Relaxation and Activation Energies for an Interstitial Neutral Defect in an Alkali Halide Lattice. II*

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(Received 31 October 1963)

The distortion around and the relaxation energy for a Cl^0 interstitial atom in a NaCl lattice has been obtained for various positions of the Cl^0 by a method involving the exact calculation of electrostatic, polarization, dipole-dipole, and repulsive energies. The relaxation of from 14 to 23 neighboring ions has been taken into account, using up to nine independent parameters, in minimizing the energy relative to the perfect lattice. The following positions of the Cl^0 were investigated: the cube center, the face center, and various positions along the cube and face diagonals. The cube-center and cube-diagonal positions were always found to be stable relative to the face-center and face-diagonal positions. There are two energy minima of almost the same value along the body diagonal, one in the center of the cube and one in which the Cl^0 and Cl^- are located on either side of a normal Cl^- lattice position. These two minima are separated by a potential barrier of about 0.2 eV. The energy differences for the various configurations along the face diagonal are small with the face center the position of lowest energy. The face-center position is metastable with respect to the body-center position by about 0.03 eV. The energy difference between the body-center and face-center positions is 0.44 eV, giving an activation energy along this line of motion of 0.47 eV.

I. INTRODUCTION

THE properties of defects in the alkali halides can be described theoretically quite successfully on the basis of the point-ion model, with suitable modifications to account for the polarization energy. There is a considerable difference in technique between the study of charged and neutral defects. With a charged defect, for example a cation or anion vacancy, the effect of the additional charge has to be taken into account by considering the crystal as a polarizable medium past the initial shells, as has been done by Mott and Littleton,[1] and by minimizing the energy with respect to a few parameters associated with the ions surrounding the defect. This method has also been used by Tosi and Fumi[2] and by Tharmalingam.[3] Kurosawa[4] has improved this approach by considering the energy a function of the displacements and the polarizations of the surrounding ions and by minimizing with respect to both of these sets of parameters. In the case of a neutral defect such as an interstitial neutral atom, the polarization effects are smaller and the ions surrounding the defects can then be allowed to relax asymmetrically as far as the concept of shells is concerned. It has been found that directed chains of ions are formed in certain cases rather than a uniform isotropic displacement. The neutral divacancy has been studied by Dienes[5] and by

Tharmalingam and Lidiard[6] using exact calculations for a few parameters; Hardy[7] has investigated a substitutional potassium ion in a sodium chloride lattice by a normal coordinate expansion method due to Kanzaki[8]; and Hatcher and Dienes[9] have studied a neutral chlorine atom in an interstitial position in NaCl by an expansion method for the various energy terms.

The present approach differs from the ones mentioned above by using many more parameters which are independently varied to find the positions of minimum energy; by not grouping the ions into shells but studying their displacements separately; by investigating asymmetric defect positions; and by studying paths for the motion of the defect. The properties of Cl^0 in an NaCl lattice are discussed in this paper but the general method can be easily modified for any neutral defect, for example the H center,[10] as studied in a preliminary way by Dienes, Hatcher, and Smoluchowski.[11] Varley[12] has shown that interstitial halogen atoms may well be produced by ionizing radiation in ionic crystals. In this paper the relaxation energies are calculated for several positions of the interstitial halogen, including asymmetric ones, using crystal forces only, i.e., no special attractive potential was assumed for the interaction of Cl^0 with a neighboring Cl^-. Specifically,

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[5] G. J. Dienes, J. Chem. Phys. 16, 620 (1948).

[6] K. Tharmalingan and A. B. Lidiard, Phil. Mag. 6, 1157 (1961).
[7] J. R. Hardy, Phys. Chem. Solids 15, 39 (1960).
[8] H. Kanzaki, Phys. Chem. Solids 2, 24 (1957).
[9] R. D. Hatcher and G. J. Dienes, Phys. Rev. 124, 726 (1961).
[10] W. Kanzig, Phys. Rev. 99, 1890 (1955); W. Kanzig and T. O. Woodruff, *ibid.* 9, 70 (1959).
[11] G. J. Dienes, R. D. Hatcher, and R. Smoluchowski, Bull. Am. Phys. Soc. 8, 89 (1963).
[12] J. H. O. Varley, J. Nucl. Energy 1, 130 (1954); Nature 174, 886 (1954).

it was of interest to find out whether the Cl^0, under the influence of crystal forces alone, would tend to go to a position in the lattice where it would be closer to one Cl^- than to any other.

The method previously described by Hatcher and Dienes[9] (to be referred to hereafter as I) was an expansion technique which could not be used for asymmetrical positions. Exact expressions, based on the point-ion model, are used in this paper. As in I, some of the regular ions of the lattice are considered as movable and the others as fixed. The notation for the movable and fixed ions, the coordinate system used and the method of breaking up a sum over all the ions of the lattice into sums over the fixed and movable ions separately are the same as in I. The multiple sums over the fixed ions were carried out as far as necessary so that their energy contribution would be correct to 0.01 eV. The energy expressions were written in terms of the parameters chosen to represent the defect atom and the positions of the neighboring ions in their relaxed positions, and all calculations were referred to the energy of the perfect lattice.

The energy relative to the perfect lattice is made up of several parts

$$E = E_S + E_P + E_{PA} + E_D + E_{DA} + E_R + E_{RA},$$

where E_S is the electrostatic energy, E_P the polarization energy due to the regular ions, E_{PA} the polarization energy of the additional atom, E_D the dipole-dipole energy of the regular ions, E_{DA} the dipole-dipole contribution of the additional atom, E_R the repulsive energy of the regular ions among themselves, and E_{RA} the repulsive energy due to the presence of the additional atom. These are the energies listed in the tables for various configurations (in some cases some of the terms are zero because of symmetry). The exact expressions used for these terms are given in Secs. III, IV, V, and VI of I, the only change in the constants employed being that the value of the polarizability for Na^+ was taken as 0.26×10^{-24} cm^3 from the work of Tessman et al.[13]

With the energy expressed as a function of the parameters p_i and q_i, calculations were performed on the IBM 7090 by choosing the q_i to correspond to a particular position in the lattice for the defect atom and varying the p_i systematically from an initial set chosen as a first guess. With p_2 to p_n fixed, p_1 was varied in steps of 0.05 until a minimum with respect to p_1 was found; with this minimum position for p_1, p_2 was then varied in a similar manner and this process continued up to p_n. Then the process was repeated with a step of 0.02 for the p_i's and finally for a step size of 0.005. Some calculations were also performed for smaller step sizes, down to 0.001. Three steps were found to be necessary and sufficient, in most cases, to obtain an accuracy of

[13] J. Tessman, A. Kahn, and W. Shockley, Phys. Rev. 92, 890 (1953).
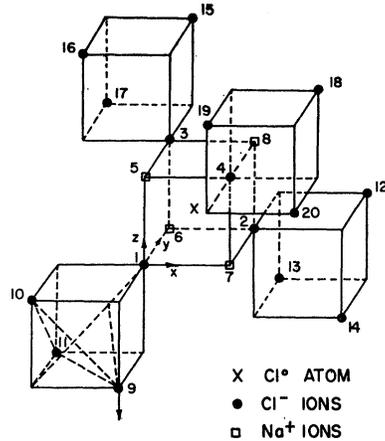
FIG. 1. Cube-center position for Cl^0 in NaCl and the ions that relax around it, showing especially the displacement of ion number 9.

0.01 eV. In each case a rather broad minimum was found in the p_i's. It was also found that the energy values depended rather strongly on the number and choice of the ions that were allowed to relax. To investigate the nature of the stability at a particular position of the defect atom the second derivatives $\partial^2 E/\partial p_i \partial p_j$, $\partial^2 E/\partial p_i \partial q_j$, and $\partial^2 E/\partial q_i \partial q_j$ were calculated in several cases. This was done by numerical differentiation after evaluating the energy for small increments in the p_i and q_i values.

