et al.[39] and 0.31 eV by Kanzaki *et al.*,[40] these latter two values being essentially equal for $T\sim 600°\mathrm{C}$ and considerably below the value obtained in the present investigation. Preliminary results of an investigation being carried out under the direction of one of us (KLK) suggest that the theoretical value of B for a calcium impurity in NaCl increases to 0.47 eV if the calcium ion is permitted to move off the lattice site,[41] a condition not permitted in previous calculations.

ACKNOWLEDGMENT

The authors wish to acknowledge the significant contribution made to this investigation by Charles Ebner.

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[39] A. Murin, S. Banasevich and Yu. Grushko, Fiz. Tverd. Tela **3**, 2427 (1961) [English transl.: Soviet Phys.—Solid State **3**, 1762 (1962)].

[40] H. Kanzaki, K. Kido, S. Oki, and S. Tamura, J. Phys. Soc. Japan **20**, 2305 (1965).

[41] P. Moore (private communication).

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Structure and Stability of *H* Centers*

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The distortion around and the relaxation energy for a substitutional $\mathrm{Cl_2^-}$ molecular ion (*H* center) in NaCl and KCl have been obtained for both the ⟨110⟩ and ⟨111⟩ orientations by a method involving the calculation of electrostatic, polarization, dipole-dipole, and repulsive energies according to the usual point-lattice model. The binding energy of the free $\mathrm{Cl_2^-}$ molecule was taken, however, from the quantum-mechanical calculations of Wahl and Gilbert. The relaxation of about 20 neighboring ions has been taken into account using five independent parameters in minimizing the energy relative to a perfect lattice. It was not found possible, with this model, to account for the preferred ⟨110⟩ orientation of the *H* center, the ⟨111⟩ direction being preferred by about 0.2 eV. It appears necessary to take into account the known fact that the hole associated with the halogen molecule is not localized on the molecule but spreads a little onto two collinear halogen ions. This effect, treated in an approximate manner, leads to an *H* center which is stable in the ⟨110⟩ direction. It also explains qualitatively the orientation of *H* centers in mixed crystals.

I. INTRODUCTION

The *H* center in the alkali halides has received extensive experimental study since its discovery by Duerig and Markham[1] in 1952. Various pieces of evidence have combined to show that it can be approximately considered as an X_2^- molecular ion. It is thus equivalent to a neutral interstitial halogen atom. The *H* center has been found to be oriented along a ⟨110⟩ direction, and it is the goal of this paper to show why it prefers that direction over the ⟨111⟩ direction, which at first sight might appear to offer more room for the $\mathrm{Cl_2^-}$ molecule. The calculations are restricted to NaCl and KCl, although the same situation is common to many other alkali halides. It should be pointed out, however, that *H* centers in certain mixed crystals have been observed to lie in the ⟨111⟩ direction.[2,3] These results are discussed briefly later on.

The *H* center may be produced by irradiation with x rays at low temperatures such as the liquid-helium temperature. Compton and Klick[4] determined the ⟨110⟩ symmetry of the center by bleaching with polarized *H*-band light. Later, detailed electron spin resonance studies of the *H* center were made by Känzig and Woodruff[5] which led to the model of an *H* center as a trapped hole localized on four colinear halogens in the ⟨110⟩ direction. Secondary splitting indicates that the hole spends most of the time on the X_2^- molecule itself and only 4–10% of the time on the two outside halogen ions.

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[1] W. H. Duerig and J. J. Markham, Phys. Rev. **88**, 1043 (1952).

[2] W. Hayes and G. M. Nichols, Phys. Rev. **117**, 993 (1960).

[3] J. W. Wilkins and J. R. Gabriel, Phys. Rev. **132**, 1950 (1963).

[4] W. D. Compton and C. C. Klick, Phys. Rev. **110**, 349 (1958).

[5] W. Känzig and T. O. Woodruff, J. Phys. Chem. Solids **9**, 70 (1958).

TABLE I. Constants used in the repulsive interaction.

	NaCl	KCl
Interionic distance	2.820 Å	3.147 Å
b	0.338×10^{-12} erg	0.338×10^{-12} erg
ρ	0.317 Å	0.337 Å
Radius of Cl^-	1.585 Å	1.585 Å
Radius of Na^+	1.170 Å	
Radius of K^+		1.463 Å

Bleaching studies have been made by Teegarden and Maurer,[6] Känzig and Woodruff,[5] and Cape and Jacobs.[7] In KCl, after warming up from 5 to 43°K, the H centers grow by about 40%, whereas the V_k centers initially present are completely bleached. At 56°K the H centers are bleached completely. The formation of an interstitial such as an H center has to be associated with the formation of a vacancy. Thus, the problem of the mechanism of H-center formation is closely related to the problem of the formation of F and α centers. Many models for this process have been proposed,[8–16] but no definite conclusions have been drawn. It is hoped that the calculation here presented may help in choosing the most satisfactory mechanism.

The method used in these calculations is essentially the same as that used by Hatcher and Dienes[17] (hereafter to be referred to as HD II). It is principally a point-ion approach with suitable modifications for the presence of a large molecular ion. The notation of HD II is used. In Sec. II, the constants and interaction potentials are give; in Sec. III, the main calculations for a Cl_2^- in the $\langle110\rangle$ and $\langle111\rangle$ directions are presented; in Sec. IV, the sensitivity of the orientations to variation in the parameters of the potential is investigated; in Sec. V, a quantum-mechanical explanation is offered for the observed preferred orientation; and finally in Sec. VI, mixed H centers are briefly discussed. Preliminary results of these investigations have been reported previously.[18,19]

II. CONSTANTS AND INTERACTION POTENTIALS

The calculation of the Coulomb and polarization interactions was described in HD II. The major questions concern the treatment of the repulsive interactions, the energy of the Cl_2^- molecule as a function of the separation of the two chlorine nuclei, and the interaction of the Cl_2^- molecule with the rest of the lattice. These items are taken up in this section.

