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MECHANISM OF POINT-DEFECT FORMATION IN IONIC CRYSTALS

Otto W. Lazareth, Jr.

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ABSTRACT

Mechanism of Point-Defect Formation in Ionic Crystals

Otto W. Lazareth, Jr.

Radiationless recombination of a V_K center and an electron to form F and H centers in KCl and KBr was studied. It was found that there is sufficient energy available for a sequence of [110] replacement collisions, involving a neutral halogen atom, to result in a stable configuration of F and H centers. In both KCl and KBr about 9 ev of energy becomes available for defect formation. In both KCl and KBr, from 5 to 7 ev is required to form the F and H centers. Zero point energy of the V_K center may be large enough to cause defocusing of the early collisions. This would result in the formation of nearby F and H centers, which in turn transform into F^+ centers (vacancies) and I centers (interstitial ions).

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Introduction:

Vacancies and defects are produced in ionic crystals by ionizing radiation.[1] The only requirement, even at 4°K, is that the photon energy be greater than the band gap. As yet, no mechanism has been proposed which gives a completely satisfactory explanation of this effect.

1. Previous Work

   a. Seitz Model of the Formation of Color Centers.[2]

Theory: Irradiation of a crystal produces excitons, some of which are trapped at the edges of dislocations, where they give the few local atoms about 7 ev of vibrational energy. One of these atoms breaks away from its lattice site and a vacancy is formed.

Shortcomings: This model does not account for the H-centers which are also observed.

   b. Varley Model and Variations.

      i. Varley Model[3]

Theory: The incident radiation multiply ionizes halogen ions, which are therefore positively charged. These ions, having nearest neighbors of the same charge, are in an unstable potential and a pertubation of the potential will force them to diffuse from their own cell into an adjacent cell. The vacancy will combine with an electron to form an F-center and the interstitial will be neutralized quickly and will combine with a halogen ion to form an H-center.

Shortcomings: Experimental data of Konitzer and Markham[4] and Kanzig and Woodruff[5] show that the F- and H-centers are at least several lattice spacings apart. The theory does not explain how this diffusion occurs. Also, the lifetime of the multiply charged ion has never been measured and therefore it cannot be shown that there is sufficient time available for diffusion to occur.

ii. Klick,[6] Williams,[7] Smoluchowski and Weigand,[8] and Howard, Vosko and Smoluchowski[9] have proposed variations of the Varley model to give an interstitial neutral atom sufficient kinetic energy to travel the required distance in the [110] direction. Howard, Vosko and Smoluchowski,[9] for example, propose two chlorine atoms moving apart in the [110] direction in a series of focussed collisions in analogy to the "dynamic crowdion" discussed by Vineyard.[10] Because of the large amount of energy available, it is probable that an electron will be transferred from the Cl^- to the Cl in such collisions, with the energy carried off by the Cl. This results in the formation of an interstitial chlorine atom or H-center, several lattice spacings away from the vacancy. The vacancy and the other chlorine atom recapture electrons leading to a normal F-center. This is the required final configuration. One problem with this theory is that the energy involved in the de-excitation collision (i.e. the transfer of an electron from a Cl^- to a Cl) has never been found.

iii. The results of Torrens and Chadderton[11] considered the Varley model and its variations and found that the motion of the positively charged ion takes place mainly along the [110] and [111] directions. However, no replacement occurs. The ion recombines with an electron and settles down on its original lattice site, in contradiction to that which occurs in the Varley model.

c. Pooley Model and Variations.

1. Pooley Model.[12]

Theory: Ionizing radiation produces holes, which are trapped as V_K centers, and electrons. The radiationless recombination of the electrons and holes of the V_K center provide sufficient kinetic energy for a halogen ion to initiate a replacement sequence of ions in the [110] direction. Replacement would occur a number of times to produce both a vacancy at the original V_K location and an interstitial ion several lattice sites from the vacancy. The [110] direction is considered because it is the direction of maximum momentum transfer. Pooley used a one dimensional model in which the ions in the [110] direction were represented by an effective potential and the polarization effects were represented by an effective charge. This model does not explain the detailed formation of H-centers.

He found that about 5 ev is needed to produce a vacancy at or near the original lattice site, and that this amount of energy is available from radiationless recombination.

Shortcomings: Torrens, Chadderton and Morgan[13] refuted the Pooley model by using two and three dimensional systems, which resulted in a 25 ev, rather than a 5 ev, threshold replacement energy. This amount of energy is not available from radiationless recombination.

Hughes, Pooley, Rahman and Runciman,[14] using a three simensional model with an effective charge and an effective dielectric constant, found a threshold replacement energy of 25 ev. This agreed with the results of Torrens, et al.[13]

ii. Pooley and Hatcher[15] have proposed a variation of the Pooley model in which charge exchange collisions, rather than replacement collisions, occur in the [110] direction and form an interstitial neutral atom several lattice sites from the vacancy, with F- and H-centers resulting. The F-center was treated an an e^- in a negative vacancy. The results of this study have not been published yet.

2. Methods.

Two previously proposed ideas are used in the model presented here: (1) as suggested by Pooley,[12] the source of energy is the recombination of a self-trapped hole (V_K center) with an electron, and (2) as suggested by Howard *et al.*,[9] the interhalogen repulsion may lead to a replacement sequence involving a neutral halogen atom, and not an ion, in the [110] direction. This replacement sequence can be either long or short. If it is long, well separated F and H centers will result. This is observed experimentally. If it is short, the newly formed F and H centers will transform into F^+ centers (vacancies) and I centers (interstitial ions). The electric field of the ion prevents the vacancy from capturing an electron,[16] resulting in a stable situation.

The present work uses a point-ion model which includes several improvements. The Gilbert and Wahl potential for the Cl_2^- molecule-ion[17] and the resonating-hole corrections used earlier in the study of the H-center[18] were used in calculating the energies of the bound molecules.

The model is a polarizable point ion one which includes a Born-Mayer repulsive potential to simulate the quantum mechanical repulsive interaction of the overlapping electron shells of two ions close to each other. It also includes the Van der Waals interaction energy. This method was used by Hatcher and Dienes,[14] for example, in the study of neutral interstitial defects in alkali halides.

The volume considered is separated into three parts. Part I consists of the defect and the N_1 ions which surround the defect. These ions are polarizable and are allowed to relax. Part II consists of N_2 ions which surround Part I. These ions are polarizable but are not allowed to relax. Part III consists of all those ions which extend from the outer boundary of Part II to infinity. The ions in Part III are neither polarizable nor allowed to relax.

The relaxations are made in the form of changes in parameters associated with the three coordinates of each of the N_1 movable ions. The energy of the lattice is found by calculating and summing the electrostatic, polarization, repulsive and Van der Waals energies. One of the parameters is changed and the energy is recalculated. The process is continued until the set of values of the parameters represents the minimum energy of the lattice. The accuracy of this minimum energy is determined by the amounts by which the parameters are changed from one step to the next.

