NUMERICAL CALCULATION OF SCHOTTKY DEFECT ENERGIES IN ALKALI HALIDES INTERACTING VIA COULOMB POTENTIAL

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BY

TAMIRU AYANA

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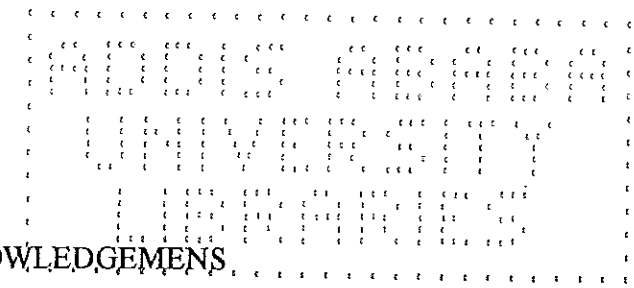
TO
MY BROTHER
MALKAMU AYANA



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Abstract

The electrostatic energy of a cluster up to 2000 ions can be calculated by numerical summation of the Coulomb interactions between all cluster ions. The energy difference between a cluster with a point defect and the corresponding perfect cluster represents the formation energy of the defect. Formation energies of Schottky-like defects in 16 alkali halides (Li-Rb, F-I) were calculated. It can be shown, that the relative positions of the vacancies and the position of the removed ions on the surface have a strong influence on the energy of the defect formation process.

I. INTRODUCTION

Vacant lattice sites and interstitials, collectively called point defects play an important role in all classes of crystalline solids for the understanding of matter transport processes, e.g., diffusion phenomena, ionic conductivity and annealing of radiation damage [1]. Many of the technologically important physical properties of crystalline solids like mechanical strength, kinetics of phase transformations, photoconductivity, color, etc. are strongly depend up on the type and concentration of point defects present in crystals. Point defects find practical applications in tunable color center lasers, in the radiation dosimeters and in high density memory devices.

Research into crystal defects is an active and rapidly advancing area of solid state science. As defects are studied in more detail, [2] using high resolution electron microscopy and other techniques, coupled with computer-assisited modeling of defect structures it is become clear that the apparently simple point defects such as vacancies and interstitials are often, more complex. Instead of single atomic defects, larger defect clusters tend to form. One of the prime interest of scientists working with defect crystals is concerned with the control of the concentration of the various defects in the crystals and hence the control of the crystal properties related to these defects [3]. The defect concentration in turn depends, first of all, on the formation energy of the defect.

Formation of a Schottky defect in ionic crystals can be seen in a simple way as the removal of two ions of opposite charge from the bulk to the surface of a crystal. The neighboring ions may relax due to interionic forces. The Schottky formation energy can be defined as the difference between the energies of the corresponding configurations: the crystal with the defect and the perfect crystal.

Calculations of the formation energies of vacancies and Schottky defects in alkali halides have been made by different workers using different methods and models. These authors deal intensively with the influence of the different parts of ionic interactions, with polarization effects and relaxation phenomena [4 -7]. The method previously employed by most workers [8] is an extended Mott-Littleton approach, calculation of the Schottky defect energies employing the simple Born-Mayer model [9] and a force balance method for the evaluation of equilibrium relaxation. According to this treatment the crystal is divided into two regions, I and II. A review of the influence of assumed models on the calculated Schottky formation energies have been given by Tosi M.P. and Fumi F.G. [5]. The publication of Scholz A.H. [4] considers a large region I containing 256 ions around a vacancy, he considered the influence of region II, the interaction of region I and region II and studied the influence of van der Waals attractive energies on Schottky formation energies. Rao K.J. and Rao C.N.R. [8] used the modified Born model which includes higher van der Waals term and appropriately adjusted repulsive terms. Tosi M.P. and Doyama M. [10] employed the repulsive parameters of Fumi and Tosi and expressed the energy of a given defect configuration, relative to the perfect crystal, as the sum of the energy required to create the defects in a rigid lattice and the relaxation energy. However less work has been done about the effect of the relative positions of the vacancies in the interior of a crystal and a position of the removed ions on the surface of a crystal.

In recent research work the possibility to calculate the electrostatic energies [11] by summation of Coulomb interactions using modern computer techniques was shown. By this method the energy of small clusters of ions is calculated and from these cluster energies the electrostatic energies of an infinite crystal can be derived by extrapolation. This method allows also to calculate the energies of the clusters with differences in the arrangements of a single

ion or few ions. Hence it is possible to calculate the energy difference between a perfect cluster and a cluster with such differences. These values are the formation energies of the corresponding point defect.

In this master thesis the calculations of the formation energies of Schottky defects in sixteen alkali halide clusters having NaCl structure have been carried out employing a very simple potential model which considers only electrostatic interactions of all ions in the cluster. These results are compared with other works which employ refined but computationally expensive potential models. From these values of Schottky formation energies a strong effects of the distance between the positive and negative ion vacancies and the positions of the relocated ions on the surface on the energy of the defect formation process, have been studied.

II. LITERATURE REVIEW

Most theoretical attention has been given to the study of the clusters of alkali halides. The reasons for these are: [1,12] the simple ionic binding character of alkali halide solids, the relative ease with which molecular scale particles or clusters of these materials can be formed and studied, and the availability of straightforward and accurate theoretical potential models for calculating the energetic interaction within the clusters. The following discussion concerns itself with some aspects of alkali halide clusters.

1. Bulk and Surface Structure of Alkali Halide Crystals

A crystal structure may be described in various ways. The most common way, and one which gives all the necessary information, is to refer the structure to the unit cell [2]. The structure is then given by the size and shape of the cell and the positions of the atoms inside the cell. At standard temperature and pressure the sixteen salts of lithium, sodium, potassium and rubidium with fluorine, chlorine, bromine and iodine have the face centered cubic; sodium chloride structure [12]. The unit cell of alkali halides with NaCl structure is shown in Fig. 1; it contains Na^+ ions at the corners and the face center positions with Cl^- ions at the edge centers and body center. The three edges of the cell a, b and c are equal in length. The three angles of the cell α (between b and c), β (between a and c) and γ(between a and b) are equal to 90 ° [2]. The crystallographic coordinates of the eight ions in the unit cell of the NaCl structure with the Na^+ in the origin of the coordinates are listed in Tab. (1). The choice of the origin is somewhat arbitrary and an equally valid unit cell could be chosen in which the Na^+ and Cl^- ions were interchanged. In this structure both anions and cations are octahedrally coordinated [2,13] with interionic distance of 0.5a , where a is a lattice constant. CsF also has this structure but the other halides have the unit cell of primitive cubic, CsCl structure, containing halide ions at the corner and alkali-metal ions at the body center or vice versa.

Tab. 1 : Crystallographic coordinates of the ions in the NaCl unit cell [2,13].

Na^+	0	0	0;	Cl^-	0.5	0.5	0.5;
	0.5	0.5	0;		0.5	0	0;
	0	0.5	0.5 ;		0	0.5	0;
	0.5	0	0.5		0	0	0.5

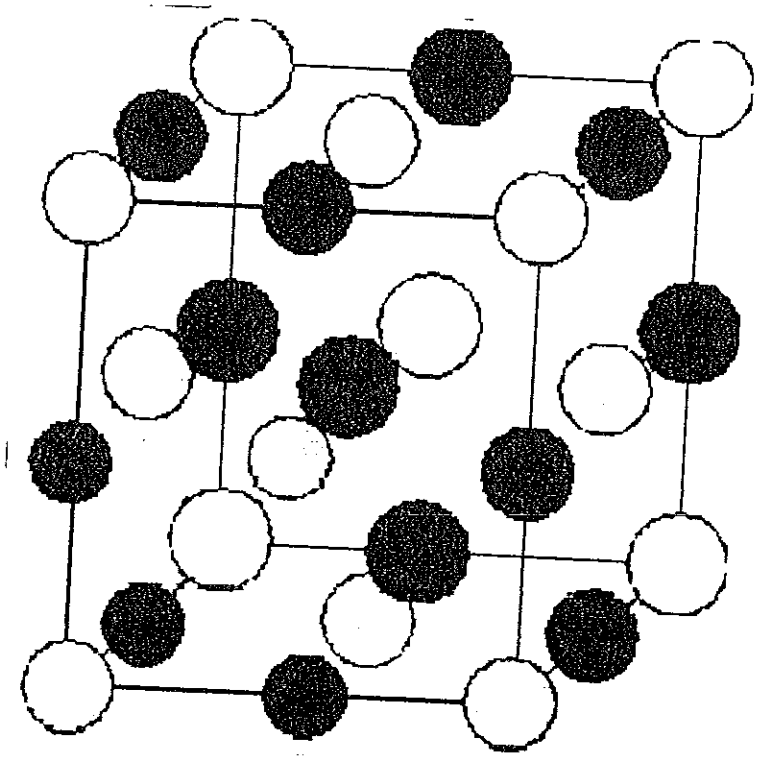


Fig. 1: A unit cell of NaCl structure

The structure of the surface plays an important role on the properties of real crystals. Therefore it is important to know as much as possible about the detail structure of the surfaces since it is known that the binding energy of an ion in the surface depends stonily on local environment [14]. In principle there are a lot of possible surface types with different arrangement of the ions in dependence of the Miller's indices [2,13].

The surface is not smooth on an atomic scale, because the addition of ions at any surface location, by various mechanisms, produces a step and different configurations of this

step causes the formation of several kinds of surface defects [15]. Hence practically a real crystal contains several defect types. Some of the simple defects that are often found on ionic crystal face and which are important with respect to Schottky defect are : a ledge (a monoatomic step on the surface, a kink (a step in the ledge) and a ledge-vacancy (a hole in the ledge). According to the NaCl structure, the correct addition of ions on the {100} surfaces is placing of ions on the top of the ions of opposite charge. If an additional layer of ions ends in a straight line in <100> direction one gets a monoatomic step on the surface [16], called a ledge (Fig. 2a). An ion deposited adjacent to a ledge has two nearest neighbors of opposite charge and six next nearest neighbors of the same charge, and therefore bound more strongly than that of an ion on the plane surface which has one nearest neighbor of opposite charge and four next neighbor of the same charge (Fig. 2b). If two ions of opposite charge are to be relocated on the surface of a crystal, which has a ledge surface position, they can be far away from each other at the different positions of a ledge or they can be in the first nearest neighboring position. However the latter configuration is energetically favorable.

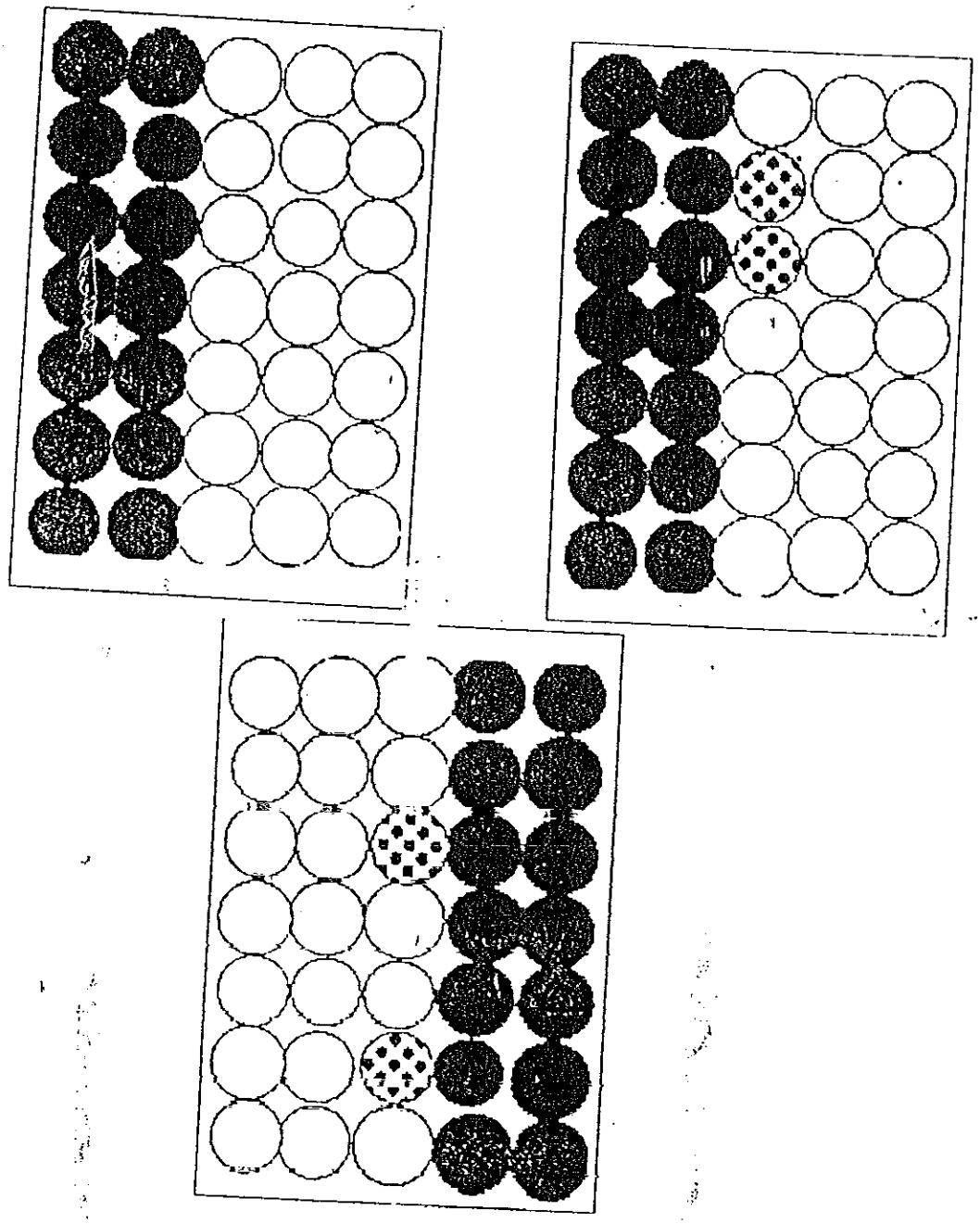


Fig. 2 : Structure of a ledge surface positions and the different possible arrangement of the relocated ions adjacent to ledge surface positions.

In most real crystals the ledges themselves are not perfect. If a configuration of a ledge changes in such a way that ions of one row, one gets a kink site (Fig . 3a). An ion deposited in a kink position has three nearest neighboring ions of the opposite charge and six next nearest neighboring ions of the same charge and is therefore bound more strongly than that of an ion adjacent to a simple ledge. If ions of opposite charge are required to be added in the kink site, they can be placed in the same kink (Fig. 3b) or in a different kink positions. Both configurations are energetically equivalent.

