CALCULATION OF SCHOTTKY DEFECT FORMATION ENERGIES IN ALKALI HALIDES BY NUMERICAL SUMMATION OF COULOMB, REPULSIVE AND VAN DER WAALS INTERACTIONS

A Thesis

Submitted to the School of Graduate Studies

Addis Ababa university

In partial fulfillment of theyequirements

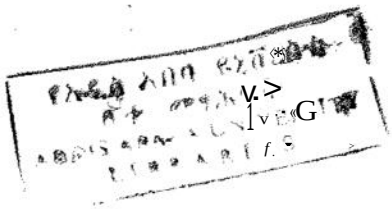
for the Degree of Master of Science

in Chemistry

BY

SISAY CHANYALEW

JUNE 2000



ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

CALCULATION OF SCHOTTKY DEFECT FORMATION ENERGIES IN ALKALI HALIDES BY NUMERICAL SUMMATION OF COULOMB, REPULSIVE AND VAN DER WAALS INTERACTIONS

BY

ISISAY CHANYALEW

DEPARTMENT OF CHEMISTRY

FACULTY OF SCIENCE

APPROVED BY:

Dr. V. Marx
Advisor

Dr. V. J. T. Raju
Examiner

Dr. Yonas Chebude
Examiner

ACKNOWLEDGMENT

I would like to express my deep gratitude to my advisor Dr. V. Marx for arousing my interest iti the area of solid state chemistry and for his invaluable advice and material support during the entire period.

I wish to express my thanks to all the staff members of the department of chemistry in particular to Dr. Wendimagegne Mamo for his friendly assistance.

I am also thankful to my friends in CSA, Ato Terefe Getaneh, Ato Assefa Dagne and my brother and my parents.

I would like to thank *ETHIOPIAN AIR LINES* for granting me the opportunity to study to my second degree.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Schottky formation energy of some sixteen alkali halides with NaCl structure and cluster size of 1728 ions was calculated using numerical summation of Coulomb, repulsive and Van der Waals interaction. The energy difference between a cluster with a point defect and the corresponding perfect cluster represents the formation energy of defects. It could be shown that the structure of vacancies in the bulk and the surface position of the removed ion have a strong influence on the formation energy Schottky defects.

1. INTRODUCTION:

The occurrence of ionic conductance and of self and impurity diffusion in classical ionic conductors, such as alkali halides first suggested the existence of point defects in these crystals [1]. Schottky type point defects are the most common type of defects in all alkali halides. They are stoichiometric defects which occur when a pair of vacant sites, an anion vacancy and a cation vacancy, are formed [2]. Theoretical calculation of defect properties are veiy useful for predicting those properties of defects which are yet uncertain experimentally. They help to determine which models can reasonably be used in the interpretation of experimental results.

The formation energy of Schottky defects can be considered as the energy required for the movement of ion pairs from the bulk to the surface of the crystal. This energy in ionic solids includes components like Coulomb interaction of charges, repulsive interactions due to overlap of electron cloud, van der Waals forces which arise from the interaction of induced electronic dipole moments, zero point energy from the lowest occupied vibrational mode, vacancy pair interactions, polarization effects and surface structure effects.

Quantitative evaluation of the formation energy is used in the control of defect concentration, rate of defect migration and other properties in the intrinsic range. The experimental methods used to study defect properties are measurement of some convenient properties like lattice parameters, density, electrical and thermal properties and spectroscopic techniques. Ionic conductivity measurement of alkali halides are often used to evaluate Schottky formation energy.

Different theoretical methods and models have been reported for the calculation of defect energies in alkali halides. Two different types of models, the polarizable point ion model and the shell model, are widely used by different workers. In both models the modified Mott-Littleton [3] method is used to evaluate defect formation energy. However the theoretical methods employed so far are not efficient methods to treat different vacancy configurations in the bulk and the effect of surface structure on the removed ions in the surface.

In recent research work the possibility to calculate the electrostatic energies [4,5] by numerical summation of the coulomb interaction using modern tecliniques 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 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 Schottky formation energies of some sixteen alkali halides having the NaCl structure are evaluated using this method by considering the Coulomb, repulsive and van der Waals interactions. These results are compared with other theoretical works which uses the modified Mott-Littleton approach. The effect of surface structure, defect configuration and vacancy diffusion on the formation energy of Schottky defects, are also considered.

2. LITERATURE REVIEW

2.1 **Defect studies in alkali halides**: The simple ciystal structure of alkali halides provides an environment of high symmetry for impurities and native defects, making defect structure determination easier experimentally and simplifies theoretical calculations. Often defect-related phenomena have been studied in alkali halides with the hope that they could first be understood in these materials and that this understanding would lead to insight into defect properties of more complicated ionic crystals [6].

2.2 **Experimental methods of defect studies**: A small concentration of impurities or native defects can dominate many important bulk properties like electrical conductivity, optical and mechanical properties [7]. The experimental tools used to study such property variations include measurement of matter transport parameters like conductivity and diffusion parameters, measurement of density or macroscopic dimension changes and spectroscopic techniques. Macroscopic expansion or density measurements are direct way of studying defect concentration. However the liigh temperature involved often makes this a difficult technique to apply to ionic crystals [8].

Electrical conduction in alkali halides is known to be primarily ionic. The conductivity as well as the self diffusion can be explained by the motion of cation and anion vacancies in the lattice. The magnitude of the ionic conductivity depends on the number of vacancies present, which in turn depends very much on the purity and thermal history of the crystals [8].