The Expressions for the Energies: (The subscripts i and j used below refer to the ions in the lattice.)

a. The Electrostatic Energy:

$$E_{ij}^{estat} = 1/2 \sum_{\substack{i,j \\ i \neq j}} \frac{q_i q_j}{|\bar{r}_{ij}'|} - 1/2 \sum_{\substack{i,j \\ i \neq j}} \frac{q_i q_j}{|\bar{r}_{ij}|} \qquad (1)$$

where q_i and q_j are the charges of ions i and j respectively and $\bar{r}_{ij} = \bar{r}_i - \bar{r}_j$ = the vector distance between ions i and j in their unrelaxed positions in a perfect lattice, and $\bar{r}_{ij}' = \bar{r}_i' - \bar{r}_j'$ = the vector distance between ions i and j in their relaxed positions. The Ewald method of summation is used to calculate this series exactly.

b. The Polarization Energy:

$$E_{ij}^{pol} = -1/2 \sum_i \bar{p}_i \cdot \bar{E}_i^{chg} , \qquad (2)$$

where $\bar{p}_i = \alpha_i \bar{E}_i^{total}$, the dipole of the ith ion, and $\bar{E}_i^{chg} = \sum_j \frac{q_i \bar{r}_{ij}'}{|r_{ij}'|^3}$, the field due to charge only acting on the ith ion. $\bar{E}_i^{total}$ is the total field at the ith ion. The polarization energy of the ions in Part I is calculated as a function of all ions under consideration. The polarization energy of the ions in Part II is calculated, in a reasonable approximation, as a function of the ions in Part I only.

c. The Repulsive Energy:

$$E_{ij}^{rep} = 1/2 \sum_{i,j} bc_{ij} e^{(R_i + R_j)/\rho} e^{-r_{ij}'/\rho} - 1/2 \sum_{i,j} bc_{ij} e^{(R_i + R_j)\rho} e^{-r_{ij}/\rho} \qquad (3)$$

where b = a constant which is the same for all alkali halides, c_{ij} = the Pauling coefficients,[19] R_i and R_j = the radii of ions i and j, and ρ = the hardness parameter which has different values for different alkali halides. We use this Born Mayer form of the repulsive potential with values of the constants obtained from Tosi and Fumi.[20]

d. The Van der Waals Energy.

$$E_V = - \sum_{\substack{i,j \\ i \neq j}} 1/2 \left(\frac{C_{ij}}{|\bar{r}_{ij}'|^6} - \frac{D_{ij}}{|\bar{r}_{ij}'|^8}\right) + \sum_{\substack{i,j \\ i \neq j}} 1/2 \left(\frac{C_{ij}}{|\bar{r}_{ij}|^6} - \frac{D_{ij}}{|\bar{r}_{ij}|^8}\right) \qquad (4)$$

where C_{ij} and D_{ij} are constants, with different values for different alkali halides, obtained from Hajj,[21] and Mayer and Mayer.[22]

3. The results consist of:

a. The structure and dynamics of the V_K center.

b. The distribution of kinetic energy between the two Cl^- ions formed by the V_K + e recombination.

c. The availability of sufficient energy and proper direction for a replacement sequence to occur.

d. The mechanism and activation energy of the replacement collisions in the [110] direction involving Cl^o atoms which result in the formation of an H-center, and also the mobility of the H-centers.

e. The probability that the moving Cl^- ion does not lose its electron to the vacancy but becomes a nearby interstitial to form an F^+ and an I center.

Please note that all crystal energies are given with respect to the energy of the perfect crystal. Also, all calculations refer to KCl unless specified otherwise.

A. The Structure and Dynamics of the V_K Center

In addition to its internal vibration which changes its length along the [110] direction, the Cl_2^- molecule-ion of the V_K center vibrates as a whole around its ideal position in the lattice and librates in the (001) and $(1\bar{1}0)$ planes.

1. The first case (vibration) was treated as a point simple harmonic oscillator, with potential energy:

$$V = 1/2k'x^2 \tag{5}$$

where k' is the spring constant and x the distance from equilibrium. Using the coordinates and energies of orientations in Figure 1, the spring constant is:

$$k' = \frac{2(V_1 - V_2)}{x_1^2 - x_2^2} = .50 \text{ ev/Å}^2 \tag{6}$$

Using this result and the mass of the Cl_2^-, the angular frequency ω, of the motion is:

$$\omega = (\frac{k}{m})^{1/2} = 8.24 \times 10^{12} \text{ cycles/sec} \tag{7}$$

Using the index of refraction, n = 1.49 for KCl, the wave number, $|k|$, is:

$$|k| = \frac{\omega n}{c} = 400 \text{ cm}^{-1}, \tag{8}$$

where c is the speed of light.

In the range of temperatures of interest (about 50^oK), the displacements of the ions are determined primarily by their zero point energy rather than by thermal excitation. The zero point energy, E_o, is:

$$E_o = 1/2\ \hbar\omega = .00271 \text{ ev} \tag{9}$$

where $\hbar$ is Planck's constant, h, divided by 2π. This energy corresponds to a maximum displacement, x_{max}, of

$$x_{max} = (\frac{2E_o}{k'})^{1/2} = .10 \text{ Å} \tag{10}$$

from the equilibrium position. Thus, from the harmonic behavior assumed in the above method, the Cl_2^- spends about 1/3 of its time displaced from between .09 Å to .10 Å from its equilibrium position.

2. In the second case [libration of the Cl_2^- in the (001) plane], the Cl_2^- is treated as a dumbbell simple harmonic oscillator pivoted at its center. The potential energy is:

$$V = \frac{1}{2} k' \ell\theta^2 \tag{11}$$

where k' is the spring constant, ℓ is the length of the dumbbell arm, and θ is the angle between the actual and equilibrium direction. The kinetic energy is:

$$E_k = I\dot{\theta}^2 \tag{12}$$

where I is the moment of inertia for one ball of the pendulum.

Using the coordinates and energies of orientations given in Figure 2, $k'\ell$ was found to be 5.48 ev. From this information, the angular frequency, ω, is:

$$\omega = (\frac{k'\ell}{2I})^{1/2} = 2.04 \times 10^{13} \text{ rad/sec.} \tag{13}$$

Using the index of refraction, the wave number $|k|$ is:

$$|k| = 1020\ \text{cm}^{-1}. \tag{14}$$

The zero point energy, E_o, is:

$$E_o = .0134\ \text{ev}. \tag{15}$$

This energy corresponds to a maximum angular deviation, θ_{max}, of:

$$\theta_{max} = \left(\frac{2E_o}{k'\ell}\right)^{1/2} = 4.0^{\circ} \tag{16}$$

Thus, the Cl_2^- molecule-ion spends about 1/3 of its time rotated at an angle between 3.5° and 4.0°, measured from its equilibrium direction.

3. It will be shown below that these displacements, together with the displacements of the surrounding K^+ ions, can affect considerably the probability of starting a replacement collision sequence in the [110] direction upon recombination of the V_K center with an electron.

B. The distribution of kinetic energy between the two Cl^- ions formed by the $V_K + e$ recombination.

The energy available from $V_K + e$ recombination consists of

1. The energy from the radiationless hole-electron recombination, plus:

2. The potential energy of the two Cl^- ions formed when the Cl_2^- bond is broken.

The hole-electron recombination energy was found by Pooley, et al.,[12] to be 6.5 ev. The potential energy of the two Cl^- ions is obtained by substituting two free Cl^- ions for the V_K center and by placing them and the surrounding ions in the same position that they have in the V_K center configuration. This energy is 2.5 ev. (Fig. 3).

The total energy available, from the radiationless recombination, is therefore about 9.0 ev. It was determined, in Part A, that the Cl_2^- ion probably will not be in a symmetrical orientation at the time of recombination. Consequently it is readonable to expect that the two Cl^- ions will have unequal energies immediately after recombination

For KBr, the corresponding energies are:

1.	Hole-electron recombination energy[12]	5.8 ev
2.	Two free Cl^- ions and neighboring ions in the same positions as the V_K center	2.8 ev

From the above, the total energy available, from the radiationless recombination, is about 8.6 ev.

C. The availability of sufficient energy and proper direction for a replacement sequence to occur.

The possibility of initiating a Cl^- replacement sequence was investigated using a dynamic Torrens-Chadderton procedure[11] modified to take into account the polarization effects in a consistent point-ion treatment. As a model, the crystal is treated as a rectangular solid (see Figure 4) containing 204 movable ions surrounded by 1434 stationary ions for a total of 1638 ions. There are nine layers of ions in the solid. The fourth, fifth and sixth layers contain the movables. The fifth layer contains the ion labelled "C", which is given the initial kinetic energy.