The repulsive interaction chosen for the problem was of the Born-Mayer form

$$C_{12}b\exp\left(\frac{r_1+r_2}{\rho}\right)\exp\left(\frac{-r_{12}}{\rho}\right).$$

This form represents the interaction between two ions of radii r_1 and r_2 with C_{12} the appropriate Pauling coefficient b a universal constant independent of the particular ions, ρ the hardness parameter, and r_{12} the separation between the ions. The constants used in the calculations were those obtained by Tosi and Fumi[20] by their extensive analysis of ionic-crystal data. The values used are shown in Table I.

A value for the effective radius of a $Cl^{-1/2}$ ion is necessary as interactions between the H center and other ions were considered on the basis of representing the Cl_2^- ion as two $Cl^{-1/2}$ ions equally spaced about the lattice site. This radius was obtained by averaging that for Cl^- and one calculated for Cl^0 from the average r value of the $3p$ wave functions of the Cl^0 atom. To have a basis for comparison, the average r for the p state of the Cl^- electrons was also calculated and the Cl^0 radius adjusted accordingly. The Cl^0 radius turns out to be 1.64 Å while the radius of the $Cl^{-1/2}$ ion is 1.725 Å. The C_{12} constants for interaction with $Cl^{-1/2}$ ions were chosen using a charge of $(-\frac{1}{2})$.

The interaction energy of the Cl_2^- itself, as a function of the separation of the chlorine nuclei, was obtained in two ways. In some preliminary calculations, a simplified potential was obtained from the arithmetic mean of the Cl^--Cl^- repulsive interaction and the Morse potential for Cl_2. The repulsive Cl-Cl potential was obtained by the statistical method of Abrahamson *et al.*[21] This interaction potential for Cl_2^- showed a slight amount of binding ($\sim$0.2 eV) at an equilibrium separation of 2.95 Å. A much better potential became available when a quantum-mechanical treatment was undertaken by Wahl and Gilbert,[22] who calculated molecular orbitals and the potential energy curve for the ground state ($^2\Sigma_u{}^+$) of the free Cl_2^- by a self-consistent field method. The Wahl-Gilbert interaction as used in our calculations is shown in Fig. 1. In this interaction, the binding energy is 0.93 eV, considerably larger than the 0.2 eV obtained from the simplified potential. The equilibrium separation is now 2.70 Å, somewhat less than the 2.95 Å obtained previously. The Cl_2^- molecular ion is larger than

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[6] K. Teegarden and R. J. Maurer, Z. Physik **138**, 284 (1954).

[7] J. Cape and G. Jacobs, Phys. Rev. **118**, 946 (1960).

[8] H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).

[9] J. H. O. Varley, Nature **174**, 886 (1954).

[10] R. E. Howard and R. Smoluchowski, Phys. Rev. **116**, 314 (1959).

[11] D. Dexter, Phys. Rev. **118**, 934 (1960).

[12] C. C. Klick, Phys. Rev. **120**, 760 (1960).

[13] R. E. Howard, S. Vosko, and R. Smoluchowski, Phys. Rev. **122**, 1406 (1961).

[14] F. E. Williams, Phys. Rev. **126**, 70 (1962).

[15] V. H. Ritz, Phys. Rev. **133**, A1452 (1964).

[16] T. M. Srinivasen and W. D. Compton, Phys. Rev. **137**, A264 (1965).

[17] R. D. Hatcher and G. J. Dienes, Phys. Rev. **134**, A214 (1964).

[18] G. J. Dienes, R. D. Hatcher, and R. Smoluchowski, Bull. Am. Phys. Soc. **8**, 89 (1963).

[19] G. J. Dienes, R. D. Hatcher, R. Smoluchowski, and W. D. Wilson, in Proceedings of the Washington Conference on Interstitials and Vacancies, May 1966 (unpublished).

[20] M. P. Tosi and F. G. Fumi, J. Phys. Chem. Solids **25**, 45 (1964).

[21] A. A. Abrahamson, R. D. Hatcher, and G. H. Vineyard, Phys. Rev. **121**, 159 (1961).

[22] A. C. Wahl and T. L. Gilbert (private communication). See also Bull. Am. Phys. Soc. **10**, 1097 (1965).

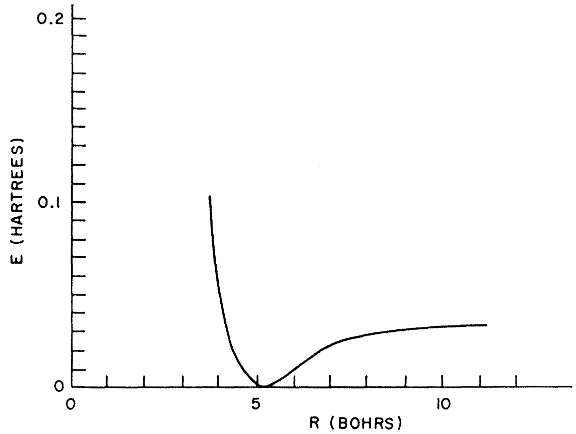

FIG. 1. The Cl_2^- interaction potential. From the work of Gilbert and Wahl.

the Cl_2 molecule as is to be expected because of the lower binding. The ground state of the Cl_2^- is nondegenerate, and therefore crystal-field splitting should not be present. In our calculations the Wahl-Gilbert potential was replaced by

$$V=-0.25-8.83(r-0.8)+35.0(r-0.8)^2-36.7(r-0.8)^3,$$

with r in units of the lattice spacing in NaCl. Although the potential for Cl_2^- was obtained for the free ion, it should also hold reasonably well in a crystal environment. It is to be expected that the H center will be squeezed somewhat in the crystal, but not very much, as the repulsive part of the potential in quite steep. The electron density curves for Cl_2^-, also calculated by Wahl-Gilbert, show a strong separation of the charge density into two groupings around the separate nuclei. This is the justification for our considering the interaction between neighboring ions and the Cl_2^- molecule as equivalent to separate interactions between individual chlorine ions.