The question of the stability of a particular Cl^0 position in the lattice is an important one and the expressions developed to test for stability are given in the Appendix. In Sec. II the results are given for the defect at cube-center and face-center positions as well as for several intermediate positions in between. In Sec. III the relaxation energies for asymmetrical positions are calculated with the defect located along a cube and a face diagonal. In Sec. IV the activation energies for various types of motion are considered and the limitations of the present method and possible improvements are discussed.

II. RELAXATION ABOUT SYMMETRICAL POSITIONS

A. Relaxation about the Cube-Center Position

A Cl^0 atom was placed at the center of a cube of ions, as shown in Fig. 1, and twenty of the surrounding ions were allowed to relax using four parameters to describe their positions. A fifth parameter was reserved for the defect atom itself to allow it to move slightly off the symmetrical position $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ in the x direction. Many calculations were performed to ascertain which of the surrounding ions would most affect the relaxation energy. These showed that the important ions to be relaxed are not necessarily the ones closest to the defect atom. The eight ions immediately surrounding the defect were, of course, included among these and two parameters were assigned to them, p_1 to the four Cl^-'s
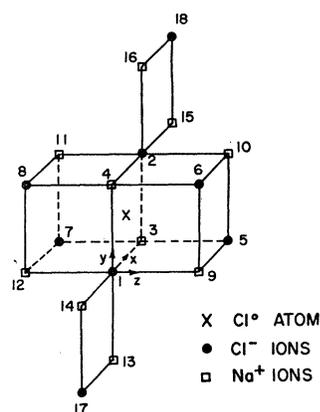
Fig. 2. Face-center position for Cl^0 in NaCl and the ions that relax around it.

X Cl° ATOM
● Cl^- IONS
□ Na^+ IONS

TABLE I. Parameters and energy contributions for the cube-center position.

Ions	Parameter	Value	Displacement of a typical ion (the first) of the group
1, 2, 3, 4	p_1	0.135	$-p_1, -p_1, -p_1$
5, 6, 7, 8	p_2	0.159	$-p_2, -p_2, p_2$
9–20	p_3	0.055	$-p_4, -p_3-p_4, -p_3-p_4$
	p_4	−0.014	
Cl^0	$p_5=q$	0.0	$p_5, 0, 0$
Electrostatic			−2.57 eV
Polarization			−1.37
Dipole-dipole			0.07
Repulsive—regular ions			5.25
Repulsive—additional atom			−7.25
Energy relative to perfect lattice—defect present and no relaxation			8.52
Energy relative to perfect lattice			2.65 eV

which were allowed to relax radially, and p_2 to the four Na^+'s which were also allowed to relax radially, where p_1 and p_2 are the x components of the displacements of these ions. The other twelve ions concerned are those numbered 9–20 in Fig. 1. They are Cl^- ions in cubes containing a Cl^- of the first group diagonally removed from the defect atom. Each of these ions were allowed to relax in the same way with the use of two parameters p_3 and p_4. These two parameters were chosen so that these ions could relax radially outwards from a point on the diagonal of the cube. In this way their tendency to move away from the similar Cl^-'s in the same cube and from the Cl^- nearest to the defect atom could be taken into account. As expected these Cl^- ions chose to relax about a point in between the position which the Cl^- nearest to the defect takes and the place where the plane containing the three similarly treated Cl^- ions cuts the diagonal. It is to be noted that the Na^+ ions of these diagonally situated cubes were not allowed to relax. Separate calculations showed their relaxations would have a small effect on the energy. The same is true of Cl^- ions in positions such as $(1, -1, 0)$. The type of displacement thus obtained is a chain-like relaxation in particular directions rather than an isotropic displacement in terms of shells. The displacements in the three rectangular directions for ion number 9 were chosen to be $(-p_4, -p_3-p_4, -p_3-p_4)$ so that the rectangular components of the points along the diagonal about which that ion relaxes is given by p_4/p_3. The amount of the displacement depends in a different way on p_3 and p_4. The fifth parameter p_5 was taken to be a displacement along the x direction of the defect atom, to see whether the central position was a maximum or minimum.

The position of minimum energy relative to the perfect lattice was found by the process already described using step sizes down to 0.001 (in terms of the nearest-neighbor distance as 1) in order to find how critical these parameters were in changing the energy. The best values obtained for the parameters, the corresponding displacements and the various contributions to the energy are shown in Table I. A rather

broad minimum was obtained; varying the parameters by 0.001 from their best positions gave rise to energy changes of less than 0.0003 eV. The x coordinate of the point about which ion number 9 and similar ions relax turned out to be -0.255, considerably further down along the diagonal than the -0.135 value for ion number 1, which otherwise might have been chosen as the center of relaxation of ion number 9. Comparison with the calculations in I, when only the eight immediate neighbors were allowed to vary, shows that the inclusion of the extra ions caused the relative energy to be decreased by 0.9 eV. This difference is due to a combination of each of the various types of energy as can be seen by comparing Table I with Table II of I. Allowing $p_5(q)$ to vary slightly shows that $\partial E/\partial q$ is 0 and $\partial^2 E/\partial q^2$ is positive, which indicates that this position is a stable one. A variation of 0.05 in the x direction for p_5 caused an increase of 0.027 eV in the energy.

B. Relaxation about the Face-Center Position

The neutral chlorine atom was placed at the center of a cube face as shown in Fig. 2 and eighteen of the surrounding ions were allowed to relax, using six parameters. As in the cube-center position calculation, the ions chosen to relax were those whose contributions were appreciable in terms of energy contributions of 0.01 eV. The ions immediately surrounding the defect atom, the four nearest neighbors of these Cl^- ions, and those in the neighboring two cubes were included in the calculation. The parameters and typical displacements are shown in Table II. The displacement of ions 17 and 18 resembles the chain-like displacements of the Cl^- ions obtained in part A. It will be noticed that the displacement of ions 17 and 18 is about 40% of that of ions 1 and 2 so that this type of displacement may continue for several more ions before becoming negligible. Because of this directional effect ions 13, 14, 15, and 16,

TABLE II. Parameters and energy contributions
for the face-center position.

Ions	Parameters	Value	Displacement of a typical ion (the first) of the group
1, 2	p_1	0.227	$-p_1$, $-p_1$, 0
3, 4	p_2	0.210	p_2, $-p_2$, 0
5, 6, 7, 8	p_3	0.009	p_3, $-p_3$, $2p_3$
9, 10, 11, 12	p_4	0.026	$-p_4$, $-p_4$, $2p_4$
13, 14, 15, 16	p_5	0.015	0, $-p_5$, 0
17, 18	p_6	0.095	$-p_6$, $-p_6$, 0

Electrostatic	-1.61 eV
Polarization	-1.11
Dipole-dipole	0.03
Repulsive—regular ions	4.22
Repulsive—additional ions	-14.38
Energy relative to perfect lattice—defect present and no relaxation	15.94
Energy relative to perfect lattice	3.09 eV

which lie off the chain direction, have only one sixth of the displacement of ions 17 and 18. Limitations of the program precluded investigation of ions further away; however, all ions as close to the defect as those considered movable in Fig. 2 were examined for their contributions. An improvement in the choice of parameters would have been to assign two parameters to ions 5–8, and also to ions 9–12, so that the center about which their relaxation occurred could be determined. This would have meant 8 parameters and even more when the derivatives were calculated to determine stability. It is estimated that these two modifications would have reduced the energy, but probably by not as much as 0.1 eV.