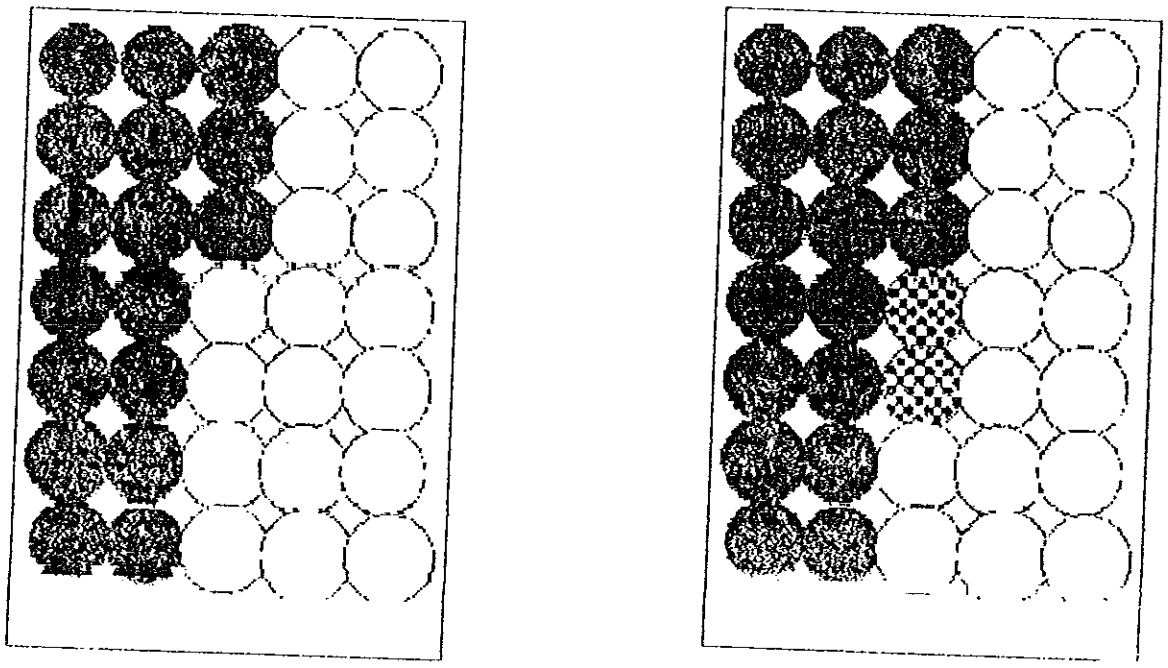
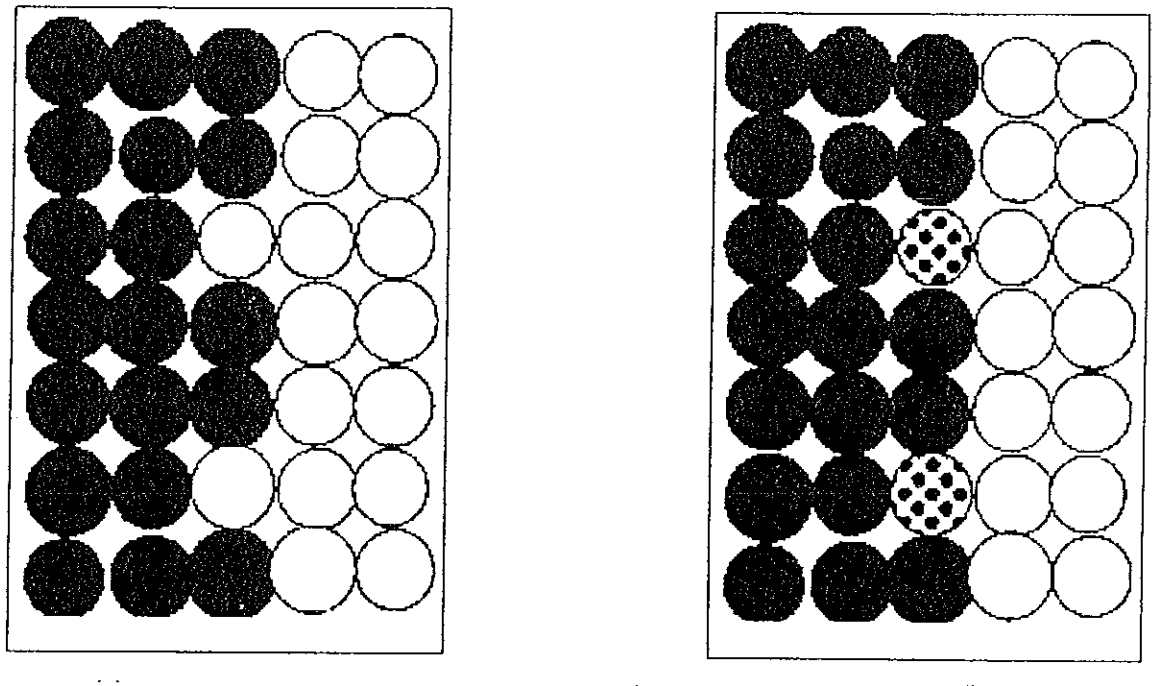


Fig. 3: (a) Structure of a kink surface and (b) the relocated ions in the kink surface position.

If a single ion is removed from a ledge one gets a vacancy in a ledge or ledge-vacancy (Fig. 4a). An ion deposited in a ledge-vacancy has four nearest neighboring ions of opposite charge and six next nearest neighbor of the same charge (Fig . 4b) and therefore bounded more strongly than that of an ion in a kink position.



(a) (b)

Fig. 4: (a) Structure of the ledge-vacancy and (b) the relocated ions in the ledge-vacancy.

2. Lattice Energy of ALKALI HALIDE CRYSTALS

The lattice energy, U_L, of an ionic crystal can be defined [18] as the energy change involved per mole when gaseous sodium (Na^+) and chloride (Cl^-) ions are brought from infinity to their respective equilibrium position in the lattice, e.g.

$$Na^+ (g) + Cl^- (g) \rightarrow NaCl (s), \qquad \Delta H = U_L \text{ --------- (1)}$$

The lattice energy can be theoretically calculated as well as experimentally estimated [13].

2.1 Theoretical Evaluation of Lattice Energy

In the case of compounds consisting of ions, the lattice energy U_L, can be spilited into several terms according to [19]

$$U_L = U_M + U_R + U_{VW} + U_Z \text{ ----------(2)}$$

where U_M, U_R, U_{VW} and U_Z represent the Madelung, the Born repulsion, the van der Waals and the zero point vibrational energy respectively.

In the case of alkali halide crystals the Born repulsion term contributes about 10-15%, whereas the zero point vibrational and van der Waals terms contribute about 1% each and, being of opposite sign, tend to cancel each other [2]. Thus the Madelung term U_M makes a dominant contribution to the lattice energies of ionic crystals.

2.1.1 The Madelung term, $-U_M$

The electrostatic energy of an ionic crystal (Madelung part of the lattice energy) arises from the electrostatic interaction of the point charges with which the ions have been replaced in the theoretical consideration of the problem. It can be calculated by the summation and the Madelung constant methods.

The summation method: two point charges $Z_i e$ and $Z_j e$ separated by a distance, r_{ij}, experience an electrostatic interaction force, F, given by the Coulomb law [2]:

$$F = \pm \frac{Z_i Z_j e^2}{r_{ij}^2} \text{ ---------- (3)}$$

And their Coulomb potential energy, V, is given by

$$V_{ij} = \int_{\infty}^{r} F dr = \pm \frac{Z_i Z_j e}{r_{ij}} \quad \text{---------- (4)}$$

If the ions have opposite charges, the Coulomb interaction is attractive which has negative sign otherwise it is repulsive interaction with a positive sign. The total electrostatic energy U_M, of n such charges in ionic clusters can be calculated by summation of all the electrostatic interactions of the charged ions in the cluster [12]. By designating the lattice site by i or j and the distance between the sites by r_{ij}, the Coulomb energy of the crystal is given by the sum of the Coulomb interaction energies of all pairs of the charged ions.

$$U_M = -\frac{1}{2} \Sigma'_{ij} \frac{Z_i Z_j e}{r_{ij}} \quad \text{----------(5)}$$

The summation i and j range over all the sites in the lattice and the prime on the summation indicates an exclusion of terms for which i = j. The factor $\frac{1}{2}$ avoids the counting of pairs of charge twice, $Z_i e = Z_+ e$ or $Z_- e$ depending up on whether the lattice site is occupied by a positive or a negative ion. This numerical summation can be performed easily by using the computer technique. A personal computer with 80486 processor and a frequency of 60 MHz, for example, can calculate the electrostatic energy of a cluster which contains about 10,000 ions, in less than one hour. The energy of an infinite crystal can be derived by extrapolation. In addition to the calculation of the Madelung energies for the perfect clusters it is also possible to evaluate the energies of clusters with the modification(s) in the arrangement of a single or a few ions, only by this computer summation method. Therefore the electrostatic part of the cluster energies can be calculated for the perfect and the defect clusters. The difference of these two energies, is the Madelung energy required to form the corresponding point defect in the perfect cluster.

The Madelung constant method: for simple crystal structures, like alkali halide crystals the above summation can be replaced by a mathematical sequence. The analytical solution of this mathematical sequence yields the Madelung constant, A, as in equ. (6)

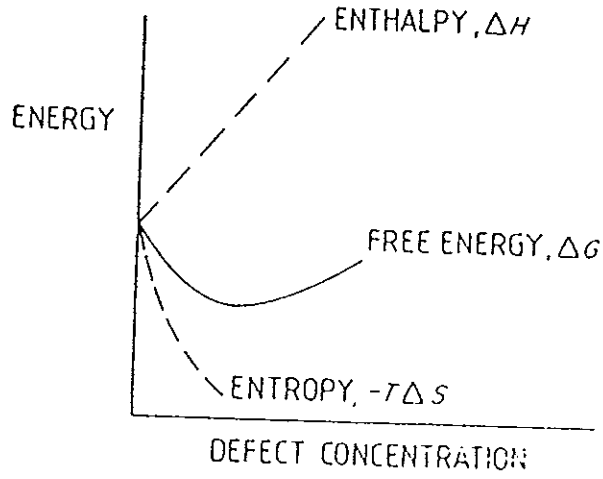


Fig . 5 : Energy changes on introducing the defects into a perfect crystal.

3.2 Point Defects in Ionic Crystals

Point defects (zero dimensional) involve only one lattice point or site, e.g. vacancies or interstitials. More reasonable models for point defects were proposed by [27] I. Frenkel in 1928 and W. Schottky in 1930. There are different types of point defects in ionic crystals (Fig. 6). However those defects for which the energy of formation is smallest will predominate [1,2]. The most frequently occurred point defects in alkali halide crystals are: Schottky (a pair of vacancies) and Frenkel (vacancy-interstitial pair) defects [25,26].

3.2.1 Schottky defect

The Schottky defect is a pair of vacant sites, an anion and a cation vacancy. To compensate for the vacancies, there should be two extra ions at the surface of the crystal for each Schottky defect. There are equal numbers of anion and cation vacancies in order to preserve local electroneutrality as much as possible, both inside and at the surface of the crystal [2]. The

Schottky defect is the predominant point defect in alkali halides. The Schottky equilibrium in a crystal of NaCl, for example, can be treated by assuming that a pair of oppositively charged ions are removed from the bulk of the crystal, leaving vacancies behind and relocated at the crystal surface. This can be represented by the following equation [2];

$$M^{+} + X^{-} + V_M^{s} + V_X^{s} \leftrightarrow V_M + V_X + M^{+,S} + X^{-,S} \text{ ----------(10)}$$

where V_M , V_X V_M^{S} , V_{Cl}^{S}, M^{+}, X^{-}, $M^{+,S}$ and $X^{-,S}$ represent cation and anion vacancies, vacant cation and anion surface sites, normally occupied cation and anion sites and occupied cation and anion surface sites respectively. The notations used are based on Kroger's [28] notation. From this equation, an equation relating, the concentration of Schottky defects, the number of ion pairs, the Schottky formation energy and the temperature can be derived using the law of mass action. If n is the number of Schottky defects, N the total number of cation-anion pairs and E_S the average energy required to create a Schottky defect. Hence an equation relating the above quantities is given by [18]

$$n = N \exp -\left(\frac{E_S}{2KT}\right) \text{----------(11)}$$

where K is the Boltzmann's constan. Thus, the number of Schottky defects depends on:
the total number of ion pairs, the average energy required to produce a Schottky defect and the temperaturrature.

The simplest arrangement of cation and anion vacancies is obtained by removal of the two nearest neighboring ions from the interior of the crystal. In this case the distance between the centers of the vacancies is $\frac{a}{2}$. There are also other arrangements of vacancies in Schottky defect which can be obtained by varying the distances between the vacancies.

The presence of a vacancy does not imply that one lattice site is vacant while all the surrounding particles remain in their original position. The first nearest neighboring ions may be displaced slightly outward from their regular positions, and the second nearest neighboring ions assume positions slightly displaced towards the vacancy, hence in the neighborhood of the

vacancy the distortion of the lattice occurs. However at greater distance away from the vacancy the lattice is unperturbed [23]. Moreover the surrounding ions to the vacancy become polarized due to the effective charges of the vacancies. This polarization causes the formation of dipoles induced in the ions by the Coulomb field of missing ion [20,22,30] and the surrounding ions in turn create a reaction potential, V, at the location of the charge. This makes also another energy contribution, termed as polarization energy, to the total energy of the defect crystal.

The positive and negative ion vacancies of a Schottky defect bear opposite effective charges in the alkali halide lattice, and hence one has to expect that they will attract each other as a result of Coulomb field between them. They may even combine to form pair of vacancies on adjacent lattice site [19]. These pairs are electrically neutral but they are dipolar [25,26], pairs can therefore attract each other to form larger aggregates or clusters [2].

3.2.2 Frenkel Defect

The particles which left a normal site to create a vacancy may end up in an interstitial sites, i.e., the sites which according to crystal structure should not be occupied [14]. These particles are called interstitials. A Frenkel defect involves equal numbers of interstitials and vacancies of one component of a compound. It is a predominant point defect in silver halides with silver ions as interstitials [23,27].

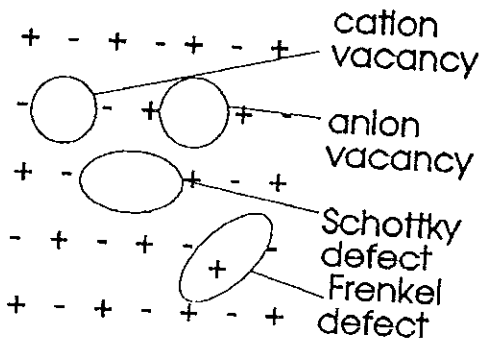


Fig. 6 : Some point defects in alkali halide lattice

4. Theoretical Studies of Formation Energies of Schottky Defect

The total energy of the defect crystal, U_L, is the sum of the Coulombic, polarization, van der Waals and repulsive terms [17], i.e.,

$$U_L = U_{coul} + U_{pol} + U_{vw} + U_{rep} \text{ ----------(12)}$$

The subscripts "coul", "pol", "vw", and "rep" represent the Coulombic, polarization, van der Waals and repulsive terms respectively.

The first important attempt to deal theoretically with Schottky defects in the alkali halides were due to Jost and Schottky [5] a few years after Frenkel had introduced the concept of point defects. Jost noted that the formation energy, E_S, of Schottky defect is equal to the difference of two energies, the lattice energy, U_L, per ion pair which is necessary to form a Schottky defect in a rigid, nonpolarized lattice and the polarization energy [5,6]. He represented the vacancy by a spherical cavity of radius R and effective charge e inside a homogenous dielectric medium. The dielectric medium is polarized by the charge and an electrostatic potential is set up at the vacancy which causes the polarization energy in the defect crystal. Therefore according to Jost model the Schottky formation energy, E_S, can be expressed as

$$E_S = U_L - \frac{e^2}{2}\left(1 - \frac{1}{\varepsilon}\right)\left(\frac{1}{R_+} + \frac{1}{R_-}\right) \text{----------(13)}$$

where R_+ and R_- are the radius of cation and anion vacancies respectively and ε is a dielectric constant of the medium. Although such a rough estimation can not obviously give reasonable value for E_S, it allows to understand why experimental E_s values are much smaller than U_L.

An important step forward in making an estimate of the formation energy of Schottky defects quantitatively was taken by Mott and Littleton and they treat the polarization energy in a better way than Jost [6]. According to Mott-Littleton the crystal is divided into two regions. An inner region containing a vacancy with the nearest neighboring ions (region I) and the outer region includes the rest of the crystal (region II) [1]. All interactions between ions of the inner region are explicitly described. The outer region is assumed to behave harmonically. They calculated the Schottky defect energies using the simple Born-Mayer ionic model and a force balance method for the evaluation of equilibrium relaxation of region I. They wrote the electrostatic energy, U_+^v, part required to extract the positive ion as [1,4,5]

$$U_+^v = A\frac{e^2}{r} + e\frac{V}{2} \qquad \text{----------(14)}$$

where V is an electrostatic potential at vacant site due to the polarization of the rest of the lattice (region I and II). The same formula holds for creation of the negative ion vacancy and they calculated the formation energy, E_S, of the Schottky defect as [1,5]

$$E_S = U_+^v + U_-^v - U_L \qquad \text{----------(15)}$$

Two relevant criticisms can be made on Mott-Littleton approach, namely, that it neglects the elastic distortion of the crystal around the defect and it does not consider explicitly the repulsive interaction between non-nearest neighbors.

A review of the influence of assumed models on the calculated Schottky formation energies have been given by Tosi M.P. and Fumi F.G. [5]. They have used two different forms, Born-Mayer and Huggins-Mayer, for repulsive potential. The values that they found for the different contributions to the energy to form a Schottky defect in NaCl are listed in Tab. 2 and compared with values given by Mott-Littleton.

Tab. 2 : Formation energy of Schottky defect in NaCl crystal, in eV.

	Mott - Littleton	Fumi and Tosi	
		B.M. repul.	H.M. repul.
Positive ion vacancy			
Ae^2/r	8.94	8.94	8.94
eV/2	-3.55	-3.43	-3.42
Repulsive	-0.75	-0.58	-0.72
U_+^v	4.64	4.93	4.80
Negative ion vacancy			
Ae^2/r	8.94	8.94	8.94
eV/2	-3.04	-3.17	-2.90
Repulsive	-0.72	-0.88	-0.90
U_-^v	5.18	4.89	5.14
E_s	1.93	1.91	2.12

The values of Fumi and Tosi for the formation energies of Schottky defects in NaCl and KCl are collected in Tab. 3 and are compared with Mott-Littleton and with experimental values.

Tab. 3: Formation energies of Schottky defects in NaCl and KCl in eV

	Mott- Littleton	Fumi and Tosi		experimental
		B.M. repul.	H.M. repul.	
NaCl	1.93	1.91	2.12	2.02
KCl	2.14	2.18	2.21	2.1-2.4

The Publication of Scholz A.H. [4] considered a large region I containing 256 ions around a vacancy. He considered the influence of region II, the interaction of region I and region II and studied the influence of van der Waals attractive energies on Schottky formation energies. Tosi M.P. and Doyama M. [21] employed the repulsive parameters of Fumi and Tosi and expressed the energy of a given defect configuration, relative to the perfect crystal, as the sum of the energy required to create the defects in a rigid lattice and the relaxation energy.

