

EMPIRICAL CORRECTION OF THE INTERIONIC POTENTIAL

For

SOME DIFFUSION PROCESSES

in

ALKALI HALIDES

A Thesis

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at

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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.

CONTENTS

	PAGE
ACKNOWLEDGEMENTS.....	(ii)
ABSTRACT.....	(iii)
CHAPTER I INTRODUCTION.....	(1)
CHAPTER II MODEL AND THEORETICAL METHOD	
2.1 The BSG method of ion size correction.....	(11)
2.2 Treatment of lattice relaxation.....	(15)
2.3 The shell model	
A. Introduction.....	(17)
B. The polarization of the simple shell model.....	(20)
C. Calculation of shell model parameters.....	(24)
CHAPTER III CALCULATIONS, RESULTS AND DISCUSSION	
3.1 Corrections to the pairwise repulsive energy.....	(28)
3.2 Zeroth-order approximation to the odd parity F - center saddle point energy.....	(32)
3.3 Estimate of the ionic polarization energy.....	(42)
3.4 Estimate of the activation energy for step diffusion of the F-center.....	(47)
3.5 Summary.....	(49)
CHAPTER IV FUTURE WORK AND APPLICATIONS	
A. Prediction of the activation energy for step diffusion of the F-center in NaCl.....	(50)
B. The reorientation and dissociation energies of impurity F- centers.....	(50)
C. The activation energy for capture of anion vacancies by F ⁺ - centers.....	(52)

D. Reorientation of the Sr^{2+} - vacancy dipole in RbCl.....	PAGE (54)
REFERENCES.....	(55)
APPENDIX: SUMMATION BY EVJEN'S METHOD FOR THE LATTICE OF NaCl	
STRUCTURE.....	(58)

CHAPTER I

INTRODUCTION

Recently, Brown and Vail¹ (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 - center² (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 - centers³ (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' centers⁴ and to the reorientation of the cation vacancy-divalent ion dipole, such as strontium - doped $RbCl$ ⁵ (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.