In this calculation step sizes down to 0.005 were used to determine the configuration of minimum energy, and estimates were made on the basis of the results obtained in part A with step sizes of 0.001 as to the error involved in stopping at 0.005. The error was estimated to be less than that arising from not including additional parameters. The best values obtained for the parameters and the various contributions to the energy are shown in Table II. Comparison with the results in I, where only the four immediate neighbors were varied shows the same decrease of the relative energy (0.9 eV) as in the case A. Thus, the activation energy, taken as the difference in energy between the face-centered and body-centered configurations, is very closely the same as obtained previously. The present results must be considered more accurate because of the inclusion of a large number of movable ions and parameters. It is surprising that the displacements of the nearest neighbors turn out to be so close when comparing these results with those of I; here 0.227 is obtained for the Cl⁻'s whereas 0.200 was obtained in I; here 0.210 is obtained for the Na⁺'s whereas 0.215 was obtained previously. The question whether this position for the defect atom is a maximum or a local

minimum one in the energy is an important one in obtaining the activation energy. In I it was assumed to be a maximum in all three directions. With the parameters as given in Table II, and by assigning another parameter to the displacement of the defect atom itself out of the plane, $\partial^2 E/\partial q^2$ was calculated and found to be positive, indicating that the face-center position is a minimum with respect to this direction. Within this approximation the face-centered position is also a minimum with respect to displacement of the Cl⁰ in the x or y directions. This result was established by assigning three parameters to the Cl⁰ and calculating the matrix S of the Appendix. With q_1, q_2, q_3 the parameters chosen for displacements in the x, y, z directions, respectively, then with the symmetry already present in Fig. 2, it follows that $\partial^2 E/\partial q_1^2 = \partial^2 E/\partial q_2^2$ and $\partial^2 E/\partial q_1 \partial q_3 = \partial^2 E/\partial q_2 \partial q_3 = 0$. The calculations showed that $\partial^2 E/\partial q_1 \partial q_2 < \partial^2 E/\partial q_1^2$ and that $\partial^2 E/\partial q_1^2$, and $\partial^2 E/\partial q_2^2 > 0$ so that $|S| > 0$ and the position considered is thus a minimum one in all three directions of displacement of the defect atom. According to these calculations, therefore, the face-center position is a metastable one. However, the parameters of Table II are symmetric with respect to each side of the plane so that if the defect atom moves in the positive direction the parameters on either side would be the same as for the defect in a fixed position at the center of the face. This approximation may be a poor one and the stability conditions must be investigated more carefully. This is done in the next section.

C. Stability Conditions at the Face-Center Position

The stability conditions described in the Appendix were applied to the face-center configuration. A single direction of displacement for the defect was chosen and the parameters p_i were split up into two groups l_i and r_i depending on whether they lie to the left or the right of the plane perpendicular to the defect's displacement. It was also assumed that the l_i and r_i change into each other if the direction of the defect's displacement is reversed. It is now easy to show that whereas with complete symmetry $\partial^2 E/\partial p_i \partial q = 0$ this condition is now changed to

$$\partial^2 E/\partial l_i \partial q + \partial^2 E/\partial r_i \partial q = 0.$$

The condition $dp_i/dq = 0$ is changed into

$$dl_i/dq + dr_i/dq = 0$$

and the expression for the second derivative becomes

$$d^2\epsilon/dq^2 = \partial^2 E/\partial q^2 - 2 \sum_i (\partial^2 E/\partial r_i \partial q)^2/\partial^2 E/\partial r_i^2; \quad (1)$$

this equation has been obtained by eliminating the expression depending on the l_i parameters from Eq. (A18). It is interesting to compare Eq. (1) with the equation which results when the complete symmetry is imposed

$$d^2\epsilon/dq^2 = \partial^2 E/\partial q^2.$$
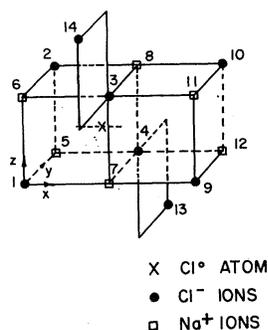
FIG. 3. Intermediate position for Cl^0 in NaCl and the ions that relax around it.

X Cl^0 ATOM

● Cl^- IONS

□ Na^+ IONS

TABLE III. Parameters and energy contributions for the (0.9, 0.5, 0.5) position.

Ions	Parameters	Value	Displacement of a typical ion (the first) in the group
1, 2	p_1	0.020	$-2p_1,\ -p_1,\ -p_1$
3, 4	p_2	0.220	$0,\ -p_2,\ p_2$
5, 6	p_3	0.035	$-2p_3,\ p_3,\ -p_3$
7, 8	p_4	0.200	$0,\ -p_4,\ -p_4$
9, 10	p_5	0.000	$2p_5,\ -p_5,\ -p_5$
11, 12	p_6	0.015	$2p_6,\ -p_6,\ p_6$
13, 14	p_7	0.090	$0,\ p_7,\ -p_7$
Electrostatic			-1.69 eV
Polarization			-1.06
Dipole-dipole			0.03
Repulsive—regular ions			4.19
Repulsive—additional atom			-13.54
Energy relative to perfect lattice—defect present and no relaxation			15.18
Energy relative to perfect lattice			3.11 eV

The second term on the right-hand side of Eq. (1) is positive since $\partial^2 E/\partial r_i^2 > 0$, r_i being one of the variable parameters and the energy already having been minimized with respect to the variable parameters. Thus the relaxation of the symmetry lowers the value of $d^2\epsilon/dq^2$. If $\partial^2 E/\partial q^2 < 0$ then $d^2\epsilon/dq^2 < 0$ and the position is a maximum. If, however, $\partial^2 E/\partial q^2 > 0$, whereas in the complete symmetry case the position would be judged to be a minimum, now the second term of Eq. (1) has to be evaluated.

A nine parameter calculation was performed for the face-center position of the Cl^0 defect. With reference to Fig. 2, the ion group 5, 6, 7, 8 was split up into two groups 5, 6, assigned one parameter, and 7, 8 assigned another. Similarly ions 9, 10 were assigned one parameter and ions 11, 12 a different one. Calculations for the quantities appearing in the matrix W (see Appendix) were obtained by numerical differentiation on varying each of the parameters through two steps separately and in conjunction with other parameters, so that $\partial^2 E/\partial p_i \partial q$ and $\partial^2 E/\partial p_i \partial p_j$ could be obtained. Evaluating $|W|$ and its principal minors showed each of these quantities to be positive, thus indicating that the face-center position is a minimum with respect to motion in the z direction. A more accurate calculation would have involved an investigation of each of the three directions of displacement involving about eight additional parameters. Taking the results as obtained in the symmetry calculation together with the calculation of this section indicates very strongly that the face-center position is a minimum in any direction of motion of the defect atom from its symmetry position although the minimum is only a very shallow one as will be seen in part D and Fig. 4. Thus, it is concluded that the face-center position is a metastable one although an absolute proof would be very difficult to obtain.

D. Relaxation about Intermediate Positions between Cube Center and Face Center

Two direct calculations were performed to determine the energies of positions intermediate between the cube center and face center along the line joining them. The results of part C could also be verified by such a

calculation, in which the relaxation around the intermediate position was calculated directly. In the first calculation the defect was placed at (0.9, 0.5, 0.5) and fourteen ions were varied using seven parameters as shown in Fig. 3. The ions chosen to be varied were picked from those used in part B since the Cl^0 is so close to the position there (1.0, 0.5, 0.5) The Na^+ ions in the plane of the face-center position and its nearest neighbors were not employed this time as they did not contribute a large amount previously. However, a larger number of parameters was necessary because of the lack of symmetry. To simplify the calculation further, the ions chosen were allowed to relax from the center of the face rather than the actual position of the Cl^0, so that the program could be used for other intermediate points. The parameters and the displacements are listed in Table III. It will be noticed that the ions which along with ion number 1 are chained together as found in part A were not included in this calculation since an additional 16 ions with six additional parameters would have had to be included. An estimate of the influence of these ions was made in the second calculation of this set. The best values of the parameters and the various energy terms are given in Table III. In the program the contributions to the energy due to the polarization energy of the defect atom and its dipole-dipole contributions were calculated but found to be small. Since the defect atom has moved from the face-center symmetry position it is now in an electric field but one that apparently is too small to appreciably polarize the atom on the point-ion model. It will be noted that p_2 and p_4 have approximately the same values as in part B where they correspond to p_1 and p_2, respectively (Table II). Similar comparisons can be drawn between corresponding pairs of parameters. It will be noted especially that ions 9 and 10 suffer no displacement and thus there is no need to consider the

TABLE IV. Parameters and energy contributions
for the (0.75, 0.5, 0.5) position.