For each ion, the electric forces of charges and dipoles, the Born-Mayer repulsive force and the Van der Waals force are calculated. To save computer time, the calculation of the dipole field is simplified by calculating it one time step behind the regular calculation. A time step for the calculation is chosen. It is of the order of $\frac{d_o}{10v_o}$, where d_o is the lattice constant and v_o is the initial velocity of the defect. Starting with a particular configuration, the values of the forces, the new velocities and the new positions are calculated. The expressions for the position, x, the acceleration, a, the velocity, v, and the forces, F, of the ith ion are:

$$\bar{x}_i(t + \Delta t) = \bar{x}_i(t) + \Delta t \cdot \bar{v}_i(t + \frac{\Delta t}{2}) \tag{17}$$

where Δt is the time step.

$$\bar{a}_i(t) = \dot{\bar{v}}_i(t) = \frac{\bar{F}_i(t)}{m_i} , \tag{18}$$

where m is the mass of the ion.

$$\bar{a}_i(t) \approx \frac{\bar{v}_i(t + \frac{\Delta t}{2}) - \bar{v}_i(t - \frac{\Delta t}{2})}{\Delta t} \tag{19}$$

$$\bar{v}_i(t + \frac{\Delta t}{2}) \approx \frac{\bar{x}_i(t + \Delta t) - \bar{x}_i(t)}{\Delta t} \tag{20}$$

The total force, $\bar{F}_i^{\text{total}}$, is:

$$\bar{F}_i^{\text{total}} = \bar{F}_i^{\text{estat}} + \bar{F}_i^{\text{pol}} + \bar{F}_i^{\text{rep}} + \bar{F}_i^{\text{VdW}} \tag{21}$$

where $\bar{F}_i^{\text{estat}}$ is the electrostatic force, $\bar{F}_i^{\text{pol}}$ is the polarization force, $\bar{F}_i^{\text{rep}}$ is the repulsive force and $\bar{F}_i^{\text{VdW}}$ is the Van der Waals force. Now,

$$\bar{F}_i^{\text{estat}} = q_i \sum_{\substack{j \\ i \neq j}} \frac{q_j \bar{r}_{ij}}{|\bar{r}_{ij}|^3} \tag{22}$$

where q_i and q_j are the charges of particles i and j respectively, and $\bar{r}_{ij}$ is the length vector between those two particles.

$$\bar{F}_i^{\text{pol}} = q_i \sum_{\substack{j \\ i \neq j}} \frac{1}{|\bar{r}_{ij}|^3} [-\bar{p}_j + \frac{3(\bar{p}_j \cdot \bar{r}_{ij})\bar{r}_{ij}}{|\bar{r}_{ij}|^2}] + \bar{p}_i \cdot \bar{\nabla}_i \mathcal{E}_i^{\text{total}} , \tag{23}$$

where $\bar{p}_i$ and $\bar{p}_j$ are the dipole moments of particles i and j respectively, and $\mathcal{E}_i^{\text{total}}$ is the total electric field acting on ion i. Also,

$$\bar{P}_i = \alpha_i \bar{\mathcal{E}}_i^{\text{total}}, \tag{24}$$

where α_i is the polarizibility of particle i.

$$\bar{F}_i^{\text{rep}} = - \bar{\nabla}_i E_{ij}^{\text{rep}}, \tag{25}$$

where E_{ij}^{rep} is the repulsive energy between particles i and j and is given by equation (3).

$$\bar{F}_i^{\text{VdW}} = -\bar{\nabla}_i E_{ij}^{\text{VdW}} \tag{26}$$

where E_{ij}^{VdW} is the Van der Waals interaction energy between particles i and j and is given by equation (4).

The results displayed in Figures 5, 6 and 7 show that different values of the initial kinetic energy of the moving ion result in different final configurations of the crystal. The figure shows the [110] components of the positions of the ions labelled in Figure 4. That is, the viewer is looking in a direction perpendicular to the [110] direction. Each line represents 10 time steps. The results for 10, 15 and 20 ev imparted to the Cl^- ion originally located at (0,0,0) are:

1. 10 ev - insufficient energy for defect formation.
2. 15 ev - a vacancy is formed at (0,0,0) and the Cl^- ion originally at (3,3,0) becomes an interstitial at (3.5,3.5,0).
3. 20 ev - a vacancy is formed at (0,0,0) and the Cl^- ion originally at (6,6,0) becomes an interstitial at (6.5,6.5,0).

Therefore 12-15 ev of kinetic energy must be imparted to a Cl^- ion in the KCl lattice in a [110] direction to initiate a Cl^- collision sequence leading to the formation of a stable interstitial Cl^- ion (I center) and a negative ion vacancy (F^+ center). Since only about 9 ev is available, this process, therefore, is not possible.

For KBr, the same process requires about 25 ev, with only about 9 ev available.

D. The mechanism and activation energy of the replacement collisions in the [110] direction involving Cl^{o} atoms which result in the formation of an H center, and also the mobility of the H centers.

Another possible mechanism is one in which the Cl^- ion moving in the [110] direction loses an electron to become a Cl^{o} and the electron is used in the formation of an F-center at the origin.[9,15] The values of the relevant energies were calculated using an F-center model in which the charge is distributed among the nearest K^+ and Cl^- ions. The fraction, f, of the charge of the electron was shared equally among the six nearest K^+ ions, and the remainder of the charge, 1-f, was shared equally among the 12 next nearest Cl^- ions. The fraction f was treated as a variable parameter. It's value was determined by varying it until the F-center energy found using the model was in reasonable agreement with 2.3 ev which is the result of the following calculation:

1. Ionization energy of an F-center	2.2 ev
2. Self energy of a vacancy with the same displacements as the F-center[23]	5.1 ev
3. Energy of an electron in the conduction band	- .6 ev

From the above, the F-center energy is found to be 2.3 ev.

The value of the parameter, f, was found to be 50%, in reasonable agreement with electron-nuclear double resonance results.[24] It will be shown below that the value of this parameter is not critical for the general results presented here.

Two cases were studied using this F-center model. In the first case, the Cl^- ion travels in the [110] direction to (.5,.5,0), loses its electron to become a Cl^o at the same location, and an F-center is formed at (0,0,0). The required energy consists of two parts. The first is the energy of an F-center at (0,0,0) and a Cl^o atom at (.5,.5, 0). See Figure 8. This energy is 4.6 ev. The second part is the electron affinity of a Cl^- ion, which is 3.6 ev. Therefore this process requires 8.2 ev. Since additional energy is needed to move the Cl^o into the next cell, it is concluded that there is not enough energy for this process to occur.

In the second case, the Cl^- ion travels to (.5,.5,0) and two processes occur simultaneously. The Cl^- loses its electron to the origin to form an F-center and the newly formed Cl^o combines with the Cl^- at (1,1,0) to form an H-center. See Figure 9. The energies required for this process to occur are listed in Table 1. Calculations were made for several values of both the charge distribution parameter, f, and the position of the H center. The results show that neither factor is critical in the determination of the required energy. That is, if their values are changed slightly, the qualitative results are the same. Therefore, this simultaneous formation of F and H centers is energetically possible in both KCl and KBr. Using the kinetic energy of the Cl^- ion, the H center moves along the [110] direction as a replacement sequence and stable F and H centers result.

It is to be noted that the asymmetrical distribution of the kinetic energy imparted to the two ions of the V_K center, described in

Part B, is essential for two reasons: (1) 4.5 ev is insufficient to form F and H centers and (2) there is no evidence for the formation of two adjacent F centers which would occur if the energy were shared equally.