The Tessman, Kahn, and Shockley[23] values of the polarizabilities have been used for Na^+, K^+, and Cl^-. For Cl^0, we have taken the ratio of the polarizability with five and with six $3p$ electrons, multiplied it by the polarizability of Cl^-, and obtained 2.61×10^{-24} cm^3 for the neutral chlorine atom. The polarizability of $Cl^{-1/2}$ was taken to be the average of that for Cl and Cl^-, or 2.785×10^{-24} cm^3. Occasionally in the calculations a charge other than 1 or $\frac{1}{2}$ on the ions was assumed. In these cases, the polarizabilities were interpolated accordingly.

III. RELAXATION FOR THE H CENTER ORIENTED IN $\langle 111\rangle$ AND $\langle 110\rangle$ DIRECTIONS

Several sets of calculations were performed to evaluate the relaxation of ions neighboring the H center. In each set the H center was oriented symmetrically about the (0,0,0) position, first in a $\langle 111\rangle$ direction, then in a $\langle 110\rangle$ direction, and of the order of 20 ions were assigned displacement parameters so that, in general, they moved away from the (0,0,0) position. Those ions were chosen which affected most the final result as verified by trial and error. The symmetry of the configurations permitted the use of a small number of displacement parameters. The specific choices of ions and parameters are listed in tables pertaining to the particular calculations. In each case, the energy relative to a perfect lattice, not containing the defect, was found by evaluating the electrostatic, polarization, dipole-dipole, repulsive, and attractive contributions from the various ions. The method of calculation was essentially the same as that of HD II and the basic expressions are the same. For the electrostatic terms no approximations were needed. In the polarization terms, the effect of an induced dipole on one ion in changing the electric field at another ion, and thereby affecting the value of the induced dipole at that ion, was not included. Some tests were made to verify that, as expected, this correction would be small since the defect preserves the neutrality of the lattice. The polarization series was carried as far as the dipole-dipole interaction, and appeared to be converging well. The repulsive terms were also treated exactly insofar as the contributions from as many neighbors as necessary were included to give energies well within the desired accuracy of the calculation. The attractive term arose from the internal Cl_2^- interaction.

As far as the electrostatic interaction of the Cl_2^- with neighboring ions was concerned, the Cl_2^- was considered as consisting of two $Cl^{-1/2}$ ions. An alternative would have been to consider it as a single charge located at the lattice site. This did not appear appropriate since it is known that the wave functions for the Cl_2^- spread out considerably in the axial direction; and in this case, not only are the two halves of the Cl_2^- separately polarizable, but the field due to the two halves will affect the dipoles on neighboring ions. An ion far away sees just a single charge while a nearby ion experiences a charge

TABLE II. Displacement parameters and energies for set (c) parameters for NaCl for Cl_2^- in $\langle 111\rangle$ orientation.

Ions	Parameter	Value	Displacement of typical ion (the first) of the group
1,2	p_1	0.255	p_1,p_1,p_1
3–8	p_2	0.060	$-p_1p_2,(1-p_1)p_2,(1-p_1)p_2$
9–14	p_3	0.105	$(1-p_1)p_3,-1.6p_1p_3,-1.6p_1p_3$
15,16	p_4	0.000	p_4,p_4,p_4
17–22	p_5	0.010	$-p_5,-p_5,-p_5$
23–26	...	0	
Electrostatic			0.18 eV
Polarization			−0.50
Dipole-dipole			0.04
Repulsive, regular ions			2.28
Repulsive, H center			−0.76
Energy relative to perfect lattice (defect present and no relaxation)			0.81
Energy relative to perfect lattice			2.05 eV

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[23] J. Tessman, A. Kahn, and W. Shockley, Phys. Rev. 92, 890 (1953).

distributed nearly like the charge density calculable from the wave functions. In dealing with the Cl_2^- molecule itself, all interactions between the two centers were considered as being included in the Gilbert-Wahl potential. In treating the repulsive interaction between a $Cl^{-1/2}$ and a nearby ion, the Born-Mayer expression was employed with the hardness parameter appropriate to the lattice, and a radius for the $Cl^{-1/2}$ obtained as described above. The distance of a $Cl^{-1/2}$ center from the origin was always taken as one of the unknown parameters, and usually the other center was chosen to lie in a symmetrical position with respect to the first.

The energy was calculated first for an initial, estimated set of values of the displacement parameters, and then the parameters were varied until minima were found for the energy with respect to each of them. This process was iterated on a high-speed computer until an accuracy of about 0.01 eV was obtained.

Calculations were made for:

(a) Born-Mayer potentials and a simplified Cl_2^- interaction.

(b) Born-Mayer potentials and Wahl-Gilbert interaction potential.

(c) Born-Mayer potentials with Tosi-Fumi constants and Wahl-Gilbert interaction potential.

(The numerical values of the constants are listed in Table I.) All three sets were used for NaCl; however, only the last was used for KCl. Results for (a) and (b) will be mentioned briefly and details will be given only for set (c) which is considered to be the best combination of potentials.

The over-all conclusions from the constants and potentials used in set (a) were that the $\langle 111\rangle$ direction is favored over the $\langle 110\rangle$ by 0.2 eV for NaCl. Since the binding energy for the Cl_2^- in this approximation is quite a bit smaller than that obtained from the Wahl-Gilbert potential, it was expected that the use of the latter might change the situation in many respects. For set (b), for the $\langle 111\rangle$ direction, the energy of formation of an *H* center relative to a perfect lattice turned out to be 2.00 eV. The separation of the two $Cl^{-1/2}$ centers in this calculation was 2.48 Å compared to a separation in the free molecule of 2.70 Å. The crystal compresses the molecule and at the same time lowers the binding energy from 0.93 to 0.76 eV. This loss is, however, offset by the electrostatic and polarization terms. The minimum in the total energy was quite broad, so that slightly changing the displacement parameters around their minimum values did not change the energy appreciably. For the $\langle 110\rangle$ direction and a similar number of parameters and relaxing ions, the energy relative to the perfect lattice was 2.09 eV. Although the difference is small, it appears to be real in that small changes in the parameters and constants used in the program usually change both the $\langle 111\rangle$ and $\langle 110\rangle$ calculations in the same way. The difference is less than the 0.20 eV obtained by using the simplified version of the interaction for the Cl_2^-; however, it is not small enough to say that it lies within the error of the calculation. The separation of the two centers is now 2.47 Å, close to that for a $\langle 111\rangle$ direction It thus appears that the Cl_2^- maintains the same size in swinging around from a $\langle 111\rangle$ to a $\langle 110\rangle$ direction.