Rao K.J. and Rao C.N.R. [8] used the modified Born model which includes the van der Waals term and appropriately adjusted repulsive terms. The calculated values of Schottky formation energies are collected in Tab. 4.

Tab. 4 : Calculated Schottky formation energies of various alkali halides .

(a) By Scholz A.H.

Alkali halide	Schottky formation energies, in eV	
	without van der Waals	with van der Waals
NaCl	1.50	1.56
NaBr	1.56	1.65
KCl	1.90	1.90
KBr	1.94	1.96
(b) By Rao K.J and Rao C.N.R.		
KCl	2.2	-
KBr	2.11	-
KI	2.87	-
RbCl	1.17	-
RbBr	1.99	-
RbI	1.88	-
(C) By Tosi M.P. and Doyama M.		
NaCl	1.94	-
KCl	2.00	-
RbCl	2.10	-

All the calculations were performed for an infinite separation distances of the vacancies, however since anion and cation vacancies have opposite effective charge there exists a

long-range Debye-Huckel electrostatic interaction between them. In addition the authors did not also consider the different types of surface sites, and hence the different types of surface positions at which the ions can be deposited that can affect significantly the value of Schottky formation energy.

5. Experimental Methods for Measurement of Formation Energies of Schottky Defect.

Measurement of the transport processes, e.g., electrical conductivity [31-37] and diffusion phenomena [38-44] in ionic crystals can provide the most important information about formation energies, mobility, and concentration of defects [1,29].

5.1 Measurement of the Formation Energies of Schottky Defects by Ionic Conductivity

When a potential difference is applied between two opposite faces of an ionic crystals an electric current may be detected. In alkali halides of NaCl structure type cations are more mobile than anions hence ionic conductivity in these crystals occurs predominantly through the motion of positive ion vacancies [32]. Such vacancies may be either of thermal origin or may be incorporated in to the lattice due to the divalent cation impurities to maintain charge neutrality. The expression for the ionic conductivity, σ, due to cation vacancies is [33]

$$\sigma = ne\mu = \left(\frac{4a^2e^2\upsilon_0}{KT}\right) n \exp\left(-\frac{E_m}{KT}\right) \quad \text{----------(16)}$$

where n is the concentration of cation vacancies, μ their mobility, *a* the distance between the nearest neighbor ions, E_m the activation energy for the motion of the cation vacancies, υ_0 the frequency factor (which contains an effective lattice vibrational frequency multiplied by entropy factor) and e and KT their usual significance.

This equation suggests that data for conductivity as a function of temperature can be plotted as $\ln\sigma T$ Vs T^{-1}. If the slope of a plot is equal to - E/K, the quantity E, which represents an effective activation energy is equal to E_m plus an energy associated with the temperature dependence of n. A schematic diagram of conductivity plot for a typical crystal doped with a divalent cation impurity is shown in Fig. (7).

In the intrinsic conductivity region at higher temperature (region I) the concentration of thermally induced vacancies is greater than the vacancy concentration associated with the doppant. Hence the number of cation vacancies, n, is temperature dependent, which is given by equ. (11), so the overall conductivity in the intrinsic region is given by

$$\sigma = A \exp -\left(\frac{E_m + E_S/2}{KT}\right) \text{----------(17)}$$

where the pre-exponential factor, A, contains several constants. Thus in this region the effective activation energy E_I is

$$E_I = E_m + E_S/2 \text{ ----------(18)}$$

A compilation of experimental results, by various authors, gives [32]. E_I as 1.86 ± 0.03 eV for NaCl and 1.95 ± 0.03 eV for KCl. In the low temperature, extrinsic region (region II) the number of thermally generated intrinsic vacancies is very small and, unless the crystal is very pure, is much less than the concentration of extrinsic vacancies. Hence the concentration of vacancies is dominated by the impurity level and is constant, equal to the concentration of divalent cation impurities [33-37]. Thus in this region the conductivity is given by an equation

$$\sigma = A' \exp\left(-\frac{E_m}{KT}\right) \text{ ----------(15)}$$

where the pre-exponential factor, A', contains several constants Thus the effective activation energy, E_{II} can also be written as

$$E_{II} = E_m \text{ ----------(16)}$$

A compilation of experimental results, by various authors, gives [33] E_{II} as 0.80± 0.03 eV for NaCl and 0.84± 0.05 eV for KCl. Based on the above considerations one can determine E_S and E_m separately from a knowledge of E_I and E_{II} . A wide discrepancy in the value of E_m for NaCl exists among different authors, ranging from 0.72 eV to 0.85 eV [32].

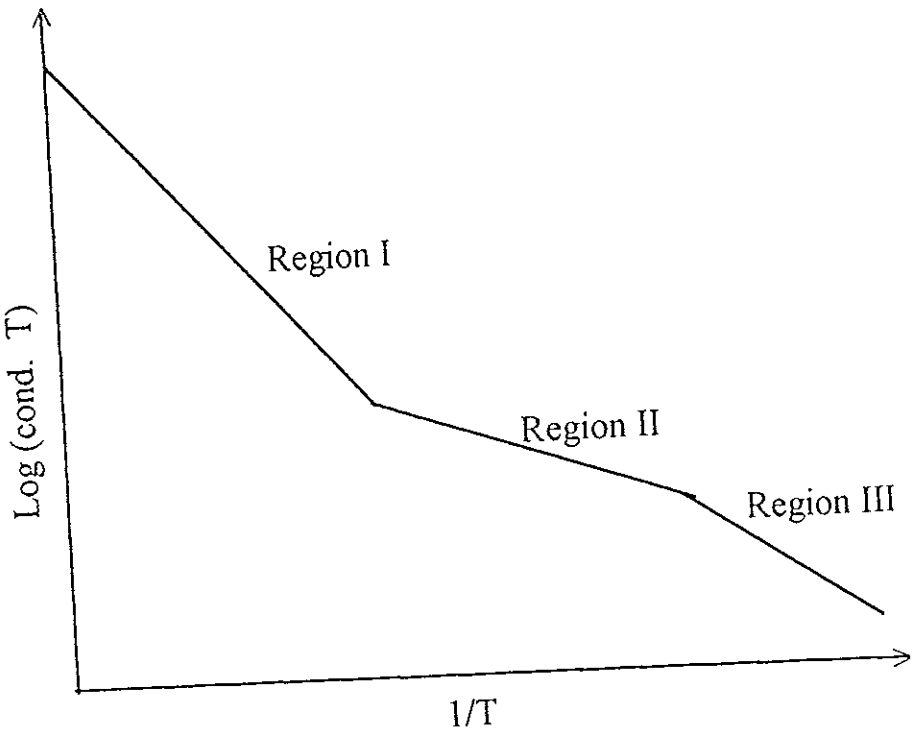


Fig. 7: Schematic ionic conductivity of doped NaCl crystals.

5.2 Measurement of the Formation Energies of Schottky Defects by Diffusion Method

When there is a concentration gradient of impurity or vacncies, there will be a diffusion of these through the solid. It has been agreed that in alkali halide crystals diffusion occurs mainly through the continual movement of t. At equilibrium the impurities or vacancies will be distributed uniformly. The net flux J_N of ions of one species in a solid is related to the gradient of the concentration N of this species by a relation called Fick's first law [13]:

$$J_N = -D \text{ grd } N \text{ ----------(17)}$$

where J_N is the number of atoms or ions crossing unit area in unit time; the constant D is the diffusion coefficient or diffusivity.

The diffusion coefficient is often found to vary with temperature as:

$$D = D_o \exp\left(-\frac{E_D}{k_B T}\right) \text{ ----------(18)}$$

where the pre-exponential factor, D_0 is a constants, E_D is the activation energy for diffusion.

Thus the migration of vacancies in the bulk or the whole volume of the lattice of alkali halide crystals predominates at high temperatures. When the diffusion is governed by the intrinsic cation and anion vacancy concentration as in the case at high temperature or in pure materials, the slope of lnD vs. 1/T curve gives $E_D = E_m + E_S/2$ [38,39]. Consequently one can write the self diffusion coefficient, D, as [38,39]:

$$D = D_0 \exp\left(-\frac{E_S/2+E_m}{k_B T}\right) \text{----------(19)}$$

At lower temperatures the intrinsic vacancy concentration falls below that resulting from divalent cation impurities, which introduces cation vacancies into the lattice, and hence the concentration of cation vacancies is independent of temperature and determined only by the impurity concentration [40,41]. This leads to a break in the lnD vs. 1/T curve and the slope in the lower temperature region gives only E_m. Hence the gradient of an intrinsic curve is greater than that of an extrinsic curve and if both the intrinsic and extrinsic gradients can be measured then E_m and E_S may be determined separately.

If there are no contribution to diffusion from neutral defects the information obtained from diffusion measurement is similar to that of obtained from conductivity. If the mechanisms of ionic migration under the influence of external electric field and concentration gradient are the same, then coefficient for a trace self-diffusion, D_T, and the conductivity, σ, are related by [22,31] Nernst-Einstein equation :

$$D_T = \frac{KT}{NZ^2e} \text{----------(20)}$$

III. METHODOLOGY AND COMPUTATIONAL DETAILS

The major part (85-90 %) of the cohesive energy in ionic crystals is due simply to electrostatic interactions among the ions considered as fixed point charges. Therefore the simple potential model which is used throughout this work will not be an oversimplification. Because the binding in alkali halides is almost purely ionic, an alkali halide cluster is best viewed as being composed of ions held together by Coulomb forces. Hence the simplest pair potential which describes ionic bonding has the form of:

$$V_{ij} = -\frac{Z_i Z_j e}{r_{ij}} \text{----------(21)}$$

where V_{ij} is the potential energy between the ions i and j with respective charges $Z_i e$ and $Z_j e$ and r_{ij} is the distance between the charges. Then the total electrostatic energy of a finite cluster of N ions as a function of position takes the form:

$$V_M = -\frac{1}{2}\Sigma'_{ij}\frac{Z_i Z_j}{r_{ij}} \text{----------(22)}$$

Fast Turbo Pascal-6.0 computer programs were constructed in order to perform this summation.

1. Qualitative Description of a Turbo Pascal-6.0 Programs

To calculate the electrostatic energies of clusters using Turbo Pascal-6.0 programs the following steps should be performed.

A. Creation of a start cell in crystallographic coordinates (by BORN501.EXE program)

B. Multiplication of the start cell to get the larger cluster (by BORN502.EXE program)

C. Transformation of the crystallographic coordinates into physical coordinates (by BORN503.EXE program)

D. Modification of the crystallographic or of the physical files (by BORN504.EXE program)

E. Calculations of the cluster energies by numerical summation of Coulomb interactions (by BORN505.EXE program)

F. Show the file of the clusters (by BORN506.EXE program)

A. Creation of a Start Cell with Crystallographic Positions (by BORN501.EXE).

This program generates a start cell in crystallographic coordinates. The program writes records with the crystallographic coordinate x, y, z and the charges in a file. Files with crystallographic coordinates have the extension CRY. As start cell the unit cell of the NaCl structure is used. The positions and charges used in this work are listed in Tab. (5).

The number of ions in the start cell can be varied as required. In crystallographic notation, the length of the unit cell is considered as unity. The position of each ion in the cluster is described by a fraction or multiple of this distance. Most alkali halides crystallize in the NaCl structure. The Bravais lattice is face centered cubic; the basis consists of one Na atom and one Cl atom separated by one-half of the body diagonal of a unit cube. There are four units of NaCl in each unit cube, with atoms in the crystallographic positions.

Tab. 5: Crystallographic coordinates and charges of the ions in the start cell

Record	x	y	z	charge
1	0	0	0	1
2	0	0.5	0.5	1
3	0.5	0	0.5	1
4	0.5	0.5	0	1
5	0.5	0.5	0.5	-1
6	0.5	0	0	-1
7	0	0.5	0	-1
8	0	0	0.5	-1

B. Multiplication of the Start Cell to get Larger Clusters. (by BORN502.EXE program).

This program multiplies the start cell according to the relation $N = 8xn^3$. N is the number of ions in the larger cluster and n is a multiplication factor. Hence the program allows to build up larger clusters from the start cell created with BORN501.EXE. To do this a new file is created with additional records. If one adds 1 to the x coordinate of the first position of the start cell one get the first position of the next unit cell in x-direction. In the same way one can get the first position of the next unit cell in y and z directions by the addition of 1 to the y and z coordinate respectively. By addition of larger integer numbers, one can get larger clusters. In this work, however, we have used only cluster with the same number of unit cells in all directions. Hence when we say a cluster with n = 6, six unit cells are stacked together in all directions to form a cluster with $(8 \times 6^3) = 1728$ ions. The records of these crystallographic files with extension CRY are the same for all sixteen alkali halides.

C. Transformation of Crystallographic Coordinates into Physical Coordinates (by BORN503.EXE program)

In the crystallographic notation, ionic space coordinates were defined by crystallographic axes of the NaCl structure. Born 503 transforms the crystallographic coordinates of each ion into physical coordinates. Since the alkali halides have a cubic structure, one can transform the crystallographic coordinates into the physical coordinates by only multiplication with the lattice constant. In this way we get sixteen different physical files for the sixteen different alkali halides from only one crystallographic file. The file names of physical files have the extension PHY. All the lattice constants necessary for the calculation are collected in Tab. 6.

Tab. 6: Lattice constants of alkali halides in Angstroms.

Alkali halide	Lattice constant	Alkali halide	Lattice constant
LiF	4.0270	LiBr	5.5013
NaF	4.6400	NaBr	5.9772
KF	5.3470	KBr	6.5966
RbF	5.6516	RbBr	6.8890
LiCl	5.1396	LiI	6.0000
NaCl	5.6402	NaI	6.4730
KCl	6.2931	KI	7.0655
RbCl	6.5810	RbI	7.3420

D. Modification of Crystallographic or Physical Files (by the BORN504.EXE program)

This program is used to modify the positions or charges of ions in a given cluster. The program has other options. It deletes or appends an ion or group of ions. Hence the program changes a single ion position in the cluster to introduce defects in the perfect cluster. Generally it allows us to:

1. insert an additional ion position
2. delete an ion position
3. change of an ion position

E. Calculation of the Electrostatic Energy of the Clusters (by the BORN505.EXE program)

Born 505 calculates the coulombic interactions of ions i and j first by calculating the distance between them. In crystallographic coordinates, this distance is simply the square root

of the sum of the squares of the coordinate differences. The distance, r_{ij}, between two ions with the coordinates a_1, b_1, c_1 and a_2, b_2, c_2 is calculated by equ. (23).