Since both the F and H centers are neutral and each gives rise to an increase in the volume of the crystal, they tend to repel each other, adding to their stability.

H center mobility.

H centers become mobile at 56°K in KCl.[25] This corresponds to an activation energy of .15 ev. An attempt to calculate this value with the present model was accomplished by finding the difference in energy between state 1 and state 2 shown in Figure 10. State 1 is an H center in its normal configuration. Its energy is .7 ev. State 2 is the saddle point configuration of a moving H center. The fractions of charges on the negative Cl ions are found from the following analysis (see Figure 11):

Position in Crystal	a	b	c	d	e
Charge at Start of H center motion	-1	$-\frac{1}{2}\ -\frac{1}{2}$	0	-1	-1
Charge at Saddle point of H center motion	q_1	q_2	q_3	q_4	q_5
Charge at End of H center motion	-1	-1	0	$-\frac{1}{2}\ -\frac{1}{2}$	-1

At the start of the process, the H center is located at position b and at the end of the process, it has moved to location d. Assuming that a $Cl^{-1/2}$ ion moves from location b to location d, it is concluded that:

$q_3 = -1/2$

$q_1 = q_5 = -1$ (no change)

$q_2 = q_4 = -3/4$.

Using these values of the charges of the negative Cl ions, the H center saddle point energy is found to be 1.1 ev. (See Figure 10.)

This leads to an activation energy of 1.1 - .7 = .4 ev, which is reasonably close to the experimental value of .15 ev.

E. The probability that the moving Cl^- ion does not lose its electron to the vacancy but becomes a nearby interstitial to form an F^+ and an I center.

F^+ and I centers are produced under the influence of ionizing radiation.[26,27] There is strong experimental evidence[28] that they are not formed directly but are formed from F and H centers which are bombarded with either incident ionizing radiation or with the strong radiation released during electron-hole recombination. Also, if the F and H centers are close to each other, an electron may tunnel from the F center to the H center. There are indications that the F and H centers should be close together for the resulting F^+ and I centers to be stable.[16] Therefore, the replacement sequence must be short and therefore the line connecting the two Cl^- ions (produced from the V_K center) cannot be in the [110] direction.

Two ways in which this condition can occur are:

1. The condition for the propagation of a focussed collision sequence[29] along a row of atoms is $D < 4R$, where D is the spacing along the row and R is the energy dependent hard sphere atomic radius. This condition is not satisfied for the initial collision between the Cl^- ion originating in the V_K center and the nearest Cl^- ion in the [110] direction.

2. As previously discussed, the zero point librational displacement of the nearest Cl^- ion (as well as that of other ions in the neighborhood) may shorten the replacement sequence.

The formation energy of an F^+ and an I center, assuming direct motion of the Cl^- ion from its on-site position to a stable interstitial position, was found from the following calculations which are displayed in Figure 12. The configuration of the crystal at the beginning of the process is that of the perfect crystal. The saddle points configuration is one in which the moving Cl^- ion passes through the cell wall at (1.1, .5,.5). The value of x is greater than 1.0 because the four ions nearest the moving Cl^- ion are pushed out by the motion of that ion. The final configuration has the Cl^- ion in the center of the adjacent cell with its coordinates as (1.5,.5,.5). The energies of the three cases are:

1.	Start (perfect crystal)	0 ev
2.	Saddle point	3.6 ev
3.	End	3.0 ev

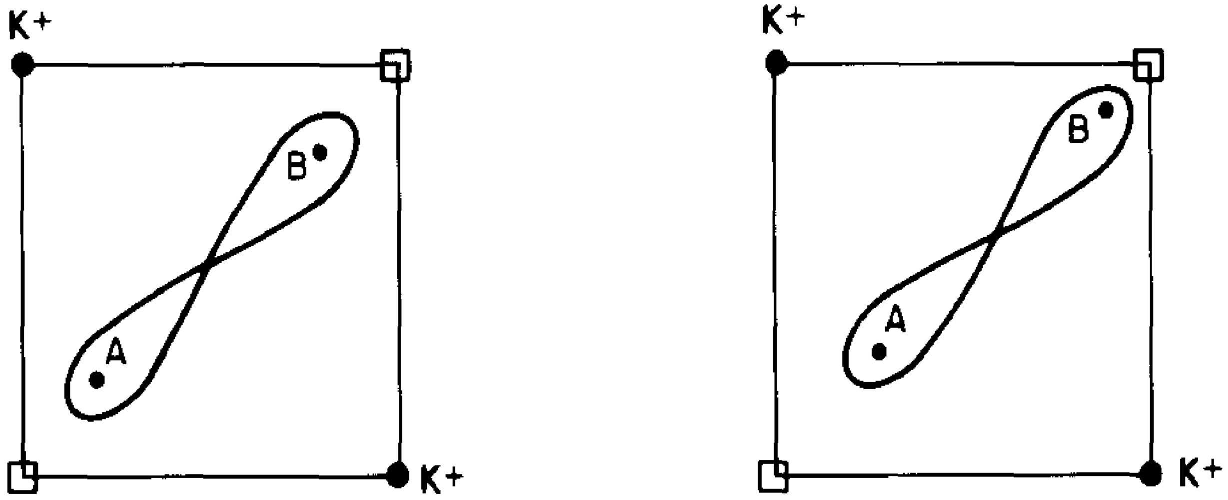
Therefore the energy required to form the F^+ and I center from a perfect crystal, by direct motion of a Cl^- ion, is about 4 ev, and the final state is a metastable state.

TABLE 1

Energy Requirements for Defect Production

Crystal	Position of Anion	Fraction of F-center charge on positive ions	Energy to put anion at position (ev)	Energy to convert to F + H (ev)	Energy to form F + H from V_K (ev)
KCl	(.50,.50,0)	.6	5.0	2.0	7.0
		.5	5.0	1.0	6.0
		.4	5.0	-0.1	4.9
	(.55,.55,0)	.5	6.0	-1.0	5.0
KBr	(.55,.55,0)	.5	4.8	1.3	6.1

ENERGY OF THE V_K CENTER AS A FUNCTION OF A TRANSLATIONAL DISPLACEMENT.



V_K CENTER IN EQUILIBRIUM POSITION

ION A AT (0.2, 0.2, 0)

ION B AT (0.8, 0.8, 0)

ENERGY = 4.97 eV

V_K CENTER DISPLACED IN THE [110] DIRECTION

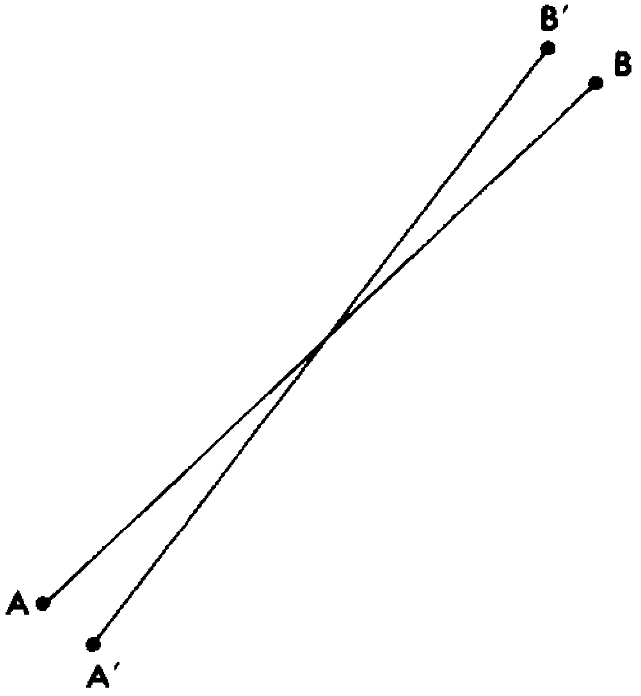
ION A AT (0.3, 0.3, 0)

ION B AT (0.9, 0.9, 0)

ENERGY = 5.02 eV

FIGURE 1

ENERGY OF A V_K CENTER AS A FUNCTION OF ROTATIONAL DISPLACEMENT



IONS A—B REPRESENT THE V_K CENTER IN ITS EQUILIBRIUM POSITION.

