

EMPIRICAL CORRECTION OF THE INTERIONIC POTENTIAL

For

SOME DIFFUSION PROCESSES

in

ALKALI HALIDES

A Thesis

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ABSTRACT

We investigate a procedure for correcting the Born-Mayer repulsion in a defect in an alkali-halide crystal. The procedure is to use the experimental value of the activation energy for anion vacancy diffusion to determine the correction for ions adjacent to the saddle-point. Then, using a non-polarizable point ion lattice, with an odd-parity electronic trial wave function in adiabatic approximation self-consistently minimizing the energy with respect to electronic wave function parameters and ionic displacements, we obtain a zeroth-order approximation to the energy of the odd parity saddle point F - center. From this we estimate the activation energy of F - center step diffusion in KCl to be 1.6 eV, in agreement with the experimental result of Wolf. We also predict the activation energy of F - center step diffusion in NaCl. The method is critically analysed, and its relevance to other defect processes involving the saddle point configuration in NaCl - type alkali halides is indicated.

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CHAPTER I

INTRODUCTION

Recently, Brown and Vail<sup>1</sup> (1970) obtained fair agreement for the step diffusion activation energy of the F-center (Fig. 1) by a procedure which was not entirely consistent. They have pointed out that the main difficulty in this problem is that one cannot use the perfect lattice ion-ion repulsion at the saddle point, where inter-ionic spacings and coordinations are quite different from the perfect lattice case, and this is supported by comparison of detailed calculation with experiment in section (3.1) of the present work. The same difficulties arise in investigating other defects with non-harmonic distortion. Some defect problems to which the saddle-point configuration is relevant are (i) the reorientation and dissociation of the  $F_A$  - center<sup>2</sup> (Fig. 2), which is an F - center with an adjacent impurity; and (ii) the activation energy of the various reorientation and dissociation processes of  $F_B$  - and  $F_C$  - centers<sup>3</sup> (Fig. 3), in which two, and three impurity alkali ions, respectively, are adjacent to the F - center. The number of possible step diffusion processes for  $F_A$  -,  $F_B$  -, and  $F_C$  - centers is 18. Furthermore, the saddle point configuration is relevant to energies for the capture of anion vacancies by  $F'$  centers<sup>4</sup> and to the reorientation of the cation vacancy-divalent ion dipole, such as strontium - doped  $RbCl$ <sup>5</sup> (Fig. 4). Therefore the determination of some appropriate interionic potential for the saddle point configuration, which is the main object of this work, is an important problem for a variety of point defects.

FIGURE 1

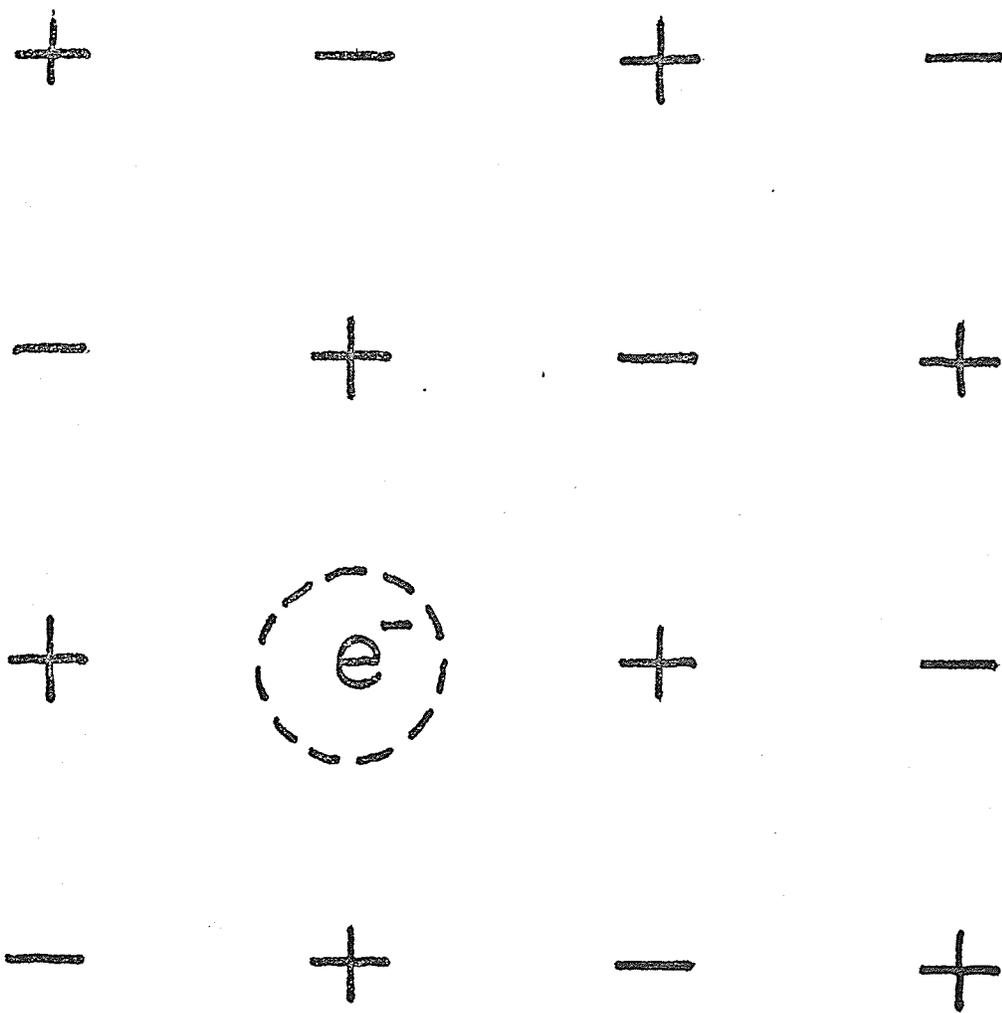
(a) Ordinary F-center in a NaCl-type alkali halide.

+ denotes the cation

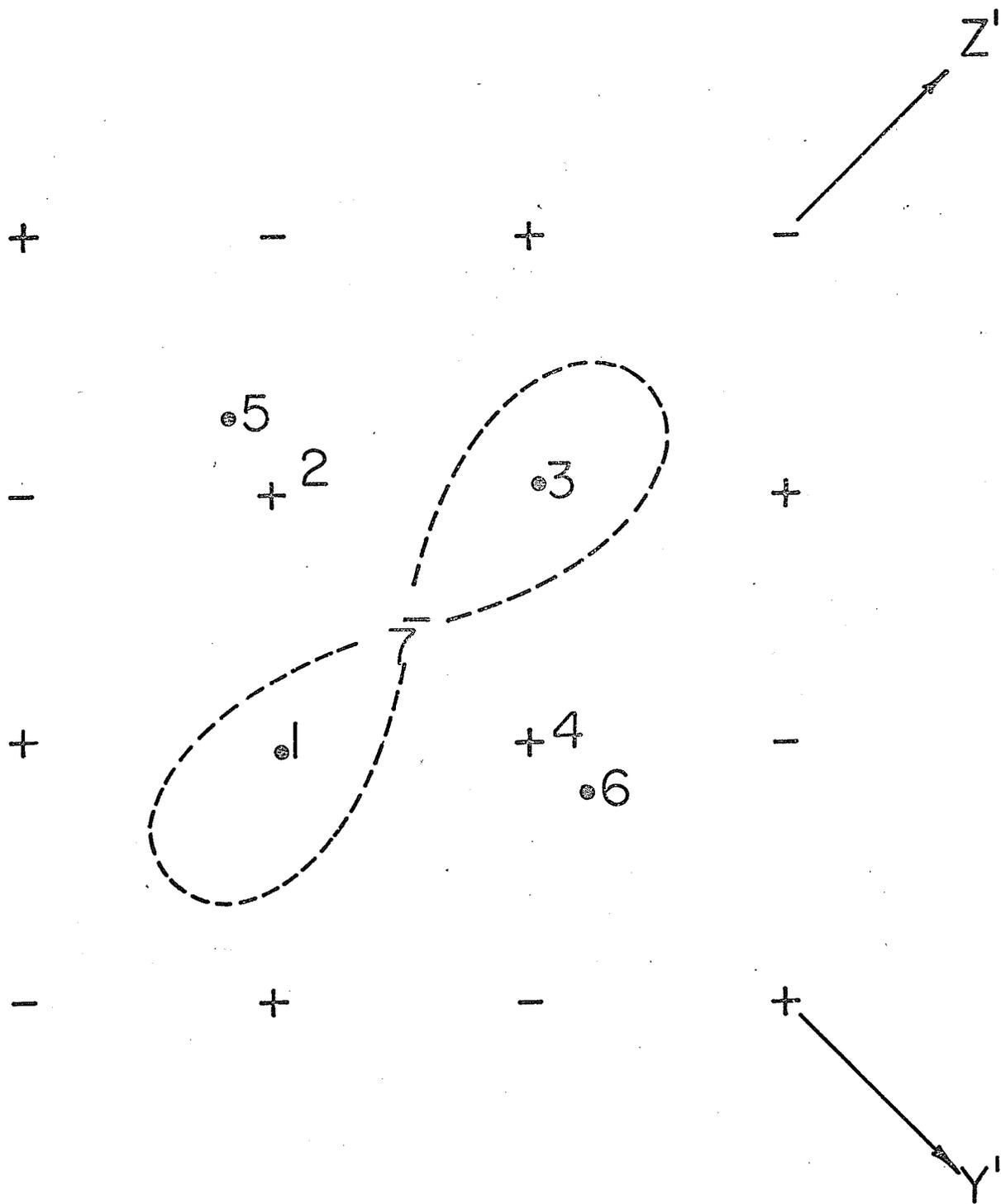
- denotes the anion

$e^-$  denotes the trapped electron

(b) Saddle point configuration of the F-center. Position (7) is the saddle point, in which a negative ion lies halfway between two vacant negative ion sites (1) and (3). Two straddling positive ions (2) and (4) will be displaced to (5) and (6) due to the interaction with the saddle point negative ion. The F-center electron is shared by the two negative ion sites (1) and (3). The energy of this configuration relative to that of figure 1(a) gives a measure of the activation energy for step diffusion of the F-center.



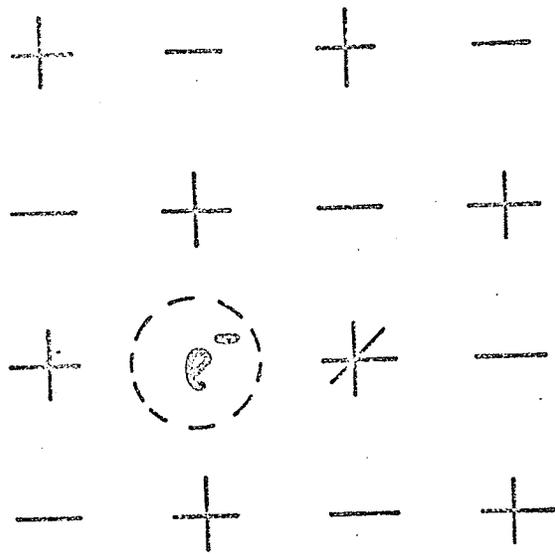
(a)



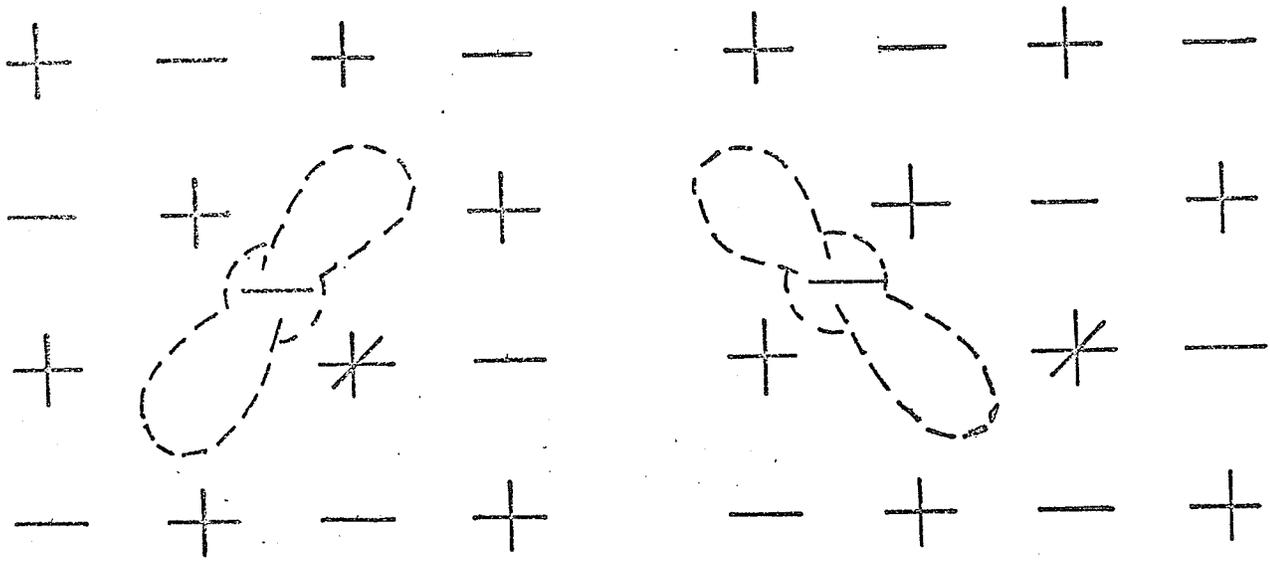
(b)

FIGURE 2.

Saddle point configuration for reorientation  
and dissociation processes of  $F_A^-$  center  
\* denotes an impurity cation and  $e^-$  denotes  
the trapped electron.