Ill the intrinsic conductivity region the number of vacancies, n, is temperature dependent and is given by $n = Nexp\left(\frac{-E_J}{2RT_J}\right)$, where N is the total number of ionic sites. The conductivity measured hi the this region is related to the activation energy for the formation of one mole of Schottky defect (Ef) and the activation energy for migration of vacancies ($E_{„}$) by the relation $\sigma \simeq A\exp\left(-\frac{E_{„} + Ej\ 12}{RT}\right)$ where the pre-exponential factor A, includes several constants, including the vibrational frequency of the potentially mobile ions [9]. Some of the values of Schottky formation energy obtained by different workers [10] are listed in table bellow.

Table 1. Experimentally evaluated Schottky defect energies.

Halide	Ef (eV)	Halide	Ef (eV)	Halide	Ef (eV)
LiF	2.68,2.34	NaBr	1.68, 1.72	RbF	-
LiCl	2.12	Nal	2.27	RbCl	-
LiBr	1.80	KF	2.64	RbBr	-
Lil	1.34	KCl	2.49, 2.30, 2.59	Rbl	2.1
NaF	2.42	KBr	2.39, 2.53		
NaCl	2.20, 2.4-2.5	KI	2.21		

Although the conductivity of different alkali halides have been measured many times and in many different laboratories, there is not a good agreement on the value of formation energy of Schottky defects. The experimental methods do not consider surface structure and vacancy configuration effects during conductivity measurements.

The variation in the above Schottky formation energy values is therefore the possibility of the presence of different Schottky defect configurations, surface structure effect and the presence of other types of point defects in lower concentration. Most of what is known about point defects on ionic surfaces concerns electronic structure, and most of that has been obtained from electron spectroscopies such as ultraviolet photoelectron spectroscopy (UPS) and electron energy loss spectroscopy (EELS) [11].

2.3 Theoretical study of defect energies: Theoretical calculations are very useful for predicting which models can reasonably be used in the interpretation of experimental results. Most calculations of defect properties are made for a static lattice. The basis of earlier methods is to setup the energy function of the solid, describing each ion by its displacement from its perfect lattice position and its electronic dipole moment and then minimizing the energy with respect to these parameters [12]. The function contains I) electrostatic terms coming from interaction among the ionic charges and dipoles, ii) short range repulsion coming from ionic overlap iii) self energies of polarization and iv) van der Waals attractions.

Different theoretical methods and models have been reported by different worker for the calculation of defect energies in alkali halides. One of the basic questions in such work is how accurately do the calculated results represent the model employed. The question was specially pertinent for charged defects in view of the long-range polarization field to which they give rise. To enable explicit calculations to be carried out, it is necessary to divide the crystal into two regions.

The method previously employed by most workers is an extended Mott-Littleton [13] approach of dividing the crystal into a small inner region containing the defect (region I) and the rest of the crystal (region II) . The object of this is to choose region I large enough so that one can describe the displacement and polarization of the ions in region II in a harmonic approximation. This provides the link with the dielectric, elastic, and lattice dynamical properties of the crystal. The inner region is energy minimized tlnough modeling of the lattice relaxation by interatomic potentials until equilibrium is acliieved [14].

The error in such calculated results arise from the limitations of the model used to represent the ciystal. Boswarva and Lidiard [15] made comprehensive study of how the Schottky energy of an alkali halide changed as the interionic potential was altered. But they did not consider the interaction between the two regions and van der Waals forces. Scholz [16] in his calculation increased the size of region I and considered the interaction of ions in region I with those in region II and van der Waals interactions. His values for Schottky formation energies are too low compared with the experimental data. Further for lithium halides the approaches led to

Table 2. Theoretical result of Schottky formation energy (eV) from different approaches

Interaction considered	[15]	[16]	[17]	[19]	[20]	[10]
Coulomb	x	x	x	x	x	X
Born repulsion	x	x	x	x	x	x
Van der Waals		x	x	x	x	x
Polarization	x	x	x	x	x	x
Relaxation	x	x	x	x	x	x
Model	P.I	P.I	S.M	P.I	P.I	S.M
LiF	1.904			2.71	2.72	2.66
LiCl	1.244				1.72	2.16
LiBr	1.060				1.53	2.01
LiI	0.766				1.29	-
NaF	2.517			3.23	3.24	2.98
NaCl	1.945	1.56	2.227	2.27	2.48	2.54
NaBr	1.754	1.65	2.001	2.23	2.23	2.40
NaI	1.465			1.84	1.87	2.14
KF	2.211				2.72	2.52
KCl	2.105	1.90	2.341	2.50	2.57	2.56
KBr	1.985	1.96	2.247	2.42	2.46	2.45
KI	1.802			2.29	2.28	2.34
RbF	1.995				2.34	2.42
RbCl	2.097			2.44	2.46	2.44
RbBr	1.979			2.37	2.41	2.46
RbI	1.848			2.29	2.29	2.30

P.I and S.M refer to the point ion and shell models used, respectively.

The area of interest in any of these calculations is how accurately do the calculated results represent the model employed. For this a number of modifications and approaches have been made as shown above. The major emphasis for modifications were made on the type of model, method of approximations, derivation of repulsive parameters and potential models used.