ION A AT (0.2, 0.2, 0)

ION B AT (0.8, 0.8, 0)

ENERGY = 4.97 eV

IONS A′—B′ REPRESENT THE V_K CENTER ROTATED ABOUT ITS CENTER.

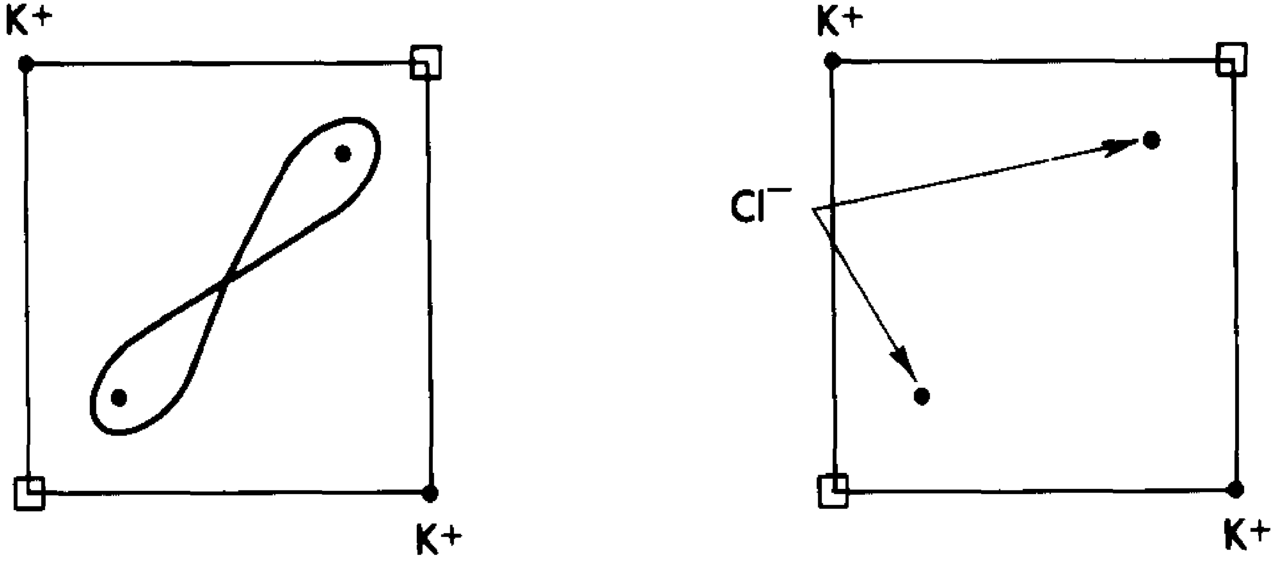
ION A′ AT (0.25, 0.15, 0)

ION B′ AT (0.75, 0.84, 0)

ENERGY = 5.03 eV

FIGURE 2

POTENTIAL ENERGY OF TWO Cl^- IONS AFTER THE Cl_2^- BOND IS BROKEN.



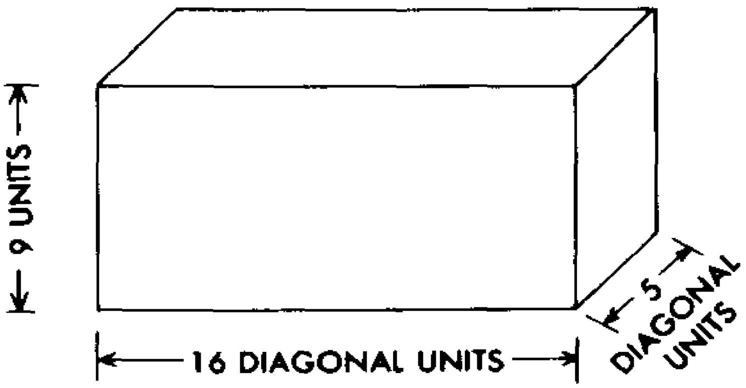
V_K CENTER
ENERGY = 4.97 eV

2 Cl^- IONS IN THE
V_K CONFIGURATION.
ENERGY = 2.5 eV

FIGURE 3

MODEL OF IONS USED IN THE DYNAMIC METHOD.

(a) THREE DIMENSIONAL VIEW.



(b) CROSS SECTION SHOWING THE FIFTH (MIDDLE) LAYER.

ION "C" IS GIVEN THE KINETIC ENERGY.

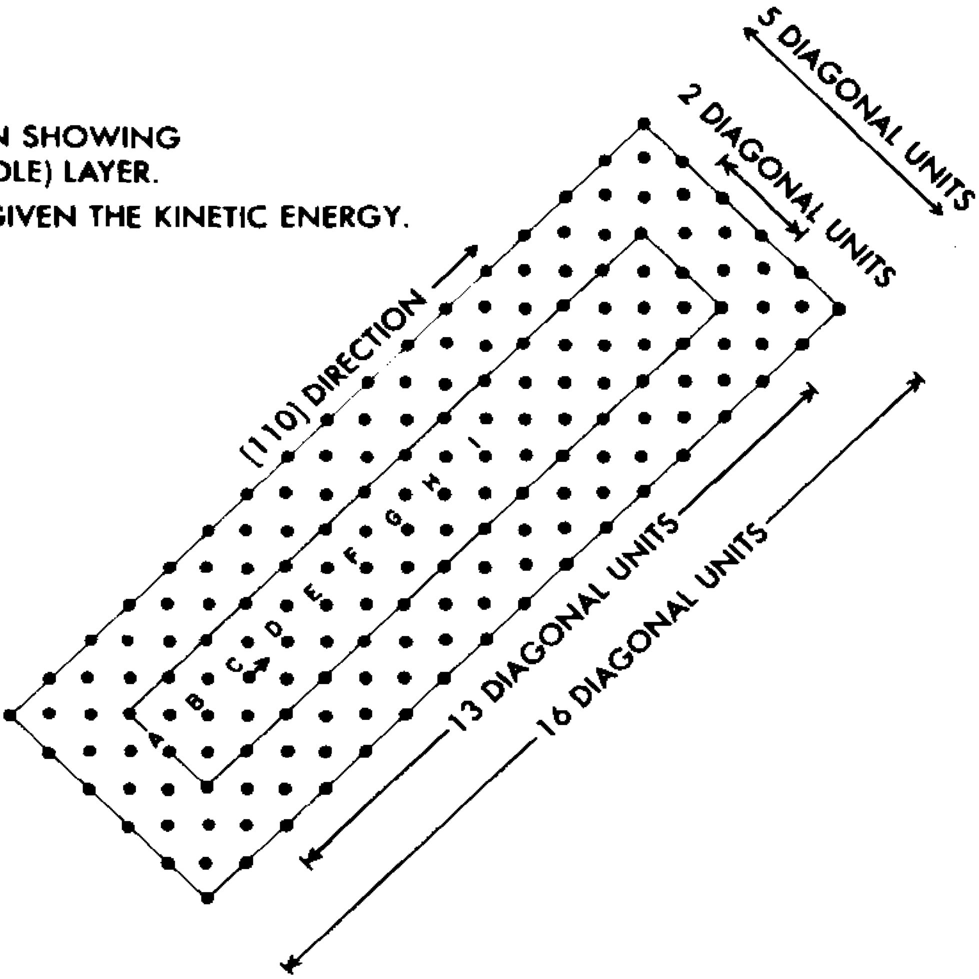


FIGURE 4

[110] COMPONENTS OF THE POSITIONS OF THE IONS LABELLED IN FIGURE 4. ION "C" IS GIVEN 10 eV OF KINETIC ENERGY.