(a) ground state

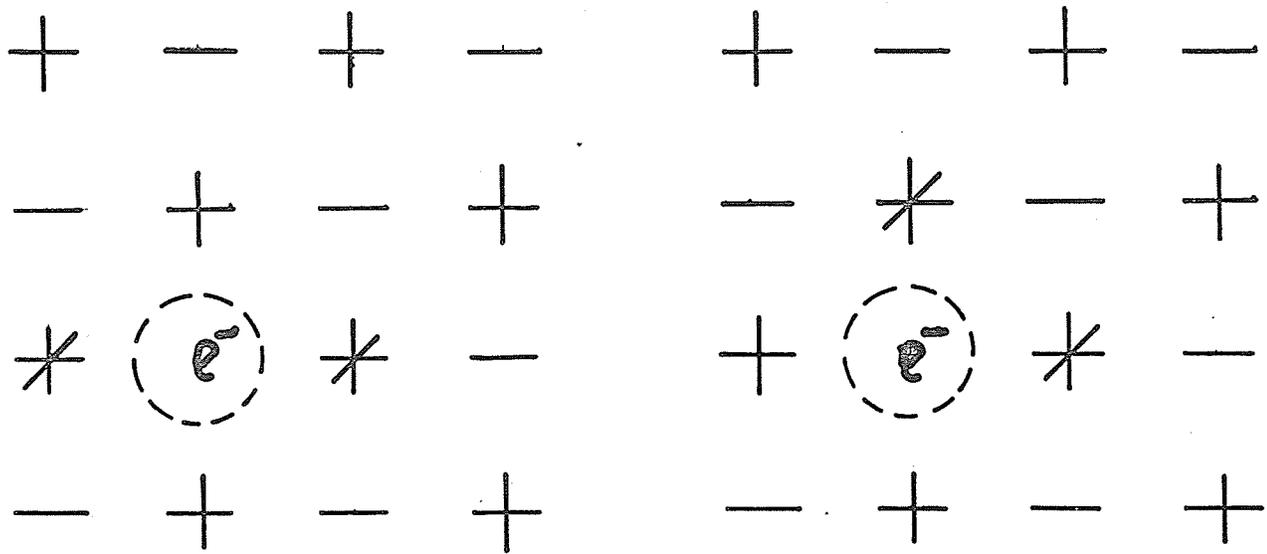


(b) reorientation

(c) dissociation

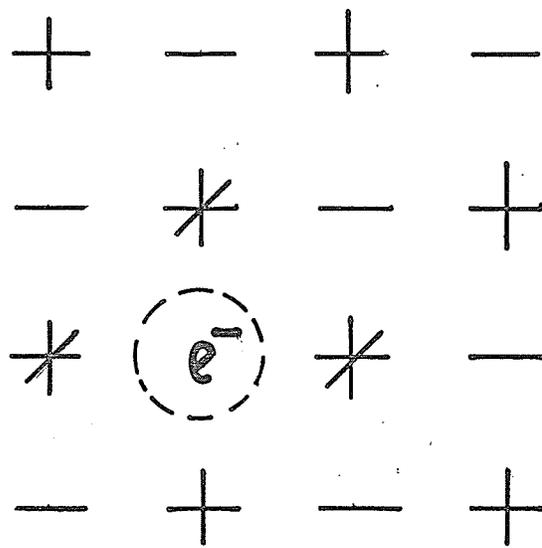
FIGURE 3.

$F_B$  - and  $F_C$  - centers. \* denotes an impurity cation and  $e^-$  denotes the trapped electron.



(a)  $F_B$ -Centre

(b)  $F_{B'}$ -Centre

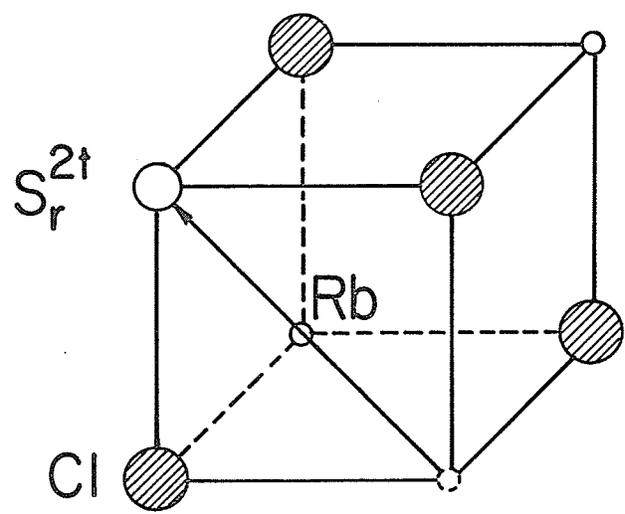


(c)  $F_C$ -Centre

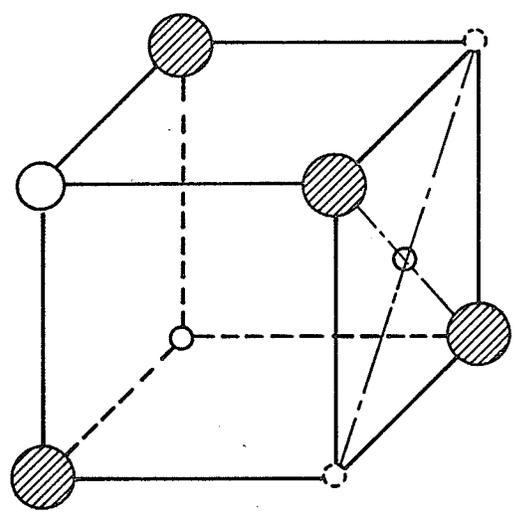
FIGURE 4.

Model for reorientation of the  $S_r^{2+}$  - vacancy  
dipole in RbCl

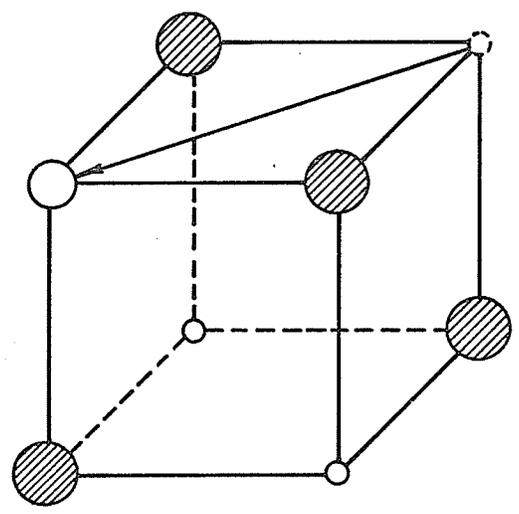
- ⊗ denotes the  $Cl^-$  ion
- denotes the  $Rb^+$  ion
- ⊙ denotes the cation vacancy
- denotes the impurity cation  $S_r^{2+}$
- ↗ denotes the direction of the dipole moment.



INITIAL STATE



INTERMEDIATE STATE  
(SADDLE POINT)



FINAL STATE

We use Born's model of the ionic crystal, which has point ions with unit charge, positive and negative, bound by long range coulomb interaction, and stabilized by short range repulsive forces between nearest neighbours. The repulsive force is due to the overlap of the closed electron shells of different ions, and is partly due to the exclusion principle. It is determined by the charge distribution where neighbouring ions overlap, and is affected by the lattice polarization due to both ionic displacement and ionic polarization. There exist several forms for the repulsive potential, containing empirical parameters. However, the most important character of the repulsive force is that it is very sensitive to the interionic distances, increasing strongly with decreasing ionic spacing.

The most widely used representation of the repulsive force is due to Born and Mayer<sup>6</sup>. It takes the nearest neighbour interionic potential to have the form

$$w(r) = A e^{-r/\rho} \tag{1.1}$$

where  $r$  is the distance between the two ions and  $A$  and  $\rho$  are parameters determined from macroscopic experimental data. Therefore, part of the non-pairwise contribution is included in these parameters. The Born-Mayer potential describes some properties of the perfect lattice in ionic crystals quite well, but is inadequate for defects where the ionic configuration is quite different from the perfect lattice. The saddle point configuration of the F - center is such a defect. Here, we have sought to get the corrected pairwise repulsive energy at the saddle point and <sup>to</sup> calculate the activation energy for F-center step diffusion in KCl. Wolf<sup>7</sup> has defined two possible processes of F - center diffusion: The dominant

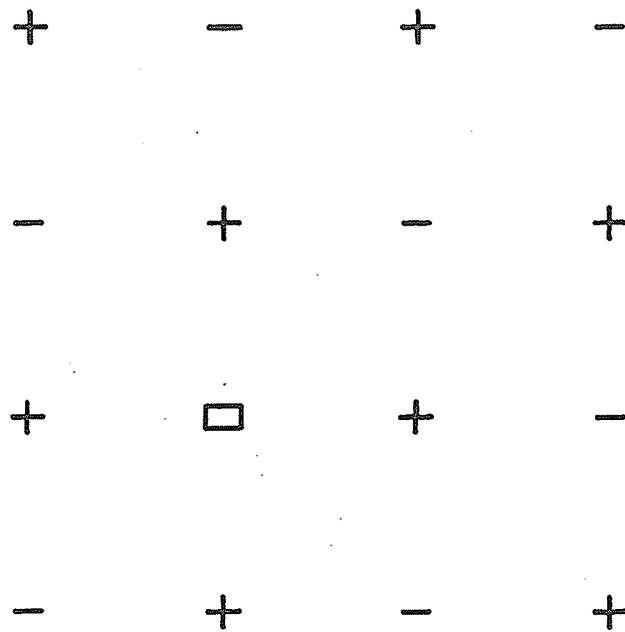
process occurs when the F - electron is thermally ionized and migrates through the conduction band, to be recaptured at a distant anion vacancy; a second diffusion process occurs when one of the twelve negative ions, nearest to the F - center, interchanges positions with the F - center. The second process is termed 'step diffusion' by Wolf. He estimates the activation energy for step - diffusion in KCl to be  $1.6 \pm 0.2$  eV at around 500° K.

The method which we have used avoids quantum mechanical treatment of the ions. The idea is to determine the effective repulsive interaction involved in the activation of anion vacancy diffusion and then to use it in other defects which involve the same basic lattice configuration. This can be done by correcting the repulsive interaction for the saddle point ion and its two nearest neighbours (Fig. 5) so as to produce agreement between the calculated value and the experimental value for the activation energy for anion vacancy diffusion.

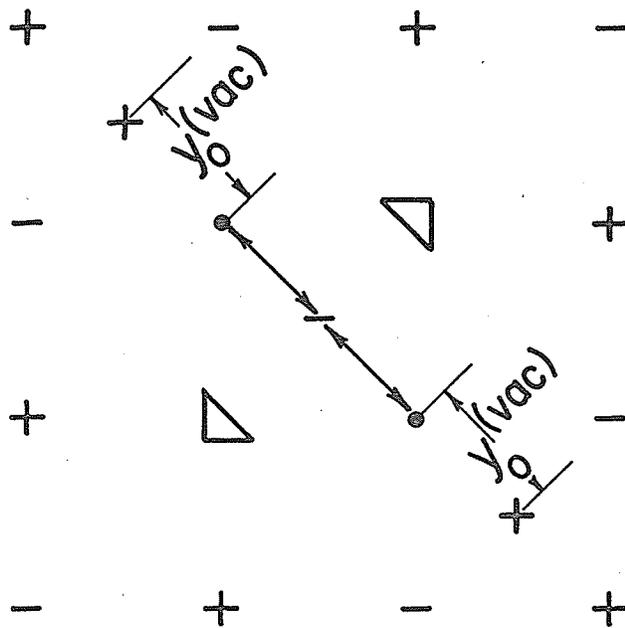
In separate calculations, A and  $\rho$  in  $A e^{-r/\rho}$  will be corrected, since we have only one piece of experimental data, namely, the activation energy for anion vacancy diffusion, and we wish to see whether the result is sensitive to the choice of the parameter. The empirically corrected parameter plays a role similar to that of a configuration coordinate, since it replaces, or embodies, a whole set of necessary corrections to our simple model, including part of the displacement polarization and ionic polarization and some of the approximations in actual calculations. Using a non-polarizable point ion lattice with an odd-parity electronic trial wave function, in adiabatic approximation, including the ion size correction due to Bartram, Stoneham and Gash<sup>8</sup> (hereafter referred to as BSG), we obtain the zeroth order

FIGURE 5.

Model for activation of anion vacancy diffusion  
in a NaCl-type alkali halides.



ORDINARY ANION VACANCY



SADDLE POINT ANION VACANCY

estimate of the saddle point F-center's energy. This energy minimizes the defect system's energy with respect to electronic parameters, and with respect to the non-harmonic displacement  $y_0$  of the straddling positive ions (Fig. 6) self-consistently, with the rest of the lattice (Region II) undistorted. This leads to an estimated activation energy of step diffusion in F-center for KCl which is in agreement with the experimental result of Wolf<sup>7</sup>. We also predict the activation energy of F-center step-diffusion in NaCl.

In chapter II, we will specify the model and method briefly, including description of the BSG ion size correction for the electron-ion interaction, the method of lattice statics (Kanzaki method<sup>9</sup>) for lattice distortion, and the shell model for ionic polarization. In chapter III, we will describe the calculation of (1) corrections to the pairwise repulsive energy; (2) zeroth order approximation to the odd-parity F-center saddle point energy; (3) estimate of the ionic polarization energy by considering only nearest negative neighbours to the saddle point, using the shell model; (4) estimate of the activation energy for F-center step diffusion. In Chapter IV, we will discuss further possible application and extensions of this work.

FIGURE 6.

Region I and Region II of the F-center saddle point defect in a NaCl-type alkali halide.

+

-

+

-

$Z'$

-

+

+

-

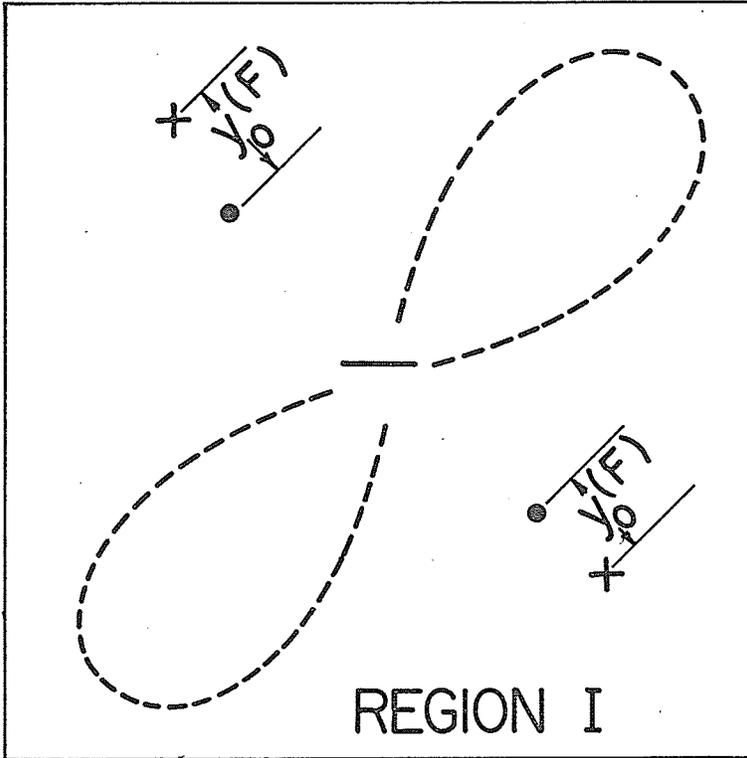
-

+

-

+

$Y'$



REGION I

REGION II

CHAPTER II

MODEL AND THEORETICAL METHOD

In this chapter, we discuss briefly the model and theoretical methods that we have used in the present work. Our calculations are based on the Born model. In the Born model, the ions are replaced by point charges, but one knows that the ions are composed of a core surrounded by an electronic cloud. We take account of the extended-ion effect by using the BSG ion-size correction, which is a point-ion correction based on the pseudopotential method. The lattice relaxation around the defect can be rigorously taken into account by the Kanzaki method. In the present work, we use the Kanzaki method only up to the zeroth order approximation, since our objective is to correct the interionic repulsion at the saddle point, in estimating the activation energy for F - center step diffusion. Finally, we describe the shell model in some detail, in order to be able later to obtain a rough estimate of the ionic polarization energy.