The symmetry possessed by the infinite periodic arrangement of atoms in perfect crystalline solids makes the calculation of the bulk structure relatively forward. The existence of even a perfect surface also destroys some of the crystals symmetry, and theoretical methods for calculating the electronic and geometric properties of perfect surfaces are less mature than their bulk counter parts [11]].

In both the above theoretical and experimental values the influence of defect configurations and surface structure on Schottky formation energy were not considered. The Schottky formation energy were obtained by calculating the cation and anion vacancy formation energy separately i.e. energy required to remove an ion to infinity and the cohesive energy per ion pair ($E_c = W_1 + E_+ + E_-$ where W_1 is the cohesive energy of ion pairs, E_+ and E_- are the energy required to take an ion to infinity) [21]. In these cases the single defect considered separately will cause significant polarization. All the methods that have been used earlier could not be used to deal with defect configuration. For this aspect of study numerical summation of interionic interaction, which is employed in this work, is relevant. In numerical summation near neighbor Schottky pair defects can be considered and this will avoid the polarization effect as it will be neutralized by the ion pairs.

Numerical summation method was first employed in this field by Marx [5,22] for the calculation of the Madelung contribution to lattice energy. Schottky formation energy of alkali halides was also calculated using this method for ions interacting via Coulombic interactions [4]. Further improvement of the Schottky formation energy obtained are made in this work by including repulsive and van der Waals interactions.

3. METHODOLOGY AND COMPUTATIONAL DETAILS

For the evaluation of interatomic potentials one has to first develop potential model. An interatomic potential model is a mathematical representation of the potential energy of the system as a function of particle coordinates [23].

The total potential $U(r_{ij})$ in ionic solids is normally decomposed into Coulombic and non-Coulombic components. $U(r_{ij}) = q_i q_j e^2/4p\epsilon_o r_{ij} + V_{ij}(r_{ij})$ Were q and q are the charges on the ions I and j, and $V_{ij}(r_{ij})$ is usually referred to as the 'short-range' potential.

A number of analytical functions have been used for the evaluation of $V_{ij}(r_{ij})$, but the most popular in ionic crystal simulations, has been the Buckingham potential. $V(r)= Ae^{-r/\rho} - Cr^{-6}$ in which it is tempting to associate the attractive r^{-6} term with genuine dispersion force which includes induced dipole-induced dipole interactions. In practice, this term will normally include contributions from other attractive forces including small covalent terms. There is; however, no ambiguity about the interpretation of the exponential repulsion term which describes the 'Pauli repulsion', which comes in to play when atomic charge clouds overlap.

The general formula used in these calculations is,

$$U= \tfrac{1}{2}(\Sigma q_i q_j e^2/4\pi\epsilon_o r_{ij} + \Sigma A_{ij}\exp(-r_{ij}/\rho_{ij}) - \Sigma C_{ij}/r_{ij}^{6})$$

Where q_i, q_j are the point charges on the ion I and j, $e = 1.602 \times 10^{-19}$ C, $\epsilon_o = 8.859 \times 10^{-12}$ $C^2J^1m^{-1}$,

A_{ij}, ρ_{ij} and C_{ij} are short-range interaction parameters to be determined experimentally. The defec

formation energies are calculated by subtracting the lattice energy of the modified or defect cluster from the energy of the perfect cluster.

3.1 Numerical constants: As discussed above one of the source of variation in the calculated result lies in the selection of constants. The repulsive parameters used are taken from theoretical sources which uses the shell model or cases which consider both the dielectric and compressibility factors [24]. The lattice constants used were taken from [25]. Van der Waals parameters were calculated using Slater Kirkwood formula [26] except the van der Waals coefficient of for iodide-iodide case which were taken from Mayer [27].

$$C_{ij} = \left(\frac{3}{2}\sqrt{\frac{e^2h^2}{4\pi^2 m}}\right)\left(\frac{\alpha_i\alpha_j}{\sqrt{\frac{\alpha_i}{N_i}}+\sqrt{\frac{\alpha_j}{N_j}}}\right)$$

where α is the electrical polarizability and N is the effective electron number.

Table 3. Effective electron number 'N' and plarizability 'α' of anions and cations [28].

Cations	N	$\alpha(10^{-24}cm^3)$	Anions	N	α $(10^{-24}cm^3)$
Li^+	2	0.029	F^-	8.5	0.858
Na^+	9.5	0.290	Cl^-	17	2.947
K^+	17.25	1.133	Br^-	22	4.091
Rb^+	22.25	1.679	I^-	30.25	6.116

The results of the above formula for C_{ij} and the rest of the constants used for the calculation of lattice energy are listed in the table 2.

Table 4. Born and van der Waals parameters used in the calculation of interionic interactions.