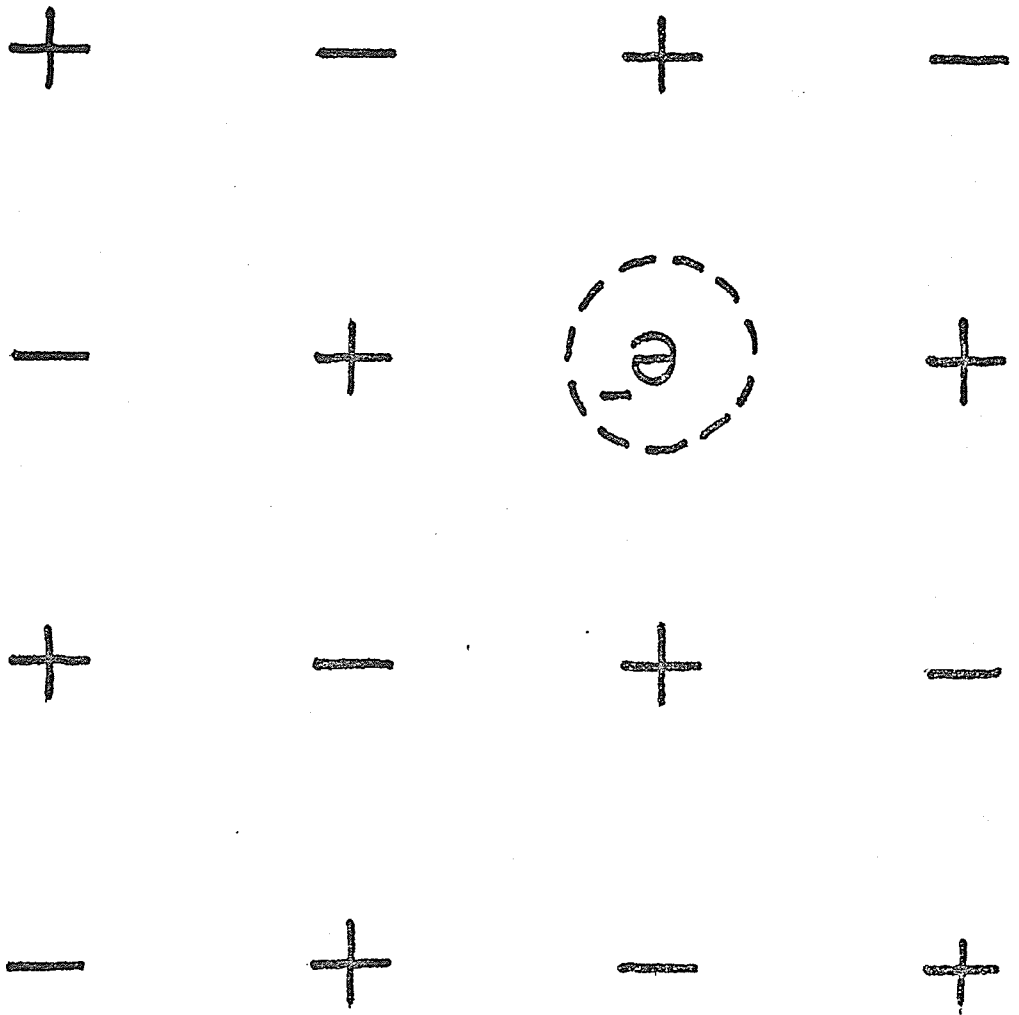
+ denotes the cation

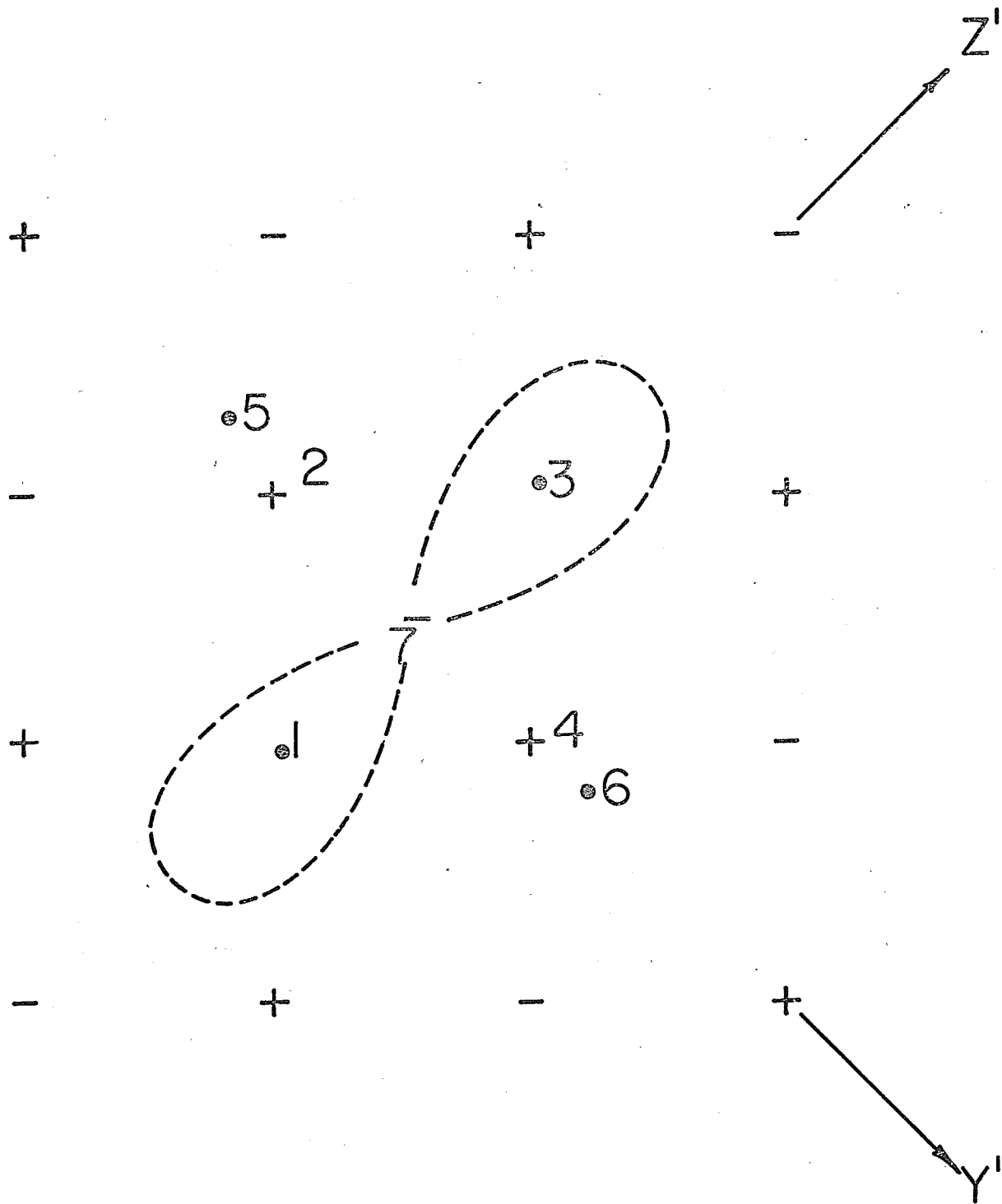
- denotes the anion

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 half-way 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.