2.1 The BSG Method of Ion Size Correction

The pseudopotential equation <sup>10, 11</sup> is given by

$$(T + V_p) |\phi\rangle = E_v |\phi\rangle \quad (2.1)$$

where  $V_p$  is the pseudopotential, defined by

$$V_p = V + V_R \quad (2.2)$$

and  $V_R$  is the repulsive potential arising from orthogonalizing the

smooth envelope function  $\phi$  of the electron (F - center in this case) to the filled ion-core states. The orthogonalized function is

$$|\phi_F\rangle = N(1 - P) |\phi\rangle, \quad (2.3)$$

where  $N$  is the normalizing constant, and  $P$  is the core projector, that is

$$P = \sum_c |\psi_c\rangle \langle \psi_c|, \quad (2.4)$$

where  $|\psi_c\rangle$  is the free ion core wave function.

Bartram, Stoneham and Gash<sup>8</sup>, herein denoted BSG, used the above pseudopotential formalism, in the approximation of non - overlapping ion cores, and neglecting the variation of the trial pseudo wave function  $\phi$  over the ion cores. They then got an approximate pseudopotential

$$V_P = V_{PI} + \sum_{\gamma} [A_{\gamma} + (\bar{V} - U_{\gamma})B_{\gamma}] \delta(\vec{r} - \vec{r}_{\gamma}). \quad (2.5)$$

The coefficient of the  $\delta$  - function is the ion - size contribution to  $V_P$ ,  $V_{PI}$  is the point - ion potential,  $U_{\gamma}$  is the potential energy of an electron at lattice site  $\gamma$  due to all the other ions in the crystal, and  $A_{\gamma}$  and  $B_{\gamma}$  are constants characteristic of the ionic species at  $\gamma$ , given by

$$A_{\gamma} = \int (1 - P_{\gamma}) (V_{\gamma} - V_{PI_{\gamma}}) d\tau - \int P_{\gamma} V_{PI_{\gamma}} d\tau \quad (2.6)$$

$$B_{\gamma} = \int P_{\gamma} d\tau \quad (2.7)$$

Their values for a number of ions with closed -shell configurations are

given in BSG table 1, also,  $\bar{V}$  is defined by

$$\bar{V} = \langle \phi | V_P | \phi \rangle \quad (2.8)$$

BSG have used these results to calculate the ionization potential of alkali atoms, obtaining agreement with experiment, and to calculate the F - band energies in alkali halides and alkaline - earth fluorides, with results which are in poor agreement with experiment. BSG noticed that if the coefficients  $A_\gamma$  were reduced by a single semi - empirical factor  $\alpha = 0.53$ , agreement was obtained between the theoretically predicted and experimentally observed F - center absorption energies in the alkali halides. The same value of the empirical factor  $\alpha$  was also found to be applicable to F - center absorption energies in the alkaline-earth fluorides. The theoretical origin of this factor was not apparent.

By reviewing the derivation of BSG for the ion size correction, and their calculations for F - center absorption energy, one can see that

(1) The trial pseudo wave function  $\phi$  of equation (2.1), equation (2.3) and equation (2.8) should be the 'smoothest' pseudo wave function. In the BSG calculations, they used a Gourary - Adrian (type III) <sup>12</sup> trial wave function for the F - center ground state, and Gourary - Adrian (type II) for the F - center excited state, and not the 'smoothest' pseudo wave function. This source of error has been investigated by Weber and Dick <sup>13</sup>, and Alig <sup>14</sup>. Weber and Dick used six different types of trial pseudo wave functions for the valence electron to calculate the ionization potentials of the alkali atoms and found that the form of the trial pseudo wave functions is very important. Alig came to the same

conclusion by using different approximate forms of the trial pseudo wave functions to calculate the shifts of the  $F_{A1}$  and  $F_{A2}$  optical transitions energies from the ordinary F - center transition energy, due to the change in the ion - size corrections, for several  $F_A$  - centers. Alig did not use the empirical reduction factor  $\alpha$  for the coefficient  $A_Y$ . Furthermore, he calculated the equilibrium radial displacements of the impurity ion and of the remaining cations nearest to the vacancy in the  $F_A$  center and concluded that the Gourary - Adrian type of trial pseudo wave functions concentrate too much charge at the nearest - neighbour sites.

(2) BSG used free crystal ion core wave function in equation (2.6) and equation (2.7) instead of the true ion core wave function. Hagston<sup>15</sup> studied the expansion or contraction of the free ion function on forming a solid by considering the spin - orbit coupling constants in the alkaline earth fluorides and found them to be greater than the free ion values, which is equivalent to a contraction of the free ion wave function on forming a solid. Furthermore, Hagston has checked the semi-empirical reduction factor  $\alpha$ , by comparing the calculated and experimental values of the transferred hyperfine interaction constants for several alkali halides, and agrees with the BSG value.

In spite of the above analysis, the BSG ion size correction is considered to be a useful approximation for some many body effects, which it incorporates into the one - electron F - center wave function. At present, it appears that  $\alpha = 0.53$  should be used for the F - center absorption process, but how good this value may be for other defect configurations is still an open question.

In the present work, we take  $\alpha = 0.53$ , and use Gaussian - localized trial pseudo wave functions, as in Brown and Vail<sup>1</sup>. The equation (2.5) will be used in Chapter III as the electron - lattice interaction energy, including ion size correction.  $V_{PI}$  has been expanded in a convenient form by Brown<sup>16</sup> for the F - center saddle point, (see equation (3.17)) and the summation is carried up to the second term by Evjen's method (Appendix), which included 24 groups of ion.

## 2.2 Treatment of Lattice Relaxation

The forces due to the lattice defect introduce ion displacements and ion polarization. A great deal of work has been done following the "semi - discrete" approach of Mott and Littleton<sup>17</sup>, in which only the ions near the defect (region I) were treated as discrete, while the distant ions (region II) were regarded as a dielectric continuum. In this approach, the displacements of the ions in region I must minimize the total energy of the defect lattice. For our model, where the whole lattice is composed of discrete ions, Brown and Vail<sup>1</sup> have estimated F - center energies by the method of lattice statics, or the Kanzaki method<sup>9</sup>.

Our problem will be formulated in terms of the zeroth order approximation. In the Kanzaki method, the whole lattice is treated as discrete, and the results are exact within the harmonic approximation. The modification to include excess electrons has been made by Stoneham<sup>18</sup>, and to include non - harmonic lattice distortion in region I by Vail<sup>19</sup>, who has also briefly reviewed the subject. Hereafter, we follow Vail's notation closely.

For an excess electron defect with the trial wave function  $\phi(\vec{r}, \underline{\lambda})$ , containing variational parameters which form the components of a generalized vector  $\underline{\lambda}$ , the energy of the defect system is

$$E(\underline{\xi}, \underline{\mu}_p, \underline{\lambda}_{p,p}) = \frac{1}{2} \underline{\xi}_p^T \cdot \underline{A} \cdot \underline{\xi}_p + V_L(\underline{\xi}_p, \underline{\mu}_p) + T(\underline{\lambda}_{p,p}) + V(\underline{\xi}_p, \underline{\mu}_p, \underline{\lambda}_{p,p}) \quad (2.9)$$

where  $\underline{\mu}$  is a vector standing for the generalized coordinates of atoms in region I,

$T(\underline{\lambda}_{p,p})$  is the excess electron's kinetic energy,

$\underline{\xi}_p$  is a column matrix representing the resultant distortion field of the crystal in region II, and  $\underline{\xi}_p^T$  is its transpose.

$V_L(\underline{\xi}_p, \underline{\mu}_p)$  is the energy required to produce the atomic configuration of region I from a perfect lattice with distortion field  $\underline{\xi}$ , and it can be written

$$V_L(\underline{\xi}_p, \underline{\mu}_p) = V_{L1}(\underline{\mu}_p) + V_{L2}(\underline{\xi}_p) + V_{L3}(\underline{\xi}_p, \underline{\mu}_p) \quad (2.10)$$

$\underline{A}$  is the force constant matrix of the perfect lattice and

$V(\underline{\xi}_p, \underline{\mu}_p, \underline{\lambda}_{p,p})$  is the electron-lattice interaction energy, which can be split into

$$V(\underline{\xi}_p, \underline{\mu}_p, \underline{\lambda}_{p,p}) = V_1(\underline{\lambda}_{p,p}, \underline{\mu}_p) + V_2(\underline{\lambda}_{p,p}, \underline{\xi}_p) \quad (2.11)$$

The subscripts  $p$  and  $p'$  are necessary to distinguish between relaxed and unrelaxed states of the lattice <sup>in</sup> electronic transitions of the F-center, as described by Vail <sup>19</sup>.

Expanding this energy, equation (2.9), to quadratic terms in  $\underline{\xi}_p$ ,  $\Delta \underline{\mu}_p$ , and  $\Delta \underline{\lambda}_{pp}$ , one obtains

$$\begin{aligned}
 E(\underline{\xi}, \underline{\mu}, \lambda) &= E^{(0)} - \underline{F}_0^T \cdot \underline{\xi} + \frac{1}{2} \underline{\xi}^T \cdot (\underline{A} + \underline{F}_1) \cdot \underline{\xi} \\
 &+ \underline{\xi}^T \cdot (\underline{A} \cdot \Delta \underline{\lambda} + \underline{M} \cdot \Delta \underline{\mu}) + \Delta \underline{\lambda}^T \cdot \underline{N} \cdot \Delta \underline{\mu} \\
 &+ \frac{1}{2} \Delta \underline{\lambda}^T \cdot \underline{A}_{=1} \cdot \Delta \underline{\lambda} + \frac{1}{2} \Delta \underline{\mu}^T \cdot \underline{M}_{=1} \cdot \Delta \underline{\mu}
 \end{aligned} \tag{2.12}$$

where  $\Delta \lambda = (\lambda - \lambda^{(0)})$ ,  $\Delta \mu = (\mu - \mu^{(0)})$ , and where  $\lambda^{(0)}$  and  $\mu^{(0)}$  are the zeroth order solution of the perturbation-interaction method, that is

$$\left( \frac{\partial E}{\partial \lambda} \right)_{\underline{\xi}=0} = 0 \quad \rightarrow \quad \lambda_{pp} = \lambda_{pp}^{(0)} \tag{2.13}$$

$$\left( \frac{\partial E}{\partial \mu_p} \right)_{\underline{\xi}=0} = 0 \quad \rightarrow \quad \mu_p = \mu_p^{(1)} \tag{2.14}$$

and where  $E^{(0)}$  is constant, and the matrices  $\underline{F}_0$ ,  $\underline{F}_1$ ,  $\underline{A}_{=1}$ ,  $\underline{A}$ ,  $\underline{M}_{=1}$ ,  $\underline{N}$ , involve first and second derivatives of  $V_1$ ,  $V_2$ ,  $V_{L1}$ ,  $V_{L2}$ ,  $V_{L3}$ , and  $T$ . In the present problem, we are concerned with the zeroth order solution.

From equation (2.9), with  $\underline{\xi}_p = \underline{0}$ , the energy of the defect system reduces to

$$E^{(0)} = E(\underline{0}, \underline{\mu}_p^{(0)}, \lambda_{pp}^{(0)}) = T(\lambda_{pp}^{(0)}) + V_L(\underline{0}, \underline{\mu}_p^{(0)}) + V(\underline{0}, \underline{\mu}_p^{(0)}, \lambda_{pp}^{(0)}) \tag{2.15}$$

## 2.3 The Shell Model

### (A) Introduction

Most treatments of ionic crystal lattices have been based on the Born model (Chapter 1). In this model, the ions are assumed to be rigid, interacting with one another through long-range electrostatic

forces and through short-range repulsive forces due to the overlap between neighbours. Among the early treatments, Kellermann<sup>20</sup> provided the foundation for the development of models for static and dynamic distortions in the alkali halides. Kellermann assumed that two empirical constants are needed for the repulsive force, namely, the nearest neighbours ionic spacing, obtained from the condition of equilibrium, and the compressibility. He used the Ewald transformation in evaluating the coulomb interaction between displaced ions. The polarizability of the ions was completely neglected in his treatment. The result was that the calculated specific heat of the lattice was in good agreement with experiment but inconsistent results were obtained for the dielectric properties of the alkali halides. Even prior to Kellermann's work, Lyddane and Herzfeld<sup>21</sup> had included the polarization due to the electric field but not that due to the overlap force. That is, they let the point ion be polarizable, by assuming that they had charges  $\pm Ze$  and polarizabilities  $\alpha_{\pm}$ . However, the result was worse than Kellermann's, many of the calculated frequencies were much too low. One may conclude that it is better to neglect electronic polarizability completely than to take account of only one aspect of it.

The difficulties of the classical theory have been explained by Szigeti<sup>22</sup>. He introduced the concept of distortion polarization, or "second mechanism of polarization", which accompanies the electronic polarization of the ions, and is due to the displacement of the ions from equilibrium lattice sites. This distortion polarization is due to the action of repulsive forces between shells when neighbouring ions undergo relative displacement. The direction of distortion polarization

is opposite to that of the polarization associated with the displacement of the charged point ions, and to the electronic polarization induced by the resultant electric field.

The classical polarizable point ion model is in poor agreement with dielectric constant measurements because it neglects the simultaneous dependence of the electronic polarizability of the ions on the electric field and on the short range repulsion. It is this deficiency which the ion polarization model, or shell model, is designed to correct. It was originally developed by Dick and Overhauser<sup>23</sup> to calculate the effective ionic charge, and is undoubtedly a great improvement on the point polarizable ion models.

In the shell model, one considers each ion of the crystal to be divided in two rigid parts: a spherically symmetric electron shell representing the outer-electrons, negatively charged, and an inner core representing the other electrons and the nucleus. Each shell is bound to its core by an isotropic harmonic force and adjacent shells also interact with each other via isotropic harmonic forces. In the vibrating lattice, the shells move relative to their respective cores under the combined action of the local field and the overlap forces, thus taking account of both field polarization and distortion polarization of the ions. The contents of unit cell, namely, a single positive and single negative ion, could be described in terms of the displacements of four, rather than two variables; that is, the displacements of the cores of the two ions, and the displacements of the shells of the two ions. The core displacements and the shell displacements are not necessarily equal. Therefore, the shell model doubles the number of degrees of freedom of each

ion. This increases the work in lattice calculations since the dynamical matrix becomes a 12 x 12 matrix instead of a 6 x 6 matrix. The shell model evidently includes the harmonic approximation and normally also embodies the adiabatic assumption, by neglecting the inertia of electrons, so that the shells occupy positions of equilibrium at each instant.