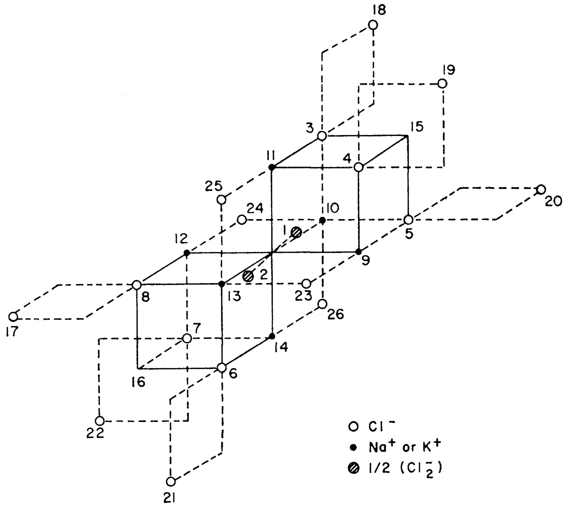

FIG. 2. Cl_2^- in a $\langle 111\rangle$ direction and the relaxing ions.

A. Set (c) Potentials for NaCl $\langle 111\rangle$ Orientation

The ions to be relaxed and the displacement parameters associated with them were chosen as shown in Fig. 2. The values obtained for the parameters on minimization and the various energies are shown in Table II. Although the energy relative to the perfect lattice has gone up only 0.05 eV as compared to set (b), there were quite large changes in some of the separate energy terms. The parameter associated with the $Cl^{-1/2}$ did not change, but the over-all relaxation of the lattice was considerably less. There was a corresponding decrease in the polarization energy. These changes were more than balanced, however, by a significant increase in the electrostatic energy. It should be noted that the final value for the total energy is rather insensitive to quite large changes in the various constants. The Cl_2^- molecule is compressed, as compared to the free molecular ion (2.70 Å), to an internuclear separation of 2.48 Å.

B. Set (c) Potentials for NaCl $\langle 110\rangle$ Orientation

Figure 3 shows the ions which were allowed to relax, and Table III gives the values for the displacement parameters and the corresponding energy terms. The same general characteristics as found in comparing set (c) and (b) before apply here, and again the total energy has increased. The net result is that the energy difference between $\langle 111\rangle$ and $\langle 110\rangle$ directions is 0.18 eV, again in favor of a $\langle 111\rangle$ orientation. The Tosi-Fumi constants generally give rise to a more compact structure, but with slightly higher energies. The less distorted nature of the neighborhood of the defect should

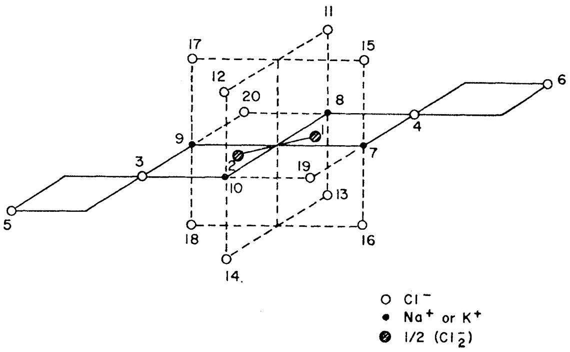

FIG. 3. Cl_2^- in a ⟨110⟩ direction and the relaxing ions.

increase the accuracy of the calculation since the influence of ions further away has been decreased. The internuclear separation of the Cl_2^- is now 2.46 Å, very close to the value found for the ⟨111⟩ orientation.

C. Set (c) Potentials for KCl ⟨111⟩ Orientation

Since the K^+ ion is larger in size than the Na^+, the ions allowed to relax in KCl are somewhat different from those in the NaCl case. More attention is paid to the neighboring K^+ ions and less to the Cl^- ions further away. For the case of Cl_2^- in a ⟨111⟩ direction, the ions chosen to relax, the parameters involved, and the corresponding energies are shown in Fig. 2 and Table IV. Eighteen movable ions were employed with five displacement parameters. The larger size of the K^+ ions caused the displacements of the neighboring ions to be smaller than in the case of NaCl, and consequently the energy relative to the perfect lattice decreased. There is a greater compactness here as compared to NaCl. The influence of the larger ion has been offset somewhat by the larger lattice constant, with the result that the separation between the $Cl^{-1/2}$ centers is a little greater than in the NaCl case. For KCl it is 2.56 Å in the ⟨111⟩ directions, introducing a little more binding into the Cl_2^- interaction energy.

TABLE III. Displacement parameters and energy contributions for Cl_2^- in ⟨110⟩ orientation with set (c) of potentials for NaCl.

Ions	Parameters	Value	Displacement of typical ion (the first) of the group
1,2	p_1	0.310	$p_1,p_1,0$
3,4	p_2	0.080	$-p_2,-p_2,0$
5,6	p_3	0.025	$-p_3,-p_3,0$
7–10	p_4	0.105	$p_4,-p_4,0$
11–18	p_5	0.010	$-p_5,p_5,p_5$
19,20	...	0	
Electrostatic			0.24 eV
Polarization			−0.65
Dipole-dipole			0.05
Repulsive, regular ions			2.51
Repulsive, *H* center			−0.73
Energy relative to perfect lattice (defect present and no relaxation)			0.81
Energy relative to perfect lattice			2.23 eV

TABLE IV. Displacement parameters and energy contributions for Cl_2^- in ⟨111⟩ orientation with set (c) of parameters for KCl.