+ - + -

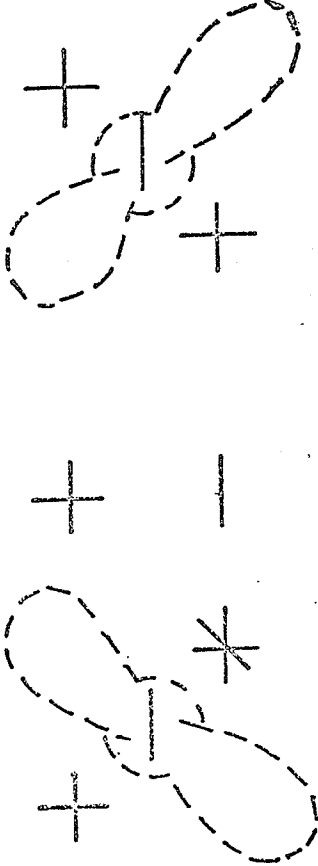
- + - +

+  -

- + - +

(a) ground state

+ - + - + - + -

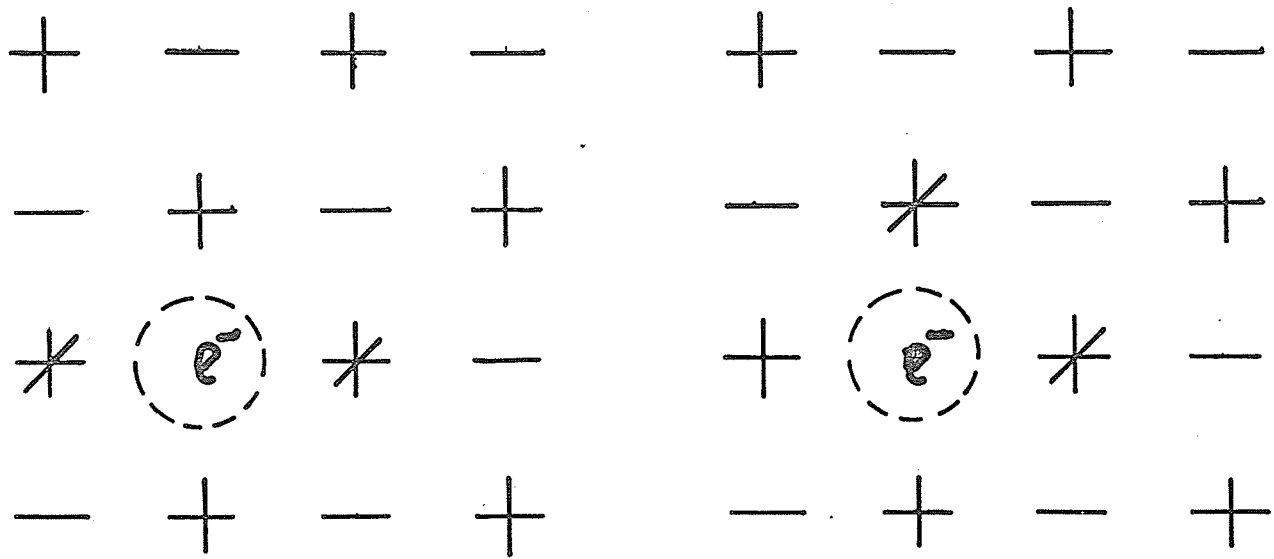
- + - + - + - +


+ - + - + - +

(b) reorientation (c) dissociation

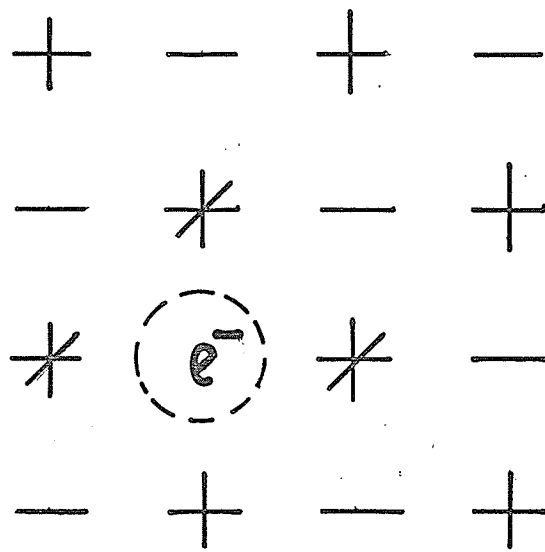
FIGURE 3.

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



(a) F_B -Centre

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

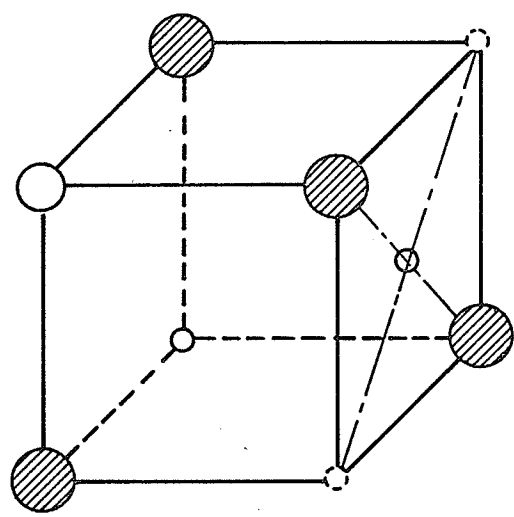
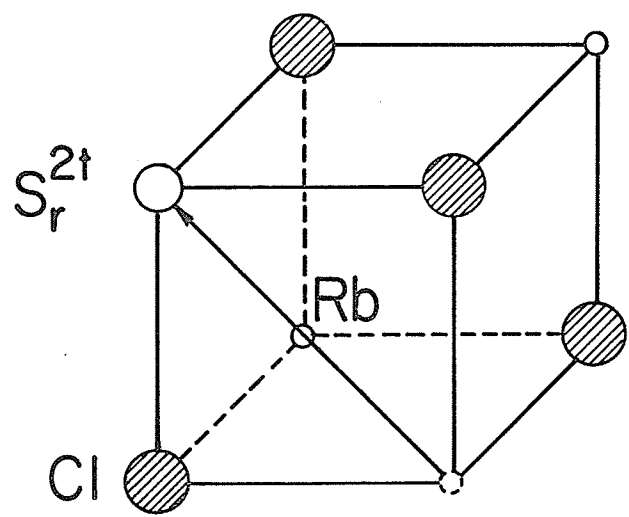


(c) F_C -Centre

FIGURE 4.