(B) The Polarization of the Simple Shell Model

In Fig. 7, the simple shell model representation of interaction between adjacent ion pairs is shown. The force constants coupling a shell isotropically to the core of the same ion are denoted by  $k_+$ ,  $k_-$  for positive and negative ions respectively, and the force constant coupling adjacent shells is denoted by  $R$ . Fig. 7 (a) shows the unpolarized state and Fig. 7 (b) the polarized state. In the polarized state, the relevant displacements for the simple shell model are

$d_+$  = the displacement of shell with respect to the core of positive ion;

$d_-$  = the displacement of shell with respect to the core of negative ion;

$\Delta_+$  = the displacement of core of positive ion;

$\Delta_-$  = the displacement of core of negative ion;

$\Delta = \Delta_+ - \Delta_-$  = relative displacement of the cores;

$M = \Delta - d_- + d_+$  = relative displacement of the shells.

The potential energy contributed by the ion polarization in the shell model can be divided into three parts:

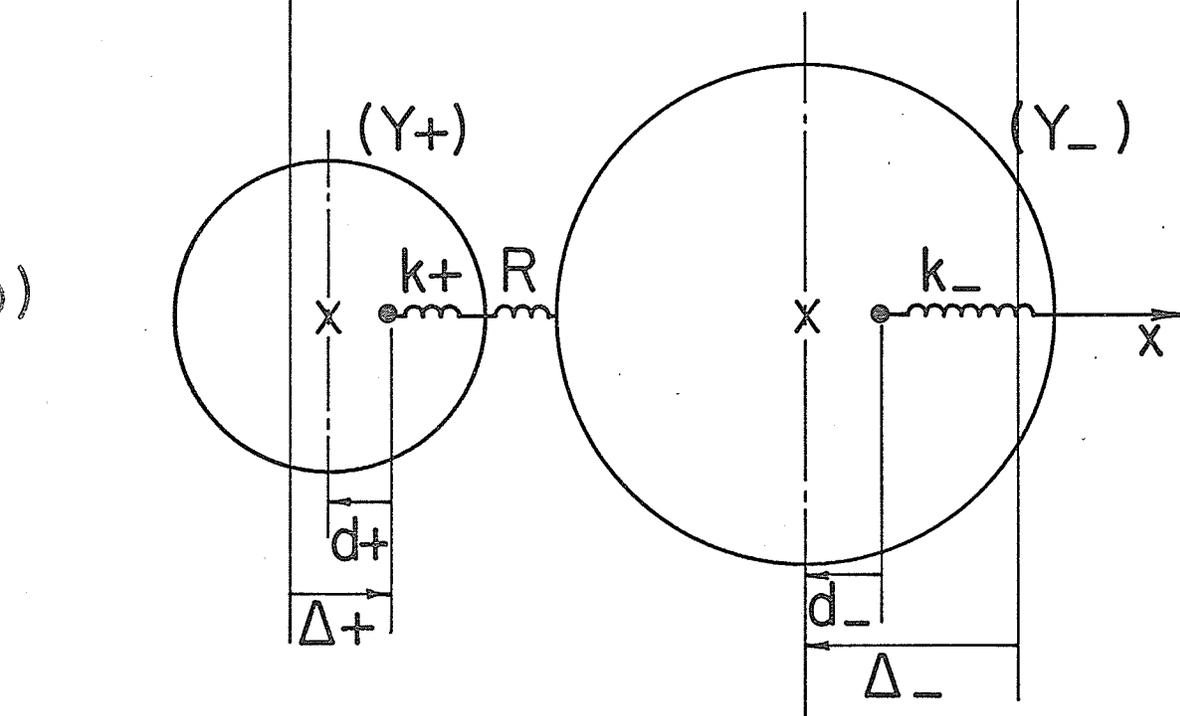
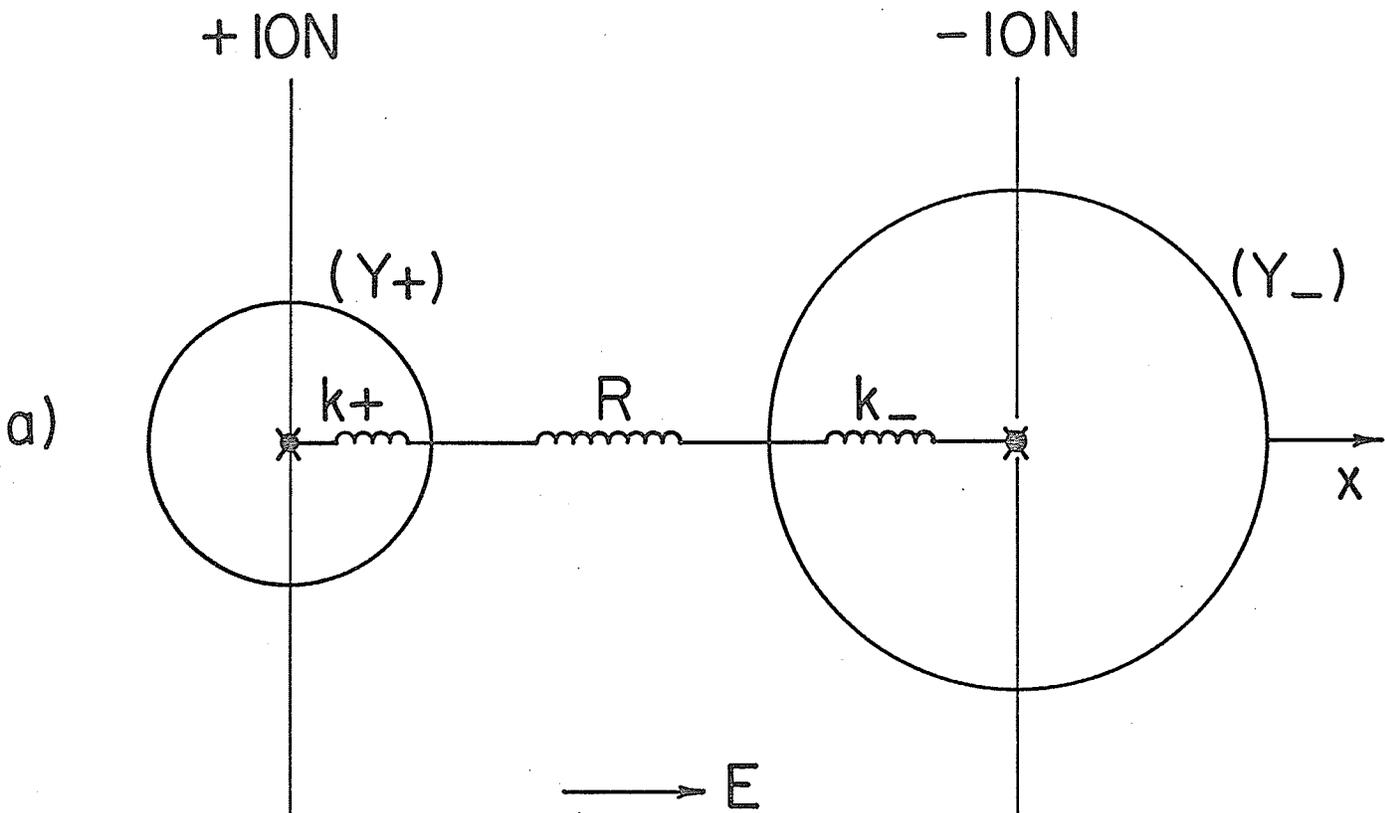
- (i) Electrostatic energy
- (ii) Short range interaction energy
- (iii) Self-energies of the ions

FIGURE 7.

Simple shell model representation of the polarization of the ion pair, assuming the direction of the polarizing field is along the positive x-axis.  $R$  is the spring constant of the spring coupling the shells between  $(+)$  ions,  $k_+$  are the spring constants of the springs coupling the core and shell of the  $(+)$  ions,  $\Delta_+$  is the core displacement of the  $(+)$  ions,  $d_+$  is the shell displacement with respect to the core of the  $(+)$  ions,  $Y_+$  is the no. of electrons on the shell of  $(+)$  ions.

- (a) unpolarized state
- (b) polarized state

- denotes core center
- x denotes shell center



(i) Electrostatic Energy

The coulomb forces may be described in terms of an electrostatic multipole expansion about the ion sites. From reference (24), P. 101 the energy of the charge distribution  $(q_j, \vec{P}_j, \dots)$  at  $\vec{R}_i^{(0)}$  is

$$w_i = q_i \phi(\vec{R}_i^{(0)}) - \vec{P}_i \cdot \vec{E}(\vec{R}_i^{(0)}) \quad (2.16)$$

where  $\vec{R}_i^{(0)}$  is the position of the  $i$ th ion site,  $q_i$  is the charge at the  $i$ th ion site,  $\vec{P}_i$  is the dipole moment at the  $i$ th ion site,  $\vec{E}(\vec{R}_i^{(0)})$  is the electric field, and  $\phi(\vec{R}_i^{(0)})$  is the electrostatic potential, and is equal to

$$\phi(\vec{R}_i^{(0)}) = \sum_{\substack{j \\ (j \neq i)}} \left\{ \frac{q_j}{|\vec{R}_i^{(0)} - \vec{R}_j^{(0)}|} + \frac{\vec{P}_j \cdot (\vec{R}_i^{(0)} - \vec{R}_j^{(0)})}{|\vec{R}_i^{(0)} - \vec{R}_j^{(0)}|^3} \right\} \quad (2.17)$$

in the dipole approximation, and the electric field  $\vec{E}(\vec{R}_i^{(0)})$  at the  $i$ th ion site is

$$\vec{E}(\vec{R}_i^{(0)}) = - [\nabla \phi(\vec{r})]_{\vec{r} = \vec{R}_i^{(0)}} \quad (2.18)$$

It becomes

$$\vec{E}(\vec{R}_i^{(0)}) = \sum_{\substack{j \\ (j \neq i)}} \left\{ \frac{q_j (\vec{R}_i^{(0)} - \vec{R}_j^{(0)})}{|\vec{R}_i^{(0)} - \vec{R}_j^{(0)}|^3} + \frac{3[\vec{P}_j \cdot (\vec{R}_i^{(0)} - \vec{R}_j^{(0)})] (\vec{R}_i^{(0)} - \vec{R}_j^{(0)}) - |\vec{R}_i^{(0)} - \vec{R}_j^{(0)}|^2 \vec{P}_j}{|\vec{R}_i^{(0)} - \vec{R}_j^{(0)}|^5} \right\} \quad (2.19)$$

Thus, the total coulomb energy of the system is

$$W = \frac{1}{2} \sum_i w_i \quad (2.20)$$

where the factor  $\frac{1}{2}$  is introduced to avoid counting each interaction twice.

From equations (2.16) to (2.20), we get

$$\begin{aligned}
 W = & \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} \frac{q_i q_j}{|\vec{R}_i^{(0)} - \vec{R}_j^{(0)}|} - \sum_{\substack{i,j \\ (i \neq j)}} \frac{q_j \vec{P}_i \cdot (\vec{R}_i^{(0)} - \vec{R}_j^{(0)})}{|\vec{R}_i^{(0)} - \vec{R}_j^{(0)}|^3} \\
 & - \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} \left\{ \frac{3 \{ [\vec{P}_i \cdot (\vec{R}_i^{(0)} - \vec{R}_j^{(0)})] [\vec{P}_j \cdot (\vec{R}_i^{(0)} - \vec{R}_j^{(0)})] \}}{|\vec{R}_i^{(0)} - \vec{R}_j^{(0)}|^5} - \frac{\vec{P}_i \cdot \vec{P}_j}{|\vec{R}_i^{(0)} - \vec{R}_j^{(0)}|^3} \right\} \quad (2.2)
 \end{aligned}$$

The first term of the equation (2.21) is contributed by monopole-monopole interaction, the second term by monopole-dipole interaction, and the last term by dipole-dipole interaction. The dipole moment of the ion in the shell model is

$$(\vec{P}_{\pm})_i = q_i (\vec{\Lambda}_{\pm})_i - Y_{\pm} e (\vec{d}_{\pm})_i \quad (2.22)$$

where (+) corresponds to positive or negative ion, respectively,  $Y$  is the number of electrons in the shell,  $\vec{\Lambda}$  is the core displacement and  $\vec{d}$  is the relative displacement of shell with respect to core.

#### (ii) Short - Range Interaction Energy

The short - range repulsive interaction should depend on displacement polarization and distortion polarization. This effect will be expressed clearly by the shell - model. In the simple shell model, the short range force is assumed to act between adjacent shells. The short - range interaction energy is

$$E_{\text{rep}} = \frac{1}{2} RM^2 + A_0 \quad (2.23)$$

where  $A_0$  is constant and is equal to the pairwise repulsive energy in non-polarizable point ion model,  $R$  is the force constant between shells of neighbouring ions, and  $\vec{M} = (\vec{\Delta} - \vec{d}_- + \vec{d}_+)$ . Thus  $E_{rep}$  involves the cross term of the  $\Delta$ 's and  $\underline{d}_+$ 's.

(iii) Self-Energies of the Ions

The self-energies of the ions are the energies contributed by the spring constant between the core and shell, which represents the electronic polarization.

$$E_{self} = \frac{1}{2} k_+ (d_+)^2 + \frac{1}{2} k_- (d_-)^2 \quad (2.24)$$

(C) Calculation of Shell Model Parameters

For carrying out a shell model calculation, one needs to evaluate the following shell model parameters

- (1) the number of electrons in the shells  $Y_{\pm}$ ;
- (2) the core - shell spring constant  $k_{\pm}$ ,
- (3) the shell-shell spring constant  $R$ .

The parameters of generalized shell models (i.e. models which include more than nearest neighbour shell-shell coupling), have been determined from "best" fits of the results derived from theoretical lattice vibration spectra with inelastic neutron scattering experiments<sup>25-29</sup>. This procedure is not unique, and there is no simple criterion for deciding between the various fits. Furthermore, the physical meaning of the extra parameters is lost when many adjustable parameters are used in the shell model.