Ions	Parameters	Value	Displacement of typical ion (the first) of the group
1,2	p_1	0.235	p_1,p_1,p_1
3–8	p_2	0.030	$-p_1p_2,(1-p_1)p_2,(1-p_1)p_2$
9–14	p_3	0.100	$(1-p_1)p_3,-1.6p_1p_3,-1.6p_1p_3$
15,16	p_4	−0.010	p_4,p_4,p_4
23–26	p_5	0.020	$p_5,-p_5,0$
17–22	...	0	
Electrostatic			0.31 eV
Polarization			−0.30
Dipole–dipole			0.02
Repulsive, regular ions			1.51
Repulsive, *H* center			−0.84
Energy relative to perfect lattice (defect present and no relaxation)			0.70
Energy relative to perfect lattice			1.40 eV

D. Set (c) Potentials for KCl ⟨110⟩ Orientation

Figure 3 and Table V show the choice of ions, parameters, and energy values for the ⟨110⟩ directions for Cl_2^- in KCl. The separation of the defect centers is 2.54 Å, approximately the same value as in C, showing, as in the case of NaCl, that the Cl_2^- remains at about the same size in the two different orientations. As for NaCl, ⟨111⟩ appears to be the favored orientation, this time by 0.17 eV.

A summary of the calculations is shown in Table VI.

IV. VARIATION OF PARAMETERS AND CONSTANTS

It has already been intimated that the energy difference of the ⟨111⟩ and ⟨110⟩ orientations appeared rather insensitive to changes in the constants and in the various parameters. This point needed more careful examination. The constants considered were the radius of the chlorine atoms (c_1), the polarizability of the Cl^- (c_2), and the hardness constant $\rho(c_3)$ used in the Born-Mayer repulsive interaction. Other variations could also be introduced as pertinent constants and were studied. The position of one of the $Cl^{-\frac{1}{2}}$ ions above the x-y plane was assigned a constant c_4. The x and y values of the $Cl^{-1/2}$ ion could also be varied independently of the z variation. Such variation was assigned the constant c_5. The five c_i mentioned above should now enter into the expression for the energy, and can be treated along the lines of the Appendix in HD II. We thus have

$$E=E(p_i,q_j,c_k),$$

with p_i being the displacement parameters of the lattice ions, q_j the displacement parameters associated with the defect, and c_k the constants. For the equilibrium position we have

$$\frac{\partial E}{\partial p_i}=\frac{\partial E}{\partial q_j}=0 \quad \text{for each } i \text{ and } j,$$

TABLE V. Displacement parameters and energy contributions for Cl_2^- on ⟨110⟩ orientation with set (c) of parameters for KCl.

Ions	Parameters	Value	Displacement of typical ion (the first) of the group
1,2	p_1	0.285	$p_1, p_1, 0$
3,4	p_2	0.045	$-p_2, -p_2, 0$
19,20	p_3	0.035	$p_3, -p_3, 0$
7–10	p_4	0.095	$p_4, -p_4, 0$
11–18	p_5	0.010	$-p_5, p_5, p_5$
5,6	⋯	0	
Electrostatic			0.41 eV
Polarization			−0.39
Dipole-dipole			0.04
Repulsive, regular ions			1.63
Repulsive, *H* center			−0.82
Energy relative to perfect lattice (defect present and no relaxation)			0.70
Energy relative to perfect lattice			1.57 eV

but, of course, it is not necessary for any such condition to hold for the c_k. If the c_k are given fixed values and equilibrium values are obtained for the p_i, q_j, then the p_i, q_j can be considered as functions of the c_k and the energy expression takes the form

$$E=E(p_i(c_k),q_j(c_k),c_k)=F(c_k).$$

To second order, the change in the energy with respect to the c_k's is

$$dF=\sum_i \frac{\partial F}{\partial c_i}dc_i+\tfrac{1}{2}\sum_{ij}\frac{\partial^2 F}{\partial c_i \partial c_j}dc_i dc_j.$$

By a similar analysis to that of the Appendix of HD II

$$\frac{\partial F}{\partial c_i}=\frac{\partial E}{\partial c_i},$$

and

$$\frac{\partial^2 F}{\partial c_i \partial c_k}=\frac{1}{|W|}\begin{vmatrix} W & P^k \\ Q^i & C_{ik}\end{vmatrix},$$

with the W defined by Eq. (A3) of HD II and

$$P^k=\begin{bmatrix} \dfrac{\partial^2 E}{\partial r_1 \partial c_k} \\ \vdots \\ \dfrac{\partial^2 E}{\partial r_n \partial c_k}\end{bmatrix}, \quad C_{ik}=\begin{bmatrix} \dfrac{\partial^2 E}{\partial c_1^2} & \dfrac{\partial^2 E}{\partial c_1 \partial c_2} & \cdots \\ \vdots & \vdots & \vdots \\ & & \cdots \dfrac{\partial^2 E}{\partial c_k^2}\end{bmatrix},$$

and

$$Q^i=\left(\frac{\partial^2 E}{\partial c_i \partial r_1}\cdots\frac{\partial^2 E}{\partial c_i \partial r_n}\right),$$

where r_n refers to the complete set of parameters p_i, and q_j. This gives for the energy change due to the constants c_k

$$dF=\sum_i \frac{\partial E}{\partial c_i}dc_i+\frac{1}{2}\frac{1}{|W|}\sum_{ik}\begin{vmatrix} W & P^k \\ Q^i & C^{ik}\end{vmatrix} dc_i dc_k \qquad (1)$$

up to second order. Equation (1) can be used for the evaluation of these changes without having to minimize separately the energy every time a new value of the constant is investigated. What is required is to find the derivatives of the energy as a function of the p's, q's, and c's, for the initially chosen values of the c_k's.