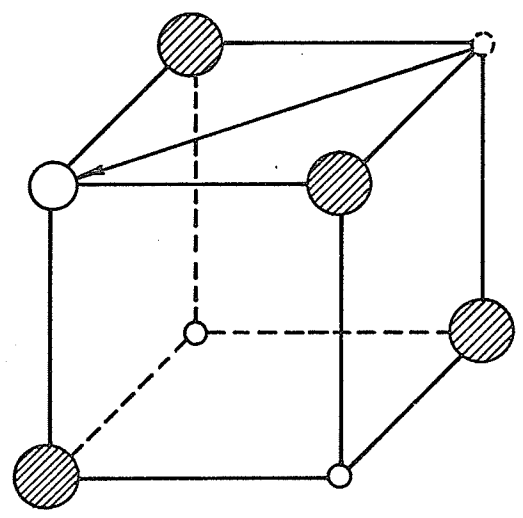
Model for reorientation of the S_r^{2+} - vacancy
dipole in RbCl

- ⊗ 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 Mayer⁶. 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 ρ 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 ^{to} calculate the activation energy for F-center step diffusion in KCl. Wolf⁷ has defined two possible processes of F - center diffusion: The dominant

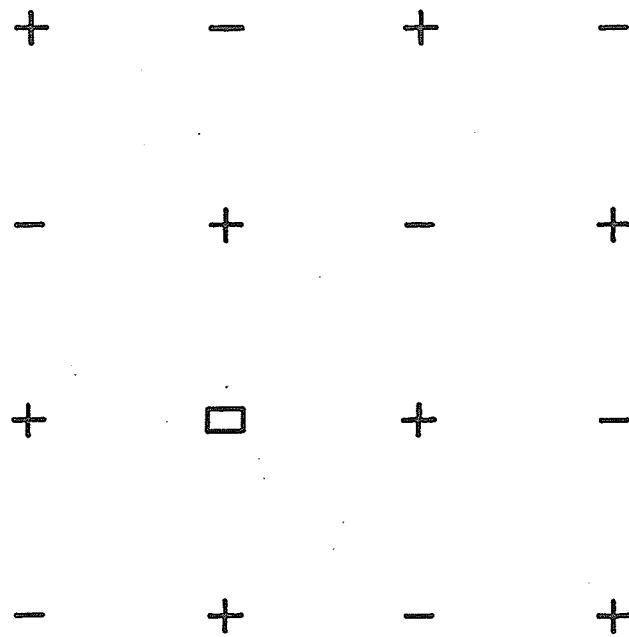
process occurs when the F - electron is thermally ionized and migrates through the conduction band, to be recaptured at a distant anion vacancy; a second diffusion process occurs when one of the twelve negative ions, nearest to the F - center, interchanges positions with the F - center. The second process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

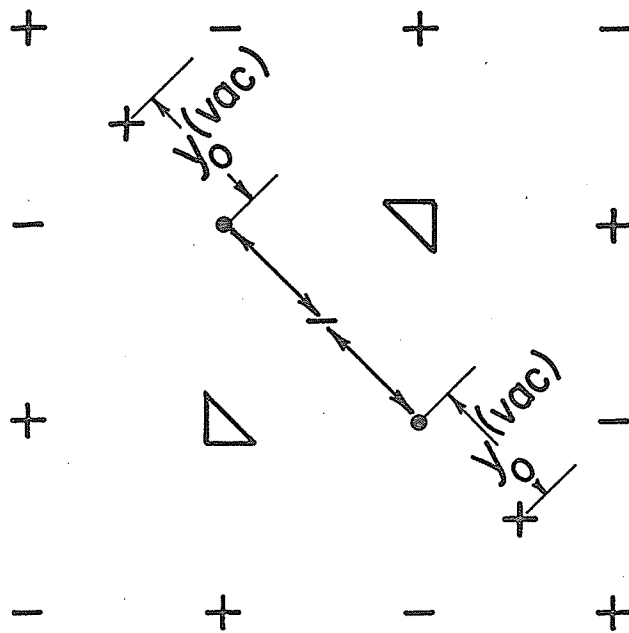
In separate calculations, A and ρ in $A e^{-r/\rho}$ will be corrected, since we have only one piece of experimental data, namely, the activation energy for anion vacancy diffusion, and we wish to see whether the result is sensitive to the choice of the parameter. The empirically corrected parameter 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 Gash⁸ (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 Wolf⁷. 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 method⁹) 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'