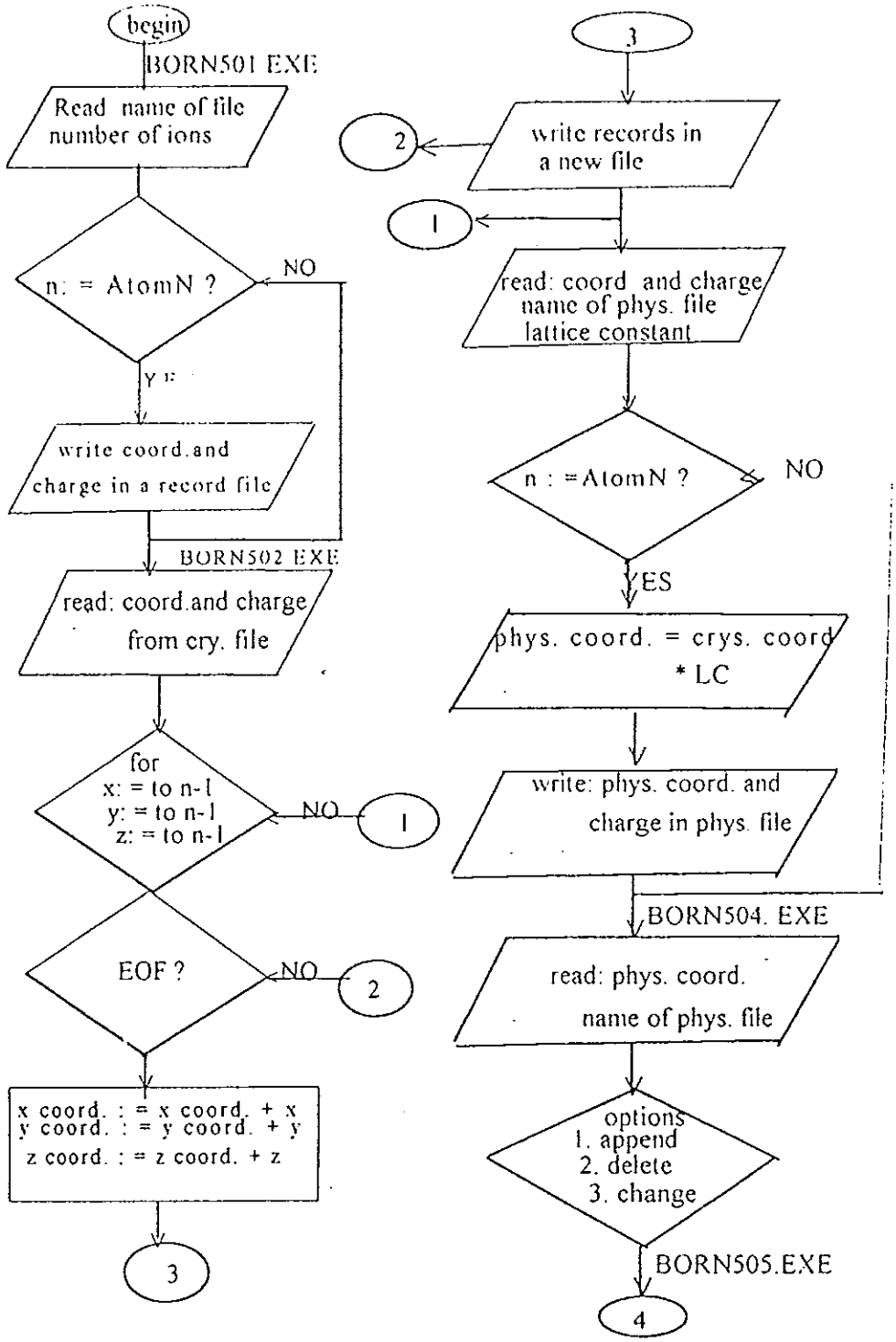
$$r_{ij} = \sqrt{(a_2 + a_1)^2 + (b_2 - b_1)^2 + (c_2 - c_1)^2} \quad \text{---------- (23)}$$

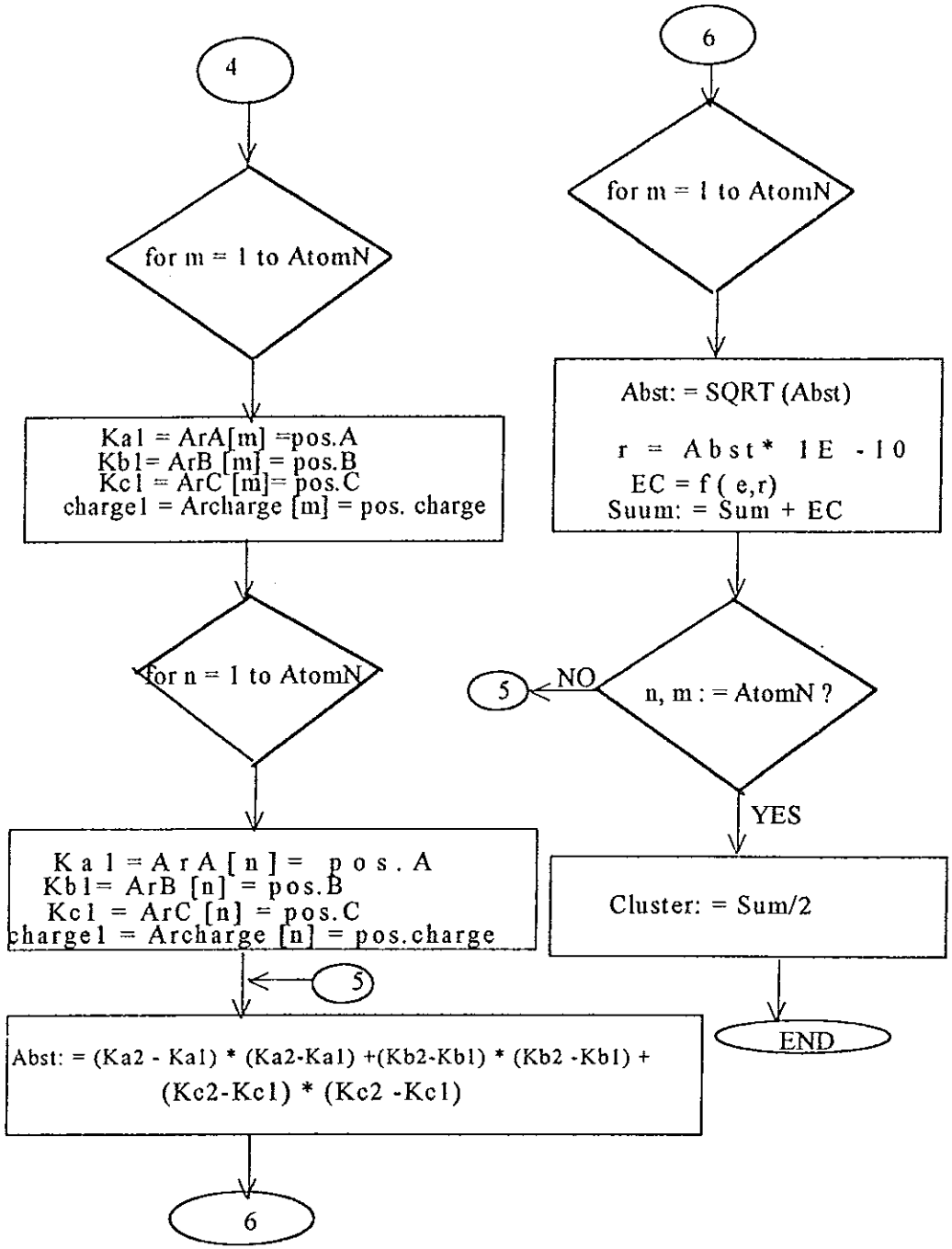
After this the electrostatic interaction energy of these two ions is calculated by using equ. (4). The electrostatic interaction energies of all ion pairs in the cluster are summed up and this value is divided by two to get the electrostatic energy of the cluster.

F. Show the File (by BORN506.EXE program)

It allows us to see the crystallographic or the physical files in the screen to check the correctness of the data records. Generalized flow chart of a program is given below. The flow chart is merely summary of the foregoing discussions using programming symbolism to show the flow of information in the programs. Flow charting is usually required at the initial stages of program development. Therefore a detailed and more sophisticated flow chart is omitted as it gives no additional information in view of the complete program listed in Appendix.

Generalized flow-charts of BORN programs




4
for m = 1 to AtomN
Ka1 = ArA[m] =pos.A
Kb1= ArB [m] = pos.B
Kc1 = ArC [m]= pos.C
charge1 = Archarge [m] = pos. charge
for n = 1 to AtomN
Ka1 = ArA [n] = pos.A
Kb1= ArB [n] = pos.B
Kc1 = ArC [n] = pos.C
charge1 = Archarge [n] = pos.charge
5
Abst: = (Ka2 - Ka1) * (Ka2-Ka1) +(Kb2-Kb1) * (Kb2 -Kb1) +
(Kc2-Kc1) * (Kc2 -Kc1)
6
6
for m = 1 to AtomN
Abst: = SQRT (Abst)
r = Abst* 1E -10
EC = f (e,r)
Suum: = Sum + EC
n, m : = AtomN ?
NO
5
YES
Cluster: = Sum/2
END

IV. NUMERICAL RESULTS AND DISCUSSION

The formation energy of a Schottky defect, E_S, is obtained by subtracting the energy of alkali halide with a perfect lattice consisting of N ions from the total energy of a similar system in which two ions of opposite charge have been removed from the bulk and placed on the surface. Therefore the Coulomb part of the Schottky formation energy, E_S^{coul}, can be calculated by subtracting the Coulomb energy of alkali halide with a perfect lattice consisting of N ions from the Coulomb energy of a similar system with a Schottky defect.

In this work the difference of the Coulomb energies of the perfect and the corresponding Schotky defect clusters, are calculated for each sixteen alkali halides to obtain the Coulomb part of the Schottky formation energies, E_S^{coul}. These E_S^{coul} values of alkali halide clusters will be discussed in terms of the following aspects:

1. Different sizes of the cluster to determine the cluster size that can represent well an infinite crystal.
2. Different types of surface sites of the crystals to show the influene of surface sites on the formation energy of Schottky defect.
3. The different separation distances of the vacancies of a Schottky defect in ionic crystals to show the dependence of formation energy of Schottky defect on the separation distance of the vacancies.
4. Formation and diffusion processes of the vacancies in ionic crystals and
5. Separation of cation and anion vacancies to show the ionic conductivity process in ionic crystals.

1. Dependence of Schottky Formation Energies on the Cluster Size

First it is important to determine the cluster size that can represent an infinite crystal and to show a strong dependence of the Schottky formation energies on the size of the alkali halide

clusters. To do this, six Schottky defects are made, for each cluster with size of n = 1-6, (where n is the multiplication factor of the start cell in one dimension) in each sixteen alkali halide cluster by removing the nearest neighboring ions from the positions in the center of the clusters to infinity. The crystallographic coordinates of the Schottky vacancies and the multiplication factors, n, of these Schottky defect clusters are shown in Tab. 7. The formation energies of the Schottky defecs in these clusters are calculated. The the values are are listed in Tab. 8 and shown graphically for LiBr, NaCl, RbCl and Nacl alkali halide clusters on Fig. 8.

Tab. 7: Crystallographic coordinates of Schottky vacancies and multiplication factors, n.

Multiplication factor	Schottky vacancies	
n	Na^+	Cl^-
1	0/0/0	0.5/0.5/0.5
2	1/0.5/0.5	0.5/0.5/0.5
3	1/1/1	1.5/1.5/1.5
4	2/1.5/1.5	2.5/1.5/1.5
5	2.5/2.5/2.5	2/2.5/2.5
6	3/3/3	3/3/3.5

Tab. 8: Schottky formation energies in alkali halide clusters with size of n =1-6, in eV.

Alkali halide	n = 1	n = 2	n = 3	n = 4	n = 5	n = 6
LiF	13.674097	17.381403	17.836436	17.841637	17.843001	17.843477
NaF	11.867583	15.085110	15.480028	15.484541	15.485724	15.486135
KF	10.298408	13.090501	13.433202	13.437118	13.438145	13.714217
RbF	9.743362	12.384972	12.709203	12.712909	12.713881	12.739915
LiCl	10.713983	13.618747	13.975276	13.979351	13.980419	13.980793
NaCl	9.763056	12.410005	12.734891	12.738603	12.739577	12.739915
KCl	8.750153	11.122485	11.413664	11.416992	11.417865	11.418169
RbCl	8.367359	10.635908	10.914349	10.917531	10.918366	10.918654
LiBr	10.009559	12.723340	13.056428	13.060235	13.061235	13.061582
NaBr	9.212606	11.710317	12.016886	12.020389	12.021310	12.021631
KBr	8.347571	10.610755	10.888538	10.891712	10.892544	10.892836
RbBr	7.993263	10.160388	10.426380	10.429420	10.430216	10.430494
LiI	9.77598	11.665818	11.971222	11.974712	11.975627	11.975945
NaI	8.506965	10.813365	11.096451	11.099687	11.100534	11.100832
KI	7.793587	9.906576	10.165923	10.168887	10.169663	10.169934
RbI	7.500080	9.533494	9.783074	9.785927	9.786674	9.786936

The calculated values of Schottky formation energies for n = 1-6 show that the formation energies initially increase rapidly with increasing the size of clusters and then become constant at larger size clusters (Tab. 8 and Fig. 8). There is a strong difference between the values for cluster sizes of n = 1and n = 2, but for clusters with size of n = 5 and n = 6 the difference is

smaller than 0.1%. Therefore the Coulomb energies of the clusters, with size of n = 6, can represent well the values in macroscopic crystal. From this we can conclude that the clusters with NaCl structure type of six unit cells magnitude (1728 ions) behaves like an infinite crystal structure with an error of about 0.1%. A unit cell of NaCl structure type can be considerd as a neutral block consisting of four cation and four anion species and the clusters are built up by stacking the unit cells face to face. Therefore the electostatic interaction energy falls off rapidly with distance for these nearly neutral groups than for the groups with an excess of charge.

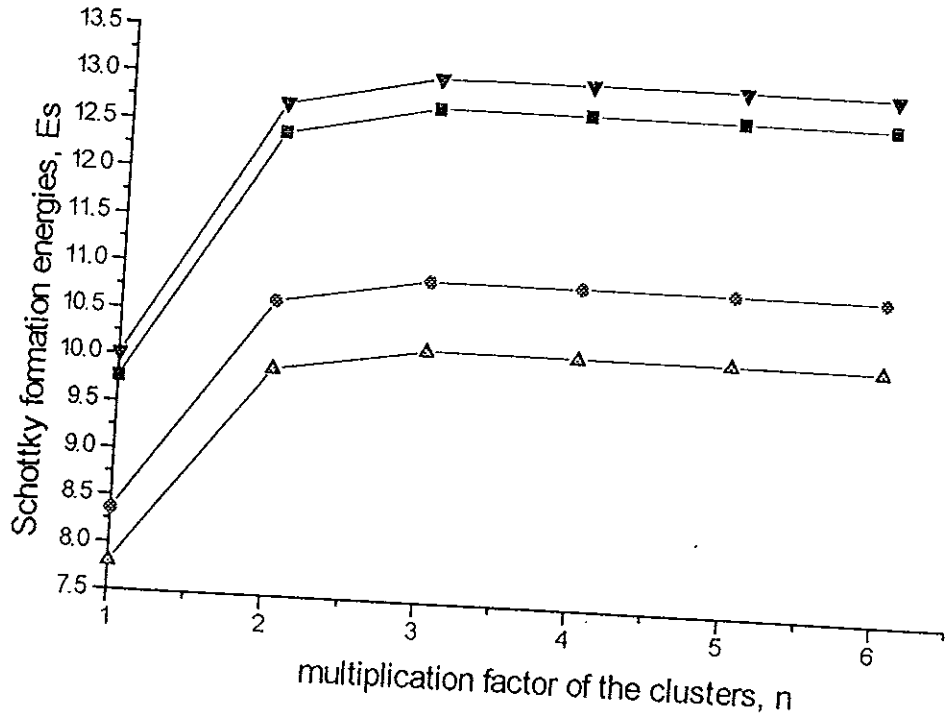


Fig. 8: Variation of Schottky formation energies with the cluster size.

2. Dependence of Schottky Formation Energies on the Surface Position

A more realistic picture of the formation of Schottky defects in ionic crystals can be seen in a simple way as the removal of two ions of opposite charge from the interior of the crystal and their deposition on the surface. However a real surface contains several kinds of lattice sites due to the presence of different kinds of defects on the surface and hence there are several different types of possible sites for the deposition of the ions on the surface of the crystal. The ions removed from the bulk may deposit on the smooth face to form a new layer, they may deposit in a position adjacent to a ledge, they may deposit in a kink, they may deposit in a ledge-vacancy or they may deposit adjacent to another type of defect. The quantity of energy released will differ for deposition at these various sites. Due to this fact the formation energies of Schottky defects in each sixteen alkali halide cluster size of n = 2-6 for the plane surface positions are calculated. The formation energies of Schottky defects in each sixteen alkali halide cluster size of n = 6, with each of the above three types of surface defects, are also calculated. The models of the perfect clusters, with each type of surface defects, are constructed for each sixteen alkali halide cluster by putting additional ions on one of their faces. In this work only {100} surfaces are considered, therefore the additional ions are placed at the corner of a square with alternating arrangements and hence the distance between two nearest neighboring ions of opposite charge is a/2 where a is a lattice constant.

2.1 Calculation of the Schottky Formation Energies for the Plane Surface Position

The Schottky defects are made in each of the sixteen alkali halide cluster size of n = 2-6 by removing the nearest neighboring ions from the bulk and put in the center of the plane surface of the clusters. The multiplication factors, n, and the crystallographic coordinates of the vacancies in the bulk and the surface positions of the deposited ions of these Schottky defect in alkali halide clusters are shown in Tab. 9.

Tab. 9: Multiplication factors, n, and the crystallographic positions of Schottky vacancies and the relocted ions on the surface.

n	Schottky vacancies		Surface positions	
	Na^+	Cl^-	Na^+	Cl^-
2	1/1/1	0.5/1/1	2/0.5/1	2/1/1
3	1/1/1	1.5/1/1	3/1/1	3/1.5/1
4	2/2/2	1.5/2/2	4/2/2	4/1.5/2
5	2.5/2.5/2.5	2/2.5/2.5	5/3/3	5/2.5/3
6	3/3/3	3/3/3.5	6/3/3	6/3/3.5

The formation energies of the Schottky defects in these clusters are calculated and the values are listed in Tab. 10.

Tab. 10: Schottky formation energy in alkali halides clusters with sizes of n = 2-6 for {100} plane surface position, in eV.