However, the simple shell model (Fig. 7) has the merit of intuitive interpretation, and it is moderately successful in lattice dynamics. Therefore, in the present work, we will use the simple shell model, assuming the overlap forces to be axially symmetric and to extend no further than first nearest neighbours. We make the further approximation that only negative ions are polarizable, that is,  $k_+ = \infty$ , since the electronic polarizability of the positive ion is small compared with that of the negative ion. It is a particularly good approximation for Li and Na salts<sup>30</sup>. Havinga<sup>31</sup>, Woods et al.<sup>27</sup> have derived the expression for this simple shell model's parameters in terms of the elastic constants  $C_{11}$ ,  $C_{12}$ , the high frequency dielectric constant  $\epsilon$ , and the low frequency dielectric constant  $\epsilon_0$ . From ref (27) equations (2.3.9), (2.3.12), (2.3.13) and (2.3.1), we have

$$\frac{4\pi\alpha_-}{3v} = \frac{\epsilon - 1}{\epsilon + 2} \quad (2.25)$$

$$\left[ \frac{(z - d')^2 e^2}{R - e^2 d'^2 / \alpha_-} \right] = \frac{3v}{4\pi} \left( \frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon - 1}{\epsilon + 2} \right) \quad (2.26)$$

where  $v$  is the volume of a unit cell,  $r_0$  is the lattice spacing,  $\alpha_-$  is the polarizability of the free ions,  $Ze$  is the charge on the positive ion, and  $d'$  is the mechanical polarizability of the ion. It is a measure of the polarizability of the negative ion under the short range forces, and is defined as

$$d' = - \frac{RY_-}{(k_- + R)} \quad (2.27)$$

where  $R$  is the force constant between shells, and is given by

$$R = \frac{6 r_o (C_{11} + 2C_{12})}{3} \quad (2.28)$$

and the polarizability of the free ions related to the shell model parameters by

$$\alpha_- = \frac{Y_-^2 e^2}{k_- + R} \quad (2.29)$$

Therefore, for given values of  $C_{11}$ ,  $C_{12}$ ,  $\epsilon$  and  $\epsilon_o$ , we get the values of  $\alpha_-$ ,  $d'$ , and  $R$  from equations (2.25), (2.26) and (2.28), from which the simple shell model parameters  $Y_-$ ,  $k_-$  is calculated by equations (2.27) and (2.29).

In table (1), all the experimental values of  $C_{11}$ ,  $C_{12}$ ,  $\epsilon$  and  $\epsilon_o$  used for the calculation of shell model parameters are given, and table (2) gives the results of these calculations. The calculation for NaI is used for checking and comparing with ref. (27).

TABLE 1 EXPERIMENTAL VALUES USED FOR  
CALCULATION OF SHELL MODEL PARAMETERS

parameters	unit	NaI <sup>27</sup>	NaCl <sup>29</sup>	KCl <sup>25</sup>
$r_0$	$\text{\AA}$	3.21	2.81	3.12
$v$	$\text{\AA}^3$	66.00	44.20	60.80
$C_{11}$	$10^{11} \text{ dynes/cm}^2$	3.59	4.88	4.60
$C_{12}$	$10^{11} \text{ dynes/cm}^2$	0.75	1.26	0.58
$\epsilon$	$10^{12} \text{ Hertz}$	2.91	2.31	2.15
$\epsilon_0$	$10^{12} \text{ Hertz}$	6.18	5.91	4.57

TABLE 2 CALCULATED VALUES OF  
SHELL MODEL PARAMETERS

Parameters	unit	NaI	NaCl	KCl
R	$10^4 \text{ erg/cm}^2$	3.22	4.16	3.60
$K_-$	$10^5 \text{ dyne/cm}^2$	2.55	1.35	2.66
$Y_-$	electrons	2.76	1.57	2.29

CHAPTER III

CALCULATIONS, RESULTS AND DISCUSSION

3.1 Corrections to the Pairwise Repulsive Energy

In order to correct the pairwise repulsive energy at the saddle point, we have to calculate the energy of the ordinary vacancy  $E_o^{\text{vac}}(\tilde{\xi})$  and the energy of the saddle point vacancy  $E_{\text{s.p.}}^{\text{vac}}(\xi, \underline{\mu})$ . Then, the activation energy for vacancy diffusion can be written as

$$E_{\text{act}}^{\text{(vac)}} = \{ E_{\text{s.p.}}^{\text{(vac)}}(\xi, \underline{\mu}) - E_o^{\text{vac}}(\tilde{\xi}) \} \quad (3.1)$$

where  $\xi$  and  $\tilde{\xi}$ , are the distortion fields in region II of the saddle point vacancy and ordinary vacancy, respectively. In the problem of the vacancy, there is no excess electron, so the electron - lattice interaction energy  $V$  and the kinetic energy of the excess electron, should be set equal to zero in equation (2.1):

$$T = V = 0 \quad (3.2)$$

Let  $\underline{\mu} = y_o^{\text{(vac)}}$ , the displacement of the positive ions straddling the saddle point (see Fig. 5). Then the saddle point energy of the vacancy becomes

$$E_{\text{s.p.}}^{\text{vac}}(\xi, y_o^{\text{(vac)}}) = \frac{1}{2} \xi^T \cdot \underline{A} \cdot \xi + V_L(\xi, y_o^{\text{(vac)}}) \quad (3.3)$$

and the energy of the ordinary vacancy becomes

$$E_o^{\text{vac}}(\tilde{\xi}) = \frac{1}{2} \tilde{\xi} \cdot \underline{A} \cdot \tilde{\xi} + \tilde{V}_L(\tilde{\xi}) \quad (3.4)$$

The evaluation of the energies in equations (3.3) and (3.4)

could be done quite accurately, using the Kanzaki method to calculate the distortion fields  $\underline{\xi}$  and  $\tilde{\xi}$  in region II. In this problem, since we have only one piece of empirical data, we can only correct one parameter in the repulsive potential. Then, the corrected parameter will play a role similar to that of configuration coordinate since it includes a whole set of necessary corrections, such as the displacement and ionic polarization, the contribution to the energy of region II, and some assumptions in the detailed calculation. Furthermore, we want to use the corrected repulsive potential in the saddle point F-center to calculate the odd - parity saddle - point F-center energy in the zeroth order approximation. Therefore, we calculate the energies of ordinary and saddle-point vacancies in zeroth order ; that is without lattice relaxation in region II. Equation (3.3) and equation (3.4) become:

$$E_{s.p}^{vac}(y_o^{(vac)}) = V_L(y_o^{(vac)}) \quad (3.5)$$

$$E_o^{vac} = \tilde{V}_L(0) \quad (3.6)$$

where  $V_L(y_o^{(vac)})$ ,  $\tilde{V}_L(0)$  are the energies required to create the lattice defect of the saddle point and ordinary vacancy configurations, respectively, without allowing for any relaxation of the lattice in Region II.

The next step is to evaluate  $V_L(y_o^{(vac)})$  and  $\tilde{V}_L(0)$ . Our calculation is based on the Born model, described in Chapter I. The ionic interaction can be written as the sum of Coulomb (c) and repulsive (R) parts:

$$\omega = \omega^{(c)} + \omega^{(R)} \quad (3.7)$$

In the present work, we use the Born-Mayer repulsive form, so  $\omega^{(R)} = A e^{-r/\rho}$ , where  $A$  and  $\rho$  are the repulsive parameters, determined from the equilibrium ionic spacings and compressibility, with only nearest neighbour repulsive interaction included. Therefore, equation (3.7) becomes

$$\omega = \frac{1}{2} \sum_{lK, l'K'} \frac{q_K q_{K'}}{r} + \sum_{\substack{lK, l'K' \\ \text{(n.n.)}}} A e^{-r/\rho} \quad (3.8)$$

where  $r = |\vec{r}(l'K') - \vec{r}(lK)|$ ,  $\vec{r}(lK)$  is the position of the  $K$ th ion in  $l$ th unit cell,  $q_K$  is the ionic charge of an ion of type  $K$  and (n.n.) stands for "nearest neighbour".

The corrected repulsive parameters will be used in the interaction between the saddle point ion and the adjacent straddling positive ions, and the bulk values of Born-Mayer repulsive parameters will still be used for the repulsion of the rest of the ion pairs.

We formulate the procedure for calculating the energy  $V_L$  required to create the saddle point defect as follows (Fig. 1):

- (1) remove negative ion from lattice site labelled 3
- (2) remove negative ion from lattice site labelled 1
- (3) remove positive ion from lattice site labelled 2
- (4) remove positive ion from lattice site labelled 4
- (5) put in negative ion at saddle-point labelled 7
- (6) put in positive ion at lattice site labelled 5
- (7) put in positive ion at lattice site labelled 6

We then obtain the energy required to create the saddle point vacancy defect  $V_L$ , as follows:

$$\begin{aligned}
 V_L(y_o^{(\text{vac})}) = & (4M + \frac{2}{\sqrt{2}} - 4) - 20 A e^{-r/\rho} + 4 A e^{-\sqrt{a^2+y_o^2} - \sqrt{2} a y_o/\rho} \\
 & + 4 A e^{-\sqrt{a^2+y_o^2}/\rho} - 1/(\sqrt{2} + y_o/a) - 2/(\sqrt{2}/2 + y_o/a) \\
 & + B + C + 2A' e^{-(\sqrt{2}a/2 + y_o)/\rho'} \tag{3.9}
 \end{aligned}$$

This energy is in units of  $(e^2/a)$ , where  $e = 4.8 \times 10^{-10}$  e.s.u.

$a$  is the interionic spacing,  $M$  is the Madelung constant,  $B$  is the coulomb energy of a positive ion displaced by  $y_o$  to position 5 in Fig. 1, from a perfect lattice site 2 when the two negative ions at lattice sites labelled 1 and 3 are missing and  $C$  is the Coulomb energy of a positive ion displaced by  $y_o$  from perfect lattice site 4 when the two negative ions at 1 and 3 are missing and the positive ion at 2 has been displaced to 5.

The last term of equation (3.9) is the pairwise repulsive energy of the straddling positive ions interacting with the negative ion at the saddle point. It has two parameters, namely,  $A'$  and  $\rho'$  to be corrected, but we have only one piece of experimental data. Therefore, we let one of the parameters equal the perfect lattice value and determine the other.

The energy required to create the ordinary vacancy defect is

$$\tilde{V}_L(o) = M - 6 A e^{-r/\rho} \tag{3.10}$$

in units of  $(e^2/a)$ .

To determine the corrected value  $\rho'$  or  $A'$  at the saddle-point in zeroth order, we have to minimize the saddle point energy with respect to the displacement  $y_o^{(\text{vac})}$ , while choosing a value of  $\rho'$  or  $A'$  which leads to the experimental activation energy. From equation (2.14), we get

$$\left( \frac{\partial}{\partial y_0} E_{s.p}^{(vac)} \right)_{\xi=0} = 0 \quad (3.11)$$

We use different values of the corrected repulsive parameter in the minimization process of equation (3.11) until a specific value of the corrected repulsive parameters leads to a minimum value of  $E_{s.p}^{(vac)}$  in agreement with the  $E_{act}^{vac}$  (experimental) (see Fig. 8 and Fig. 9), that is:

$$\{ E_{s.p}^{(vac)} - E_0^{(vac)} \} = E_{act}^{vac} \quad (\text{experimental}) \quad (3.12)$$

The experimental value for the activation energy for anion vacancy diffusion is 0.945 eV for KCl<sup>32</sup>, and 1.01 eV for NaCl<sup>33</sup>.

The results of these calculations are shown in table 3. The corrections to the pairwise repulsive energy at the saddle point are seen to be large, compared to the uncorrected energy of 0.312 eV for KCl, and 0.278 eV for NaCl, but neither they nor the saddle point spacing,  $(y_0^{(vac)} + 1/\sqrt{2})$  in units of perfect lattice spacing, are much different for the two cases  $(\rho', A)$  or  $(\rho, A')$ . (See Fig. 10)

### 3.2. Zeroth-Order Approximation to the Odd Parity F-Center Saddle Point Energy

We now use the corrected repulsive parameter from the vacancy saddle point, which has been calculated in section (3.1), in the ion-pair interaction in the saddle-point F-center. We want to use it to calculate the odd-parity saddle-point F-center's energy, by minimizing the defect system's energy with respect to electronic parameters, and with respect to the non-harmonic displacement  $y_0^{(F)}$  of the straddling positive ions. This will give the zeroth order approximation, which neglects lattice

FIGURE 8.

Corrected repulsive parameter  $\rho'$  for the activation energy for anion vacancy diffusion in KCl.

ACTIVATION ENERGY  $E_{act}^{vac}$  (eV)

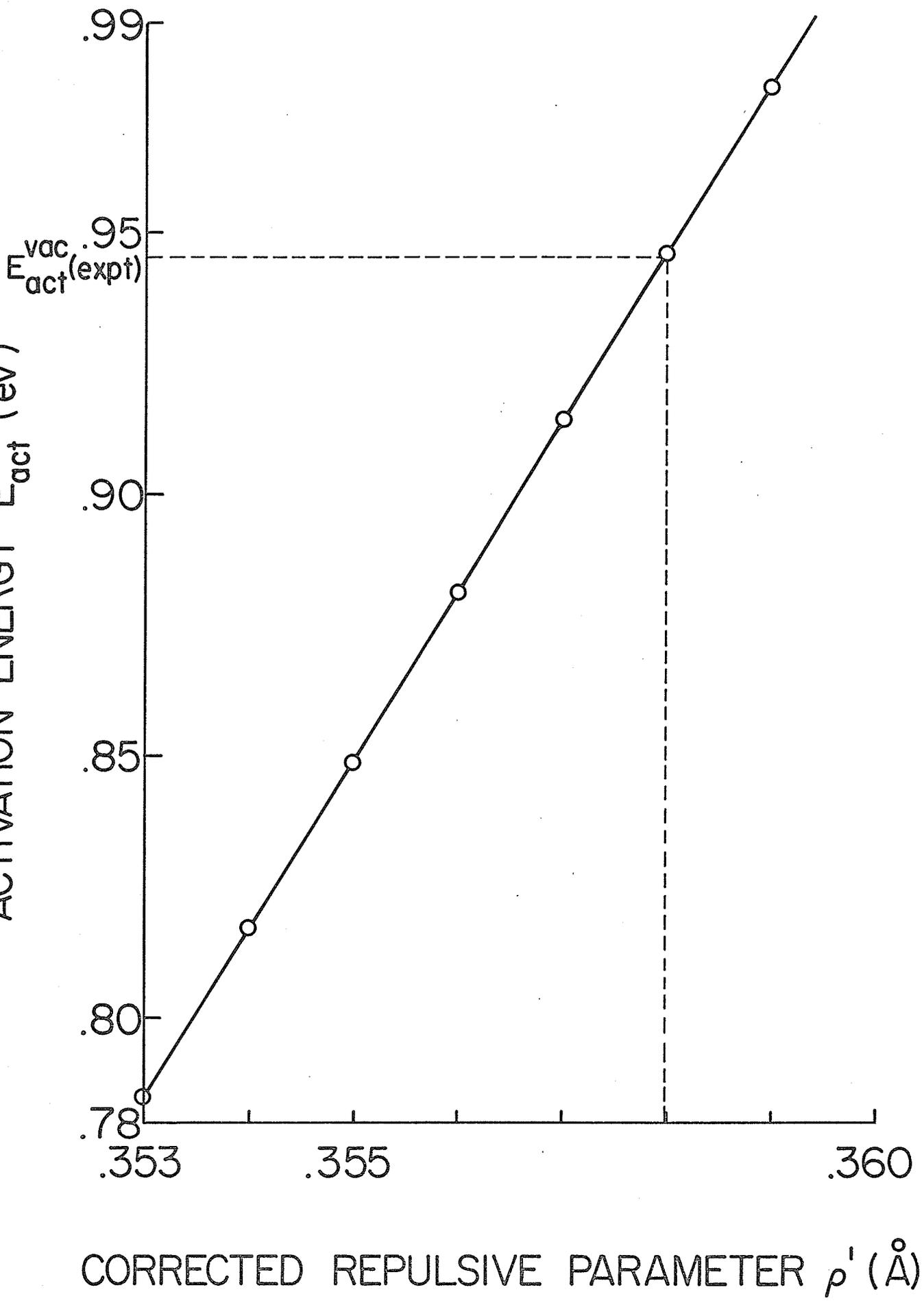


FIGURE 9.