-

+

+

-

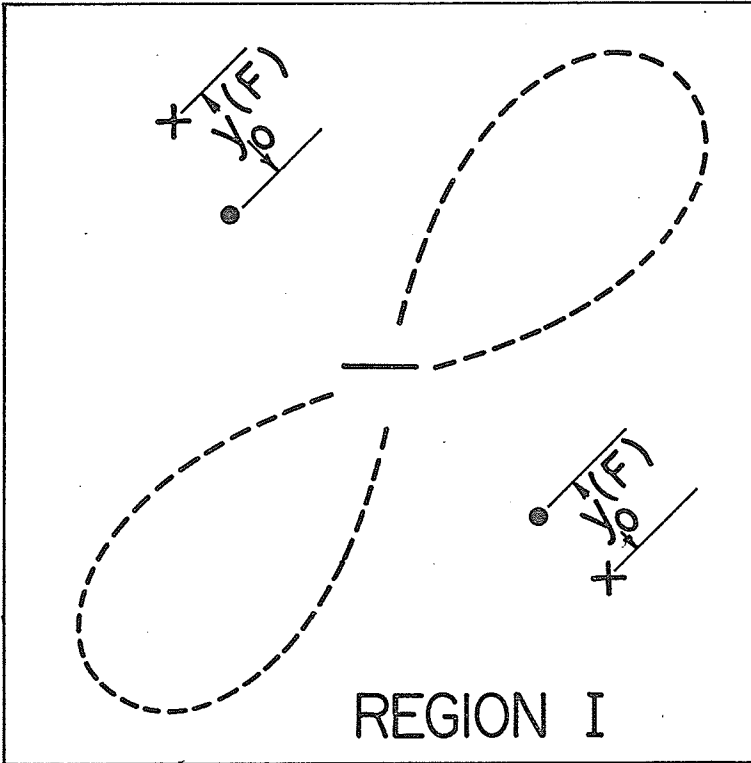
-

+

-

+

Y'



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 ^{10, 11} 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 ϕ 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 Gash⁸, 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 ϕ 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 δ - function is the ion - size contribution to V_P , V_{PI} is the point - ion potential, U_{γ} is the potential energy of an electron at lattice site γ due to all the other ions in the crystal, and A_{γ} and B_{γ} are constants characteristic of the ionic species at γ , 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_γ 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 α 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 ϕ 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) ¹² 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 ¹³, and Alig ¹⁴. 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 α 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. Hagston¹⁵ 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 α , 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 Vail¹. 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 Brown¹⁶ 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 Littleton¹⁷, 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 Vail¹ have estimated F - center energies by the method of lattice statics, or the Kanzaki method⁹.

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 Stoneham¹⁸, and to include non - harmonic lattice distortion in region I by Vail¹⁹, 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 ⁱⁿ electronic transitions of the F-center, as described by Vail ¹⁹.

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, Kellermann²⁰ 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 Herzfeld²¹ 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 α_{\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 Szigeti²². 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 Overhauser²³ 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;

Δ_+ = the displacement of core of positive ion;

Δ_- = 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, Δ_+ 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