Alkali halide	n = 2	n = 3	n = 4	n = 5	n = 6
LiF	9.48645	9.597560	9.789848	9.654742	9.818913
NaF	8.233176	8.342463	8.509604	8.392167	8.534869
KF	7.144555	7.228678	7.373505	7.271747	7.395398
RbF	6.759491	6.866602	7.004175	6.907514	7.024972
LiCl	7.432862	7.521201	7.671888	7.566013	7.694666
NaCl	6.773153	6.854428	6.991757	6.895266	7.012515
KCl	6.070448	6.142195	6.265254	6.178789	6.283854
RbCl	5.804883	5.873438	5.991113	5.908432	6.008900
LiBr	6.944165	7.026349	7.167172	7.068212	7.188400
NaBr	6.391276	6.466874	6.596438	6.505403	6.616023
KBr	5.791156	5.860972	5.978397	5.895893	5.996147
RbBr	5.545353	5.610881	5.723296	5.644312	5.740289
LiI	6.366989	6.443162	6.572251	6.519854	6.591763
NaI	5.901736	6.971420	6.091058	6.043430	6.109143
KI	5.406827	5.471125	5.580740	5.506639	5.597308
RbI	5.203206	5.265455	5.370949	5.296827	5.386896

2.2 Calculations of Schottky Formation Energies for the Ledge Surface Position

The models of the clusters with the ledge type of surface sites are constructed for each sixteen alkali halide cluster size of n = 6 by putting 84 additional ions on one of their faces. These are used as the perfect clusters. The crystallographic coordinates of these additional

ions put on the faces of the clusters are listed in Tab. 11 and shown schematically on Fig. 9. The two nearest neighboring ions are removed from the bulk and placed adjacent to these ledge surface sites in nearest neighbor position and these are the corresponding Schottky defective clusters. The crystallographic coordinates of the Schottky vacancies in the bulk of the clusters are :

Na^+ 3/3/3 ; Cl^- 3/3/3.5

The crystallographic coordinates of the deposited ions on the surface of the clusters are :

Na^+ 6/2.5/3.5 ; Cl^- 6/3/3.5

The the formation energies of these Schottky defects in these clusters are calculated and the values are listed in Tab. 12.

Tab. 11: Crystallographic coordinates of the additional ions put on the faces of the cluster size of n = 6 to make ledge surface position

No.	Ion	crystal. coord.	No.	Ion	Crystal.coord.
1	Na^+	6 0 0	43	Na^+	6 2.5 1.5
2	Cl^-	6 0.5 0	44	Cl^-	6 2 1.5
3	Na^+	6 1 0	45	Na^+	6 1.5 1.5
4	Cl^-	6 1.5 0	46	Cl^-	6 1 1.5
5	Na^+	6 2.0 0	47	Na^+	6 0.5 1.5
6	Cl^-	6 2.5 0	48	Cl^-	6 0 1.5
7	Na^+	6 3.0 0	49	Na^+	6 0 2
8	Cl^-	6 3.5 0	50	Cl^-	6 0.5 2
9	Na^+	6 4.0 0	51	Na^+	6 1 2
10	Cl^-	6 4.5 0	52	Cl^-	6 1.5 2
11	Na^+	6 5.0 0	53	Na^+	6 2 2
12	Cl^-	6 5.5 0	54	Cl^-	6 2.5 2
13	Na^+	6 5.5 0.5	55	Na^+	6 3 2
14	Cl^-	6 5 0.5	56	Cl^-	6 3.5 2
15	Na^+	6 4.5 0.5	57	Na^+	6 4 2
16	Cl^-	6 4 0.5	58	Cl^-	6 4.5 2
17	Na^+	6 3.5 0.5	59	Na^+	6 5 2
18	Cl^-	6 3.0 0.5	60	Cl^-	6 5.5 2
19	Na^+	6 2.5 0.5	61	Na^+	6 5.5 2.5
20	Cl^-	6 2 0.5	62	Cl^-	6 5 2.5
21	Na^+	6 1.5 0.5	63	Na^+	6 4.5 2.5
22	Cl^-	6 1 0.5	64	Cl^-	6 4 2.5
23	Na^+	6 0.5 0.5	65	Na^+	6 3.5 2.5
24	Cl^-	6 0 0.5	66	Cl^-	6 3 2.5
25	Na^+	6 0 1	67	Na^+	6 2.5 2.5
26	Cl^-	6 0.5 1	68	Cl^-	6 2 2.5
27	Na^+	6 1 1	69	Na^+	6 1.5 2.5
28	Cl-	6 1.5 1	70	Cl-	6 1 2.5
29	Na^+	6 2 1	71	Na^+	6 0.5 2.5
30	Cl^-	6 2.5 1	72	Cl^-	6 0 2.5
31	Na^+	6 3 1	73	Na^+	6 0 3
32	Cl^-	6 3.5 1	74	Cl^-	6 0.5 3
33	Na^+	6 4 1	75	Na^+	6 1 3
34	Cl^-	6 4.5 1	76	Cl^-	6 1.5 3
35	Na^-	6 5.5 1	78	Na^+	6 3 3
38	Cl^-	6 5 1.5	80	Cl^-	6 3.5 3
39	Na^+	6 4.5 1.5	81	Na^+	6 4 3
40	Cl^-	6 4 1.5	82	Na^+	6 5 3
42	Cl^-	6 3 1.5	84	Cl^-	6 5.5 3

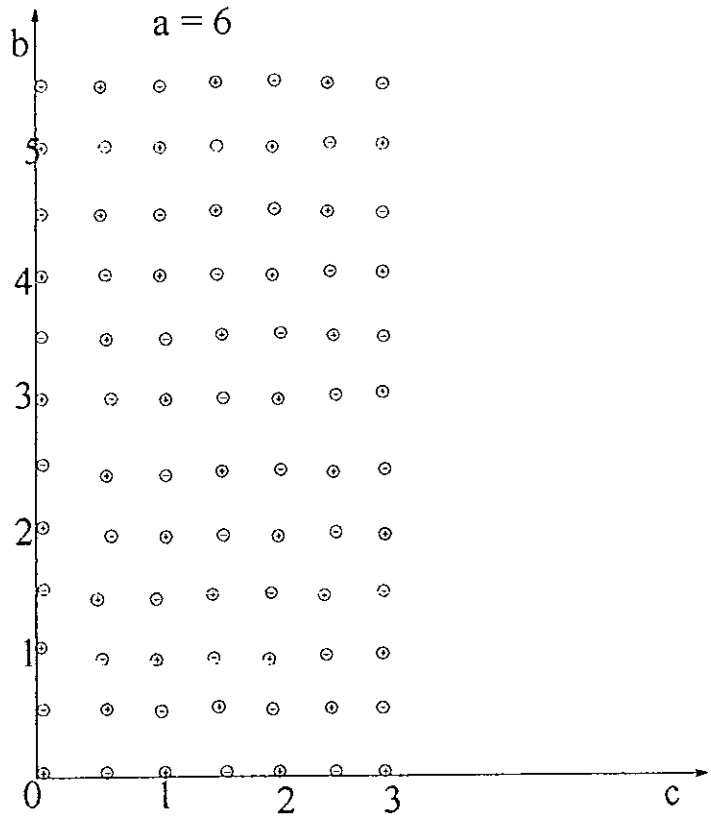


Fig. 9: Schematic representation of additional ions put on the faces of the cluster size of n = 6 to make ledge surface position

Tab. 12: Energies of the perfect, the defect and the corresponding Schottky formation energies of alkali halide cluster size of n = 6 for a ledge surface position, in eV.

Alkali halide	perfect cluster	defect cluster	difference
LiF	11096.88075	11088.64202	8.23873
NaF	9630.886396	9623.708715	7.177681
KF	8357.441108	8351.199647	6.241461
RbF	7906.994867	7901.127894	5.866973
LiCl	8694.667246	8688.238541	6.428705
NaCl	7922.973008	7917.106034	5.866974
KCl	7100.972594	7095.729767	5.242827
RbCl	6790.335008	6781.30050	5.044433
LiBr	8123.011833	8117.02003	5.991803
NaBr	7476.271644	7470.716743	5.554901
KBr	6774.294525	6769.238942	5.055583
RbBr	6486.750417	6481.944492	4.805925
LiI	7447.872996	7442.318096	5.55490
NaI	6903.617597	6898.499599	5.117998
KI	6324.722089	6319.978579	4.743510
RbI	6086.516773	6081.991671	4.525102

2.3 Calculation of Schottky Formation Energies for the Kink Surface Position

The models of the clusters with the kink type of surface sites are constructed for each sixteen alkali halide cluster size of n = 6 by adding 76 ions on one of their faces. These are used as the perfect clusters. The crystallographic coordinates of these ions which are added on

the faces of the clusters to form the kink surface position are listed in Tab. 13 and shown schematically on Fig. 10. The two nearest neighboring ions are removed from the bulk of the clusters and put in these kink surface positions. These are the corresponding Schottky defective clusters. The crystallographic coordinates of the Schottky vacancies in the bulk of the clusters are:

Na^+ 3/3/3 ; Cl^- 3/3/3.5

The crystallographic coordinates of the ions at the surfaces of the clusters are:

Na^+ 6/3/3 ; Cl^- 6/2.5/3

The formation energies of these Schottky defects in these clusters are calculated and the values are listed in Tab. 14.

Tab. 13: Crystallographic coordinates of the additional ions put on the faces of the cluster size of n = 6 to make the kink surface position

No.	Ion	Crystal. coord.	No.	Ion	Crystal. coord.
1	Na^+	6 0 0	39	Na^+	6 4.5 1.5
2	Cl^-	6 0.5 0	40	Cl^-	6 4 1.5
3	Na^+	6 1 0	41	Na^+	6 3.5 1.5
4	Cl^-	6 1.5 0	42	Cl^-	6 3 1.5
5	Na^+	6 2.0 0	43	Na^+	6 2.5 1.5
6	Cl^-	6 2.5 0	44	Cl^-	6 2 1.5
7	Na^+	6 3.0 0	45	Na^+	6 1.5 1.5
8	Cl^-	6 3.5 0	46	Cl^-	6 1 1.5
9	Na^+	6 4.0 0	47	Na^+	6 0.5 1.5
10	Cl^-	6 4.5 0	48	Cl^-	6 0 1.5
11	Na^+	6 5.0 0	49	Na^+	6 0 2
12	Cl^-	6 5.5 0	50	Cl^-	6 0.5 2
13	Na^+	6 5.5 0.5	51	Na^+	6 1 2
14	Cl^-	6 5 0.5	52	Cl^-	6 1.5 2
15	Na^+	6 4.5 0.5	53	Na^+	6 2 2
16	Cl^-	6 4 0.5	54	Cl^-	6 2.5 2
17	Na^+	6 3.5 0.5	55	Na^+	6 3 2
18	Cl^-	6 3.0 0.5	56	Cl^-	6 3.5 2
19	Na^+	6 2.5 0.5	57	Na^+	6 4 2
20	Cl^-	6 2 0.5	58	Cl^-	6 4.5 2
21	Na^+	6 1.5 0.5	59	Na^+	6 5 2
22	Cl^-	6 1 0.5	60	Cl^-	6 5.5 2
23	Na^+	6 0.5 0.5	61	Na^+	6 5.5 2.5
24	Cl^-	6 0 0.5	62	Cl^-	6 5 2.5
25	Na^+	6 0 1	63	Na^+	6 4.5 2.5
26	Cl^-	6 0.5 1	64	Cl^-	6 4 2.5
27	Na^+	6 1 1	65	Na^+	6 3.5 2.5
28	Cl^-	6 1.5 1	66	Cl^-	6 3 2.5
29	Na^+	6 2 1	67	Na^+	6 2.5 2.5
30	Cl^-	6 2.5 1	68	Cl^-	6 2 2.5
31	Na^+	6 3 1	69	Na^+	6 1.5 2.5
32	Cl^-	6 3.5 1	70	Cl^-	6 1 2.5
33	Na^+	6 4 1	71	Na^+	6 0.5 2.5
34	Cl^-	6 4.5 1	72	Cl^-	6 0 2.5
35	Na^+	6 5 1	73	Na^+	6 0 3
36	Cl^-	6 5.5 1	74	Cl^-	6 0.5 3
37	Na^+	6 5.5 1.5	75	Na^+	6 1 3
38	Cl^-	6 5 1.5	76	Cl^-	6 1.5 3

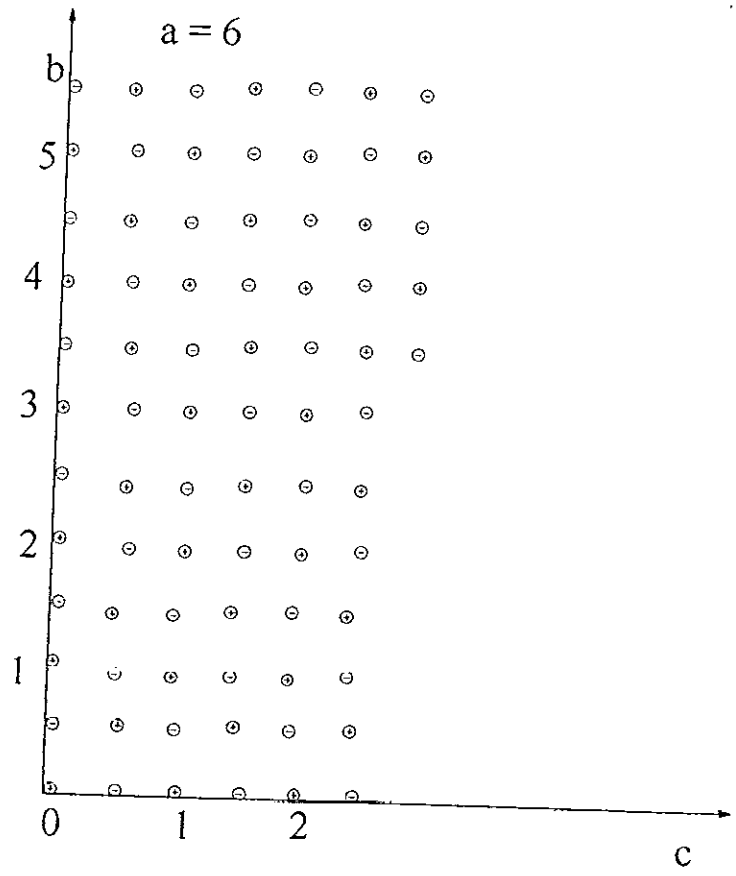


Fig. 10: Schematic representation of addition ions on the faces of the cluster size of n = 6 to make kink surface position

Tab. 14: Energies of the perfect clusters, the defect cluster and the corresponding Schottky formation energies of alkali halide cluster size of n = 6 for a kink surface position, in eV.

Alkali halide	Perfect cluster E/cluster	Defect cluster E/cluster	Difference E/cluster
LiF	11045.70077	11040.39553	5.305240
NaF	9586.447193	9581.828512	4.618681
KF	8318.868879	8314.874344	3.994535
RbF	7870.544735	7866.737444	3.807291
LiCl	8654.597066	8650.415287	4.181779
NaCl	7886.460461	7882.653169	3.807292
KCl	7068.267338	7064.834535	3.432803
RbCl	6759.002945	6755.757386	3.245500
LiBr	8085.563067	8081.693361	3.869706
NaBr	7441.818779	7438.198732	3.620047
KBr	6743.024805	6739.779246	3.245559
RbBr	6456.853819	6453.733088	3.120731
LiI	7413.544961	7409.924913	3.620048
NaI	6871.786146	6868.478172	3.307974
kI	6295.512052	6292.516115	2.995937
RbI	6058.448880	6055.521635	2.927245

2.4 Calculations of Schottky formation energies for a ledge-vacancy surface position.

The models of the clusters with the ledge-vacancy type of surface sites are constructed for each sixteen alkali halide cluster size of n = 6 by putting 82 additional ions on one of their

faces. These are used as the perfect clusters. The crystallographic coordinates of these additional ions put on the faces of the clusters are listed in Tab. 15 and shown schematically on Fig. 11. The two nearest neighboring ions are removed from the bulk and put in these ledge-vacancy surface sites to form the corresponding Schottky defective clusters. The crystallographic coordinates of the Schottky vacancies in the bulk of the clusters are:

Na^+ 3/3/3 ; Cl^- 3/3/3.5

The crystallographic coordinates of deposited ions on the surface of the clusters are:

Na^+ 6/2/3 ; Cl^- 6/3.5/3

The formation energies of these Schottky defects in these clusters are calculated and the values are listed in Tab. 16.