Alkali	x (10^{-16})J				x (10^{-10})m			x (10^{-79} Jm^6)	
halide	A(A-A)	A(A-H)	A(H-H)	ρ(A-A)	ρ(A-H)	ρ(H-H)	C(A-A)	C(A-H)	C(H-H)
LiF	1.84608	0.7769	1.80432	0.1364	0.2614	0.2753	0.088	1.62	38.92
LiCl		2.20896	1.96352		0.2786	0.3214		4.57	363.4
LiBr		2.66084	4.71712		0.2882	0.3164		5.94	615.1
LiI		14.2315	8.8040		0.2617	0.3066		8.57	906.24
NaF	12.6362	2.55072	1.80432	0.1709	0.2555	0.2753	2.94	9.62	38.92
NaCl		3.70352	1.96352		0.2903	0.3214		27.43	363.4
NaBr		4.14896	4.71712		0.3014	0.3164		35.65	615.1
NaI		5.9288	8.8040		0.3099	0.3066		51.46	906.24
KF	6.07504	3.88288	1.80432	0.2603	0.2770	0.2753	39.53	38.18	38.92
KCl		6.58864	1.96352		0.3048	0.3214		111.9	363.4
KBr		4.7104	4.71712		0.3295	0.3164		145.5	615.1
KI		9.34784	8.8040		0.3264	0.3066		210.8	906.24
RbF	10.89296	3.53488	1.80432	0.2704	0.2945	0.2753	98.35	61.03	38.92
RbCl		5.69584	1.96352		0.3233	0.3214		180.4	363.4
RbBr		6.67184	4.71712		0.3321	0.3164		234.6	615.1
RbI		8.4512	8.8040		0.3431	0.3066		340.3	906.24

3.2 Turbo Pascal-6.0 programs: The Turbo Pascal programs were designed to take coordinate positions for r_{ij}, charge of an ion and interionic parameter values to evaluate the cluster energies. All the programs developed for the step wise development of the clusters and evaluation of cluster energy are named Born 50n.EXE where n=1-5.

3.2.1 Generation of a start cell: A start cell was generated from eight coordinate positions and the respective charge of part of a face centered cubic unit cell. The start cell coordinates and charges form the first file generated by using the first Turbo Pascal program named Born 501.EXE.

Table 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

3.2.2 Multiplication of the start cell: The start cell generated was then multiplied to six layers in all three dimensions by a second program named Born 502.EXE. Cluster size of six was selected from previous work [4] approach and for reasons of computer speed. Cluster size $N= 8 \times n^3$, where n is the number of layers considered, and in this case n=6 therefore cluster size $N= 8X6^3 =1728$ ions.

3.2.3 Modification of crystallographic files: Modification of the above perfect cluster file is required to form defects and different surface structures. This is done by taking the coordinates

of a particle from the bulk and there by taking it to the surface or infinity. The program named Born 504.EXE is used for deleting and adding coordinate positions.

Modification to form a ledge surface was done by adding additional coordinates of half a layer on top of the (100) surface of the perfect crystal. In this case the program modifies the existing file until the last coordinate specified in the program. A similar analogy is used in the formation of kink surfaces except in this case only half a row is added to the above ledge surface.

3.2.4 Conversion in to physical files: The cluster mentioned above is in the crystallographic coordinate system and requires conversion in to physical coordinate system and its conversion is done by using the program named Born 503.EXE. This conversion makes use of the particular lattice constant of each alkali halide.

Table 6. Lattice constant a of alkali halides in Angstrom.

Alkali halide	a	Alkali halide	a	Alkali halide	a	Alkali halide	a
LiF	4.072	LiCl	5.1396	LiBr	5.5013	LiI	6.0000
NaF	4.640	NaCl	5.6402	NaBr	5.9772	NaI	6.4730
KF	5.347	KCl	6.2931	KBr	5.5966	KI	7.0655
RbF	5.6516	RbCl	6.5810	RbBr	6.8890	RbI	7.3420

3.2.5 Calculation of cluster energy: The next program Born 505N.EXE takes any of the above physical file and requests for repulsive and van der Waals parameters and evaluate the cluster energy as a sum of the Coulombic, repulsive and van der Waals energies. The Coulombic and

4. NUMERICAL RESULTS AND DISCUSSION

4.1 Defect formation energy of clusters of different surface structure: 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 bulk of the crystal and their deposition on the surface [29]. In this work the above programs and methods are employed to calculate the Schottky defect formation energies of some sixteen alkali halides of cluster size n=6, where the removed ions are placed on a plane, ledge and kink surface structure.

In this work only the (100) surface positions are considered. Clusters with the above types of surface structures, are constructed for each of sixteen alkali halide clusters by putting additional ions on this face of the cluster.

4.1.1 Deposition of the removed ions on a plane surface: A cluster of size n=6 was generated using the above computer programs. Cluster generation is done by a simple three dimensional multiplication of the start cell for all sixteen alkali halides and consecutive conversion to physical file by using the respective lattice constant. Schottky defects for all sixteen alkali halides were then formed by removing a pair of nearest neighbor ions from the center of the bulk and placing them at the center of the (100) surface position. This is done by modifying the above generated perfect cluster. The removed ion pair coordinates and their position on the surface are the following.

	Schottky vacancy	Surface position
Cation	3,3,3	6,3,3
Anion	3,3.5,3	6,3.5,3

The formation energies for both the perfect and defect cluster were calculated separately by using the above generated unmodified and modified crystals respectively. The calculated values for both the individual ionic interactions and the total Schottky formation energy are tabulated in table bellow.

Table 7. a) Calculated contribution of each interionic interactions in a perfect cluster.

