energy necessary to remove a positive ion from a NaCl crystal as 4.62 ev and that for a negative ion as 5.18 ev. A direct comparison cannot be made because the electrostatic terms are dominant for charged defects whereas the repulsive terms dominate for a neutral defect. However, it is to be noted that the values are a little larger than those calculated here for the energy necessary to place a neutral atom in the lattice.

By letting

$$\nu e^{-U/kT} = 1,$$

where  $\nu$  is the peak vibration frequency of the crystal, about  $5 \times 10^{12}$ /sec for NaCl,  $U$  is the activation energy,  $k$  is Boltzmann's constant, and  $T$  the absolute temperature, one can estimate the temperature for sig-

nificant mobility to exist. For  $U=0.45$  ev this temperature is 178°K, and for 0.56 ev the corresponding temperature is 222°K. Delbecq *et al.*<sup>20</sup> report that at 173°K the  $\text{Cl}_2^-$  centers are beginning to move through the lattice in KCl. It should be mentioned, however, that we have not used the model of a molecular ion, although it would be possible to extend the calculations with the inclusion of some specific attractive forces.

In order to investigate the effect of altering the repulsive constant used in the  $\text{Cl}^- - \text{Cl}^0$  interaction energy, calculations were performed with the values 1800 and 2600 instead of 2190. This was done without the dipole-dipole corrections, to give an activation energy of 0.44 ev for the 1800 case and 0.47 ev for the 2600 case, compared to 0.45 ev for the 2190 case as used in these calculations. In each case the relaxation energies and energies relative to the standard configuration change considerably, but when differences are taken the results are remarkably uniform.

### X. DISCUSSION

The activation energy calculated here cannot be considered to be very accurate for several reasons. First, only the nearby ions were allowed to relax, whereas the next shell of ions should also be considered. This can be done using the methods and expressions developed in the first few sections, either by a method of successive approximations or by assigning certain values to the  $\Delta \mathbf{r}_N$ 's and testing for minimum values in the relaxation energy. Second, the dipole-dipole energy should be included in a more systematic way, rather than as an estimate, and again the methods developed here show this to be possible. Third, it should be investigated whether placing the additional atom in a position a little away from the symmetry sites would not yield lower energies. This also can be investigated by the methods here. All three of these points are at present being calculated on an IBM 704 computing machine. Finally, the most stable configuration may have lower symmetry than that assumed here, i.e., the interstitial atom may find a lower energy position at a considerable distance from the cube or square centers. For such configurations, new expansions around these positions for the electric field and thus the polarization and dipole-dipole energies will be necessary. In this way it can be investigated whether or not the additional

TABLE V. Energies entering into the activation energy, in ev.

	Cube-center	Square-center
Energy for introduction of additional atom	8.48	16.00
Relaxation energy	-4.97	-12.04
Energy relative to standard configuration	3.51	3.96
Activation energy	0.45	

<sup>20</sup> C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **111**, 1235 (1958).

atom tends to form a molecular ion because it tends to drift naturally, i.e. without any specific attractive energy terms, to a position nearer the anion than is possible in the configurations considered here. A preliminary calculation in this direction is not conclusive.

It will also be necessary in accurate future work to take into account the polarization models of Lundquist<sup>9</sup> and Woods *et al.*,<sup>11</sup> for ions and atoms that are close together and to consider other than exponential forms for the repulsive interactions.<sup>12,13</sup>

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## Magnetic Field Dependence of the Superconducting Penetration Depth in Thin Specimens

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The magnetic field dependence of the superconducting penetration depth for very thin films as predicted by the Ginzburg-Landau theory is considered. The results obtained depend upon the boundary conditions on the film. For the usual case of equal magnetic fields on opposite sides of the film, the penetration depth increases smoothly toward infinity as the critical field is approached, corresponding to a second-order phase transition. For the less common case of unequal fields on opposite sides, the penetration depth increases toward a finite value as the critical field is approached, corresponding to a first-order phase transition. The results for the latter case are shown to agree remarkably well with the very precise experiments of Garwin, Erlbach, and Sarachik on the field dependence of the penetration depth of a 250 Å film of Pb. The penetration depth in zero field as a function of thickness is also considered.

### I. INTRODUCTION

THE magnetic field dependence of the superconducting penetration depth has provoked considerable interest. This interest has been chiefly concerned with bulk superconductors. Because most bulk superconductors satisfy the nonlocal condition (coherence length  $\xi$  greater than penetration depth  $\lambda$ ), the interpretation of experimental results can be quite difficult. The reason for this difficulty is that there is as yet no satisfactory theory that considers nonlocal effects in the presence of a strong magnetic field. One way to skirt this problem is to limit the coherence length by making the dimensions of the superconductor small, as in the case of a thin evaporated film. By making the thickness  $d$  of the film, and hence  $\xi$ , less than  $\lambda$ , the superconductor will satisfy the local limit ( $\xi < \lambda$ ). There is fortunately a satisfactory local theory that is valid for all fields up to the critical field; it is the non-linear phenomenological theory of Ginzburg-Landau<sup>1</sup> (GL). Since the GL equations have been derived from the microscopic theory by Gor'kov,<sup>2</sup> the solutions of the GL equations will have the same rigor as those of the microscopic theory. Thus, by considering thin films the nonlocal problem can be avoided, and the comparison

between theory and experiment can be made with considerably less ambiguity. Therefore, in this paper we shall consider the magnetic field dependence of the penetration depth in *thin* specimens.

In the GL theory the penetration depth,  $\lambda$ , is inversely proportional to the order parameter,  $\psi$ , which is a function of coordinates, magnetic field, and temperature. However, if  $d/\lambda \ll \kappa^{-1} \approx 10$ , where  $d$  is the thickness of the specimen and  $\kappa$  is the nonlinear coupling constant of the theory, then  $\psi$  (and  $\lambda$ ) is independent of coordinates. Thus, if we restrict ourselves to this condition, the dependence on coordinates is eliminated and the field dependence of the penetration depth may be expressed as

$$\lambda(T,0)/\lambda(T,H) = \psi(T,H)/\psi(T,0). \quad (1)$$

Thus the problem of finding the field dependence of  $\lambda$  reduces to solving the GL equations for  $\psi(T,H)/\psi(T,0)$  for a specific geometry and specific boundary conditions.

There is evidence<sup>3</sup> that  $\lambda(T,0)$  increases as the thickness decreases, and Tinkham<sup>4</sup> has suggested a simplified way of calculating this increase. In Sec. IIA a more fundamental calculation of this effect will be presented. The field dependence of the penetration depth for equal and unequal values of the field on opposite sides of the film will be considered in Sec. IIB. In Sec. III comparison of these results with an experiment of Garwin, Erlbach, and Sarachik<sup>5</sup> will be made.

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