Corrected repulsive parameter  $A'$  for the  
activation energy for anion vacancy diffusion  
in KCl.

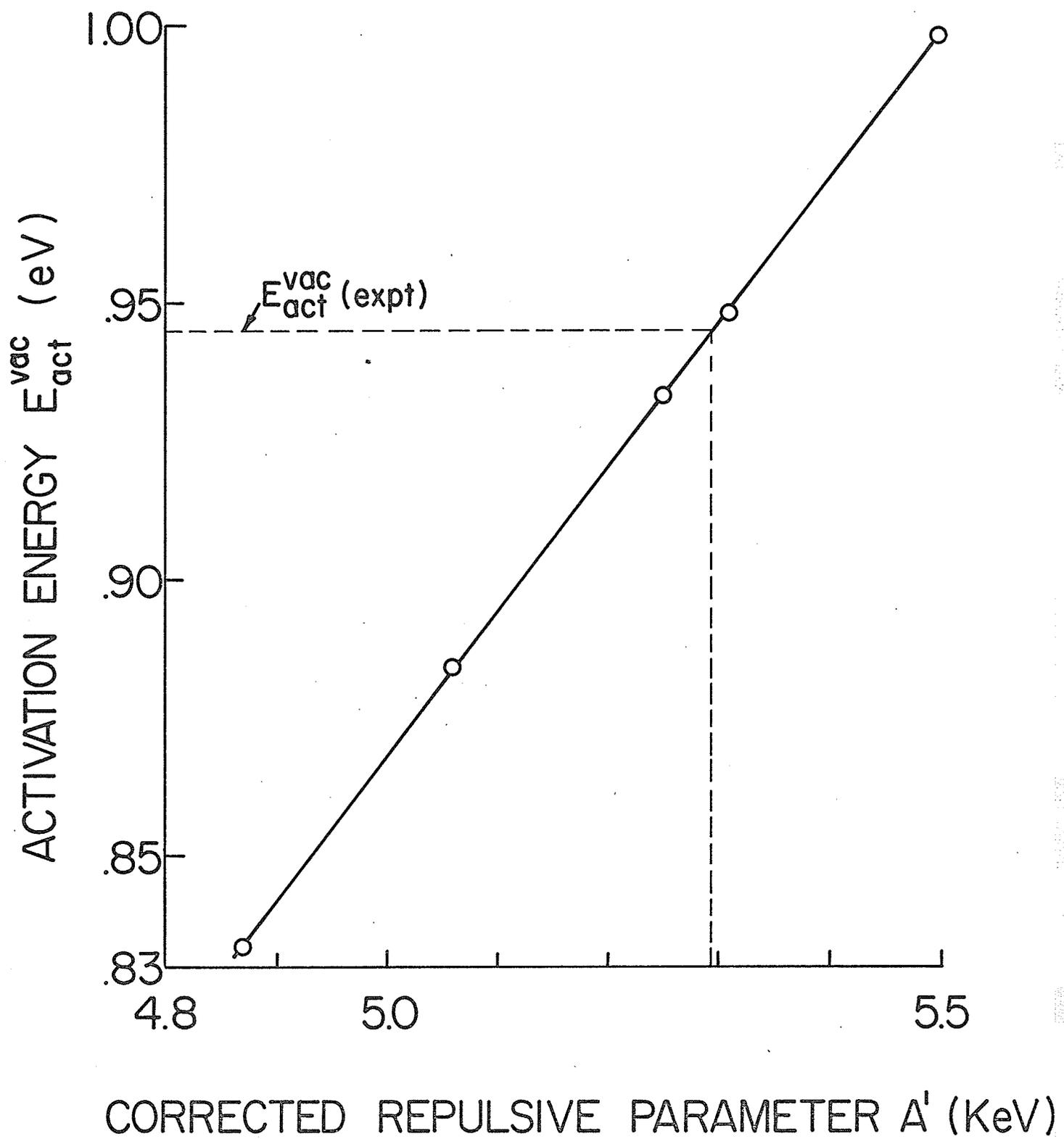
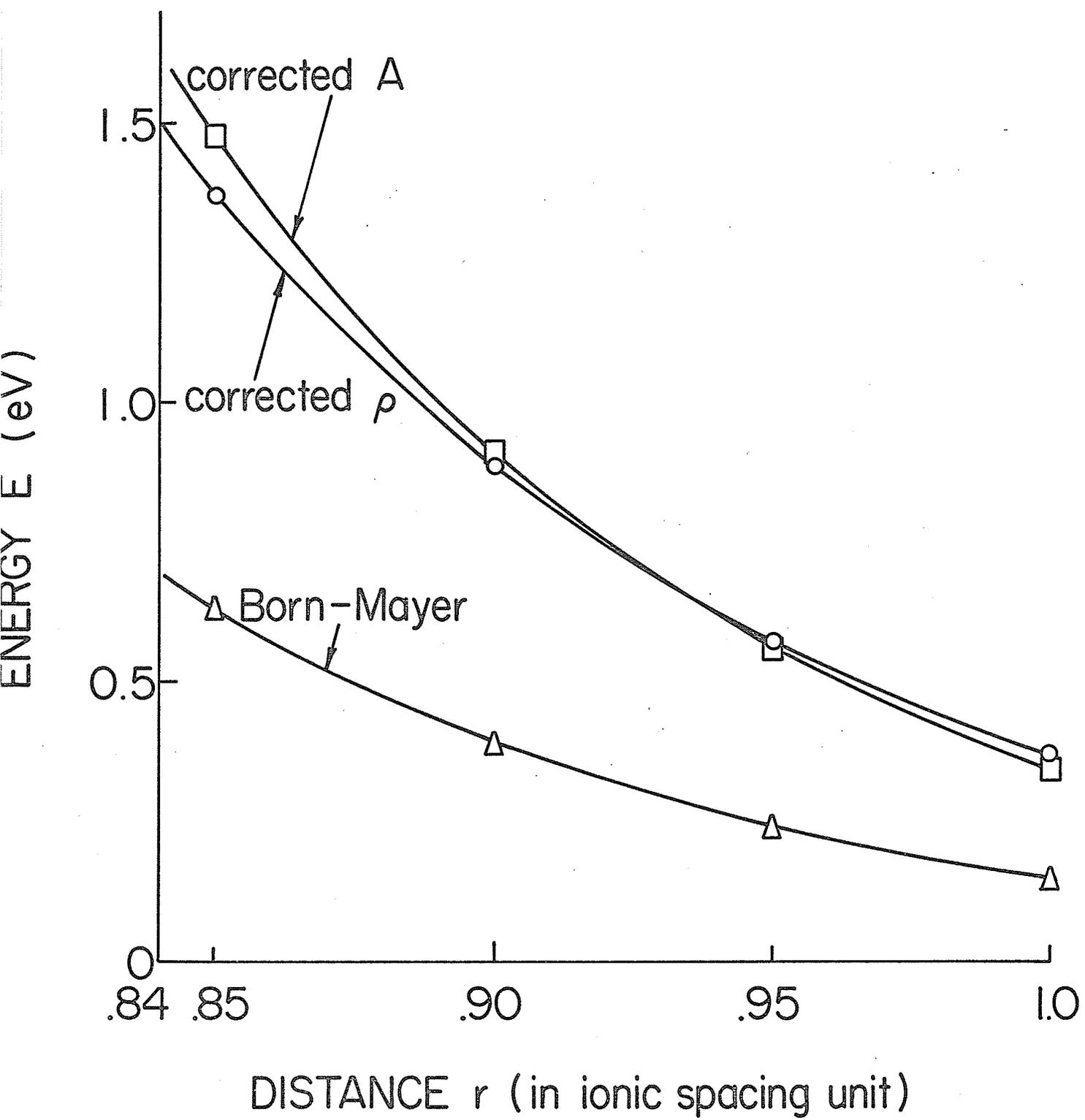


TABLE 3 CORRECTED REPULSIVE PARAMETERS  
FOR SADDLE POINT VACANCY

crystal	parameter	corrected	corrected pair-wise Energy (eV)	$(y_0+1/\sqrt{2})$ (unit of interionic spacing)
KCl	$\rho = 0.324 \overset{\circ}{\text{A}}^{34}$	$0.358 \overset{\circ}{\text{A}}$	0.740	0.923
KCl	$A = 2.26 \text{ Kev}^{34}$	5.29 Kev	0.680	0.931
NaCl	$\rho = 0.328 \overset{\circ}{\text{A}}^{34}$	$0.378 \overset{\circ}{\text{A}}$	0.858	0.944
NaCl	$A = 0.919 \text{ Kev}^{34}$	2.68 Kev	0.740	0.957

FIGURE 10.

Interionic repulsive energy for KCl.



relaxation in region II. The odd-parity state is the higher of the two states for the saddle point which have been considered by Brown and Vail<sup>1</sup>.

The change of the saddle point spacing  $(y_0 + 1/\sqrt{2})$  between a zeroth order calculation and a more accurate higher order calculation, has been evaluated by Brown. (Ref. (35), Table 9) and has been found to be small. Brown, using the perfect lattice Born-Mayer potential throughout, got the value of  $(y_0 + 1/\sqrt{2})$ , in units of perfect lattice spacing to be 0.845 for the zeroth order approximation and 0.832 from the Kanzaki treatment, where the region II is relaxed. Thus, the pairwise repulsive energy will not likely change much (see. Fig. 10). Therefore, the use of the zeroth order approximation is considered to be justified in the present work.

The relaxed odd-parity F-center saddle point energy is, from equation (2.9), with  $P' = P$ .

$$E(\xi_p, \mu_p, \lambda_{pp}) = \frac{1}{2} \xi_p^T \cdot \underline{A} \cdot \xi_p + V_L(\xi_p, \mu_p) + T(\lambda_{pp}) + V(\xi_p, \mu_p, \lambda_{pp}) \quad (3.13)$$

where  $T(\lambda_{pp}) =$  the kinetic energy of the electron

$$T(\lambda_{pp}) = \langle \phi | \tilde{T} | \phi \rangle \quad (3.14)$$

where  $\tilde{T} =$  the kinetic energy operator

$\phi = \phi(\lambda_{pp})$  is the trial pseudo-wave function for the odd-parity saddle-point state

$$\text{and } V(\xi_p, \mu_p, \lambda_{pp}) = \langle \phi | V_P(\xi_p, \mu_p) | \phi \rangle \quad (3.15)$$

where  $V_P(\xi_p, \mu_p)$  is the pseudopotential due to all the ions in the defect lattice (equations(2.5)). The odd-parity gaussian-localized trial wave

function  $\phi_{s.p}^{(o)}$  was chosen as the trial pseudo wave function  $\phi$ . It has the form

$$\phi_{s.p}^{(o)}(\vec{r}) \sim Z' \exp [-(\alpha_{s.p}^{(o)} r)^2] \sim r P_1(\cos \theta) \exp [-(\alpha_{s.p}^{(o)} r)^2] \quad (3.16)$$

in which  $\alpha_{s.p}^{(o)}$  is the variational parameter  $\underline{\lambda}$ ,  $P_\ell(\cos \theta)$  is the Legendre polynomial of order  $\ell$ , and  $\theta$  is the spherical polar angle relative to the  $Z'$  axis in Fig. 1. The trial pseudo-wave function turns out to be well localized in the two-well potential of the saddle point configuration. It has zero amplitude at the saddle point.

The interaction energy between the excess electron and the lattice was treated by the method of BSG. From equations (2.5) and (3.15).

$$V(\xi_p, \mu_p, \lambda_{pp}) = \langle \phi | V_{PI} | \phi \rangle + \sum_Y [A_Y + (\bar{V} - U_Y) B_Y] |\phi(r)|^2 \quad (3.17)$$

in which,  $V_{PI}$  is the potential energy of an electron in the presence of the point ion lattice, and may be written as

$$V_{PI}(\vec{r}) = -2 \sum_i \frac{Q_i}{|\vec{r} - \vec{r}_i|} \quad (3.18)$$

The factor 2 is introduced because the energy is expressed in Rydbergs. Equation (3.18) can be expanded in Legendre polynomials

$$V_{PI}(\vec{r}) = -2 \sum_i Q_i \sum_{\ell=0}^{\infty} \frac{1}{r_{>}} \left[ \frac{r_{<}}{r_{>}} \right]^\ell P_\ell(\cos r_i) \quad (3.19)$$

where  $r_{>}$  is the  $\left\{ \begin{array}{l} \text{larger} \\ \text{smaller} \end{array} \right\}$  of  $|\vec{r}|$  and  $|\vec{r}_i|$

After pages of algebra, and transformation into the primed coordinates of Fig. 1, Brown<sup>16</sup> got the following convenient expression.

$$\begin{aligned}
 V_{PI}(\vec{r}) = & -2 \sum_{\substack{i \\ (r_i \neq 0)}} \left(\frac{Q_i}{r_i}\right) - 2 \sum_{\substack{i \\ (r_i \neq 0)}} Q_i \left(\frac{r^2}{r_i^3}\right) P_2(\cos \theta) P_2(\cos \theta_i) \\
 & + 2 \sum_{\substack{i \\ (r_i \leq r) \\ (r_i \neq 0)}} Q_i \left[\frac{1}{r_i} - \frac{1}{r}\right] - \frac{2Q_0}{r} + 2 \sum_{\substack{i \\ (r_i \leq r) \\ (r_i \neq 0)}} Q_i \left[\frac{r^2}{r_i^3} - \frac{r_i^2}{r^3}\right] P_2(\cos \theta) P_2(\cos \theta_i) \quad (3.20)
 \end{aligned}$$

where  $\theta_0$  is the charge on the ion at  $\vec{r}_i = 0$ , and the summation is over all the ions in the defect lattice. Using equation (3.20) in (3.17), some of the terms can be evaluated explicitly and the rest can be represented as an error function, which is an available Fortran built-in function for the IBM 360 computer.