Halide	Coulomb(10^{-18} J)	Born rep. (10^{-18} J)	van der Waals(10^{-18} J)
LiF	-1695.8	192.944	-49.793
LiCl	-1328.7	114.243	-88.608
LiBr	-1241.3	100.079	-97.593
LiI	-1138.1	74.829	-120.583
NaF	-1471.7	143.547	-48.761
NaCl	-1210.7	109.910	-74.403
NaBr	-1142.5	100.712	-80.965
NaI	-1055.0	83.380	-95.781
KF	-1277.1	120.955	-67.327
KCl	-1085.1	103.867	-85.609
KBr	-1035.2	101.543	-90.384
KI	-966.5	88.893	-99.874
RbF	-1208.3	116.631	-78.671
RbCl	-1037.7	103.529	-96.091
RbBr	-991.3	99.789	-99.284
RbI	-930.1	90.818	-108.001

The contribution of the Born repulsion term is in the order of 9 to 19 %, whereas the van der Waals terms contribute about four to twelve percent of the value of the total energy. The van der Waals contribution are higher when the size difference between the cation and anion is greater and generally when the size of ions increases.

But the van der Waals forces for the iodide cases show magnitude which are even greater than the Born repulsion and this shows that the van der Waals parameters used are higher for the Born parameters used in this calculation. This will in turn have an influence of increasing the cluster energy. The influence on the Schottky formation energy is relatively lower as the difference of two cluster energies will be taken.

Table 7. b) Calculated values of Schottky formation energies for a plane surface cluster.

Alkali halide	Energy of perfect cluster (10^{-18} J)	Energy of defect cluster(10^{-18} J)	Schottky formation energies(10^{-18} J)
LiF	-1552.61	-1551.28	-1.327
LiCl	-1303.03	-1301.84	-1.196
LiBr	-1238.82	-1237.67	-1.156
LiI	-1183.89	-1182.74	-1.146
NaF	-1376.94	-1375.74	-1.200
NaCl	-1175.23	-1174.17	-1.058
NaBr	-1122.75	-1121.70	-1.048
NaI	-1067.37	-1066.36	-1.004
KF	-1223.50	-1222.41	-1.095
KCl	-1066.87	-1065.89	-0.972
KBr	-1024.04	-1023.10	-0.942

KI	-977.48	-976.57	-0.908
RbF	-1170.34	-1169.28	-1.055
RbCl	-1030.22	-1029.27	-0.949
RbBr	-990.76	-989.83	-0.919
RbI	-947.28	-946.39	-0.894

The calculated Schottky formation energy value in this case is by far larger than the experimental and other theoretical considerations and this shows that plane surface is not a likely structure of cluster or surface deposition sites.

4.1.2 Deposition of the removed ions on a ledge surface: The perfect cluster generated above was modified by adding seven row of additional ions on the (100) surface. This makes a step or a ledge on the surface of the cluster. The additional consecutive coordinate positions include the following coordinate positions which makes a total of additional 48 ion positions.

1.	6,0,0 ...	6,5.5,0	5.	6,0,2 ...	6,5.5,2
2.	6,0,0.5 ...	6,5.5,0.5	6.	6,0,2.5 ...	6,5.5,2.5
3.	6,0,1 ...	6,5.5,1	7.	6,0,3 ...	6,5.5,3
4.	6,0,1.5 ...	6,5.5,1			

The modification of this cluster to make a defect cluster once again requires the removal of ion pairs from the bulk and placing the removed ion on the ledge surface. The removed ion pair and surface coordinate positions are the following,

	Schottky vacancy	Surface position
Cations	3,3,3	6,3.5,3.5
Anions	3,3.5,3	6,3,3.5

The calculated value of the contribution of each part to the cluster energy and the Schottky formation energies are tabulated bellow.

Table 8. a) The contribution of each interionic interaction to the Schottky formation energy.

Halide	Coulomb(10^{-18} J)	Born rep. (10^{-18} J)	van der Waals(10^{-18} J)
LiF	-1.24	0.247	-0.00696
LiCl	-1.04	0.145	-0.0126
LiBr	-0.97	0.128	-0.0129
LiI	-0.87	0.095	-0.0122
NaF	-1.06	0.182	-0.0057
NaCl	-0.9	0.14	-0.0103
NaBr	-0.82	0.128	-0.0112
NaI	-0.79	0.106	-0.0102
KF	-0.96	0.153	-0.0089
KCl	-0.81	0.132	-0.0114
KBr	-0.79	0.129	-0.0121
KI	-0.69	0.112	-0.0116
RbF	-0.91	0.148	-0.0104
RbCl	-0.78	0.1311	-0.0127
RbBr	-0.74	0.1265	-0.0128
RbI	-0.71	0.1147	-0.0125

The contribution of the Born repulsion in this case varies from 9 to 24% while the van der Waals is in between 5 to 12% of the Schottky formation energy. The values obtained show the significance of the near neighbor interactions to defect formation energies.

Table 8. b) Schottky formation energy and cluster energies of perfect and defect cluster.

Alkali Halide	Perfect cluster(10^{-18} J)	Defect cluster(10^{-18} J)	Formation energies (10^{-18} J)
LiF	-1627.80	-1626.71	-1.095
LiCl	-1366.31	-1365.34	-0.977
LiBr	-1299.04	-1298.09	-0.943
LiI	-1204.44	-1203.56	-0.880
NaF	-1443.65	-1442.66	-0.988
NaCl	-1232.27	-1231.40	-0.871
NaBr	-1177.24	-1176.41	-0.833
NaI	-1095.74	-1094.95	-0.788
KF	-1282.81	-1281.92	-0.894
KCl	-1118.63	-1117.84	-0.797
KBr	-1073.75	-1072.98	-0.770
KI	-1011.06	-1010.33	-0.729
RbF	-1227.08	-1226.22	-0.863
RbCl	-1080.21	-1079.44	-0.775
RbBr	-1031.79	-1031.05	-0.742
RbI	-982.26	-981.54	-0.713

In every case the formation energy decreases as the ionic size increases due to the major contributor, the Coulombic, part which is significantly influenced by increase in interionic distance. The Schottky formation energy is lower than the case of deposition on a plane surface

and this is because of an increase in the near neighbor interaction during deposition on the ledge surface.