Tab. 15: Crystallographic coordinates of the additional ions put on the faces of the cluster with size of n = 6 to make ledge-vacancy surface position

No.	Ion	crystal. coordinates	No.	Ion	Crystal. coordinates
1	Na^+	6 0 0	43	Na^+	6 2.5 1.5
2	Cl^-	6 0.5 0	44	Cl^-	6 2 1.5
3	Na^+	6 1 0	45	Na^+	6 1.5 1.5
4	Cl^-	6 1.5 0	46	Cl^-	6 1 1.5
5	Na^+	6 2.0 0	47	Na^+	6 0.5 1.5
6	Cl^-	6 2.5 0	48	Cl^-	6 0 1.5
7	Na^+	6 3.0 0	49	Na^+	6 0 2
8	Cl^-	6 3.5 0	50	Cl^-	6 0.5 2
9	Na^+	6 4.0 0	51	Na^+	6 1 2
10	Cl^-	6 4.5 0	52	Cl^-	6 1.5 2
11	Na^+	6 5.0 0	53	Na^+	6 2 2
12	Cl^-	6 5.5 0	54	Cl^-	6 2.5 2
13	Na^+	6 5.5 0.5	55	Na^+	6 3 2
14	Cl^-	6 5 0.5	56	Cl^-	6 3.5 2
15	Na^+	6 4.5 0.5	57	Na^+	6 4 2
16	Cl^-	6 4 0.5	58	Cl^-	6 4.5 2
17	Na^+	6 3.5 0.5	59	Na^+	6 5 2
18	Cl^-	6 3.0 0.5	60	Cl^-	6 5.5 2
19	Na^+	6 2.5 0.5	61	Na^+	6 5.5 2.5
20	Cl^-	6 2 0.5	62	Cl^-	6 5 2.5
21	Na^+	6 1.5 0.5	63	Na^+	6 4.5 2.5
22	Cl^-	6 1 0.5	64	Cl^-	6 4 2.5
23	Na^+	6 0.5 0.5	65	Na^+	6 3.5 2.5
24	Cl^-	6 0 0.5	66	Cl^-	6 3 2.5
25	Na^+	6 0 1	67	Na^+	6 2.5 2.5
26	Cl^-	6 0.5 1	68	Cl^-	6 2 2.5
27	Na^+	6 1 1	69	Na^+	6 1.5 2.5
28	Cl^-	6 1.5 1	70	Cl^-	6 1 2.5
29	Na^+	6 2 1	71	Na^+	6 0.5 2.5
30	Cl^-	6 2.5 1	72	Cl^-	6 0 2.5
31	Na^+	6 3 1	73	Na^+	6 0 3
32	Cl^-	6 3.5 1	74	Cl^-	6 0.5 3
33	Na^+	6 4 1	75	Na^+	6 1 3
34	Cl^-	6 4.5 1	76	Cl^-	6 1.5 3
35	Na^+	6 5 1			
36	Cl^-	6 5.5 1	77	Cl^-	6 2.5 3
37	Na^+	6 5.5 1.5	78	Na^+	6 3 3
38	Cl^-	6 5 1.5			
39	Na^+	6 4.5 1.5	79	Na^+	6 4 3
40	Cl^-	6 4 1.5	80	Cl^-	6 4.5 3
41	Na^+	6 3.5 1.5	81	Na^+	6 5 3
42	Cl^-	6 3 1.5	82	Cl^-	6 5.5 3

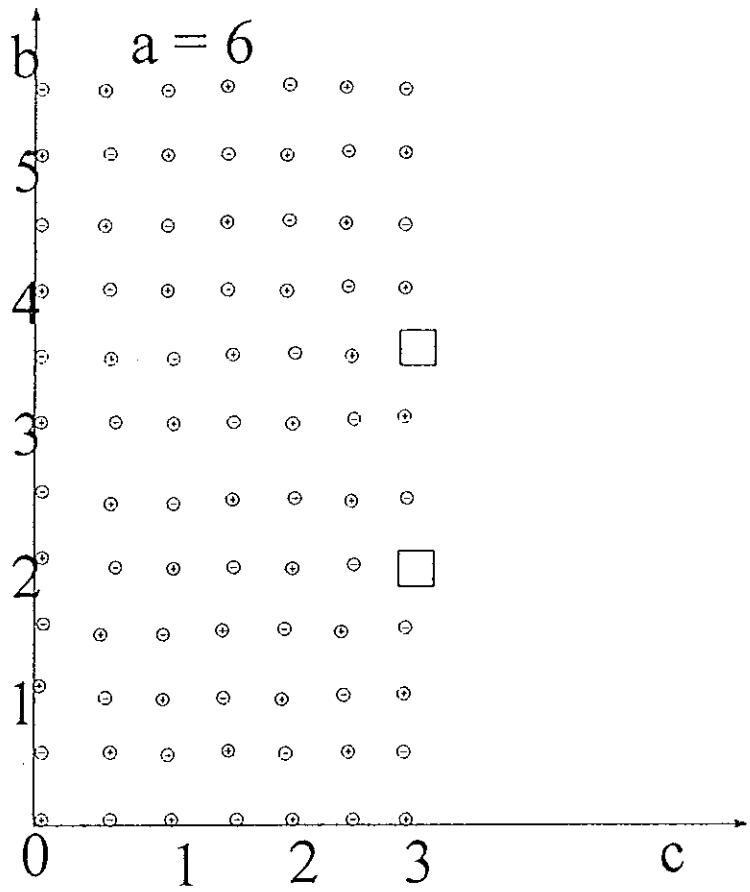


Fig. 11: Schematic representation of additional ions on faces of the cluster size of n = 6 to make ledge-vacancy surface position .

Tab. 16 : Energies of the perfect, the defect cluster and the Schottky formation energies of alkali halide cluster size of $n = 6$ for a ledge-vacancy surface position, in eV.

Alkali halide	Perfect cluster E/cluster	Defect cluster E/cluster	Difference E/cluster
LiF	11077.28256	11079.030170	1.747610
NaCl	9613.847207	9615.345158	1.497951
KF	8342.648845	8344.021967	1.373122
RbF	7893.013995	7894.262287	1.248292
LiCl	8679.313251	8680.686373	1.373122
NaCl	7908.992135	7910.240427	1.248292
KCl	7088.427257	7089.550720	1.123463
RbCl	6778.351475	6779.412523	1.061048
LiBr	8108.656472	8109.967179	1.310707
NaBr	7463.039746	7464.225624	1.185878
KBr	6762.310920	6763.371968	1.061048
RbBr	6475.266129	6476.327177	1.061048
LiI	7434.703513	7435.889391	1.185878
NaI	6891.446748	6892.507796	1.061048
KI	6313.549874	6314.548508	0.998634
RbI	6075.756451	6076.730119	0.973668

As can be seen from Tables 10, 12, 14 and 16 the calculated values of Schottky formation energies are very large for plane and ledge surface positions. The values for the kink and ledge-vacancy surface positions are smaller and in the same order of magnitude with the

Schottky defects. This can explain why experimental values show a large variation of Schottky formation energies.

The theoretical values are calculated by different authors (Tab. 17) using different models and methods. The theoretical values, we found from different literatures, are based up on the fact that the lattice energy per ion pair is required to remove each ion from the bulk, if no relaxation occurs, while half of the lattice energy per ion pair is regained when each of the removed ion is returned to to the surface. Since the electrostatic interaction energy of the ions on the surface involves only a hemisphere, the hemisphere out side the crystal being un occupied by ion. The value of relaxation energy is added if relaxation occurs during Schottky defect formation. Thus the values are calculated by assuming that the removed ions are deposited in the center of the plane surface of the crystals. Inspite of the fact that we consider, only, the coulombic part of Schottky formation energies, E_s^{coul}, the results for kink surface positions are in the same order of magnitude with that of experimental values. This shows that there are large concentration of kink sites on the surface of the crystals. In all alkali halides the calculated values are larger than the corresponding experimental ones, this is obviously due to the polarization and repulsion energy terms of defect crystals which decrease the value of Schottky formation energy. Therefore it is reasonable to say that the value of the formation energy of Schottky defects depends up on the sructure of the surface, which in turn determines the concentration of Schottky defects.

Tab. 17: Experimental and calculated values of Schottky formation energies, E_s in eV

Alkali halide	Theoretical values	Experimental values
LiF	1.24-2.57	2.34-2.68
NaF	2.29-2.97	-
KF	2.04-2.51	2.26-2.31
RbF	1.85-2.26	-
LiCl	1.08-2.56	2.20
NaCl	1.30-2.20	2.18-2.38
KCl	1.75-2.26	2.26-2.31
RbCl	1.98-2.24	-
LiBr	0.86	-
NaBr	1.31-2.01	-
KBr	1.68-2.14	2.3-2.53
RbBr	1.87-2.11	-
LiI	0.64-1.00	1.34
NaI	1.35-1.60	-
KI	1.70-1.92	1.6
RbI	1.75-1.97	-

3. Dependence of Schottky Formation Energies on Separation Distances of the Vacancies

The most simple arrangement of cation and anion vacancies in the bulk of the cluster is in the nearest neighboring position. In this case the distance between the centers of the vacancies is a/2 , where a is a lattice constant. There are also a lot of other arrangements with other larger distances between the vacancies. Here the formation energies of different arrengements

of Schottky defects are calculated to show the effect of the sepation distance of a cation and anion vacancies on the Schottky formation energies and hence propose the most realistic configuration of the Schottky pairs in the crystal structure. To do this the formation energies for Schottky-like defects, for different separation distances of the vacancies, in each sixteen alkali halide cluster size of n = 6 are calculated to study this effect by the following procedure: Six different types of Schottky-like defective clusters are made for each sixteen alkali halide by removing the ions from the sites of different separation distances. The ions removed from the interior of the cluster to infinity. The distances considered between the vacancies, in lattice constant unit are: 0.5, 0.866, 1.118, 1.5, 2.06, and 2.598. The crystallographic coordinates of the Schottky vacancies and the distances, d, between them, in lattice constant units, are listed in Tab. 18. The formation energies for these Schottky-like defects are calculated and the calculated values are listed in Tab. 19 and shown graphically for LiBr, NaCl, RbCl and NaCl clusters on Fig. 12.

Tab. 18 : The crystallographic coordinates and the distances between the vacancies.

Schottky vacancies		d
Na^+	Cl^-	
3/3/3	3.5/3/3	0.50
3/3/3	3.5/3.5/3.5	0.866
3/3/3	4/3/3.5	1.118
3/3/3	4.5/3/3	1.50
3/3/3	4.5/4/4	2.06
3/3/3	4.5/4.5/4.5	2.598

Tab. 19: Formation energies of Schottky defects in alkali halide clusters for n = 6 in dependence on the vacancy separation distances in lattice constant unit, in eV.

Alkali hal.	0.5a	0.866a	1.118a	1.5a	2.06a	2.598a
LiF	17.843477	20.860732	21.794091	22.610244	23.221321	23.53539
NaF	15.843477	18.104775	18.914825	19.623155	20.153501	20.426082
KF	13.438504	14.864137	16.41384	16.110737	17.488734	17.725273
RbF	12.714217	14.864137	15.529194	16.110737	16.546155	16.769945
LiCl	13.980793	16.344886	17.076195	17.715670	18.194464	18.440547
NaCl	12.739915	14.894180	15.560582	16.143300	16.579598	16.803840
KCl	11.418169	13.348932	13.946195	14.468457	14.859489	15.060467
RbCl	10.918654	12.764951	13.336085	14.468457	14.209426	14.401611
LiBr	13.061582	15.270279	15.953465	16.550897	16.998211	17.228115
NaBr	12.021631	14.054437	14.683265	15.233130	15.644829	15.856428
KBr	10.892836	12.734769	13.304553	13.802787	14.175828	14.367559
RbBr	10.430494	12.194246	12.739846	13.216932	13.574140	13.757733
LiI	11.975945	14.001027	14.627466	15.175241	15.585375	15.796171
NaI	11.100832	12.977935	13.558599	14.066346	14.446511	14.641903
KI	10.169934	11.889627	12.421597	12.886766	13.235050	13.414057
RbI	9.786936	11.441865	11.953802	12.401452	12.736620	12.908886

The calculated values show that the formation energies decrease with decreasing the distance between the vacancies (Tab. 19 and Fig. 12). The nearest neighboring anion and cation vacancies are energetically favorable. Therefore an energy is released and thus an energy of the crystal is lowered as the two separated Schottky pairs are approaching to each other which has an effect of partially compensating for their formation energies. Therfore there is an

elecrostaic potential energy of attraction. In general the extra energy released is caused by the Coulomb interaction of the vacancies. Thus each vacancy is surrounded by the atmosphere or the cloud of oppositely charged vacancies.At high temperature and hence at high concentrations of vacancies where the separation distance of the vacancies become small the effective formation energy becomes small. Hence vacancy concetration is greater than that would be expeted by exrapolation from the values of lower temperatures.

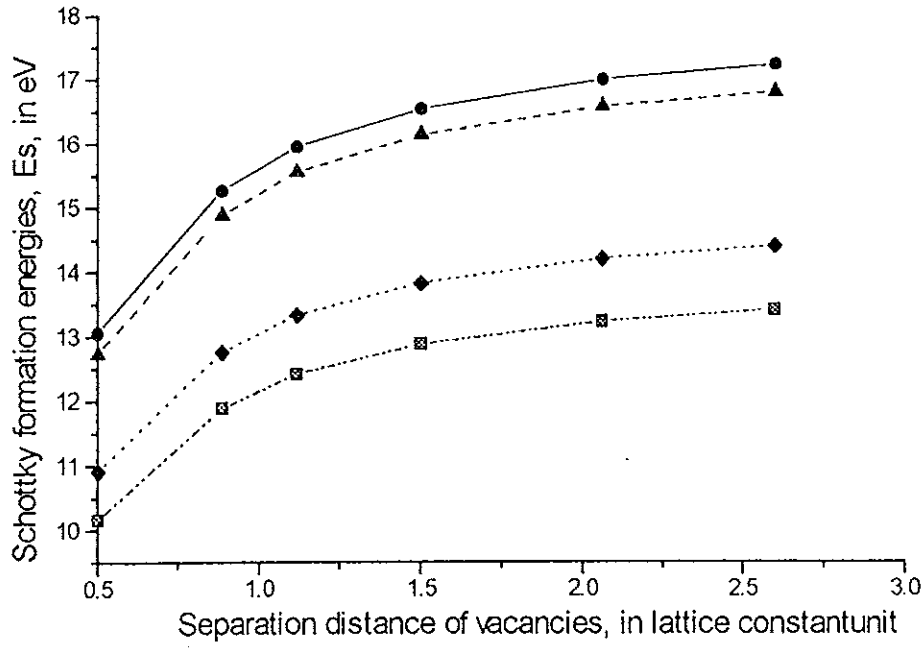


Fig. 12: Variation of Schottky formation energies with separation distance of the vacancies.

4. Diffusion of the Nearest-neighbor Vacancies through the Crystal

A quite realistic picture for the thermal formation of Schottky defects is the generation of the vacancies on the surface and their diffusion into the interior of the crystal. According to this mechnism a vacant lattice site may be formed by the jump of the ion from its initial site in the surface and become an adatom in a neighboring lattice site. This vacant site may then become occupied by another ion when the latter jumps into the vacancy. Successive jumps of this kind thus leads to the diffusion of a vacant lattice sites from the surface into the interior of the crystal. The result would be equivalent to taking an ion somewhere from the interior of the crystal and placing it at the surface.

In this part the formation and the diffusion of the vacancy-pairs by the mechnism described above is shown by the calculation of the formation energies for Schottky defects. To do this the formation energies of vacancy-pairs, for different distances of the vacancy-pairs from the surface, in each sixteen alkali halide cluster size of n = 6 are calculated to explain this diffusion process by the following procedure: six different types of Schottky defective clusters are made for each sixteen alkali halide by removing the nearest neighboring ions from the site of different distances from the surface to infinity. Therefore the first type of Schottky-like defective clusters are made by removing the nearest neighboring ions from the surface to infinity. The second type of Schottky-like defective clusters are made by removing the nearest neighboring ions, with a distance of 0.5a from the surface to infinity and so on. The crystallographic coordinates of the Schottky vacancies and their distances, R, from the surface of the clusters, in lattice constant units, are listed in Tab. 20.

Tab. 20: Crystallographic coordinates of Schottky vacancies and their distances, R, from the surface, in lattice constant unit.

Schottky vacancies		R
Na^+	Cl^-	
3/3/0	3/3.5/0	0
3/3.5/0.5	3/3/0.5	0.5
3/3/1	3/3.5/1	1.0
3/3.5/1.5	3/3/1.5	1.5
3/3/2	3/3.5/2	2.0
3/3.5/2.5	3/3/2.5	2.5

The formation energies of the Schottky-like defectis in these clusters are calculated and the values are listed in Tab. 21 and shown graphically for four clusters on Fig. 13 .

Tab. 21: Schottky formation energies in alkali halide cluster size of $n = 6$ in dependence on the distance from the surface of the clusters, in eV.