Ions	Parameter	Value	Displacement of a typical ion (the first) in the group
1, 2	p_1	0.050	$-1.5p_1,\ -p_1,\ -p_1$
3, 4	p_2	0.200	$0.5p_2,\ -p_2,\ p_2$
5, 6	p_3	0.070	$-1.5p_3,\ p_3,\ -p_3$
7, 8	p_4	0.200	$0.5p_4,\ -p_4,\ -p_4$
9, 10	p_5	-0.005	$2.5p_5,\ -p_5,\ -p_5$
11, 12	p_6	0.015	$2.5p_6,\ -p_6,\ p_6$
13, 14	p_7	0.075	$0,\ p_7,\ -p_7$
Electrostatic			-1.90 eV
Polarization			-1.16
Dipole-dipole			0.05
Repulsive—regular ions			4.49
Repulsive—additional atom			-10.59
Energy relative to perfect lattice—defect present and no relaxation			12.08
Energy relative to perfect lattice			2.97 eV

chain of ions associated with them. The energy relative to the perfect lattice has increased slightly from that obtained for the face-center position (3.11 eV compared to 3.09 eV, Tables II and III; this small change has, however, been the result of several larger changes in the various energy terms. The results of part C are hereby verified in that the face-center position is a minimum.

A similar calculation was carried out at the (0.75, 0.5, 0.5) position with parameters and displacements assigned to the ions as shown in Table IV and Fig. 3. In this case the ions were chosen to relax about the position of the defect since it was now halfway between the two positions of symmetry. In a separate auxiliary calculation two additional parameters were used; one to take care of the Na^+ ions 13, 14, 15, and 16 in Fig. 2, and the other to investigate the chain displacement effect. Zero displacement was found for the variation of the Na^+ ions and the effect of Cl^-'s further away than those in Table IV was estimated to be no more than 0.03 eV. The best values of the parameters obtained in the main calculation and the various energy contributions are given in Table IV. The energy relative to the perfect lattice in this case was found to be 2.97 eV, showing that the maximum between the two symmetry positions occurs between distances 0.75 and 0.90 in the x direction. Some calculations were also carried out at small distances from the symmetry positions in which the relaxations were assumed to be the same as those at the symmetry positions. From all of these results, together with those from parts A and B, one can construct a plot of energy versus distance along the x direction as shown in Fig. 4. The maximum appears to be at about $x=0.87$. For motion along the x direction the system passes through this maximum and therefore there is an additional contribution of 0.025 eV to the activation energy. To do a more accurate
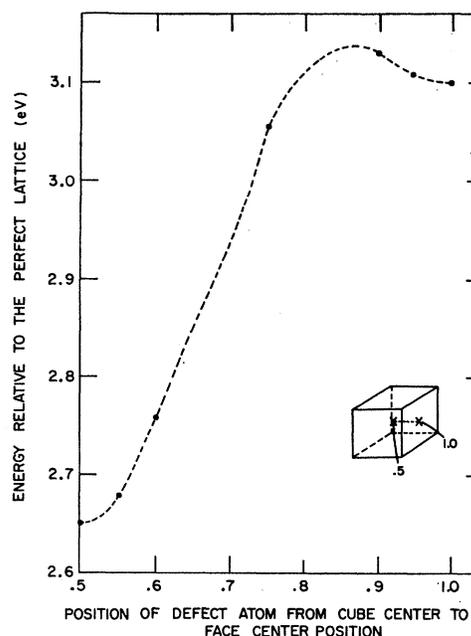
FIG. 4. Energy relative to the perfect lattice for intermediate positions of Cl^0 defect between cube-center and face-center positions.

calculation of the activation energy would require finding the relaxation about many more positions for the Cl^0 removed slightly from the line between the two symmetry positions. Such a calculation, because of the much lower symmetry, would require many more parameters. Thus, it is quite difficult to find the actual path taken by the Cl^0 in its migration in the lattice without taking into account many more positions. The path chosen here seems to be a reasonable one.

III. RELAXATION ABOUT ASYMMETRICAL POSITIONS

A. Relaxation about a Position for the Cl^0 Along the Cube Diagonal

The work of Kanzig et al.[10] has shown that a molecular ion Cl_2^- is formed in a lattice, situated around the former position of a Cl^- ion. Accordingly a study was made here to find where positioning the defect atom along the diagonal and allowing its position to vary would yield a stable configuration. One of the Cl^- ions was selected to be the partner of the Cl^0 in these calculations and this Cl^- was allowed also to vary in its position along the diagonal. The usual minimization process was carried out using these two parameters as well as several others involving the neighboring ions. In this calculation 19 ions were allowed to relax in addition to the Cl^0, using nine parameters. The relaxations of all ions were initially chosen to be radially outward from the (0,0,0) position as shown in Fig. 5. A slight change was added later to investigate the effect of allowing ions 17, 18, and 19 to be given a displacement perpendicular to this original one. In all
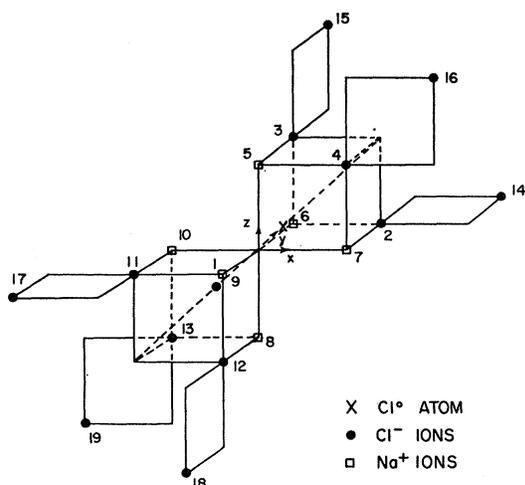
FIG. 5. Asymmetric cube-diagonal position for Cl^0 in NaCl and the ions that relax around it.

cases the parameters chosen measure the displacements along the coordinate axes. The particular parameters and displacements assigned to the ions are given in Table V. The effect of chains of ions is retained here, in the sense that ion number 2 for example affects the motion of ion number 14. In this way six of the outlying ions enter into the calculation whereas some of the closer ones are not appreciably affected. Although the Cl^0 was chosen along the diagonal at a position not at the center of the cube, there is still considerable symmetry present. However the ions nearest the Cl^- primarily concerned had to be given different parameters

TABLE V. Parameters and energy contributions for asymmetric position along the cube diagonal.

Ions	Parameter	Value	Displacement of a typical ion (the first) in the group
1	p_1	0.425	$-p_1, -p_1, -p_1$
Cl^0	p_2	0.196	p_2, p_2, p_2
2, 3, 4	p_3	0.034	$p_3, p_3, 0$
11, 12, 13	p_4	0.166	$-p_4, -p_4, 0$
14, 15, 16	p_5	0.010	$p_5, p_5, 0$
17, 18, 19	p_6	0.063	$-p_6, -p_6, -p_9$
5, 6, 7	p_7	0.182	$0, 0, p_7$
8, 9, 10	p_8	0.094	$0, 0, -p_8$
17, 18, 19	p_9	−0.008	$-p_6, -p_6, -p_9$

Electrostatic	−2.16 eV
Polarization—regular ions	−1.23
Dipole-dipole—regular ions	0.11
Polarization—additional atom with relaxation	18.01
Polarization—additional atom (no relaxation) relative to perfect lattice	−18.06
Dipole-dipole—additional atom	0.01
Repulsive—regular ions	4.91
Repulsive—additional atom	−138.56
Repulsive energy relative to perfect lattice—defect present and no relaxation	139.58
Energy relative to perfect lattice	2.61 eV

from those nearest the Cl^0 to conserve the asymmetry. Table V contains the best values found for the parameters involved and the energy contributions. The repulsive energy parts had necessarily to be large here, because in the term for the energy relative to the perfect lattice with the defect present and with no relaxation the Cl^0 atom is very close to the (0,0,0) position. This term is, however, balanced by the relaxation. A similar balancing occurs in the polarization energies. This is the first time these terms have shown up, necessary now because of the position of the Cl^0 so far away from a symmetry position. The final value for the energy of the relaxed configuration is 2.61 eV, very close to that for the cube-center position in II A, 2.65 eV. Because of the inaccuracies of the method, caused by the exclusion of many nearby ions and the approximate parameterization of the ones treated, it is impossible to decide which of the two configurations really has the least value for the energy. Because of the dominant role played by the repulsive terms it is likely that choosing different forms for the repulsive interaction could change the picture considerably. The influence of the repulsive terms can be seen here by noting that the motion of ions 11, 12, and 13 is much larger than that of ions 2, 3, and 4; the former group being closer to the Cl^-, the latter to the Cl^0. It will be noted that the Cl^0 and Cl^- do not take up positions equidistant from the (0,0,0) position. The Cl^0 comes much closer to it than the Cl^-, which correspondingly pushes its nearest neighbors further away than the Cl^0 does.