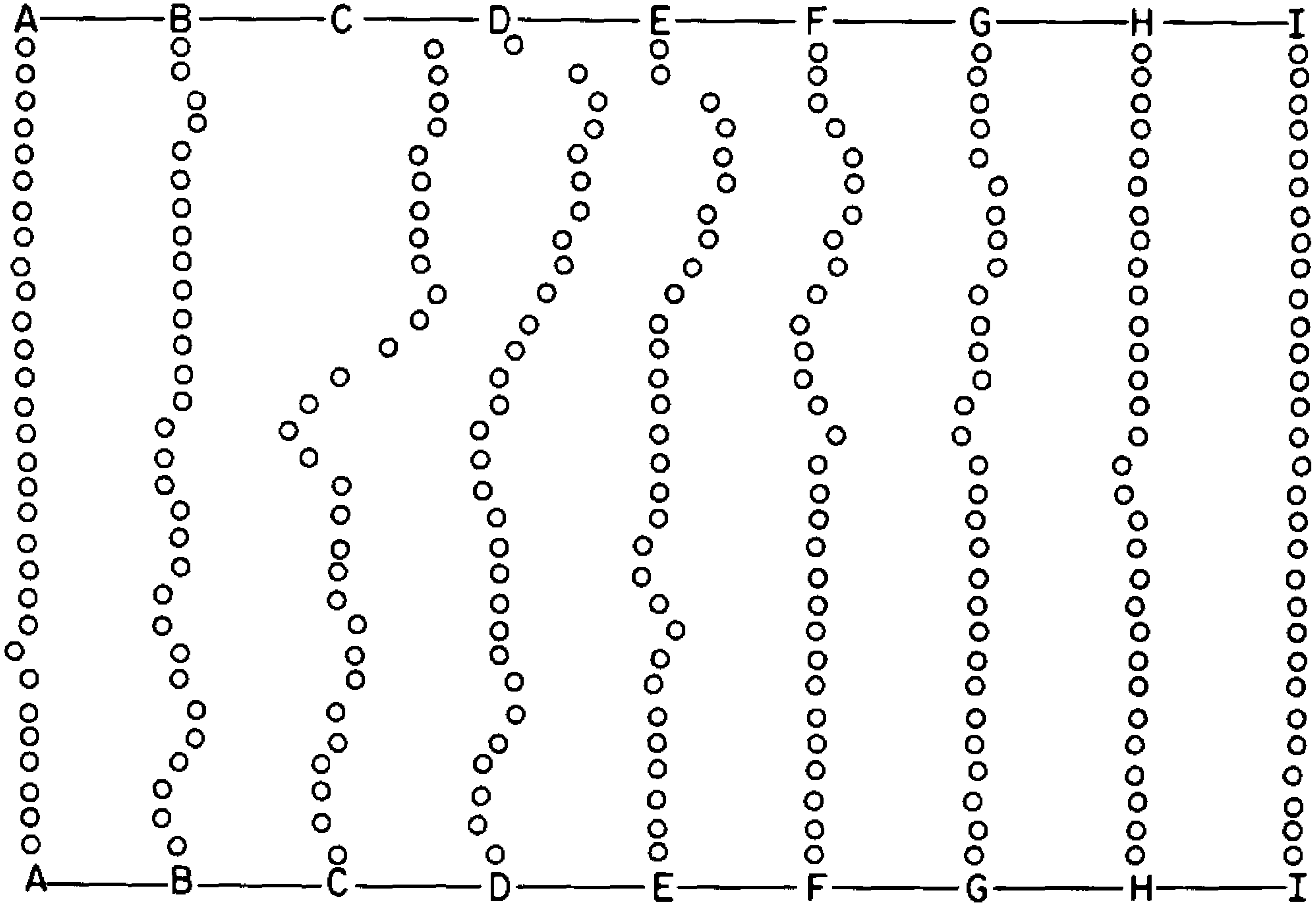


FIGURE 5

[110] COMPONENTS OF THE POSITIONS OF THE IONS LABELLED IN FIGURE 4. ION "C" IS GIVEN 15 eV OF KINETIC ENERGY.

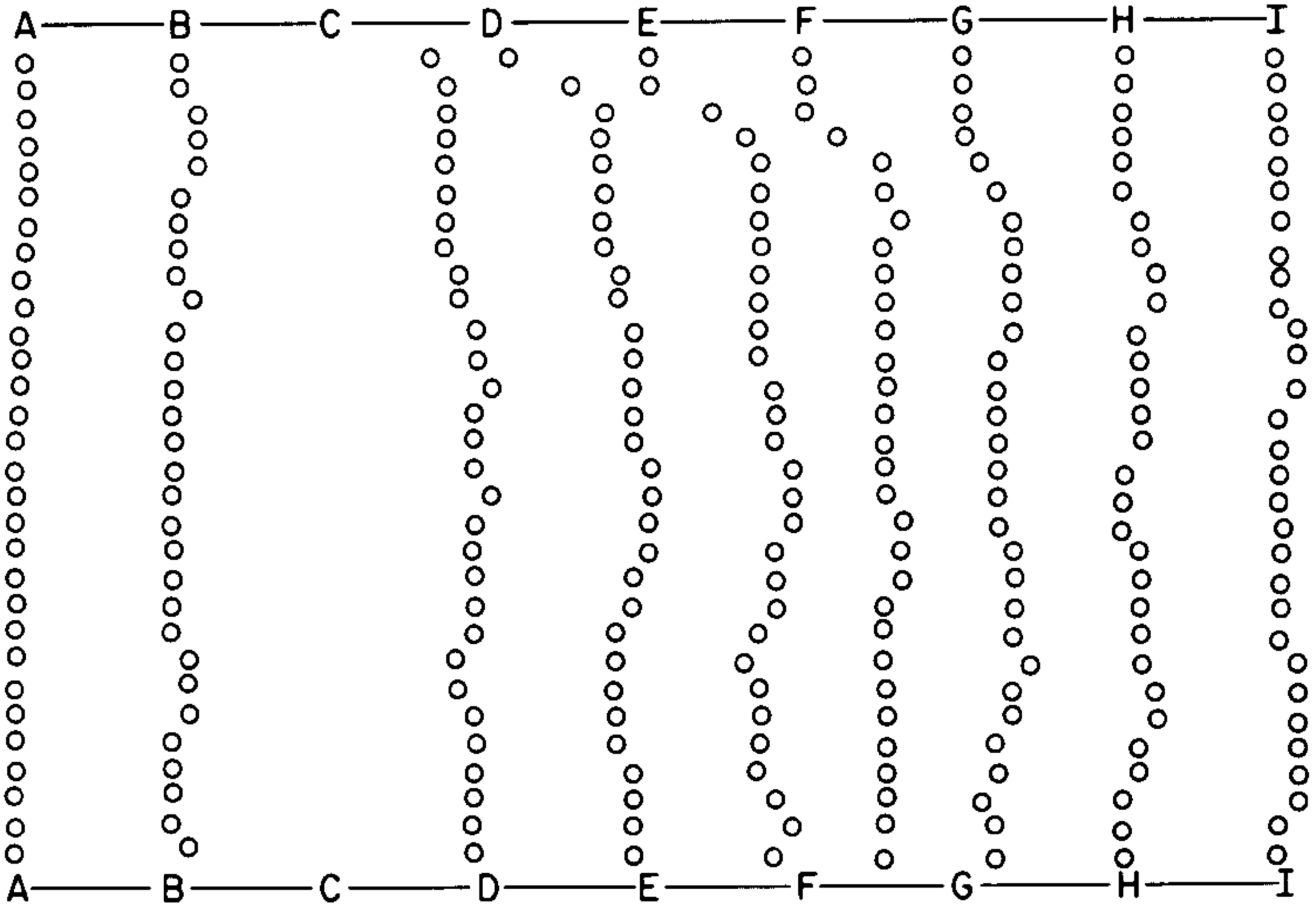


FIGURE 6

[110] COMPONENTS OF THE POSITIONS OF THE IONS LABELLED IN FIGURE 4. ION "C" IS GIVEN 20 eV OF KINETIC ENERGY.