Alkali hal.	0	0.5	1.0	1.5	2.0	2.5
LiF	16.899680	17.846847	17.842383	17.837283	17.840813	17.839044
NaF	14.689661	15.512965	15.509085	15.504652	15.507721	15.506184
KF	12.728482	13.441868	13.438505	13.434665	13.437324	13.435992
RbF	12.090929	12.768582	12.765388	12.761740	12.764265	12.763000
LiCl	13.243565	13.985821	13.982322	13.978327	13.981092	13.979707
NaCl	12.069488	12.745941	12.742752	12.739110	12.741632	12.740369
KCl	10.815365	11.421528	11.418671	11.415408	11.417667	11.416535
RbCl	10.342132	10.921772	10.919040	10.915919	10.918079	10.916997
LiBr	12.372210	13.065628	13.062360	13.058627	13.061211	13.059916
NaBr	11.387074	12.025279	12.022271	12.018835	12.021213	12.020021
KBr	10.320180	10.898590	10.895864	10.892750	10.894906	10.893826
RbBr	9.879815	10.433544	10.430934	10.427953	10.430017	10.428983
LiI	11.345318	11.981183	11.978187	11.974763	11.977133	11.975945
NaI	10.514661	11.103971	11.098021	11.101194	11.100218	11.099117
KI	9.633726	10.173663	10.168210	10.171118	10.170223	10.169214
RbI	9.271578	9.791217	9.785970	9.788767	9.787906	9.786936

The calculated values of formation energy of vacancy-pair show that the Schottky-like defect arises with relatively small energy at the surface and becomes larger and constant in the interior of a crystal (Tab. 21 and Fig. 13). The limiting values are the formation energies of Schottky-like defects in the corresponding clusters. The formation energy for the Schottky-like

defect by this mechanism is determined essentially by the energy expended during the first few jumps. Once the vacancies are separated from their sources by several lattice distances, the potential energy of the crystal becomes essentially independent of the lattice sites occupied by the vacancies. There appears to be a greater concentration of vacant sites on, and perhaps near, the the suface of alkali halide crystal than is in the interior. It seems reasonable to assume that surface diffusion is more rapid than bulk diffusion. Hence the surface of the crystal acts as an efficient source for vacancies and thus preserve themal equlibrium concentration. The vacancies which are generated at the surface diffuse in to the interior of the crystals due to the concentration gradient. At equilibrium the Schottky defects distribute uniformly throughout the crystal. Therefore an establishment of the thermal equilibrium of vacancies requires the migration of vacancies from the surface to the interior of the crystal. If the mobility of the vacancies or rather of the ions neighboring the a vacancy is small, this equilibration process requires a very long time.

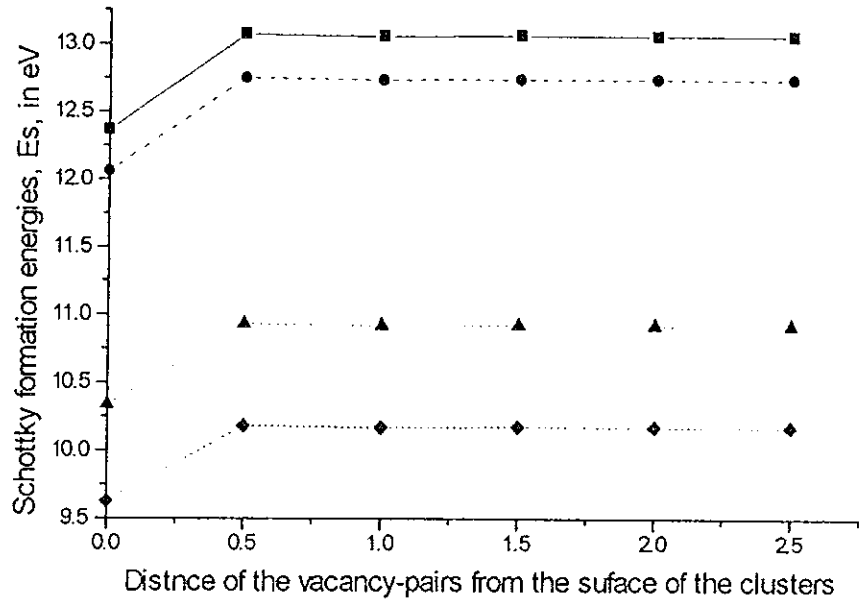


Fig. 13: variation of formation energies of vacancy-pairs with the distance from the surface of the clusters.

5. Diffusion of Cation and Anion Vacancies to Opposite Directions

The conductivity in alkali halides can be explained in terms of the motion of the cation and anion vacancies to opposite directions. The positive ion vacancies with negative effective charge move towards the anode; similarly the negative ion vacancies with positive effective charge move towards the cathode [31-37]. Hence a quite realistic picture of the electrical conductivity of alkali halide clusters, which is caused by Schottky defects, requires the separation of the cation and anion vacancies from each other. Therefore Schottky pairs, with different configuration, requires different effective activation energgies for the conductivity process. However due to the coulomb interaction of vacancies each vacancy in ionic crystal is

Tab. 23: Formation energies of Schottky-like defects, where the vacancies move from the center to the opposite directions in the alkali halide cluster size of n = 6, in eV.

Alkali halide	0.5a	1.5a	2.5a	3.5a	4.5
LiF	17.844361	22.610260	23.567313	23.970652	24.215514
NaF	15.486902	19.613168	20.453783	20.803836	21.016350
KF	13.439170	17.028524	17.749312	18.053080	18.237493
RbF	12.714847	16.110747	16.792683	17.080083	17.254558
LiCl	13.981486	17.715682	18.465556	18.781582	18.973438
NaCl	12.740546	16.143311	16.826629	17.114606	17.289433
KCl	11.418735	14.468467	15.080892	15.338991	15.495681
RbCl	10.919195	13.835510	14.421142	14.667950	14.817785
LiBr	13.062229	16.550908	17.251480	17.546727	17.725968
NaBr	12.022227	15.233140	15.877933	16.149672	16.252642
KBr	10.893376	13.802796	14.387044	14.633269	14.782750
RbBr	10.431011	13.216941	13.776392	14.012165	14.155301
LiI	11.976539	15.175251	15.817593	16.088301	16.252645
NaI	11.101382	14.066356	14.661760	14.912686	15.065021
KI	10.170438	12.886774	13.432250	13.662134	13.801694
RbI	9.787421	12.401460	12.926392	13.147619	13.281924

Tab. 24: Separation energies per lattice constant for a pair of Schottky defects in alkali halide cluster size of n = 6, in eV.

alkali halide	1.5a/0.5a	2.5a/1.5a	3.5a/2.5a	4.5a/3.5a
LiF	4.765899	0.957053	0.403339	0.244862
NaF	4.136266	0.830615	0.350053	0.212524
KF	3.047030	0.720788	0.303768	0.184413
RbF	3.39590	0.681940	0.287396	0.174475
LiCl	3.734196	0.749874	0.316026	0.191856
NaCl	3.402760	0.683318	0.287977	0.174827
KCl	3.049732	0.612425	0.258099	0.156690
RbCl	2.916315	0.585632	0.246808	0.149835
LiBr	3.488679	0.700572	0.295247	0.179241
NaBr	3.210913	0.644793	0.271739	0.164971
KBr	2.909420	0.584248	0.246225	0.149481
RbBr	2.78593	0.559451	0.235773	0.143136
LiI	3.198712	0.642342	0.270708	0.164344
NaI	2.964974	0.595404	0.250926	0.152335
KI	2.716336	0.545476	0.229884	0.139560
RbI	2.614239	0.524932	0.221227	0.134305

The calculated values of Schottky formation energies show that the formation energy decreases as the separation distance of the vacancies decreases(Tab. 23 and Fig. 14). The vacancy-pair has the smallest formation energy of all other arrangements of Schootky pairs. Therefore the energy of separation of a pair of Schottky-like defects is the largest for the

vacancy-pair and the other Schottky-like defects, with the larger separation distances of vacancies. The value of relative extra energy released increases with decreasing the separation distance of vacancies of Schottky-like defects (Tab. 24 and Fig. 15). These values show that the vacancies that are practically present in the association form due to Coulomb interaction of cation and anion vacancies must first acquire the additional energy needed to dissociate themselves from the association before they move to the anode. As a result, the effctive activation energy required for the conductivity of these associated vacancies is greater than the activation energy required for the motion of separated or free cation vacancies. Thus the mobility or the conductivity is less than expected at high concentrations of vacancies, where the separation distance of the vacancies of vacancies becomes small.

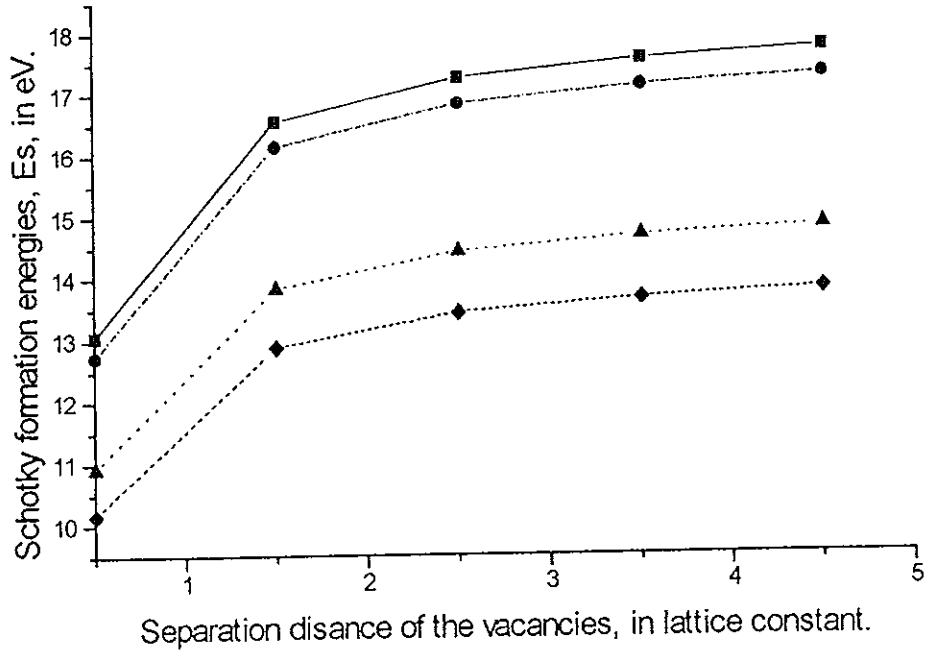


Fig. 14: Variation of Schottky formation energies with one dimensional separation distances of the vacancies.

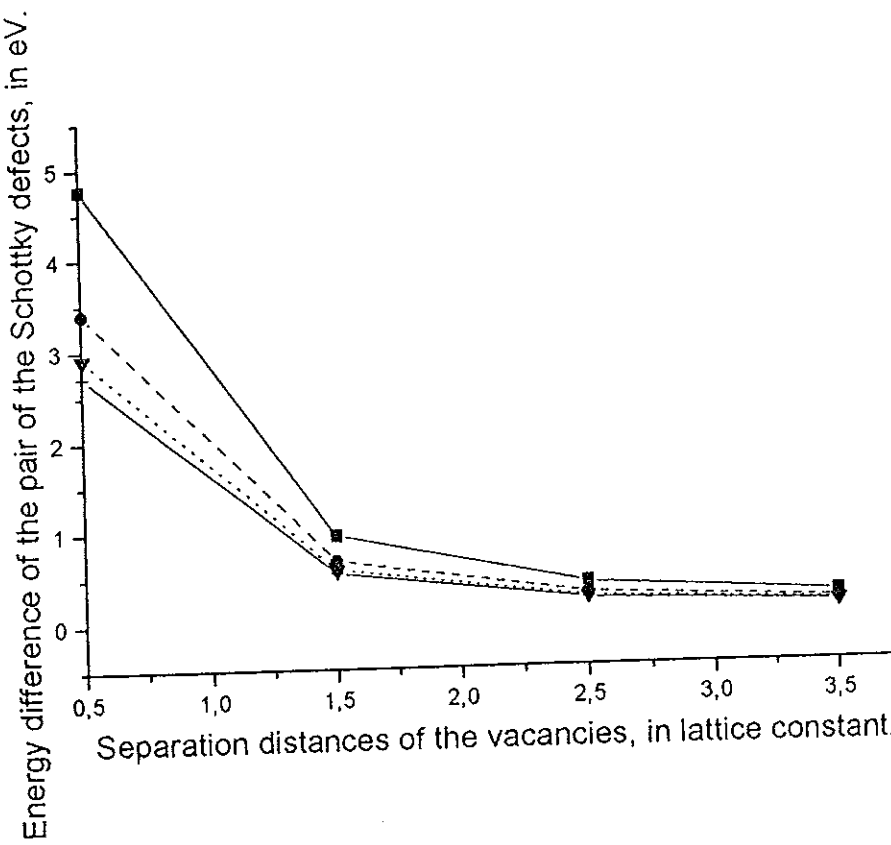


Fig. 15: Energy differences of a pair of Schottky defects separating by a distance of one lattice constant.

V. CONCLUSION

The formation energies of Schottky-like defects in each sixteen alkali halide clusters size of n = 1-6 are calculated and we found that the cluster size with n = 6 can represent well an infinite crystal, with an error of approximately 0.1%.

The effect of different types of surface defects on the formation energies of Schottky defects have been assessed by constructing the models of the perfect clusters with three different types of surface defects. We found that the values of Schottky formation energies for different types of surface sites are quite different and hence the surface structure affects significantly the formation energies of Schottky defects. Therefore the values show that relocated ions favor attachment in kink and ledge-vacancy surface positions. Since the kinks are the most probable surface positions for alkali halides, most of the deposited ions are bound in the kink surface positions and hence the values of the Schottky formation energies for the kink surface positions are reasonable.

The formation energies of Schottky pairs with different relative configurations are calculated and we found that the Schottky formation energy decreases with decreasing separation distance of vacancies. This shows that the formation energy decreases at high temperatures and hence at high concentrations of vacancies where the separation distance of the vacancies becomes small. Therfore the vacancies are not randomly distributed in the solid, each vacancy is surrounded with the cloud of oppositely charged vacancies.

The values of Schottky-like formation energies are calculated by constructing the models of Schottky-like defective clusters that can explain the diffusion and conductivity proceesses in alkali halide crystals. The values show that the surfaces of the crystals are sources and sinks of the vacancies and hence preserves the thermal equlibrium concentration. Additional activation energy is required to dissociate the closely associated cation and anion vacancies and hence the

relation of conductivity and concentration of vacancies deviates from linearity at concentration of vacancies.

Generally the formation energies of Schottky-like defects, with different arrangements of cation and anion vacancies in the bulk and at different surface positions of the deposited ions calculated, in this work show clearly that there is a wide range of possible energies. This can explain why experimental techniques to determine defect energies show a large energy distribution [1].