Let  $\frac{\mu}{p} = y_0^{(F)}$ , the outward displacement of the straddling positive ions from their perfect lattice sites, and  $\frac{\lambda}{pp} = \alpha_{s.p}^{(0)}$ , the variational parameter of the odd-parity trial pseudo wave function, in zeroth order approximation. From equations (3.13), (3.17) and (3.20), with  $\xi$  set equal to zero, the saddle-point F-center energy becomes

$$\begin{aligned}
 E_{s.p}^{(F)}(y_0^{(F)}, \alpha) = & V_L(0, y_0^{(F)}) + \langle \phi(\alpha) | T | \phi(\alpha) \rangle + \langle \phi(\alpha) | V_{PI}(y_0^{(F)}) | \phi(\alpha) \rangle \\
 & + \sum_{\gamma} [A_{\gamma} + (\bar{V} - U_{\gamma}) B_{\gamma}] |\phi(\alpha, r)|^2 \quad (3.21)
 \end{aligned}$$

We minimize the saddle point energy (3.21), using the odd-parity form (3.16) for the F-center pseudo wave function, thus determining  $\alpha_{s.p}^{(0)}$  and  $y_0^{(F)}$  self-consistently, as follows:

$$\left(\frac{\partial}{\partial \alpha_{s.p}^{(0)}} E_{s.p}^{(F)}\right)_{y_0^{(F)}} = 0 \quad (3.22)$$

$$\left( \frac{\partial}{\partial y_o^{(F)}} E_{s.p}^{(F)} \right)_{\alpha_{s.p}^{(o)}} = 0 \quad (3.23)$$

To calculate the contribution of the ion-size correction, we note that in equation (3.17)

$$\bar{V} = \langle \phi | V_p | \phi \rangle \quad (3.24)$$

In the processes of minimization, we included an iterative procedure, that is, for a fixed value of  $\bar{V}$ , we minimized  $E_{s.p}^{(F)}$  with respect to  $y_o^{(F)}$  and  $\alpha_{s.p}^{(o)}$  self-consistently, and then we recalculate  $\bar{V}$  from equation (3.24) using the updated value of  $\alpha_{s.p}^{(o)}$  in  $\phi$ , and use this new  $\bar{V}$  to do the minimization processes again, until the convergence of  $\bar{V}$  is obtained (i.e. until two consecutive estimates of  $\bar{V}$  differ by less than 0.001 Ry.).

The results of the calculation are quoted in table 4 for KCl and NaCl. We find  $(y_o + 1/\sqrt{2}) = 0.909$ , which is close to the vacancy value  $(y_o + 1/\sqrt{2}) = 0.923$  for KCl, and the corrected pairwise repulsive energy at the F-center saddle point differs from that for the vacancy by slightly less than 10%. This means that the positive ions adjacent to the saddle-point F-center are near, both in position and energy, to the values for which the corrected repulsion was derived, namely those of the saddle point vacancy. Furthermore, the result is relatively insensitive to the choice of the parameter  $A, \rho$  to be corrected. (See Fig. 10, with  $y_o = 0.91$ ).

TABLE 4 ENERGY OF ODD-PARITY SADDLE-POINT F-CENTER

Crystal	corrected parameter	$(y_0^{(F)} + \frac{1}{\sqrt{2}})^*$	$\alpha_{s.p}^{(0)}$	corrected pair-wise energy (eV)	energy (eV)
KCl	$\rho = 0.358 \text{ \AA}$	0.909	0.808	0.802	5.37
KCl	$A = 5.29 \text{ Kev}$	0.918	0.807	0.745	5.38
NaCl	$\rho = 0.378 \text{ \AA}$	0.922	0.829	0.945	6.42
NaCl	$A = 2.68 \text{ Kev}$	0.939	0.827	0.848	6.46

\*  $\alpha_{s.p}^{(0)}$  has units of reciprocal ionic spacing, and  $(y_0^{(F)} + 1/\sqrt{2})$  has units of ionic spacing

### 3.3 Estimate of the Ionic Polarization Energy

In the calculation of section (3.1) and section (3.2) the polarization energy is excluded. One can see that the neglect of electronic polarization is probably a fairly good approximation for a highly localized symmetric F-center state, but it is not clear that it will be an adequate one for the saddle point configuration. In the vacancy or ordinary F-center saddle-point problem, one can assume that the polarization of the positive ion is negligible since the polarizability of the positive ion is much smaller than the negative ion. The negative saddle point ion interacts with two straddling positive ions symmetrically (Fig. 6) and therefore its polarization will likely be zero. The four negative ions which lie nearest to the saddle point, "above" or "below" the two straddling positive ions in Fig. 6, are expected to be the most strongly polarized ions. In the following discussion, the polarization of the other ions in region II will be neglected.

The simple shell model, which is used, has been discussed in section (2.3). For simplicity, we add a further restriction to the simple shell model, namely that cores are not displaced. This would not be a good assumption in estimating the energy of the defect, since the contribution to the polarization energy by ionic displacement is larger than the distortion polarization and the directions of polarization are opposite. But we are considering the core-shell relative displacement, so part of the polarization energy due to core displacement will be included. However, the main point is that we are interested in how large the energy is which is contributed by the ionic polarization, and the order of magnitude estimate which we obtain will be useful information.

The procedure that we have followed is to include the ionic

polarization in the zeroth order calculation, even though the ions are not in region I. Therefore, when we follow it by the Kanzaki method, using the point ion model dynamical matrix, to take account of the relaxation of region II, we neglect only second order small corrections to the ionic polarization, associated with the relaxation of region II. Such a procedure might be expected to be a satisfactory first step toward the full consideration of ionic polarization in the lattice calculation. A more complete treatment<sup>36</sup> would use the shell model for all ions in the defect lattice; that is, the Kanzaki treatment would be based on the shell model dynamic matrix, and would lead to the shell displacements as well as the core displacements.

Since the defect is symmetric with respect to the  $x' - y'$  plane (Fig. 1), the polarizing field is in this plane. The first step in this problem is to determine the corrected parameter of the Born-Mayer potential from the vacancy saddle point, by the same sort of calculation as in section (3.1), including the monopole-dipole, dipole-dipole, and the self energy of the ions, as well as the monopole-monopole interaction energy and short range repulsive energy (see equation (2.21)). We minimize the saddle point energy of the vacancy with respect to  $y_o^{(vac)}$  the  $x$  - component of the shell-core displacement  $D_x$ , and the  $y$  - component of the shell-core displacement  $D_y$ , self-consistently

$$\frac{\partial}{\partial y_o^{(vac)}} (E_{s.p}^{vac})_{D_x, D_y} = 0 \quad (3.25)$$

$$\frac{\partial}{\partial D_x} (E_{s.p}^{vac})_{y_o^{(vac)}, D_y} = 0 \quad (3.26)$$

$$\frac{\partial}{\partial D_y} (E_{s.p}^{vac})_{D_x, y_o}^{(vac)} = 0 \quad (3.27)$$

In this section we deal only with KCl, and only correct the repulsive parameter  $\rho$ .

The results of the calculation are shown in the first column of table 5. One can see that the energy contributed by ionic polarization does not amount to more than a few hundredths of an eV. The corrected repulsive parameter  $\rho$  is a bit smaller than we get in section (3.1), that is, the corrected repulsive parameter we get by excluding the polarization energy, is overestimated. In other words, part of the contribution of polarization to the system is included in the corrected repulsive parameter in section (3.1). This correction to  $\rho$ , hardly more than 1%, is an upper bound, due to the fact that nearest negative ion polarization in the ordinary vacancy is not included.

The next step of the calculation is to make use of the corrected repulsive parameter  $\rho$  at the saddle point to calculate the zeroth order approximation to the odd-parity F-center saddle point energy. In this program, we have made use of the computer extensively. We minimized the saddle point energy of the F-center with respect to the four parameters  $y_o$ ,  $\alpha_{s.p}^{(o)}$ ,  $D_x$  and  $D_y$  self-consistently:

$$\frac{\partial}{\partial y_o^{(F)}} (E_{s.p}^{(F)})_{D_x, D_y, \alpha_{s.p}^{(0)}} = 0 \quad (3.28)$$

$$\frac{\partial}{\partial \alpha_{s.p}^{(0)}} (E_{s.p}^{(F)})_{D_x, D_y, y_o^{(F)}} = 0 \quad (3.29)$$

TABLE 5 CONTRIBUTION OF IONIC POLARIZATION ENERGY  
FOR VACANCY AND F-CENTER SADDLE POINT  
CONFIGURATION IN KCL

	Vacancy	F-Center
$(y_o + 1/\sqrt{2})$	0.915	0.900
$\alpha_{s.p}^o$	-	0.810
$D_x^*$	0.0032	0.0034
$D_y^*$	0.0049	0.0037
Dipole-Dipole interaction energy	$-0.114 \times 10^{-2}$	$-0.0803 \times 10^{-2}$
Dipole-Monopole interaction energy	$2.45 \times 10^{-2}$	$2.04 \times 10^{-2}$
Self energy	$1.088 \times 10^{-2}$	$0.803 \times 10^{-2}$
Total	$3.43 \times 10^{-2}$	$2.76 \times 10^{-2}$
Saddle point energy	-	5.41
corrected parameters	$\rho = 0.353$	$\rho = 0.353$
corrected pair-wise energy	0.696	0.768

\* $D_x, D_y$  refer to the negative ion in 4th quadrant in  $x' - y'$  plane

All displacements are in units of interionic spacing

All energies are in eV

$\alpha_{s.p}^o$  has units of reciprocal interionic spacing

$$\frac{\partial}{\partial D_x} (E_{s.p.}^{(F)})_{D_y, \alpha_{s.p.}^{(0)}, y_o^{(F)}} = 0 \quad (3.30)$$

$$\frac{\partial}{\partial D_y} (E_{s.p.}^{(F)})_{D_x, \alpha_{s.p.}^{(0)}, y_o^{(F)}} = 0 \quad (3.31)$$

We included the monopole-dipole, dipole-dipole, monopole-monopole interaction energy of equation (2.21), and the shell model expressions of dipole moment, short range interaction energy and self energies of the ions, of equations (2.22), (2.23), (2.24) respectively, in the saddle point F-center energy (3.21). We used Evjen's method (appendix) to calculate the lattice sum and the value of the shell model parameters which we used are given in Table 2.

The second column of Table 5 shows that the dipole-dipole, dipole-monopole and self energy of the ions are lower in the F-center saddle point defect than in the vacancy saddle point defect. The reason is that the configuration of the F-center saddle point defect is electrically more neutral than the vacancy saddle point defect. The corrected pairwise interaction energy has a difference about 10% between the F-center saddle point defect and the vacancy saddle point defect, as before. Since the total contribution of ion polarization will be seen to be much smaller than the relaxation energy due to ion displacements, a preferable way to include the ionic polarization approximately would seem to be to allow for shell-model relaxation after Kanzaki treatment of region II.

### 3.4 Estimate of the Activation Energy for Step Diffusion of the F-center

The activation energy for step diffusion is taken to be the difference between the relaxed odd parity saddle point described by  $(\underline{\lambda}, \underline{\mu}, \underline{\xi})$  and the relaxed F-center excited state, described by  $(\underline{\lambda}'', \underline{\xi}'')$ . Thus

$$E_{\text{act}} = \{E(\underline{\lambda}, \underline{\mu}, \underline{\xi}) - E(\underline{\lambda}'', \underline{\xi}'')\} \quad (3.32)$$

It is noted that the relaxed excited state of F-center is difficult to characterize in a simple model<sup>37</sup>. Most of the early theoretical calculations have assumed that the relaxed excited state is a diffuse hydrogenic 2p state. Recently, Wood and Opik<sup>38</sup> have found that the 2s level in absorption is very close to but slightly higher than the 2p level. Since the 2s - 2p splitting is so small, the states may be strongly mixed by phonons. According to the results of Bogan et al.<sup>39,40</sup>, the relaxed excited state is such a mixture of 2s and 2p states.

In the present work, a reasonable estimate of the energy  $E(\underline{\lambda}'', \underline{\xi}'')$  of the relaxed excited state for the ordinary F-center in KCl is taken from the calculation of Brown and Vail<sup>1</sup>, which is calculated for a simple p state, and is based on the same model as we have used. It is equal to 3.24 eV.

From section (3.2), using the corrected value of the repulsive parameters A and  $\rho$  in the Born-Mayer potential, we obtained a zeroth order approximation to the odd-parity F-center saddle point energy of 5.38 eV and 5.37 eV respectively (Table 4). We can give an estimate of the lattice distortion energy in region II, based on a calculation of ref. (1), by the Kanzaki method, with only slightly different values of

$y_o^{(F)}$  and  $\alpha_{s.p}^{(0)}$  (Region I). In that case, the lattice relaxation energy in region II was found to be (-0.52) eV. Furthermore, a rough estimate of the energy contributed by ionic polarization can be deduced from the shell model calculation which we have done in section (3.3). In that section (see table 5), we found that the four most strongly polarized ions contributed about 0.02 eV correction to the saddle point energy. Because of the charge neutrality of the defect system, the total ionic polarization energy will be of the same order of magnitude, namely not more than a few hundredths of an eV. Thus, ignoring the ionic polarization, we have an estimate of the odd parity saddle-point F-center energy of the order of  $\{5.37 - \theta(0.52)\} \approx 4.85$  eV, when the corrected repulsive parameters is  $\rho$ , and  $\{5.38 - \theta(0.52)\} \approx 4.86$  eV, when the corrected repulsive parameter is A.

From equation (3.32), we get the estimate of the activation energy for step diffusion of F-center

$$E_{act} \approx (4.85 - 3.24) = 1.61 \text{ eV} \quad (3.33)$$

for  $\rho$  corrected, or

$$E_{act} \approx (4.86 - 3.24) = 1.62 \text{ eV} \quad (3.34)$$

for A corrected, which is in agreement with the experimental result of Wolf <sup>7</sup>, quoted as  $1.6 \pm 0.2$  eV. The various uncertainties in our calculation suggest that it also is accurate to only two significant figures.