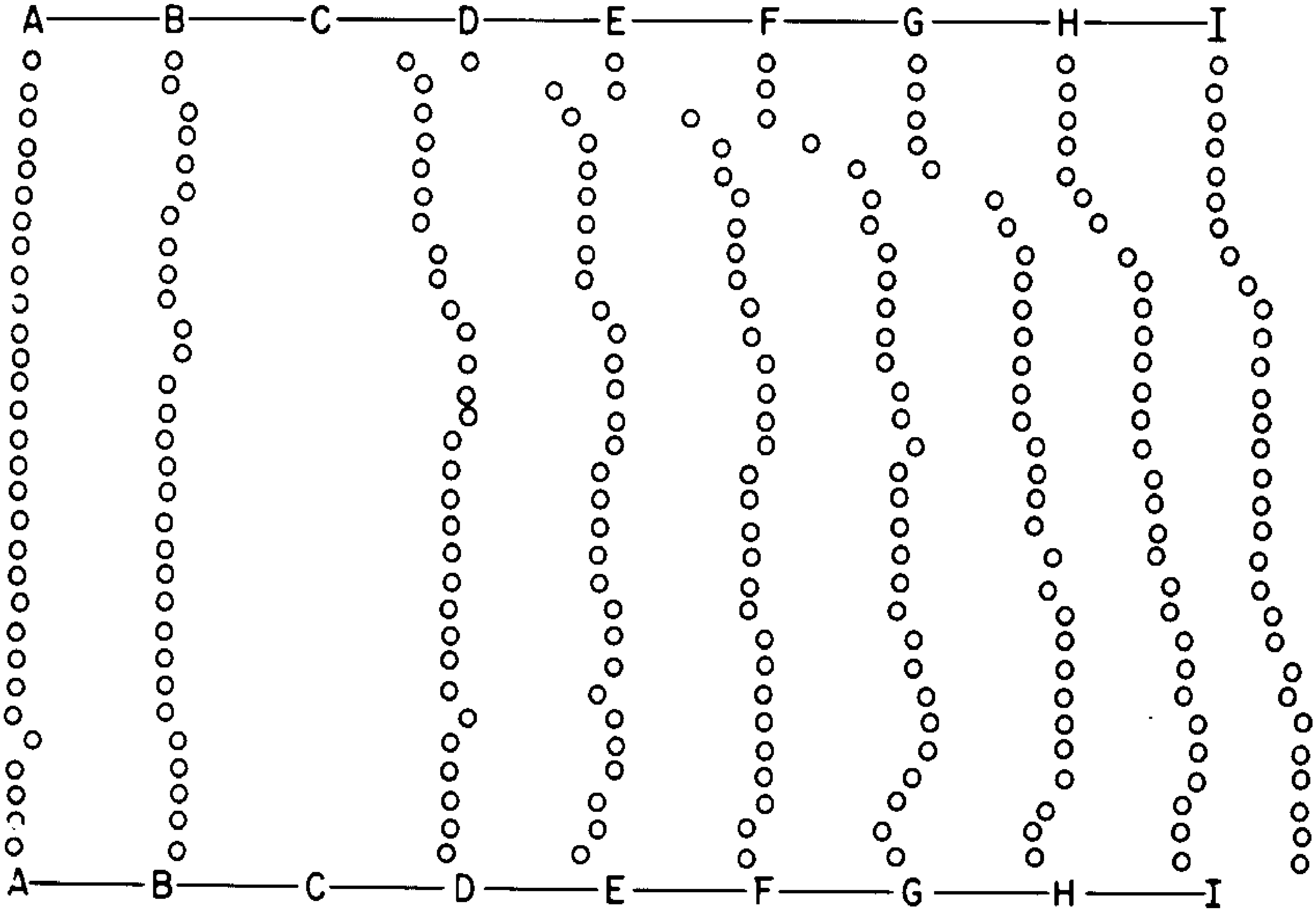
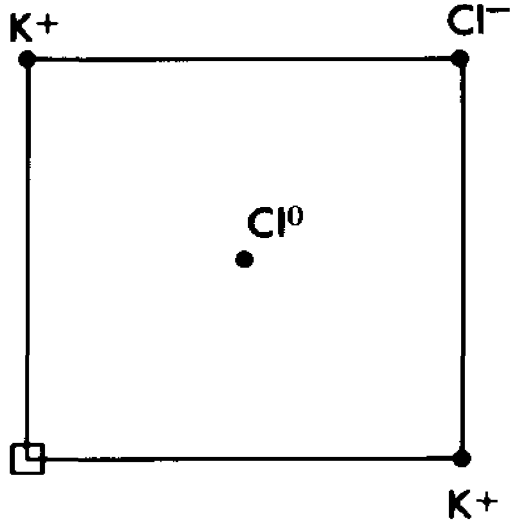


FIGURE 7

ENERGY OF A Cl^0 ATOM IN THE NEIGHBORHOOD OF AN F CENTER.



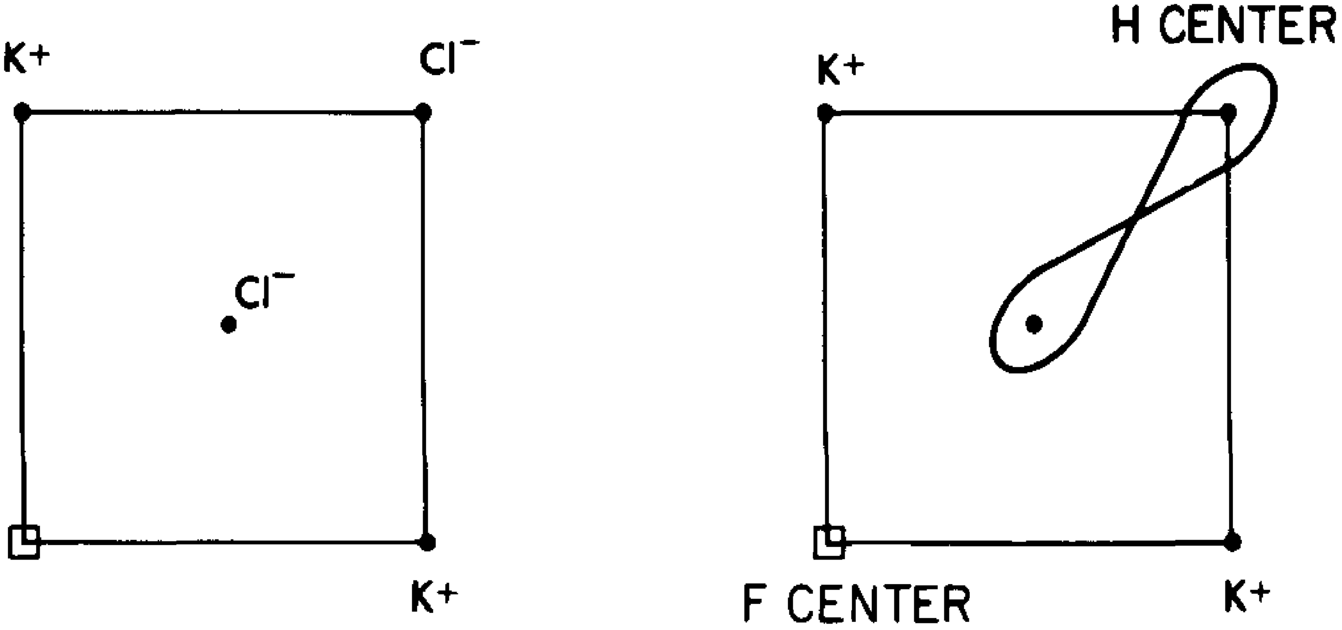
F CENTER AT (0, 0, 0)

Cl^0 ATOM AT (0.5, 0.5, 0)

ENERGY = 4.6 eV

FIGURE 8

FORMATION OF AN F AND H CENTER.