B. Relaxation about a Position along the Cube Diagonal Intermediate between the Two Minima Positions

Since the positions studied in II A and III A have very similar energies, a calculation was made for the Cl^0 fixed at a position intermediate between the two along the diagonal. The coordinates for the Cl^0 positions were chosen to be (0.348, 0.348, 0.348) and the mode of relaxation employed was patterned after that of a combination of II A and III A, although the resemblance to II A is closer than to III A. A total of 23 ions were allowed to relax using eight parameters. Figure 6 shows the ions which were chosen. This time some ions were relaxed radially from the Cl^0 position, some were relaxed into neighboring cubes and some were allowed to relax in the chain-like direction found in III A. The parameter and displacement assignments are given in Table VI. Several relaxation patterns were tried. The pattern given in Table VI gave the smallest energy values. Table VI shows the best values of the parameters which were obtained using a step size of 0.005, and the energy contributions. In this case, since the Cl^0 is further away from the (0,0,0) position the balancing terms are not as large as in III A. The energy relative to the perfect lattice was found to be 2.79 eV showing that between

TABLE VI. Parameters and energy contributions for an intermediate position (0.348, 0.348, 0.348) along the cube diagonal.

Ions	Parameter	Value	Displacement of a typical ion (the first) in the group
1	p_1	0.285	$-p_1, -p_1, -p_1$
2, 3, 4	p_2	0.300	$-0.348p_2, 0.652p_2, -0.348p_2$
5	p_3	0.065	p_3, p_3, p_3
6, 7, 8	p_4	0.145	$0.652p_4, 0.652p_4, -0.348p_4$
9, 10, 11	p_5	0.080	$-p_5, -p_5, 0$
12, 13, 14	p_6	0.045	$0, -p_6, 0$
15, 16, 17	p_7	0.025	$0, p_7, p_7$
18–23	p_8	0.015	$-1.348p_8, 0.652p_8, 1.652p_8$

Electrostatic	-2.16 eV
Polarization—regular ions	-1.02
Dipole-dipole—regular ions	0.05
Polarization—additional atom with relaxation	0.63
Polarization—additional atom (no relaxation) relative to perfect lattice	-0.63
Repulsive—regular ions	4.75
Repulsive—additional atom	-18.26
Repulsive energy relative to perfect lattice—defects present and no relaxation	19.43
Energy relative to perfect lattice	2.79 eV

the 0.196 and 0.500 values for the Cl⁰ atom along the diagonal there exists a small potential barrier of about 0.2 eV, which undoubtedly depends on the form of the potentials chosen. No attempt was made to find where the maximum of this potential barrier lay or what the nature of the region off the diagonal would be like because of the very large number of parameters needed in such a calculation. Also no attempt was made to try to link the Cl⁰ with the Na⁺ ion lying on the other side of the diagonal.

C. Relaxation about a Position for the Cl⁰ along the Face Diagonal

In addition to asymmetric positions along the cube diagonal similar positions along the face diagonal were investigated. As a matter of fact, since the H center
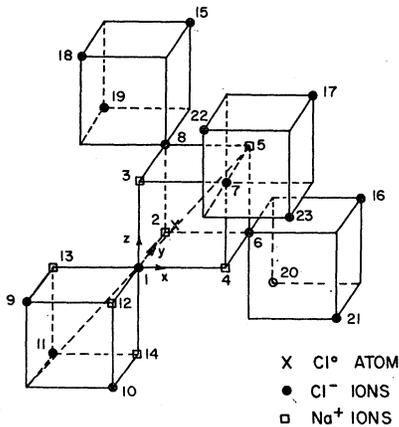
FIG. 6. Intermediate asymmetric cube-diagonal positions for Cl⁰ in NaCl and the ions that relax around it.

X Cl⁰ ATOM
● Cl⁻ IONS
□ Na⁺ IONS
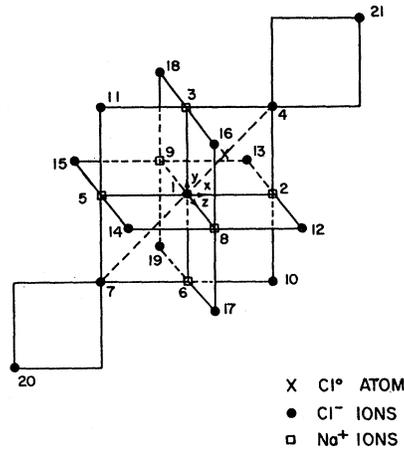
FIG. 7. Asymmetric face-diagonal position for Cl⁰ in NaCl and the ions that relax around it.

seems to be oriented along the face diagonal, these calculations were undertaken to discover how favorable such a position would be without any specifically attractive parts to the potential. The Cl⁰ was placed along the face diagonal and allowed to take a minimum position by using one parameter for its motion. Another one was used for the position of the Cl⁻ primarily concerned in this configuration, also along the diagonal. Seven other parameters were used for 20 other neighboring ions. Figure 7 shows the particular ions varied. In this case all of the nearest and next nearest neighbors of the (0,0,0) position were included as well as several of the Cl⁻ ions that would be directly affected by the directional motion of the Cl⁻ ions at the corners

TABLE VII. Parameters and energy contributions for asymmetric position along the face diagonal.

Ions	Parameter	Value	Displacement of a typical ion (the first) in the group
1	p_1	-0.316	$p_1, p_1, 0$
Cl⁰	p_2	0.410	$p_2, p_2, 0$
2, 3	p_3	-0.107	$-2p_3, p_3, 0$
4	p_4	0.160	$p_4, p_4, 0$
5, 6	p_5	0.025	$-2p_5, p_5, 0$
7	p_6	-0.150	$p_6, p_6, 0$
8, 9	p_7	0.053	$0, 0, p_7$
10–19	p_8	0.015	$p_8, -p_8, 0$
20, 21	p_9	0.061	$-p_9, -p_9, 0$

Electrostatic	-1.36 eV
Polarization—regular ions	-0.90
Dipole-dipole	0.03
Polarization—additional atom with relaxation	0.93
Polarization—additional atom (no relaxation) relative to perfect lattice	-0.95
Repulsive—regular ions	3.87
Repulsive—additional atom	-22.40
Repulsive energy relative to perfect lattice—defect present and no relaxation	23.92
Energy relative to perfect lattice	3.14 eV

TABLE VIII. Parameters and energy contributions for an intermediate asymmetric position along the face diagonal.