It is also of interest to know how the parameters p_i change with the c_k. This expression can be obtained from Eq. (A15) of HD II and is as follows:

$$\frac{\partial p_i}{\partial c_j}=-\sum_k (W^{-1})_{ik}\frac{\partial^2 E}{\partial p_k \partial c_j}, \qquad (2)$$

where W^{-1} is the reciprocal matrix to W. Again these quantities can be evaluated from the derivatives at the equilibrium condition.

The behavior of F and p_i as functions of c_j were investigated for the ⟨110⟩ and ⟨111⟩ directions for the H center for potential sets (a) and (b). The calculation was not carried over to set (c) because the above variations would be very much the same since the repulsive constants were not changed appreciably.

For the ⟨110⟩ case a change in the radius for the Cl^0 from 1.64 to 1.65 Å caused an increase in the energy of 1.3%. This is to be expected as an increase in the radius makes the repulsive energy larger; however, there is a slight countereffect in that the displacement parameters will adjust to lower the energy. An increase in ρ from 0.345 to 0.346 has an opposite effect—a decrease of about 0.7% occurs in the energy. An increase in the polarizability of the Cl^0 from 2.61 to 2.62 makes no change up to 0.1% in the energy. Although such an increase would be expected to produce a lowering of the energy, the effect of the adjustment of the displacement parameters apparently nullifies this effect. The effect of interfering with the ⟨110⟩ orientation shows that a distortion in the x, y, z directions raises the energy by a small amount. The well is quite shallow here as evidenced by the fact that a change in the z value of 0.01 (in the units used here) causes an energy change of only 0.02%. It is important to note that changes caused by the constants in the energy for the ⟨110⟩ direction are very nearly balanced by similar changes for the ⟨111⟩ direction. The variation of the energy with respect to the z value of the $Cl^{-1/2}$ shows a rather clear minimum for $z=0$, as expected from symmetry. The change in the energy due to changes in the relaxation parame-

TABLE VI. Cl_2^- in alkali halides.

Alkali halide	Orientation	Energy relative to perfect lattice, eV	Internuclear distance of Cl_2^-, Å
NaCl	⟨110⟩	2.23	2.46
	⟨111⟩	2.05	2.48
	ΔE	0.18	
KCl	⟨110⟩	1.57	2.54
	⟨111⟩	1.40	2.56
	ΔE	0.17	

TABLE VII. Dependence of the energy on small changes in the displacement parameters about the equilibrium position for a typical case ⟨110⟩.

Parameter	Value	$(\Delta E/\Delta p)\times(p/E)$
$p_1(\mathrm{Cl}^{-1/2})$	0.353	0.05
p_2 (nearest Cl^-)	0.160	0.04
p_3(next-nearest Cl^- in plane)	0.063	0.004
p_4(nearest Na^+)	0.133	0.009
p_5(next-nearest Cl^- out of plane)	0.018	0.01

ters about their equilibrium position is rather small. For a typical case these changes are shown in Table VII, from which it can be seen that the largest effects are associated with p_1, and p_2 as might be expected. p_3 has only one-tenth the effect of p_2 and it may be expected that ions farther away have an even smaller effect. It is interesting to note that the separation between the two $\mathrm{Cl}^{-1/2}$ ions decreases as both the hardness constant and the radius of the Cl^0 are raised. It was particularly important to investigate the influence of these constants because their values are quite uncertain.

In another study, the charges on the two $\mathrm{Cl}^{-1/2}$ ions were varied from their values of $-\frac{1}{2}|e|$. The charge on one of the ions was increased by an amount Δe; the charge on the other was decreased by the same amount. For the ⟨110⟩ orientation a change of $0.01|e|$ in the charge resulted in an almost negligible increase in the energy, showing that the (0.5,0.5) distribution was the stable one, but also that changes in this charge distribution would not cause much of an energy change, i.e., if part of the charge oscillated between the two ions, then stability was still present. The parameters most affected by this change in the charge are those associated with the positions of the $\mathrm{Cl}^{-1/2}$'s and the nearest colinear Cl^- ions, as expected. The other parameters show a remarkably small change. In another calculation, the charge was shared between all four of these ions in a symmetric manner, resulting again in rather small changes in the energy.

In another calculation, the Cl_2^- was oriented along directions intermediate between ⟨110⟩ and ⟨111⟩. In these cases there was less symmetry present than before, and consequently it was necessary to use seven displacement parameters involving 18 nearby ions. Equilibrium positions were found for three intermediate cases, namely, along ⟨1,1,0.5⟩, ⟨1,1,0.2⟩, and ⟨1,1,0.1⟩. The energy fell on a smooth curve with a minimum at ⟨111⟩ and a maximum at ⟨110⟩, indicating no maxima or minima in between. It is interesting to note that the separation between the $\mathrm{Cl}^{-1/2}$ ions remains about the same in each of the orientations studied, as well as in the ⟨110⟩ and ⟨111⟩ orientations.

In some of the cases the stability was examined using the analysis outlined above. If the determinant W and its principal minors are positive, then the configuration is stable. This condition was satisfied, for example, when the charge on the separate $\mathrm{Cl}^{-1/2}$'s was varied slightly showing stability about the symmetrical position.

As far as the variation of the hardness constant is concerned, the results show that a change of ρ from 0.31 to 0.37 caused the energies in the ⟨110⟩ and ⟨111⟩ directions to vary by about 0.7 eV, from the normal values of about 2.0 eV. The difference between them, however, changes very little remaining at 0.18 ± 0.03 eV.