Cl^- VACANCY AT (0, 0, 0)

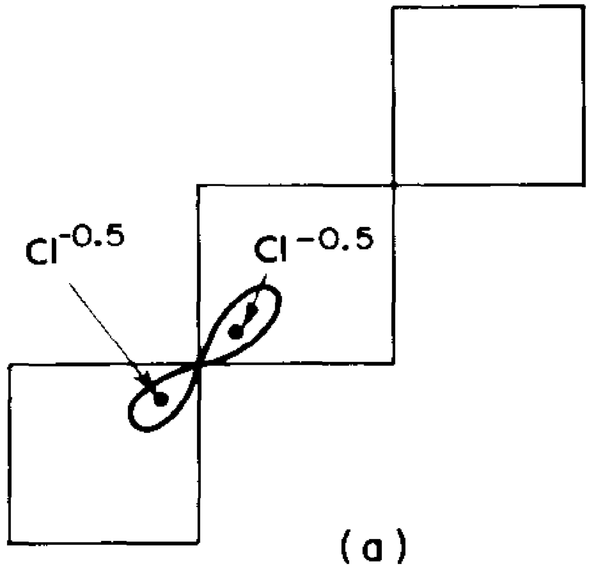
Cl^- AT (0.5, 0.5, 0)

F CENTER AT (0, 0, 0)

H CENTER CENTERED AT
(0.75, 0.75, 0)

FIGURE 9

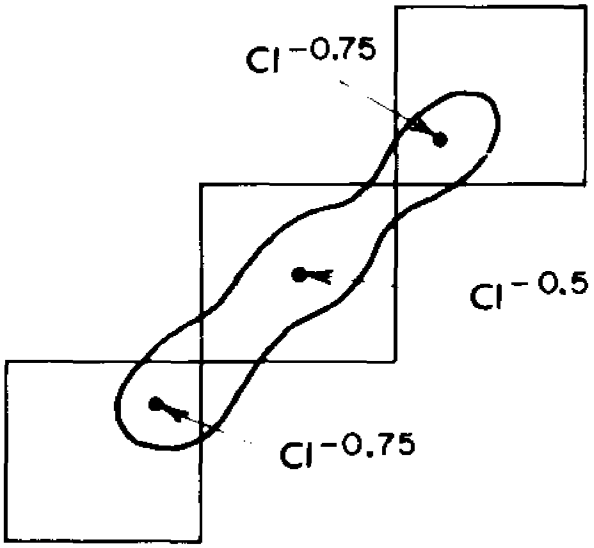
ACTIVATION ENERGY OF AN H CENTER.



(a)

H CENTER IN ITS NORMAL ORIENTATION.

ENERGY = 0.7 eV



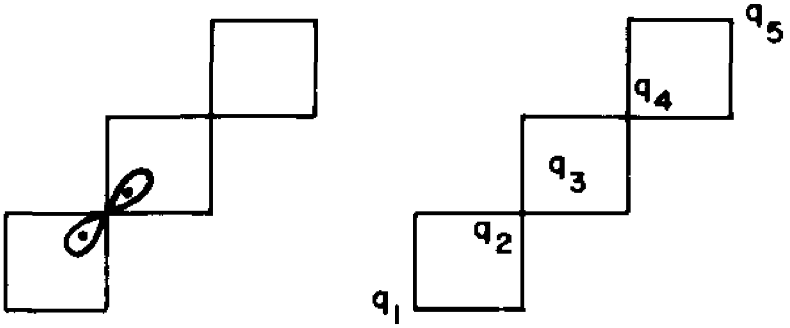
(b)

SADDLE POINT CONFIGURATION
OF A MOVING H CENTER.

ENERGY = 1.1 eV

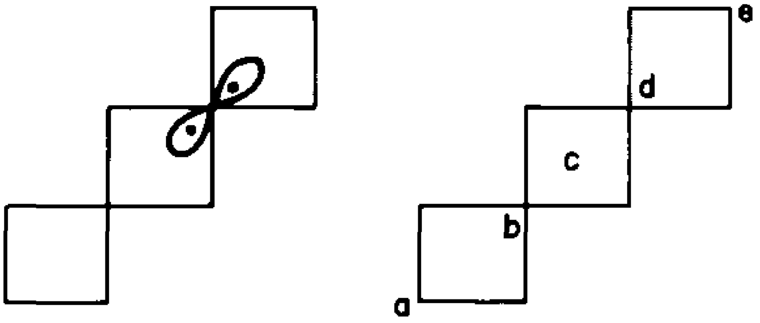
FIGURE 10

CHARGE FRACTIONS USED IN CALCULATING ACTIVATION ENERGY OF AN H CENTER.



(a) START

(b) SADDLE POINT



(c) END

(d) POSITION LABELS

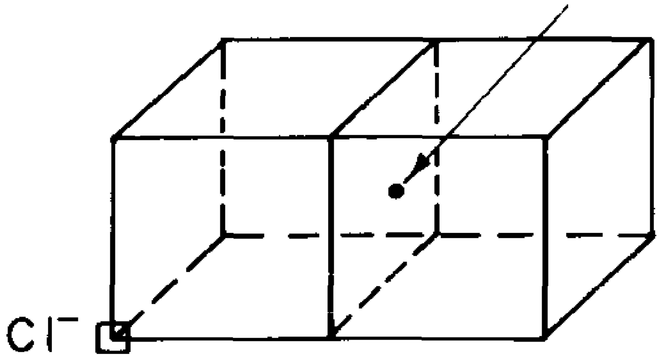
LABEL	LOCATION
a	(0, 0, 0)
b	(1, 1, 0)
c	(1.5, 1.5, 0)
d	(2, 2, 0)
e	(3, 3, 0)

FIGURE 11

FORMATION OF AN F^+ AND AN I CENTER.

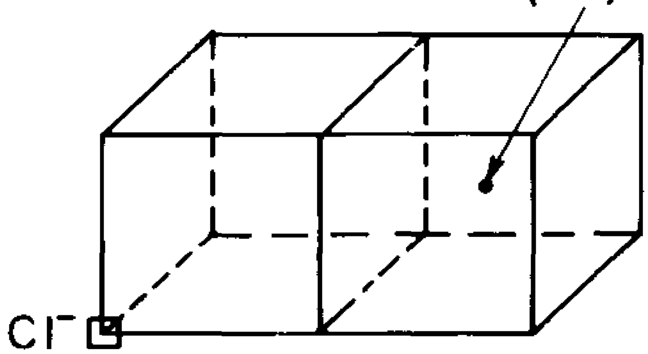
(a) START: PERFECT CRYSTAL
ENERGY = 0 eV

(b) SADDLE POINT: Cl^- AT (1.1, 0.5, 0.5)



ENERGY = 3.6 eV

(c) END Cl^- AT (1.5, 0.5, 0.5)



ENERGY = 3.0 eV

FIGURE 12

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