4.1.3 Deposition of the removed ions on a kink surface: The above ledge cluster was further modified by adding half a raw of ions with the consecutive coordinate positions from 6,5.5,3.5 to 6,4,3.5, to form a kink surface. For Schottky pair defect formation, a pair of ions were as usual removed from the bulk and placed at the kink position on the surface.

	Schottky vacancy	Surface kink position
Cation	3,3,3	6,3.5,3.5
Anion	3,3.5,3	6,3,3.5

The calculated Schottky formation energy and cluster energy of the perfect and defect kink surface clusters calculated are listed in table bellow.

Table 9. a) The contribution of the different interionic interactions to formation energy.

Halide	Coulomb(10^{-18} J)	Born rep. (10^{-18} J)	van der Waals(10^{-18} J)
LiF	-0.85	0.212	-0.00662
LiCl	-0.69	0.165	-0.01224
LiBr	-0.68	0.109	-0.01355
LiI	-0.57	0.12	-0.01185
NaF	-0.74	0.153	-0.00586
NaCl	-0.61	0.117	-0.00960
NaBr	-0.57	0.107	-0.01059

NaI	-0.53	0.087	-0.00961
KF	-0.65	0.128	-0.00777
KCl	-0.55	0.110	-0.0102
KBr	-0.57	0.107	-0.0109
KI	-0.48	0.094	-0.01044
RbF	-0.61	0.124	-0.00913
RbCl	-0.52	0.110	-0.01125
RbBr	-0.50	0.106	-0.01074
RbI	-0.47	0.096	-0.01146

The repulsion contribution is maximum when the ionic size decreases and the reverse is to van der Waals contribution. The contributions include 9 to 21% from Born part and to 0.5 to 1% from van der Waals part and the rest is Columbia.

Table 9. b) Schottky formation energies of the perfect cluster and kink surface structure.

Alkali Halide	Energy of the perfect cluster(10^{-18}J)	Energy of the defect cluster(10^{-18}J)	Formation energies of kink surface(10^{-18}J)
LiF	-1631.21	-1630.50	-0.711
LiCl	-1369.21	-1368.55	-0.669
LiBr	-1301.80	-1301.14	-0.654
LiI	-1207.00	-1206.39	-0.613
NaF	-1446.67	-1446.03	-0.648
NaCl	-1234.87	-1234.28	-0.590
NaBr	-1179.74	-1179.17	-0.575
NaI	-1098.06	-1097.52	-0.541
KF	-1285.50	-1284.90	-0.595
KCl	-1120.99	-1120.45	-0.540

KBr	-1076.02	-1075.49	-0.524
KI	-1013.20	-1012.70	-0.499
RbF	-1229.66	-1229.08	-0.578
RbCl	-1082.49	-1081.96	-0.526
RbBr	-1033.96	-1033.46	-0.503
RbI	-984.33	-983.84	-0.488

Comparison of the above three Schottky defect formation energies shows a decrease in energy from plane to a kink surface. The experimental and other recent theoretical calculations show formation energies, which are lower in value than all the above three and at least in the same order as the value of the kink surface. Incorporation of other interactions like polarization effect and relaxation may improve the results. A comparison of the above three cases and results of earlier theoretical works and experiments are shown in figure bellow.

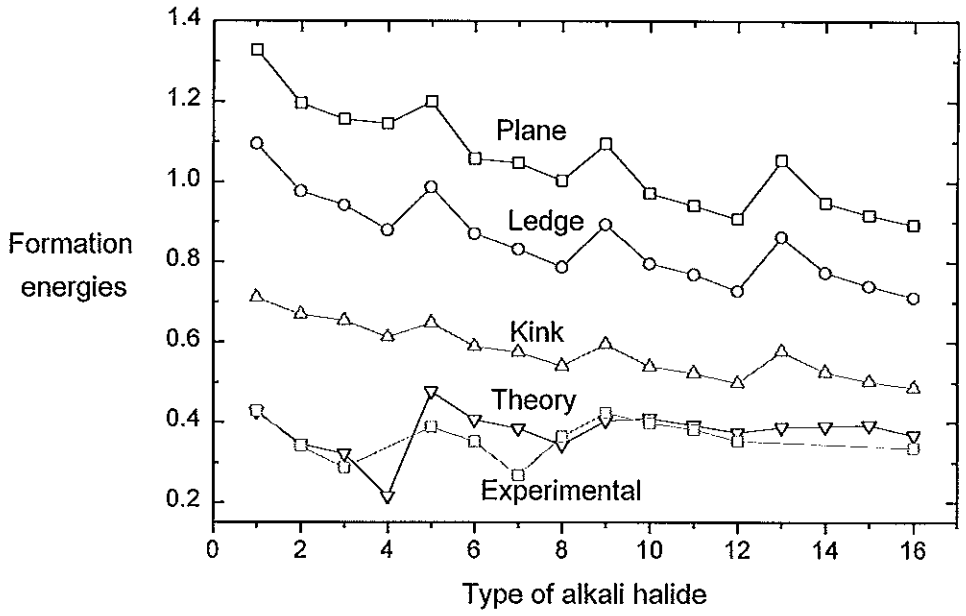


Fig. 1 Formation energies(10exp-18) during deposition on different surface structure.