Ions	Parameter	Value	Displacement of a typical ion (the first) in the group
1	p_1	−0.270	$-p_1, -p_1, 0$
2, 3	p_3	0.220	$p_3, -p_3, 0$
4	p_4	0.190	$p_4, p_4, 0$
5, 6	p_5	0.020	$-p_5, p_5, 0$
7	p_6	0.140	$-p_6, -p_6, 0$
8, 9	p_7	0.070	$0, 0, p_7$
10–19	p_8	0.020	$p_8, -p_8, 0$
20, 21	p_9	0.070	$-p_9, -p_9, 0$

Electrostatic	−1.70
Polarization—regular ions	−1.15
Dipole-dipole	0.03
Polarization—additional atom with relaxation	0.22
Polarization—additional atom (no relaxation) relative to perfect lattice	−0.22
Repulsive—regular ions	4.42
Repulsive—additional atom	−16.30
Repulsive energy relative to perfect lattice—defect present and no relaxation	17.80
Energy relative to perfect lattice	3.10 eV

of the squares neighboring (0,0,0) in which the Cl^0 and the main Cl^- lie. There is a considerable difference between the cube- and face-center positions in this respect, that is, the square configurations lead to direct effects involving one additional ion each time whereas in the cube case three similarly located Cl^- ions are often involved. The parameter and displacement assignments are given in Table VII as are the best values obtained for the parameters and the various energy contributions. It will be noticed that the Cl^0 does not move far from the face-center position, although in the cube-center position it moves to the (0.196, 0.196, 0.196) position, leading to the conclusion that the face-center configurations are much more crowded than the cube ones, and thus smaller displacements of the Cl^0 atom

TABLE IX. Summary of results.

Position of Cl^0 in NaCl	Energy relative to the perfect lattice	Energy differences in eV
Body-center, BC	2.65	
Face-center, FC	3.09	
FC−BC		0.44
Potential well around face center	∼0.03	
Activation energy from FC to BC (along line joining them)		0.47
Cl^0-Cl^- stable configuration along $\langle 111 \rangle$	2.61	
Cl^0-Cl^- intermediate configuration along $\langle 111 \rangle$	2.79	
Activation energy along $\langle 111 \rangle$		∼0.2
Cl^0-Cl^- stable configuration along $\langle 110 \rangle$	3.14	
Cl^0-Cl^- intermediate configuration along $\langle 110 \rangle$	3.10	
Activation energy along $\langle 110 \rangle$		∼0.05

are involved. Since the Cl^0 is not as close to the (0,0,0) position, the repulsive terms involving the energies relative to the standard situation are lower than in case III A. The energy relative to the perfect lattice was found to be 3.14 eV, quite close to that for the face-center position (3.09 eV). These values are too close to decide between them as to which is the smaller. The minimum position obtained here may possibly go over to the face-center position if several more ions were allowed to relax, or if the parameters had been chosen differently. It would be interesting in this connection to investigate positions for the Cl^0 slightly off the diagonal. The distance between a Cl^0 and the nearest Cl^- in this case is 1.02 units, the same as in the cube-center position; the corresponding distance in the asymmetric cube configuration is 1.07 units. It would appear then that in moving from the face to the cube configuration in the asymmetric case, there is only a small change in the Cl^0-Cl^- distance, although it is not a simple rotation that is involved because of the closeness of the Cl^0 atom to the (0,0,0) position in the cube case. A systematic study of the asymmetrical Cl^0-Cl^- along directions between the face and the cube configurations would ascertain whether a potential barrier is present similar to the one found in the symmetric case.

D. Relaxation along a Position along the Face Diagonal Intermediate between the Two Minimum Positions

A separate calculation was performed in which the Cl^0 was placed along the face diagonal intermediate between the two minimum positions (0.5, 0.5, 0) and (0.410, 0.410, 0), namely, at the position (0.455, 04.55, 0). Since the position of the Cl^0 was altered only a little, the ions of Fig. 7 were used in this calculation but with only eight parameters, since the Cl^0 position is now fixed. The parameters, displacements, and the results are given in Table VIII. Even though the position of the Cl^0 is close to that in part E, considerable differences are obtained in the separate energy terms, although the final value for the energy relative to the perfect lattice (3.10 eV) is very close to that obtained in the last example (3.14 eV) and just a little higher than that for the face center (3.09 eV). Once again, because of the inaccuracies involved it would be difficult to decide between these values. The fact that the 3.14-eV value was obtained by allowing the Cl^0 to vary and it was found to be a minimum would indicate that values quite close to it should be slightly higher in energy. Apparently the position (0.455, 0.455, 0) is close enough to the face-center position to show the slight increase necessary in order to make that position a minimum. It would also appear that no appreciable potential barrier is present for motion of the Cl^0 along the face diagonal, at least within the range of motion investigated here. Comparison of the parameter values with the face-center ones show larger variation for the Cl^- ion primarily affected

and the nearby Na^+ ions but a smaller change for the Cl^- ion further removed from the Cl^0 in the main square. The energy contributions are also quite similar.

IV. DISCUSSION

A summary of the results is presented in Table IX. On the basis of these results one may make the following comments. The calculations gave results for two types of diffusional motion for a neutral chlorine atom, although it should be recalled that the most efficient path for diffusion was not determined in either case. To go from the cube-center position to the face-center position along the line joining them and over the small potential barrier along the way requires 0.47 eV, essentially the same result as obtained in I. However, if the asymmetrical positions are stable ones, which is well possible, because of the small energy difference, then to go from the asymmetrical cube position to the asymmetrical face one, assuming no large potential hump in between, requires 0.53 eV.

The small energy difference between the point configurations and the corresponding diagonal ones is noteworthy in the sense that crystal forces alone may well push the Cl^0 into the diagonal, or H center type configurations. However, the body-diagonal or body-centered configuration is always more stable than the corresponding configurations in the crystal face. Thus, the neutral Cl^0 does not assume the Kanzig[10] configuration of the H center under the influence of crystal forces alone. The next logical step is to include an attractive potential between the Cl^0 and the nearest Cl^-, i.e., to consider the characteristics of a Cl_2^- molecule in the lattice.[11] Such calculations will be given in a later paper.

Two reorientation motions have been studied, namely, from body center to body diagonal and from face center to face diagonal. Both of these motions appear to be very easy, with motion along the face diagonal the easier of the two. These motions are not diffusional ones unless charge exchange can take place somewhere along the line. Considerations of charge exchange lead to models of H centers and their mobility which will be treated in a later paper. It would certainly be very desirable to have a program which could place the Cl^0 in any arbitrary position in the cube, vary a large number of ions with an even larger number of parameters and obtain the energy relative to a perfect lattice. Such arbitrary positions are very difficult to study even with modern computing machines. An important new type of displacement has been found in these calculations, namely, the directed chains; these displacements could have been investigated by using several more parameters to see how they spread out in different directions. It should also be remarked that a point-ion model of the lattice is not too accurate as far as polarization energies are concerned. With such large defect atoms present and the considerable overlap affecting both the repulsive as well as the polarization energies

it would be desirable to investigate various polarization models as well as other forms for the repulsive interaction. The method used here can be used for any defect which is neutral, such as a divacancy or an H center. To extend it to the case of charged defects would involve treating the ions beyond the movable ones as a polarizable medium because of the large effects that accompany the presence of the electric field associated with a net charge.

ACKNOWLEDGMENT

APPENDIX

With the defect atom assigned to a particular position in the lattice r_d relative to an origin at one of the ions of the perfect lattice and with m neighboring ions placed in positions r_i, $i = 1, \cdots, m$, with no relation as yet between r_i and r_d, the energy of the lattice with the defect present relative to the perfect lattice, may be represented by

$$E(r_1, r_2 \cdots r_m; r_d).$$

An alternative approach is to assign certain parameters to the relaxed ions and as well to the defect atom, so that the energy may be represented as

$$E(p_1, p_2, \cdots, p_n; q_1, \cdots, q_r),$$

where the parameters p_i $(i = 1, \cdots n)$ are assigned to the regular ions and q_i $(i = 1 \cdots r)$ to the defect atom. The p_i are assumed to be independent variables at present. The q_i in practice are limited to three; in some cases, however, it is convenient to consider the defect constrained to a certain plane or line, in which case two q_i or a single q_i is needed. An advantage of the parameter approach is that it reduces the number of variables required to describe the situation where some symmetry is present and is yet sufficiently general to describe any configuration.