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APPENDIX

```
program BORN501;
uses
 Crt;

type
 CrystPos= record
  A : Real;
  B : Real;
  C : Real;
  Charge : Integer;
 end;

var
 fRec: file of CrystPos;
 Pos : CrystPos;
 RecDat : String;
 IonN, n : Integer;

procedure SchrT(Fz: Byte; Ox: Byte; Oy: Byte; Txt: string);
 begin
 Textcolor(Fz);
 GotoXY(Ox, Oy);
 Write(Txt);
 end;

begin
  ClrScr;
  TextBackground(LightGray); ClrScr;
  Window(12,7,71,21);
  TextBackground(Red);
  TextColor(Yellow);
  Writeln('
');
  Writeln('                          BORN 501
');
  Writeln('
');
  Writeln('              Generation of a new start cell
');
  Writeln('
');
  Writeln('
');
  Writeln('
');
  Writeln('                        Dr. Veit Marx
');
  Writeln('                          15.10.95
');
  Writeln('
');
  Writeln('                Borland Turbo Pascal 6.0
');
  Writeln('
');
  Readln;
  Window(1,1,80,25);
  TextBackground(1); ClrScr;
  SchrT(14,30,2,'BORN 501 ');
```

```
  SchrT(14,5,5,'This program writes records with the
crystallographic ');
  SchrT(14,5,6,'coordinates a, b and c and the charge in a file.
');
  SchrT(14,5,8,'Please use the Extention .CRY        [RETURN]');
  Readln;
  ClrScr;
  SchrT(14,5,7,'Name of the File with Drive and Extention : ');
  SchrT(14,5,8,' eg A:FILENAME.CRY    : ');
  TextColor(11);
  Readln(RecDat);
  {$I-}
  SchrT(14,5,10,'Number of Ions : ');
  TextColor(11);
  repeat
   Readln(IonN);
  until IOResult=0;
  ClrScr;
  Assign(fRec,RecDat);
  Rewrite(fRec);
  For n:=1 to IonN do begin
   ClrScr;
   SchrT(14,5,2,'Ion number '); TextColor(11); Writeln(n);
   SchrT(14,5,4,'x      : '); TextColor(11);
   repeat
    Readln(Pos.a);
   until IOResult=0;
   SchrT(14,5,7,'y      : '); TextColor(11);
   repeat
    Readln(Pos.b);
   until IOResult=0;
   SchrT(14,5,10,'z      : '); TextColor(11);
   repeat
    Readln(Pos.c);
   until IOResult=0;
   SchrT(14,5,13,'charge : '); TextColor(11);
   repeat
    Readln(Pos.charge);
   until IOResult=0;
   Write(fRec,Pos);
  end;
  {$I+}
  Close(fRec);
  TextColor(14); ClrScr;
end.
```

```
program BORN502;
uses
 Crt;

type
 CrystPos= record
  A : Real;
  B : Real;
  C : Real;
  Charge : Integer;
 end;

var
 f1, f2: file of CrystPos;
 Pos1, Pos2 : CrystPos;
 RecDat1, RecDat2 : String;
 FacN, nx, ny, nz : Integer;

procedure SchrT(Fz: Byte; Ox: Byte; Oy: Byte; Txt: string);
 begin
 Textcolor(Fz);
 GotoXY(Ox, Oy);
 Write(Txt);
 end;

begin
  ClrScr;
  TextBackground(LightGray); ClrScr;
  Window(12,7,71,21);
  TextBackground(Red);
  TextColor(Yellow);
  Writeln('
');
  Writeln('                          BORN 502
');
  Writeln('
');
  Writeln('             Multiplication of the start cell
');
  Writeln('
');
  Writeln('
');
  Writeln('
');
  Writeln('                       Dr. Veit Marx
');
  Writeln('                         15.10.95
');
  Writeln('
');
  Writeln('                Borland Turbo Pascal 6.0
');
  Writeln('
');
  Readln;
  Window(1,1,80,25);
  TextBackground(1); ClrScr;
  SchrT(14,30,2,'BORN 501 ');
```

```
  SchrT(14,5,5,'This program builds a cluster by multiplication of
the start cell ');
  SchrT(14,5,6,'by the factor n in three dimensions. ');
  SchrT(14,5,8,'
[RETURN]');
  ClrScr;
  SchrT(14,5,7,'Name of the Start-Cell-File with Drive and
Extention : ');
  SchrT(14,5,8,' eg A:NAME1.CRY    : ');
  TextColor(11);
  Readln(RecDat1);
  SchrT(14,5,10,'Name of the Cluster-File with Drive and Extention
: ');
  SchrT(14,5,11,' eg A:NAME2.CRY    : ');
  TextColor(11);
  Readln(RecDat2);

  {$I-}
  SchrT(14,5,13,'Factor n : ');
  TextColor(11);
  repeat
   Readln(FacN);
  until IOResult=0;
  ClrScr;
  Assign(f1,ReCDat1);
  Assign(f2,RecDat2);
  Rewrite(f2);
  For nx:=1 to FacN do begin
   For ny:=1 to FacN do begin
    For nz:=1 to FacN do begin
     Reset(f1);
     While not EOF(f1) do begin
      Read(f1,Pos1);
      Pos2.A:=Pos1.A + nx-1;
      Pos2.B:=Pos1.B + ny-1;
      Pos2.C:=Pos1.C + nz-1;
      Pos2.Charge:=Pos1.Charge;
      Write(f2,Pos2);
     end;
     Close(f1);
    end;
   end;
  end;
  {$I+}
  Close(f2);
  TextColor(14); ClrScr;
end.
```

```
program BORN503;
uses
 Crt;

type
 CrystPos= record
  A : Real;
  B : Real;
  C : Real;
  Charge : Integer;
 end;

var
 f1, f2: file of CrystPos;
 Pos1, Pos2 : CrystPos;
 RecDat1, RecDat2 : String;
 LC: Real;

procedure SchrT(Fz: Byte; Ox: Byte; Oy: Byte; Txt: string);
 begin
 Textcolor(Fz);
 GotoXY(Ox, Oy);
 Write(Txt);
 end;

begin
  ClrScr;
  TextBackground(LightGray); ClrScr;
  Window(12,7,71,21);
  TextBackground(Red);
  TextColor(Yellow);
  Writeln('
');
  Writeln('                          BORN 503
');
  Writeln('
');
  Writeln('            Conversion of a crystallographic
');
  Writeln('                   to a physical file
');
  Writeln('
');
  Writeln('
');
  Writeln('                       Dr. Veit Marx
');
  Writeln('                         17.10.95
');
  Writeln('
');
  Writeln('                 Borland Turbo Pascal 6.0
');
  Writeln('
');
  Readln;
  Window(1,1,80,25);
  TextBackground(1); ClrScr;
  SchrT(14,30,2,'BORN 503 ');
```

```
  SchrT(14,5,5,'This program converts a file with ion positions in
crystallographic ');
  SchrT(14,5,6,'coordinate system into a file with ion positions
in physical coordinate ');
  SchrT(14,5,7,'system with the unit Angstrom.');
  SchrT(14,5,8,'Only for cubic system!');
  SchrT(14,5,9,'
[RETURN]');
  ClrScr;
  SchrT(14,5,7,'Name of the Crystallographic File with Drive and
Extention : ');
  SchrT(14,5,8,' eg A:NAME1.CRY    : ');
  TextColor(11);
  Readln(RecDat1);
  SchrT(14,5,10,'Name of the Physical File with Drive and
Extention : ');
  SchrT(14,5,11,' eg A:NAME2.PHY    : ');
  TextColor(11);
  Readln(RecDat2);

  {$I-}
  SchrT(14,5,13,'Lattice constant in Angstrom : ');
  TextColor(11);
  repeat
   Readln(LC);
  until IOResult=0;
  ClrScr;
  Assign(f1,ReCDat1);
  Assign(f2,RecDat2);
  Reset(f1);
  Rewrite(f2);
  While not EOF(f1) do begin
   Read(f1,Pos1);
   Pos2.A:=Pos1.A*LC;
   Pos2.B:=Pos1.B*LC;
   Pos2.C:=Pos1.C*LC;
   Pos2.Charge:=Pos1.Charge;
   Write(f2,Pos2);
  end;
  {$I+}
  Close(f1);
  Close(f2);
  TextColor(14); ClrScr;
end.
```

```
program BORN504;
uses
 Crt;

type
 CrystPos= record
  A : Real;
  B : Real;
  C : Real;
  Charge : Integer;
 end;

var
 f1, f2: file of CrystPos;
 Pos1, Pos2 : CrystPos;
 RecDat1, RecDat2 : String;
 NewX, NewY, NewZ: Real;
 NewCharge, n, DelN, ChaN, MenuN : Integer;
procedure SchrT(Fz: Byte; Ox: Byte; Oy: Byte; Txt: string);
 begin
 Textcolor(Fz);
 GotoXY(Ox, Oy);
 Write(Txt);
 end;

begin
  ClrScr;
  TextBackground(LightGray); ClrScr;
  Window(12,7,71,21);
  TextBackground(Red);
  TextColor(Yellow);
  Writeln('
');
  Writeln('                          BORN 504
');
  Writeln('
');
  Writeln('            Modification of a physical file
');
  Writeln('
');
  Writeln('
');
  Writeln('
');
  Writeln('                       Dr. Veit Marx
');
  Writeln('                         18.10.95
');
  Writeln('
');
  Writeln('               Borland Turbo Pascal 6.0
');
  Writeln('
');
  Readln;
  Window(1,1,80,25);
  TextBackground(1); ClrScr;
  SchrT(14,30,2,'BORN 504 ');
```

```
  SchrT(14,5,5,'This program changes single ion positions to put
defects ');
  SchrT(14,5,6,'or additional charges in the cluster.');
  SchrT(14,5,9,'
[RETURN]');
  ClrScr;
  SchrT(14,5,7,'Name of the Start File with Drive and Extention :
');
  SchrT(14,5,8,' eg A:NAME1.PHY    : ');
  TextColor(11);
  Readln(RecDat1);
  SchrT(14,5,10,'Name of the modified File with Drive and
Extention : ');
  SchrT(14,5,11,' eg A:NAME2.PHY    : ');
  TextColor(11);
  Readln(RecDat2);
  ClrScr;
  SchrT(14,30,2,'MODIFICATION');
  SchrT(14,5,5,'1  Insert of an additional ion position');
  SchrT(14,5,7,'2  Delete of an ion position');
  SchrT(14,5,9,'3  Change of an ion position                : ');
  {$I-}
  TextColor(11);
  repeat
   Readln(MenuN);
  until IOResult=0;
  ClrScr;
  Assign(f1,RecDat1);
  Assign(f2,RecDat2);
  If MenuN=1 then begin
   Reset(f1);
   Rewrite(f2);
   While not EOF(f1) do begin
    Read(f1,Pos1);
    Write(f2,Pos1);
   end;
   TextBackground(2); ClrScr;
   SchrT(15,30,2,'NEW ION POSITION');
   SchrT(15,5,5,'X : ');
   repeat
    Readln(Pos2.A);
   until IOResult=0;
   SchrT(15,5,7,'Y : ');
   repeat
    Readln(Pos2.B);
   until IOResult=0;
   SchrT(15,5,9,'Z : ');
   repeat
    Readln(Pos2.C);
   until IOResult=0;
   SchrT(15,5,11,'Charge : ');
   repeat
    Readln(Pos2.Charge);
   until IOResult=0;
   Write(f2,Pos2);
   Close(f1);
   Close(f2);
  end;
  If MenuN=2 then begin
```

```
 Reset(f1);
 Rewrite(f2);
 TextBackground(2); ClrScr;
 SchrT(15,30,2,'DELETE');
 SchrT(15,5,5,'Number of position to delete : ');
 repeat
  Readln(DelN);
 until IOResult=0;
 n:=0;
 While not EOF(f1) do begin
  Read(f1,Pos1);
  n:=n+1;
  If n <> DelN then Write(f2,Pos1);
 end;
 Close(f1);
 Close(f2);
end;

If MenuN=3 then begin
 Reset(f1);
 Rewrite(f2);
 TextBackground(2); ClrScr;
 SchrT(15,30,2,'CHANGE OF ION POSITIONS');
 SchrT(15,5,5,'Number of position to change : ');
 repeat
  Readln(ChaN);
 until IOResult=0;
 SchrT(15,5,7,'new X : ');
 repeat
  Readln(NewX);
 until IOResult=0;
 SchrT(15,5,9,'new Y : ');
 repeat
  Readln(NewY);
 until IOResult=0;
 SchrT(15,5,11,'new Z : ');
 repeat
  Readln(NewZ);
 until IOResult=0;
 SchrT(15,5,13,'new charge : ');
 repeat
  Readln(NewCharge);
 until IOResult=0;
 n:=0;
 While not EOF(f1) do begin
  Read(f1,Pos1);
  n:=n+1;
  If n = ChaN then begin
   Pos2.A:=NewX;
   Pos2.B:=NewY;
   Pos2.C:=NewZ;
   Pos2.Charge:=NewCharge;
   Write(f2,Pos2);
  end;
  If n <> ChaN then Write(f2,Pos1);
 end;
 Close(f1);
 Close(f2);
end;
```

```
 {$I+}
 TextBackground(1);
 TextColor(14); ClrScr;
end.
```

```
program BORN505;
{$N+}
uses
 Crt;
type
 CrystPos = record
  A : Real;
  B : Real;
  C : Real;
  Charge : Integer;
 end;

var
 f1: file of CrystPos;
 Pos : CrystPos;
 RecDat, AsciiDat: String;
 fText : Text;
 n, m, p : Integer;
 ArA, ArB, ArC: Array[1..2000] of Real;
 ArCharge :Array[1..2000] of Integer;
 AtomN: Integer;
 ka1, kb1, kc1, ka2, kb2, kc2, charge1, charge2: Real;
 r, Abst, Summe, Ec, Er, Ergebnis, Cluster: real;
 yn: char;
 k: Integer;

procedure SchrT(Fz: Byte; Ox: Byte; Oy: Byte; Txt: string);
 begin
 Textcolor(Fz);
 GotoXY(Ox, Oy);
 Write(Txt);
 end;

begin
  ClrScr;
  TextBackground(LightGray); ClrScr;
  Window(12,7,71,21);
  TextBackground(Red);
  TextColor(Yellow);
  Writeln('
');
  Writeln('                              BORN 505
');
  Writeln('
');
  Writeln('           Calculation of the Madelung energy
');
  Writeln('
');
  Writeln('
');
  Writeln('
');
  Writeln('                              Veit Marx
');
  Writeln('                              26.10.1995
');
  Writeln('
');
```

```
  Writeln('
');
  Writeln('                Borland  TURBO PASCAL 6.0
');
  Readln;
  Window(1,1,80,25);
  TextBackground(1); ClrScr;
  SchrT(14,30,2,'BORN 505 ');
  SchrT(14,5,5,'This program calculates the Madelung energy of a
cluster ');
  SchrT(14,5,6,'in a physical file.');
  SchrT(14,5,7,'Input data and results are written in an ASCII-
File.');
  SchrT(14,5,8,'
RETURN  ');
  Readln;
  ClrScr;
  SchrT(14,30,2,'INPUT DATA');
  SchrT(14,5,4,'Name of the physical file with drive and extention
: ');
  SchrT(14,5,5,'  eg A:NAME1.PHY : '); TextColor(11);
  Readln(RecDat);
  SchrT(14,5,7,'New ASCII-File ?  y/n  : '); TextColor(11);
  Readln(YN);
  SchrT(14,5,9,'Name of the ASCII file with drive and extention :
');
  SchrT(14,5,10,'  eg A:NAME2.ASC : '); TextColor(11);
  Readln(AsciiDat);
  ClrScr;
  Assign(fText,AsciiDat);
  If yn='y' then Rewrite(fText);
  If yn='n' then Append(fText);
  Writeln(fText,'BORN 505 Madelung energy calculation ');
  Writeln(fText,RecDat);
  Assign(f1,RecDat);
  Reset(f1);
  m:=0;      k:=0;
  While not EOF(f1) do begin
   Read(f1,Pos);
   m:=m+1;
   ArA[m]:=Pos.A;
   ArB[m]:=Pos.B;
   ArC[m]:=Pos.C;
   ArCharge[m]:=Pos.Charge;
   AtomN:=m;
  end;
  Close(f1);
  Summe:=0;
  For m:=1 to AtomN do begin
   ka1:=ArA[m];
   kb1:=ArB[m];
   kc1:=ArC[m];
   charge1:=ArCharge[m];
   For p:=1 to AtomN do begin
    ka2:=ArA[p];
    kb2:=ArB[p];
    kc2:=ArC[p];
    charge2:=ArCharge[p];
```

```
    Abst:=(ka2-ka1)*(ka2-ka1)+(kb2-kb1)*(kb2-kb1)+(kc2-kc1)*(kc2-
kc1);
    If Abst>0.01 then begin
     Abst:=SQRT(Abst);
     r:=Abst*1E-10;
     Ec:= (charge1*charge2*2.3070794E-28)/r;
     Summe:=Summe+Ec;
     k:=k+1;
     Cluster:=Summe/2;
    end;
   end;
  end;
  Ergebnis:=-(Summe*6.02205E23)/(AtomN);
  Write('Coulomb-Energy in J/mol NaCl '); Writeln(Ergebnis);
  Write('Coulomb-Energy in J/Cluster  '); Writeln(Cluster);
  Write(fText,'Coulomb-Energy in J/mol : ');
Writeln(fText,Ergebnis);
  Write(fText,'Coulomb-Energy in J/Cluster: ');
Writeln(fText,Cluster);
  Writeln(fText,' ');
  Readln;
  Close(fText);
end.
```

```
program BORN506;
uses
 Crt;

type
 CrystPos= record
  A : Real;
  B : Real;
  C : Real;
  Charge : Integer;
 end;

var
 fRec: file of CrystPos;
 Pos : CrystPos;
 RecDat : String;
 IonN, n : Integer;

procedure SchrT(Fz: Byte; Ox: Byte; Oy: Byte; Txt: string);
 begin
 Textcolor(Fz);
 GotoXY(Ox, Oy);
 Write(Txt);
 end;

begin
  ClrScr;
  TextBackground(LightGray); ClrScr;
  Window(12,7,71,21);
  TextBackground(Red);
  TextColor(Yellow);
  Writeln('
');
  Writeln('                          BORN 506
');
  Writeln('
');
  Writeln('                          Show File
');
  Writeln('
');
  Writeln('
');
  Writeln('
');
  Writeln('                        Dr. Veit Marx
');
  Writeln('                          15.10.95
');
  Writeln('
');
  Writeln('                 Borland Turbo Pascal 6.0
');
  Writeln('
');
  Readln;
  Window(1,1,80,25);
  TextBackground(1); ClrScr;
  SchrT(14,30,2,'BORN 506 ');
```

```
  SchrT(14,5,5,'This program shows the records of a
crystallographic or of a');
  SchrT(14,5,6,'physical file on monitor. ');
  SchrT(14,5,8,'
[RETURN]');
  Readln;
  ClrScr;
  SchrT(14,5,7,'Name of the File with Drive and Extention : ');
  SchrT(14,5,8,' eg A:FILENAME.CRY    : ');
  Readln(RecDat);
  ClrScr;
  SchrT(14,1,1,'No    a or x          b or y          c or z
charge    [RETURN]');
  Writeln;
  TextColor(11);
  Assign(fRec,RecDat);
  Reset(fRec);
  n:=0;
  While not EOF(fRec) do begin
   n:=n+1;
   Read(fRec,Pos);
   Write(n);
   Write('     ');
   Write(Pos.A:8:6);
   Write('         ');
   Write(Pos.B:8:6);
   Write('        ');
   Write(Pos.C:8:6);
   Write('    ');
   Write(Pos.Charge);
   Readln;
  end;
  Close(fRec);
  TextColor(14); ClrScr;
 end.
```

This thesis has been corrected and modified as recommended by members of the examining board. I certify that this is the final version of the thesis.

Advisor's Name Dr. Veit Marx

Signature