From experimental evidences of electron spectroscopy and some computed results [11], the surface of these cluster are not expected to have perfect plane surface structures. Hence there are several surface sites for a crystal depending on the thermodynamic stability and lattice structure. Because of the variety of different surface sites involved on a real surface of a crystal under investigation, an experiment designed to determine the Schottky formation energies may usually give a measure of value which is an average of several different deposition surface sites of the crystal.

Therefore the same alkali halide crystal with different concentration of each type of surface sites and hence with different surface structure may have different values of formation energy of Schottky defects. This can explain why experimental values measured in different laboratories show a large variation of Schottky formation energies.

The decrease in Schottky formation energy in the pattern specified in table, for the first three cases, is accompanied by a change in the possible number of nearest neighbor interactions, which decreases from three to one as we go from kink to plane surface. This is also manifested by a consecutive decrease in each interionic repulsion. The Schottky formation energies in every case decreases as the anion size increases for a given cation halide and in general as the cation size increases. This is mainly due to an increase in the interatomic distance as a result of increase in ionic radii displayed in the major or Coulomb part of the cluster energy.

4.2 Schottky formation energy dependence on vacancy separation distance: The most simple arrangement of cation and anion vacancies in the bulk of the cluster is the nearest neighbor position. In this case the distance between the centers of the vacancies is a/2, where a is the lattice constant. There are also a lot of other arrangements with different separation distances, hence the Schottky formation energy of the different arrangements will also differ. Here the Schottky formation energies of the different arrangements are calculated to show the effect of separation distance of anions and cations on the formation energy and hence propose the most realistic configuration of the Schottky pairs in the crystal.

To do this a kink perfect cluster was taken and Schottky pair defects was formed by taking a cation from 3,3,3 position of the bulk to 6,3.5,3.5 on surface and then moving the near neighbor anion step by step for each case and placing it at 3.5,3.5,5.5 to increase the Schottky pair separation distance Ra where a is the individual lattice constant and R is the crystallographic coordinate separation. The separation distances and corresponding calculated formation energies of these cases are listed as follows.

Cation vacancy	Anion vacancy	Separation distance(R)
3,3,3	3.5,3,3	0.5a
3,3,3	3.5,3.5,3.5	0.866a
3,3,3	3.5,3,4	1.118a
3,3,3	3,3,4.5	1.5a
3,3,3	4.5,4,4	2.06a
3,3,3	3.5,3.5,5.5	2.598a

Taking NaCl as a typical example, the calculated contribution of each part of the interionic interaction to the formation energy is shown bellow.

R	Coulomb part(10^{-18}J)	Born part (10^{-18}J)	van der Waals part(10^{-18}J)
0.5a	-1271.126	115.422	-78.2546
0.866a	-1271.0202	115.422	-78.2546
1.118a	-1270.916	115.422	-78.2553
1.5a	-1270.855	115.448	-78.3052
2.06a	-1271.473	115.445	-78.2597

The Coulomb part decreases gradually until the vacancies are far apart, the Born and van der Waals parts show non consistent behavior depending on the orientation of the vacancies.

Table 10. Schottky formation energies in (10^{-18}J) of the six different Schottky pair separations.

Alkali halide	0.5a	0.866a	1.118a	1.5a	2.06a	2.598a
LiF	0.698	1.156	1.305	1.444	1.551	1.513
LiCl	0.66	1.020	1.136	1.249	1.270	1.302
LiBr	0.644	0.988	1.090	1.196	1.199	1.245
LiI	0.605	0.919	1.016	1.112	1.113	1.157
NaF	0.637	1.044	1.164	1.291	1.377	1.351
NaCl	0.582	0.911	1.017	1.121	1.157	1.168
NaBr	0.567	0.88	0.979	1.076	1.099	1.121
NaI	0.533	0.828	0.914	1.004	1.023	1.046
KF	0.585	0.635	1.048	1.157	1.228	1.209
KCl	0.532	0.832	0.928	1.020	1.061	1.063

KBr	0.517	0.806	0.893	0.982	1.013	1.057
KI	0.491	0.767	0.845	0.927	0.954	0.966
RbF	0.570	0.903	0.876	1.112	1.178	1.170
RbCl	0.520	0.808	0.900	1.000	1.028	1.030
RbBr	0.496	0.772	0.859	0.944	0.982	0.972
RbI	0.482	0.742	0.824	0.903	0.930	0.941