To examine the stability of the p_i, q_i configuration the derivatives of E have to be evaluated as a function of small changes in the parameters, dp_i and dq_i. Thus

$$dE = \sum_{i=1}^{n} \frac{\partial E}{\partial p_i} dp_i + \sum_{i=1}^{r} \frac{\partial E}{\partial q_i} dq_i + \frac{1}{2} \sum_{ij=1}^{n} \frac{\partial^2 E}{\partial p_i \partial p_j} dp_i dp_j$$
$$+ \frac{1}{2} \sum_{ij=1}^{r} \frac{\partial^2 E}{\partial q_i \partial q_j} dq_i dq_j + \sum_{j=1}^{r} \sum_{i=1}^{n} \frac{\partial^2 E}{\partial p_i \partial q_j} dp_i dq_j$$
$$+ \cdots. \quad (A1)$$

The conditions that the energy be a minimum for a particular configuration are that

$$\partial E / \partial p_i = 0, \quad \partial E / \partial q_i = 0, \quad (A2)$$

and that

$$\tfrac{1}{2}\sum_{ij}\frac{\partial^2 E}{\partial p_i\partial p_j}dp_idp_j+\tfrac{1}{2}\sum_{ij}\frac{\partial^2 E}{\partial q_i\partial q_j}dq_idq_j+\sum_{ij}\frac{\partial^2 E}{\partial p_i\partial q_j}dp_idq_j>0$$

for all possible choices of dp_i, dq_j. But this last expression is a quadratic form in dp_i and dq_i so that the condition for a positive definite quadratic form may be used, namely, that the determinant of the coefficients and also the principal minors be positive. This determinant may be represented as $|W|$ where

$$W=\begin{bmatrix}\dfrac{\partial^2 E}{\partial p_1\partial p_1} & \dfrac{\partial^2 E}{\partial p_1\partial p_2} & \cdots & \dfrac{\partial^2 E}{\partial p_1\partial p_n} & \dfrac{\partial^2 E}{\partial p_1\partial q_1} & \cdots & \dfrac{\partial^2 E}{\partial p_1\partial q_r} \\[2mm] \dfrac{\partial^2 E}{\partial p_2\partial p_1} & & \cdots & & & & \\[2mm] \vdots & & & \vdots & & & \vdots \\[2mm] \dfrac{\partial^2 E}{\partial p_n\partial p_1} & & \cdots & \dfrac{\partial^2 E}{\partial p_n\partial p_n} & \dfrac{\partial^2 E}{\partial p_n\partial q_1} & \cdots & \dfrac{\partial^2 E}{\partial p_n\partial q_r} \\[2mm] \dfrac{\partial^2 E}{\partial q_1\partial p_1} & & \cdots & \dfrac{\partial^2 E}{\partial q_1\partial p_n} & \dfrac{\partial^2 E}{\partial q_1\partial q_1} & \cdots & \vdots \\[2mm] \vdots & & & \vdots & & & \vdots \\[2mm] \dfrac{\partial^2 E}{\partial q_r\partial p_1} & & \cdots & \dfrac{\partial^2 E}{\partial q_r\partial p_n} & & \cdots & \dfrac{\partial^2 E}{\partial q_r\partial q_r}\end{bmatrix}.$$

$$(A3)$$

W is a symmetric matrix and can be divided into four parts

$$W=\begin{pmatrix}K & L \\ M & N\end{pmatrix},$$

where K is the matrix of the derivatives with respect to the p_i's only, N is the matrix of the derivatives with respect to the q_i's only and L and M contain the mixed derivatives. Because of the symmetry of the matrix

$$M=\tilde{L},$$

where $\sim$ indicates the transpose of the matrix. K is a square matrix of dimensions $n\times n$, N is a square matrix of dimensions $r\times r$, L is a rectangular matrix of dimensions $r\times n$ and M is a rectangular matrix of dimensions $n\times r$.

The determinant of W is a bordered determinant of order $(n+r)\times(n+r)$. By pivotal condensation it may be reduced to an $(r\times r)$ determinant, by taking the pivot each time as the element in the first row and first column of the reduced determinant to obtain

the form

$$\begin{vmatrix}K & L \\ M & N\end{vmatrix}=\frac{1}{|K|^{r-1}}\begin{vmatrix}\begin{vmatrix}K & L^1 \\ M^1 & N^{11}\end{vmatrix} & \cdots & \begin{vmatrix}K & L^r \\ M^1 & N_{1r}\end{vmatrix} \\ \vdots & & \vdots \\ \begin{vmatrix}K & L^1 \\ M^r & N_{r1}\end{vmatrix} & \cdots & \begin{vmatrix}K & L^r \\ M^r & N_{rr}\end{vmatrix}\end{vmatrix}, \quad (A4)$$

where

$$L^i=\begin{bmatrix}L_{1i} \\ L_{2i} \\ \vdots \\ L_{ni}\end{bmatrix}, \quad M^i=(M_{i1}M_{i2}\cdots M_{in})$$

and L_{ij}, M_{ij}, N_{ij} are the elements in the ith rows and jth columns of the respective matrices. The bordered determinant $|W|$ has thus been reduced to a determinant of bordered determinants of a simple form. Each one of the individual determinants of Eq. (A4) may be evaluated by

$$\begin{vmatrix}K & L^i \\ M^j & N_{ji}\end{vmatrix}=|K|N_{ji}-\sum_{kl}L_{ki}M_{jl}\ (\text{cofactor of }K_{kl}).\ (A5)$$

For a single parameter only assigned to the defect, as $r=1$, $(q\equiv q_1)$, then from Eqs. (A3) and (A5)

$$|W|=|K|\frac{\partial^2 E}{\partial q^2}-\sum_{kl}\frac{\partial^2 E}{\partial p_k\partial q}\frac{\partial^2 E}{\partial p_l\partial q}\ (\text{cofactor of }K_{kl}),\ (A6)$$

and in the special case where the mixed derivatives with respect to p_i and q are zero (which will occur for example when the parameters have been chosen symmetrically about a particular position for the defect, which is then relaxed slightly from its symmetry position), then

$$|W|=|K|\,(\partial^2 E/\partial q^2),\qquad (A7)$$

and the condition for a minimum becomes very simple.

The usual situation with respect to relaxation calculations is to consider the defect in some fixed place in the lattice and the other parameters (the p_i) used to minimize the energy. The conditions

$$\partial E/\partial p_i=0,\quad i=1,\cdots n\qquad (A8)$$

then specify p_i as functions of the q_i;

$$p_i=p_i(q_1\cdots q_r),\qquad (A9)$$

so that

$$E=E(p_i(q_j);q_j)\equiv\epsilon(q_j),\qquad (A10)$$
$$i=1,\cdots n,\quad j=1,\cdots r.$$

A necessary condition that a minimum of energy be obtained subject to the restriction that the defect atom be fixed is then

$$|K|>0$$

and that the principal minors of $|K|$ be greater than 0. In this form the condition for a minimum position for the

defect is that

$$\frac{\partial \epsilon}{\partial q_j}=0, \quad j=1, \cdots r$$

and

$$S \equiv \begin{bmatrix} \dfrac{\partial^2 \epsilon}{\partial q_1{}^2} & \dfrac{\partial^2 \epsilon}{\partial q_1 \partial q_2} & \cdots & \dfrac{\partial^2 \epsilon}{\partial q_1 \partial q_r} \\ \dfrac{\partial^2 \epsilon}{\partial q_2 \partial q_1} & & & \\ \vdots & & & \\ \dfrac{\partial^2 \epsilon}{\partial q_r \partial q_1} & & & \dfrac{\partial^2 \epsilon}{\partial q_r{}^2} \end{bmatrix}$$

should have a determinant whose value and principal minors are positive. The substitution involved in Eq. (A9) is difficult to make and it is preferable to work with the original expression E for the energy. For this reason the derivatives of ϵ with respect to the q_i will now be evaluated in terms of those of E:

$$\frac{\partial \epsilon}{\partial q_i}=\frac{\partial E}{\partial q_i}+\sum_{j=1}^{n} \frac{\partial E}{\partial p_j}\frac{\partial p_j}{\partial q_i}, \tag{A11}$$

where $\partial p_j/\partial p_i$ may be obtained from Eq. (A9), or from Eq. (A8) by differentiating it with respect to the q_j, considering it as a function of the q_j only. By the latter method

$$\frac{\partial^2 E}{\partial p_i \partial q_j}+\sum_{k} \frac{\partial p_k}{\partial q_j}\frac{\partial^2 E}{\partial p_i \partial p_k}=0 \tag{A12}$$

to give a set of linear inhomogenous equations for the $n\times r$ quantities $\partial p_k/\partial q_j$. Equation (A12) may be written as

$$L^i+KT^i=0, \tag{A13}$$

where T^i is the matrix

$$\begin{bmatrix} \dfrac{\partial p_1}{\partial q_j} \\ \dfrac{\partial p_2}{\partial q_j} \\ \vdots \\ \dfrac{\partial p_n}{\partial q_j} \end{bmatrix}.$$