A separate investigation involved the effect on the polarization energy of the Cl_2^- of the nonuniformity of the electric field in the neighborhood of the ion. Considering the Cl_2^- as two separately polarizable centers as far as the rest of the lattice was concerned, the value of the average E^2 weighted with respect to the charge density of the ion will be different than the value of E^2 at the center of the ion. In addition, the most polarizable part of the ion would presumably be the outer electron shells so that the E^2 should be evaluated there. Several calculations were carried out to investigate these effects and particularly the energy differences between the ⟨110⟩ and ⟨111⟩ directions. The change in the energy amounted to less than 0.05 eV. This effect would thus appear not to explain the preferred orientation of the H center in the ⟨110⟩ directions.

V. QUANTUM-MECHANICAL CONSIDERATION OF THE *H*-CENTER ORIENTATION

The calculations of the previous sections indicate that the stability of the H center cannot be explained in terms of an X_2^- molecule embedded in the usual simple point-lattice model, in which Coulombic interactions, polarization, and the empirical Born-Mayer repulsive terms are taken into account. It is important to stress that the ⟨111⟩ orientation of an X_2^- molecule located at a halogen site is, according to this model, preferred to a ⟨110⟩ orientation within a wide range of variation of the various parameters and constants. Among the latter, one has to mention, in particular, the radius and the polarizability of the hypothetical $X^{-1/2}$ ion as well as the charge distribution among the four ions.

It appears thus that the stability of the H center must be due to a quantum-mechanical effect which is not properly accounted for by the approximate classical models. Inasmuch as an exact solution of the electronic structure of the H center, analogous to the Gilbert and Wahl[22] solution for the free Cl_2^- molecule, presents a very complicated task, it was decided to use simpler approximate methods. One of them is based on (a) the spread of the wave function of the hole associated with the H center, and the other on (b) an approximate estimate of the binding existing between the X_2^- molecule and the other two X^- ions which consitute the H center. Both these methods are described below.

A. Spread of the Wave Function

The basic idea of this model is to treat the hole associated with the X_2^- molecule as a hole trapped in a square potential well and to compare its kinetic energy for the two orientations of the molecule. In a ⟨111⟩

orientation, the two ions which lie in line with the molecule are positive metal ions which confine the hole to the X_2^- molecule. In a ⟨110⟩ direction, on the other hand, a few percent of the hole spreads to the two halogen ions which lie in line with the molecule. Intuition suggests that this effect will favor the ⟨110⟩ orientation. The calculation was made for NaCl and KCl, assuming that the size of the one-dimensional potential wells is given by the distance between appropriate chlorine nuclei plus one diameter of a chlorine ion. The internuclear distances and displacements were taken from the classical calculations given in the earlier part of this paper. Thus, for instance, for NaCl the well for the ⟨111⟩ orientation is 5.77 Å long, while for the ⟨110⟩ orientation, the hole spends most of the time in a well 5.77 Å long, and part of the time in a well 11.88 Å long.

The wave function of the hole in Cl_2^- is of the $3p\sigma_u$ character,[22] and thus, apart from nodes which are characteristic of chlorine ions themselves and have little to do with the configuration of the center, there is one node at the center of each well and those at the walls. According to Känzig and Woodruff,[5] the hole spends between 3 and 10% of the time on the two ions which adjoin the Cl_2^- molecule. One assumes thus that for NaCl, for the 10% case, 80% of the hole is confined to a 5.77 Å well, while 20% is spread over the 11.88 Å well. The resulting energy difference which favors the ⟨110⟩ orientation is 0.68 eV. This difference decreases linearly with decreasing spread of the hole and it disappears when, for both orientations, the hole is confined to the Cl_2^- molecule. Interestingly enough, for KCl one obtains within the limit of the calculation the same energy difference in favor of the ⟨110⟩ orientation.

B. Binding between Cl_2^- and the Rest of the *H* Center

The basic idea of this estimate of the binding in the *H* center in an alkali chloride is to consider a free Cl_2^- molecule as an unstable Cl_2^{-2} molecule which is stabilized by the addition of a hole. The energy-versus internuclear-distance curve for a Cl_2^{-2} configuration can be calculated using the usual Coulombic, Born-Mayer, and polarization terms. The corresponding curve for the Cl_2^- molecule is known from the work of Gilbert and Wahl.[22] The difference between these two curves gives then for each internuclear distance the amount of binding due to the addition of a hole. Knowing the fraction of time which the hole in an *H* center spends outside of the central Cl_2^- molecule, one can obtain an appropriate binding correction for the known distance between one of the chlorines of the Cl_2^-, and the nearest adjoining Cl^- ion in the ⟨110⟩ direction. This distance for NaCl and for KCl is about 3.38 Å. At this internuclear separation, the binding in the Cl_2^- molecule is 0.75 eV, while the potential of the Cl_2^{-2} configuration is 3.92 eV giving a total of 4.67 eV as the binding contribution of one hole. For an *H* center in which the hole spends 10% of the time outside of the central Cl_2^- molecule, one obtains 0.47 eV. Inasmuch as both methods give about the same result it seems reasonable to take an average value and to conclude that a 10% spread of the hole raises the energy of the *H* center in the ⟨111⟩ direction by about 0.57 eV with respect to the energy of this center in the ⟨110⟩ direction. This corrective term has to be added to the results obtained earlier with no spread. It appears that the ⟨111⟩ direction would begin to be preferred if the hole were spread by about 3%. This is just the lower limit suggested by Känzig and Woodruff.[5]

The *H* center is known to anneal out at about 60°K which gives an approximate activation energy of about 0.15 eV if one assumes a frequency factor of 10^{12}. If the rate-controlling step in this process is a rotation of the C_2l^- configuration from a ⟨110⟩ orientation to a ⟨111⟩ orientation, then a 5% spread of the hole accounts for the experimental data.

In both of these approximate methods of estimating the quantum-mechanical contribution to the stability of the *H* center the interactions with nearest-neighbor halide ions which do not lie along the axis of the Cl_2^- molecule have been neglected. The reason for this is twofold: First of all, the wave function of the $3p\sigma_u$ hole is highly concentrated along the axis of the molecule, and, secondly, the nonaxial neighbors are nearly 10% farther away from the molecule than the axial neighbors. The charge density at the centers of the former is one-tenth of that at the centers of the latter.