### 3.5 Summary

Several results of this study may be briefly summarized as follows: Firstly, the corrected pair-wise energy of ion-ion repulsion at the saddle point is much larger than the uncorrected one, which uses the perfect lattice value for Born-Mayer repulsion parameters. Secondly, the result of the calculation of the activation energy for step-diffusion of F-center in KCl, with our model, using the corrected repulsive parameters, is satisfactory. Our model ~~has~~ non-polarizable point ions, using BSG ion-size correction with semi-empirical factor 0.53, nearest neighbour ion-ion repulsive potential, self-consistent treatment of lattice and the adiabatic approximation. Thirdly, the ionic polarization energy is found, by using a simple shell model, to be small but not entirely negligible.

Finally, we should like to point out that although the results obtained with our model, using a corrected repulsive parameter, are satisfactory, it should be stressed that certain further steps should now be taken, namely, full treatment of region II by the Kanzaki method using the shell model dynamic matrix, plus determination of the relaxed excited state of the F-center, using a mixture of s- and p- type wave functions.

CHAPTER IV

FUTURE WORK AND APPLICATIONS

We have seen that empirical correction of the interionic repulsion at the saddle point gives the activation energy for step diffusion of the F-center in KCl in agreement with the experimental value of  $1.6 \pm .2$  eV by Wolf <sup>7</sup>. It can be applied or tested in several other defect problems in alkali halides.

(A) Prediction of the Activation Energy for Step Diffusion of the F-Center in NaCl

The value of the activation energy for step diffusion of F-center in NaCl, using the corrected interionic repulsion at the saddle point, is estimated below. It has not been obtained experimentally.

The odd-parity saddle point energy, which is obtained from this work is 6.42 eV, (table 4), the energy level of the relaxed excited state from ref (1) is 4.22 eV, and the estimated relaxed energy of region II based on ref (1) is  $\{-\theta (0.57)\}$  eV. Therefore, the calculated activation energy for step diffusion in NaCl is

$$\{6.42 - \theta(0.57) - 4.22\} \text{ eV} = 1.63 \text{ eV} \quad (4.1)$$

Within the limits of accuracy of the model, this is indistinguishable from the value of 1.61 eV obtained for the same process in KCl.

(B) The Reorientation and Dissociation Energies of Impurity F-centers

Impurity F-centers discussed in chapter I have an interesting variety of processes which involve the saddle point configuration, and we could apply our correction to them. They have less symmetry than F-

center, so one can get information from the impurity center which is inaccessible in the unperturbed F-center.

In the  $F_A(II)$  center  $KCl:Li$ , the dissociation process involves the same saddle point configuration as in F-center reorientation in  $KCl$ . Thus the corrected repulsive parameter can be applied and the impurity cation  $Li^+$  is a small perturbation (fig. 2). However, in  $F_A(II)$  reorientation, the saddle point involves the impurity  $Li^+$  ion (Fig 2), so our corrected parameter can only be used, at most for one side of the saddle point, namely in the  $Cl^- - K^+$  interaction. In this particular problem, the  $Li^+ - Cl^-$  spacing at the saddle point is  $\sim \theta (2.8) \overset{\circ}{\text{A}}$ , which is comparable with the  $LiCl$  crystal lattice spacing, which is  $2.57 \overset{\circ}{\text{A}}$ . Thus it may be possible to use the bulk  $LiCl$  repulsive parameters in a first order estimate. However, various other aspects of the  $F_A(II)$  reorientation problem would still remain unsolved. Similarly for the  $F_B^-$  and  $F_C^-$  center, the corrected repulsive parameters derived in this work would be useful for the treatment of the saddle point configuration, but the impurity ion contributes various new complications. There are two new major difficulties encountered in calculating the reorientation and dissociation energy of impurity centers in  $KCl$ , which do not exist in the F-center calculation.

(1) The impurity alkali ions may lie at off center positions, as the  $Li$  ion <sup>41</sup> does in the  $KCl:Li F_A$  - type II center.

(2) The repulsive parameters of the Born-Mayer potential for the interaction of impurity alkali ions and host anion is not easily determined. For this, we have to realize that the Born-Mayer repulsive parameters are obtained from the equilibrium interionic spacing and com-

pressibility, and part of the non-pairwise interaction is included. Therefore, the repulsive parameters are not simply related to the equilibrium interionic spacing but also the environments of the pair ions. Taking  $F_A(II)$ ,  $KCl:Li$  as an example, the interaction of  $Li^+ - Cl^-$  in  $KCl:Li$  is different from the interaction in the  $LiCl$  crystal, firstly, because the interionic spacing in  $KCl:Li$  is  $3.12 \text{ \AA}$  and in  $LiCl$ , it is  $2.57 \text{ \AA}$ , and secondly, the second nearest neighbours for  $Li$  in  $KCl:Li$  is  $K^+$  but in  $LiCl$ , it is  $Li^+$ , and furthermore, the coordination directions and numbers are different from those of the perfect  $LiCl$  lattice.

(C) The Activation Energy for Capture of Anion Vacancies by F'-Center

Recent work by Jaque and Agulló-López<sup>4</sup> has determined experimentally the activation energy for capture of anion vacancies by F' centers in  $NaCl$  to be  $0.48 \pm 0.06 \text{ eV}$ . The F' center consists of two electrons trapped at the lattice site of a missing negative ion. Jaque and Agulló-López conclude that the capture of anion vacancies by F' center gives rise to F-center and M-center formation through the following mechanisms:



These two resultant configurations are exemplified in Fig. 11. The empirically corrected interionic repulsion at the saddle point should be applicable to this system. Careful analysis is underway, taking proper account of the two F' electrons in the saddle point configuration to calculate this activation energy.

FIGURE 11.

The capture of an anion vacancy by an  $F'_-$  center gives rise to F-center and M-center formation,  $e^-$  denotes the trapped electron.

+ - + -

- + □ +

+ - + -

2e<sup>-</sup>

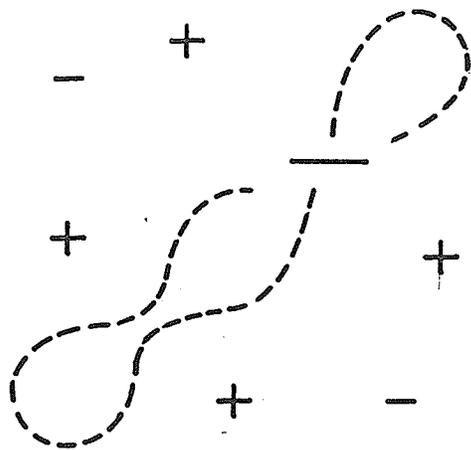
+ - +

Initial state: F' + vacancy

+ - + -

- + □ +

+ - + -



Intermediate state

+ - + -

- + e<sup>-</sup> +

+ - + -

e<sup>-</sup>

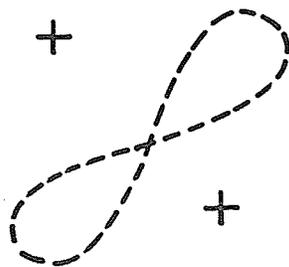
+ - +

Final state: 2F

+ - + -

- + □ +

+ - + -



Final state: M

(D) Reorientation of the  $\text{Sr}^{2+}$  - Vacancy Dipole in RbCl

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The saddle point configuration of the reorientation of the  $\text{Sr}^{2+}$  - vacancy dipole in RbCl is shown in Fig. 4. It is similar to the saddle point configuration of F-center step diffusion. Furthermore, the perturbation of the divalent impurity ion  $\text{Sr}^{2+}$  is small for it is not adjacent to the saddle point. We can obtain the corrected repulsive parameter at the saddle point for  $\text{Rb}^+ - \text{Cl}^-$  from the same sort of calculation as in section (3.1), by using the activation energy of the cation - vacancy diffusion in RbCl, which has been obtained by Arai and Mullen<sup>42</sup>. This corrected repulsive parameter can be applied to the saddle point configuration of the reorientation of  $\text{Sr}^{2+}$  - vacancy dipole in RbCl. The experimental value of the reorientation of  $\text{Sr}^{2+}$  - vacancy dipole in RbCl has recently been given by Reed et al<sup>5</sup>.

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APPENDIX

SUMMATIONS BY EVJEN'S METHOD FOR THE LATTICE

OF NaCl STRUCTURE

The difficulty of evaluating a sum

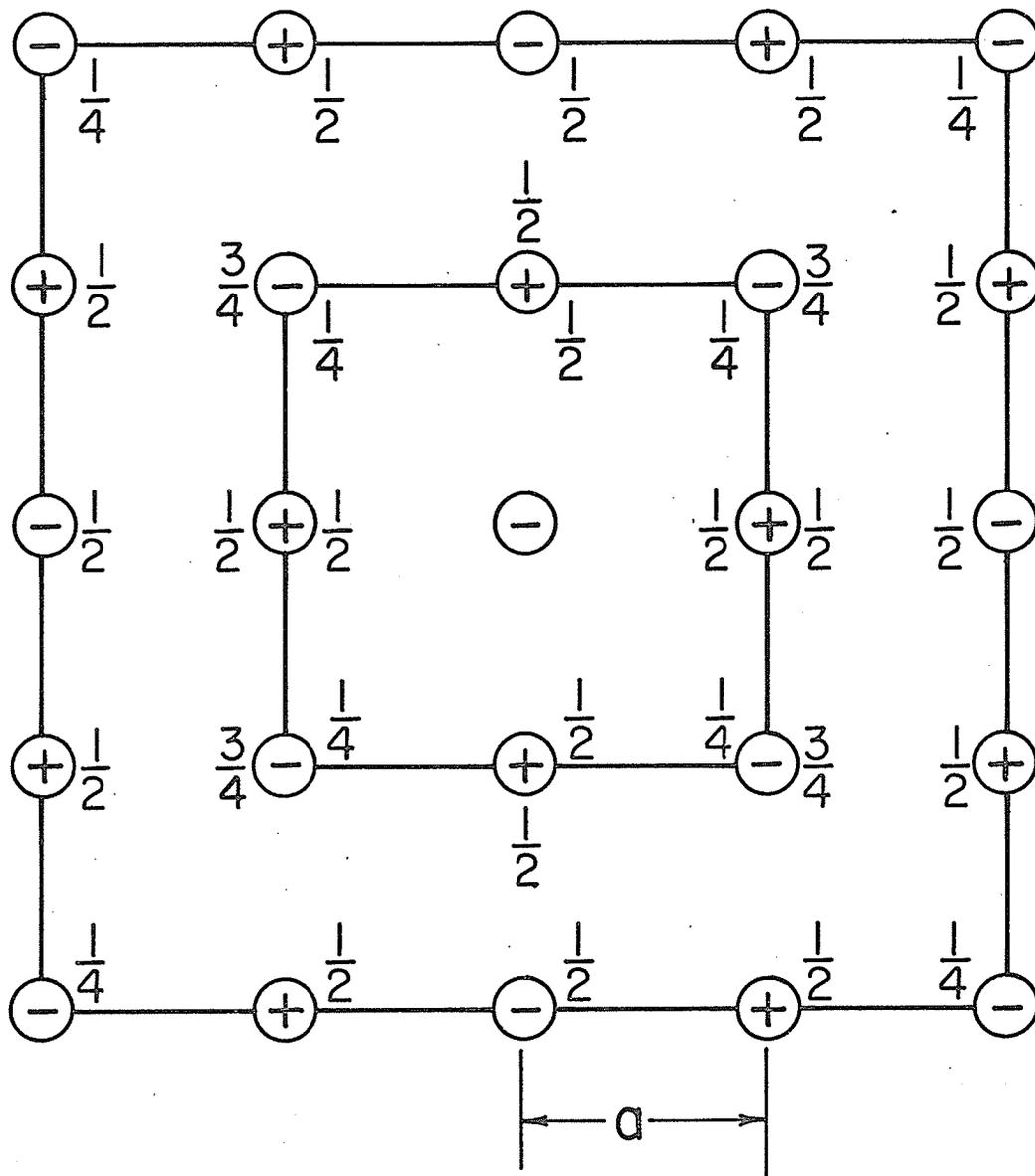
$$S_n = \sum_j' \frac{q_i q_j}{|r_j - r_i|^n} \quad (\text{A.1})$$

over the whole lattice of NaCl structure, is that the above sum is a conditionally convergent series. In equation (A.1),  $|r_j - r_i|$  is the distance of  $j$ th ion from the reference ion  $i$  and the summation excludes  $j = i$ , and  $q_j$  is the charge of the  $j$ th ion. A device for obtaining fast convergence was suggested by Evjen<sup>43</sup>. He divided the crystal into electrically neutral concentric cubes, with an ion at the center. The advantage of working with a neutral sequence is that its potential falls off faster at a distance than if the group has an excess of charge. The faces of the Evjen cubes cut through the planes of atoms. We count the charges on a cube face as half contributed to the region inside the cube and the other half to the outer region on edges as a quarter inside, and on corners as one-eighth inside. The planes of the Evjen cubes of the NaCl structure are shown in Fig. 12. The fraction denotes the fraction of an ion's charge which is contributed to the respective Evjen shells. The value of a sum at a given lattice site is obtained by summing over all ions included in successive cubical shells.

We have used the Evjen method to calculate the monopole-monopole interaction energy ( $n = 1$  in equation (A.1)) of an ion displaced by  $y_0$  from a perfect lattice site, and also the sums for  $n = 2$  and  $n = 3$  in equation (A.1).

FIGURE 12.

The planes of the Evjen cubes of the NaCl structure with sides  $2a$  and  $4a$ , where  $a$  is the nearest neighbour distance. The fractions denote the fraction<sup>of</sup> an ion's charge which contributes to the various shells.



In table 6, one can see that the first three terms of the lattice sum by Evjen method give a good approximation. In the first row, the value of the Madelung constant calculated by using Evjen cube of side  $6a$  is in good agreement with the accurate value of the Madelung constant  $\alpha = 1.747558$ , where  $a$  is the nearest-neighbour distance. The convergence for higher values of  $n$  is expected to be even faster. The last line in the table 6 is the summation for  $n = 1$  in equation (A.1) with the central atom displaced by  $0.2 a$  in (011) direction.

TABLE 6 THE FIRST THREE TERMS OF THE LATTICE

SUMS OF EQUATION (A.1) BY EVJEN'S METHOD

(units of  $e^2/a$ )

	Evjen cube of side 2a	Evjen cube of side 4a	Evjen cube of side 6a	Known accurate value
Madelung constant (n = 1)	1.4560	1.7518	1.7470	1.747558
n = 2	1.8333	2.5250	2.5190	-
n = 3	2.1318	3.2444	3.2395	-
n=1, central atom displaced by 0.2a in (011) direction	1.4553	1.7502	1.7456	-