Solving Eq. (A13) for T^i,

$$T^i=-(K^{-1})L^i, \tag{A14}$$

where K^{-1} is the inverse of K, K has an inverse since

$|K|>0$ from the condition for a minimum for variations of the p_i keeping q_j fixed. Equation (A14) gives

$$\frac{\partial p_k}{\partial q_j}=-\sum_{i}(K^{-1})_{ki}\frac{\partial^2 E}{\partial p_i \partial q_j}. \tag{A15}$$

Differentiating Eq. (A11) with respect to q_k leads to

$$\frac{\partial^2 \epsilon}{\partial q_i \partial q_k}=\frac{\partial^2 E}{\partial q_i \partial q_k}+\sum_{i}\frac{\partial^2 E}{\partial q_i \partial p_j}\frac{\partial p_j}{\partial q_k}+\sum_{i}\frac{\partial^2 E}{\partial p_j \partial q_k}\frac{\partial p_j}{\partial q_i}$$

$$+\sum_{il}\frac{\partial^2 E}{\partial p_j \partial p_l}\frac{\partial p_j}{\partial q_i}\frac{\partial p_l}{\partial q_k}+\sum_{i}\frac{\partial E}{\partial p_j}\frac{\partial^2 p_j}{\partial q_i \partial q_k}. \tag{A16}$$

Making use of the minimum conditions, Eq. (A8) and Eq. (A12), reduces the derivatives of E to

$$\partial \epsilon/\partial q_i=\partial E/\partial q_i \tag{A17}$$

and

$$\frac{\partial^2 \epsilon}{\partial q_i \partial q_k}=\frac{\partial^2 E}{\partial q_i \partial q_k}+\sum_{j}\frac{\partial^2 E}{\partial q_i \partial p_j}\frac{\partial p_j}{\partial q_k}. \tag{A18}$$

Substituting from Eq. (A15) into Eq. (A18),

$$\frac{\partial^2 \epsilon}{\partial q_i \partial q_k}=\frac{\partial^2 E}{\partial q_i \partial q_k}-\sum_{il}\frac{\partial^2 E}{\partial q_i \partial p_j}\frac{\partial^2 E}{\partial p_l \partial q_k}\frac{(\text{cofactor of } K_{lj})}{|K|}$$

$$=\frac{1}{|K|}\begin{vmatrix} K & L^k \\ M^i & N_{ik} \end{vmatrix} \quad \text{from Eq. (A5)}.$$

Therefore, the condition for a minimum becomes that

$$|S|=|W|/|K| \tag{A19}$$

[from Eq. (A14) and the above equation] is positive definite. Since $|K|$ is positive because of the minimum condition for a fixed position of the defect, this condition reduces to be that $|W|$ has to be positive definite, as found previously for the case of no initial connection between the parameters. Eq. (A19) is independent of the number of parameters used to determine the position of the defect. For a single parameter $(q_1\equiv q)$

$$|S|=\begin{vmatrix} K & L^1 \\ M^1 & N_{11} \end{vmatrix}/|K|$$

$$=N_{11}-\sum_{ij} L_i{}^1 M_j{}^1 (\text{cofactor of } K_{ij})/|K|$$

$$=\frac{\partial^2 E}{\partial q^2}-\sum_{ij}\frac{\partial^2 E}{\partial p_i \partial q}\frac{\partial^2 E}{\partial p_j \partial q}\frac{(\text{cofactor of } K_{ij})}{|K|} \tag{A20}$$

and in the special case where the mixed derivatives are zero,

$$|S|=\partial^2 E/\partial q^2. \tag{A21}$$

So far the defect has not been specified to be in a position of any particular symmetry. Each position of symmetry will simplify somewhat the expressions

obtained here. If the defect is placed in a position where

$$\epsilon(q_1 \cdots q_i \cdots q_r) = \epsilon(q_1 \cdots - q_i, \cdots q_r)$$

for each q_i, then $\partial\epsilon/\partial q_i = 0$, which satisfies one of the conditions for a minimum or maximum. It is sometimes possible to define parameters such that this type of symmetry is the case, for example, by defining the parameter to be the distance from a symmetry position. If in addition the parameters p_i are chosen so that

$$E(\cdots p_i \cdots, \cdots q_j \cdots) = E(\cdots p_i \cdots, \cdots - q_j \cdots),$$

then

$$\partial^2 E/\partial p_i \partial q_j = 0 \qquad (A22)$$

and the conditions for a minimum (with respect to this choice for the parameters) become that

$$|N| \text{ and its principal minors} > 0, \qquad (A23)$$

which reduces to

$$\partial^2 E/\partial q^2 > 0 \qquad (A24)$$

for a single defect parameter. This situation would arise again by choosing parameters symmetrically about a particular position of symmetry for the defect and then relaxing the symmetry to evaluate the required derivatives. Substituting Eq. (A22) in Eq. (A15) leads to $\partial p_k/\partial q_j = 0$ which implies that changing the q_j slightly from the values used to calculate the p_i's, does not change the values of the p_i's. Without Eq. (A22) this would not necessarily be the case showing that to ascertain the nature of a certain position the p_i's and the q_i's have to be varied. It should be pointed out that the choice implied by Eq. (A22) may force stability on the problem in the sense that a different (more realistic) choice of parameters could lead to a different type of stability.

Optical Absorption in HgTe and HgCdTe

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(Received 5 November 1963)

Absorption and reflectivity near the fundamental absorption edge have been measured in the HgTe-CdTe alloy series for CdTe concentrations of up to 28%. In the HgTe rich region, the edge shifts to longer wavelengths with decreasing temperature. For HgTe, the absorption rises to 2×10^4 cm^{-1} at $\hbar\omega = 0.6$ eV. Absorption did not decrease below 1.4×10^3 cm^{-1} at room temperature. The theory of optical absorption in zincblende compounds is reviewed. Absorption in this alloy series agrees with theory for direct transitions with an energy-independent matrix element evaluated by Kane for InSb. Analysis of reflectivity in HgTe indicates an electron effective mass of $0.02m$ at 100°C.

I. INTRODUCTION

WITH the zincblende structure HgTe and CdTe are intermetallic semiconductors. The lattice parameter varies by 0.3% between HgTe and CdTe,[1] and the compounds form solid solutions at all compositions.[2]

Measurements of the electrical properties of HgTe have been reported by several workers.[3–5] The results have usually been interpreted as indicating an energy gap near 0.02 eV, although band overlap has been suggested as an explanation for the high carrier concentrations.[6–7]

The electrical and optical properties of CdTe have also been studied.[8–10] The conduction-band minimum appears to be at the zone center,[11] and 1.6 eV (at 20°K) above the valence band as determined from the position of the exciton lines.[12] This result is in accord with observed regularities in the zincblende compounds.

Measurements of optical transmission in HgTe — CdTe alloys were reported by Lawson et al.[2] Their results indicated that the absorption edge shifted to longer wavelengths with increasing additions of HgTe in CdTe. Magnetoreflection measurements[13] are consistent with this view.

Measurements of the reflectivity of crystalline HgTe and CdTe and the transmission of thin films of CdTe

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