VI. OTHER CENTERS

It is interesting to note that Wilkins and Gabriel[3] have observed mixed $(ClF)^-$, $(BrF)^-$, and $(BrCl)^-$ centers of the *H* type in impure KCl. The first two seem to lie in the ⟨111⟩ direction, while the third one prefers the ⟨110⟩ direction. These results can be qualitatively explained in the following manner. In all these mixed centers one ion is much smaller than the other (F^-:1.16 Å; Cl^-:1.65 Å; Br^-:1.80 Å), which suggests that in each case the larger ion will tend to be as little displaced from the ideal halogen-ion site as possible. The larger ion will thus also carry most of the charge notwithstanding the few percent variation in electron affinity of the three ions. If the smaller, more displaced, partner is a chlorine then the hole will be shared between the bromine, the displaced chlorine, and the neighboring chlorine ion, all lying in one ⟨110⟩ direction. While the binding energy of $(BrCl)^-$ is not known, one can expect it to be lower than that of Cl_2^- because the corresponding neutral molecule is about 10% less tightly bound. One can conclude thus that the hole associated with the $(BrCl)^-$ center will spend most of the time on the two chlorines tending to form a Cl_2^- molecule or, in other words, the configuration will resemble that of a normal *H* center in which one of the end ions is a bromine and not a chlorine. Thus, all the arguments discussed before for the preference for the ⟨110⟩ orientation will apply. On the other hand, if the displaced partner in the $\langle 110\rangle$ direction were a fluorine the hole would tend to be concentrated on it, rather than on the adjoining bromine or chlorine which will occupy as nearly as possible normal lattice sites. This conclusion is in accord also with the fact that the binding of BrF and ClF molecules is 30% weaker than that of the Cl_2^- molecule, which implies that the corresponding $(XY)^-$ molecules are also more weakly bound than the Cl_2^- molecule. It follows that the binding effects due to the spread of the hole along the $\langle 110\rangle$ direction would be weak or even totally absent and the $\langle 111\rangle$ direction would be preferred as discussed above. This is in agreement with experiment.

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Electromodulation of the Optical Constants of Rutile in the uv

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Large light modulation has been achieved at room temperature by electroreflectance in single-crystal and by electroabsorption in polycrystalline TiO_2. The behavior is similar to that exhibited by some of the perovskite-type ferroelectrics, for instance, barium titanate, but cannot be explained by a shift of the energy levels as found in the case of potassium tantalate. The observed effects have been accounted for in terms of a strongly lifetime-broadened Franz-Keldysh tunneling, with small additional shifts of the critical points, occurring upon application of the electric field. From the electroreflectance spectra, critical points in the optical constants have been detected in good agreement with those known from absolute reflectance data. A correlation of the data with the band structure of rutile has been attempted. Spectra from polycrystalline material do not show great differences from those of single crystals.

INTRODUCTION

TWO of the authors have recently reported[1,2] electroreflectance (hereafter referred to as ER) and electroabsorption (EA) measurements in some ferroelectric materials having perovskite structure (e.g., $KTaO_3$ and $BaTiO_3$). As opposed to germanium, silicon, III-V and II-VI compounds, and other materials,[3–6] where optical field effects can usually be accounted for in terms of just Franz-Keldysh photon-assisted tunneling, in $KTaO_3$ actual shifts and splittings of certain band-structure critical points with electric field have been observed. In particular, a large field dependence was observed in the main reflectivity peak (between 4 and 5 eV for most investigated materials[7]), which corresponds approximately to the position of a classical oscillator chosen to fit the refractive-index dispersion below the fundamental energy gap. We have shown[2] that the large electro-optic effect observed in the visible in some ferroelectric materials[8] is a consequence of the above-mentioned optical field effects in the uv. Because of the large ionic and electronic polarizabilities of the transition-metal ion in ferroelectric materials having perovskite structure,[9] we interpreted the observed behavior of $KTaO_3$ as being at least in part due to changes in the overlap integrals of the transition-metal–oxygen pairs, which affect the band-structure critical points up to energies much higher than those explored in our experiments.[10]

The reason for our interest in investigating rutile (TiO_2) is that, although it does not appear to be ferroelectric over the range of temperatures from 1.6 to 1060°K, its ionic polarizability is very close to that needed for the polarization catastrophe to take place.[11] Local fields at lattice sites, when the Ti ion is ionically polarized, have been calculated to be comparable to

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[1] A. Frova and P. J. Boddy, Phys. Rev. Letters **16**, 688 (1966).

[2] A. Frova and P. J. Boddy, Phys. Rev. **153**, A606 (1967).

[3] A. Frova, P. Handler, F. Germano, and D. E. Aspnes, Phys. Rev. **145**, 575 (1966).

[4] B. O. Seraphin, R. B. Hess, and N. Bottka, J. Appl. Phys. **36**, 2242 (1965); B. O. Seraphin, Phys. Rev. **140**, A1716 (1965).

[5] K. L. Shaklee, F. H. Pollak, and M. Cardona, Phys. Rev. Letters **15**, 883 (1965); *ibid.* **16**, 48 (1966).

[6] R. Williams, Phys. Rev. **126**, 442 (1962).

[7] M. Cardona, Phys. Rev. **140**, A651 (1965).

[8] F. S. Chen, J. E. Geusic, S. K. Kurtz, J. C. Skinner, and S. H. Wemple, J. Appl. Phys. **37**, 388 (1966), and references therein.

[9] J. C. Slater, Phys. Rev. **78**, 748 (1950); S. Triebwasser, J. Phys. Chem. Solids **3**, 53 (1957).

[10] A. H. Kahn and A. J. Leyendecker, Phys. Rev. **135**, A1321 (1964).

[11] R. A. Parker, Phys. Rev. **124**, 1713 (1961); *ibid.* **124**, 1719 (1961).