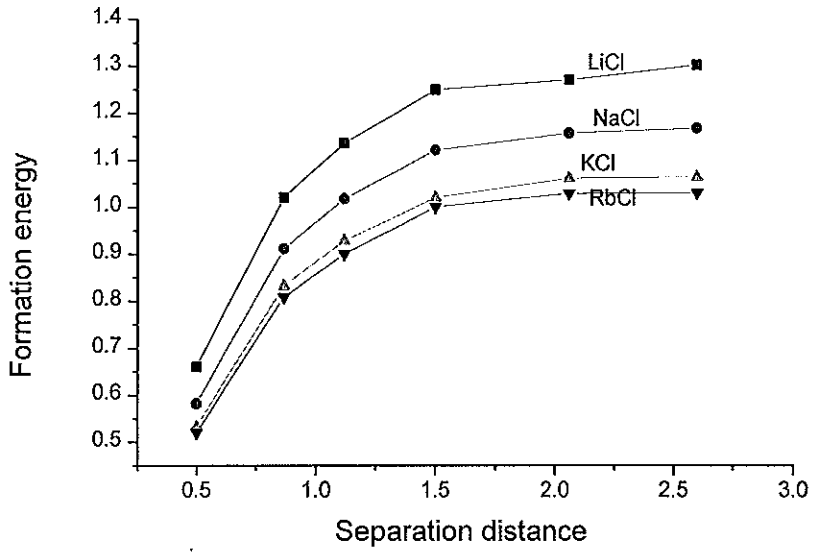


Fig 2. Schottky defect formation energy (10^{-18}J) for different separation distance of alkali Chlorides vacancies.

The calculated values show that the formation energies decrease with decreasing the distance between the vacancies. Therefore the nearest neighbor anion and cation vacancies are energetically favored. As the ions approach each other the extra energy released is caused by the increase in the attractive ionic interactions. One of the basic advantage of numerical summation is such method of dealing with defects of the required arrangement and configuration as required.

4.3 Movement of Schottky pair defects through the cluster: The realistic picture for the thermal formation of Schottky defects is the generation of the vacancies on the surface and their diffusion in to the interior of the crystal [30]. According to this mechanism a vacant lattice site may be formed by the jump of an ion from its initial site in the surface on to the neighboring lattice site. This vacant site may then become occupied by another ion when the latter jumps into the vacancy. Successive jump of this kind thus leads to the diffusion of a vacant lattice sites from the surface into the interior of the crystal. The result will be quite equivalent to taking an ion from the interior of the crystal and placing it at the surface.

In this part the formation energy for and the diffusion of the vacancy-pair by the mechanisms described above are shown by the calculation of the formation energy of Schottky defects. The Schottky pairs were first taken from the surface to infinity and then a pair of ions from the nearest neighbor position replaced the surface defect. The nearest neighbors then further replaced the vacant sites until the Schottky pairs are stabilized. This can be written in the practical defect formation terminology as the movement of the vacancy from the surface to the bulk of the

crystal during defect formation. The Schottky pairs removed and the formation energy for different vacancy positions are listed bellow.

Cation vacancy	Anion vacancy	Distance from the surface
3,3,0	3,3.5,0	0
3,3.5,0.5	3,3,0.5	0.5a
3,3,1	3,3.5,1	a
3,3.5,1.5	3,3,1.5	1.5a
3,3,2	3,3.5,2	2a
3,3.5,2.5	3,3,2.5	2.5a

Calculated values of the Schottky pair formation energies of the different Schottky pair positions from surface are tabulated bellow.

Table 11. a) Calculated Schottky formation energies (10^{-18}J) for different distance from the surface.

Halide	0	0.5a	a	1.5a	2a	2.5a
LiF	2.43778	2.53296	2.5336	2.5350	2.5357	2.5355
LiCl	2.0712	2.2135	2.2153	2.2167	2.2174	2.21746
LiBr	1.9761	2.1213	2.1277	2.1286	2.1296	2.1293
LiI	1.8357	1.9751	1.9807	1.9814	1.98207	1.98208
NaF	2.0717	2.2682	2.2698	2.2695	2.2701	2.26988
NaCl	1.8653	1.9784	1.9819	1.9822	1.9828	1.98269
NaBr	1.7858	1.9034	1.9077	1.90806	1.90864	1.9086
NaI	0.699	0.8117	0.8155	0.81588	0.81643	0.8164
KF	1.93748	2.0364	2.0379	2.0377	2.03798	2.0381
KCl	1.69736	1.8005	1.8032	1.80327	1.80378	1.8037

KBr	1.63094	1.7352	1.73828	1.738499	1.7390	1.7389
KI	1.5380	1.6395	1.6425	1.642725	1.6432	1.64314
RbF	1.8571	1.9583	1.96026	1.96101	1.96070	1.96053
RbCl	1.64196	1.7447	1.7456	1.74758	1.748086	1.74798
RbBr	1.568365	1.66593	1.66842	1.66853	1.668999	1.6745
RbI	1.496823	1.59739	1.60039	1.60056	1.1.60078	1.601

Table 11. b) Contribution of the different interionic interactions for R= 0.5a and R= 2.598a respectively.

Halide	Coulomb(10^{-18} J)		Born rep. (10^{-18} J)		van der Waals(10^{-18} J)	
	R=0	R= 2.5a	R=0	R= 2.5a	R=0	R= 2.5a
LiF	-0.773	-0.883	0.10329	0.10423	-0.00275	-0.002794
LiCl	-0.694	-0.696	0.06105	0.06159	-0.00493	-0 .00501
LiBr	-0.648	-0.650	0.05349	0.05396	-0.00543	-0.00552
LiI	-0.595	-0.596	0.0399	0.04025	-0.00475	-0.00483
NaF	-0.769	-0.771	0.0765	0.07718	-0.00265	-0.00268
NaCl	-0.633	-0.634	0.0586	0.05908	-0.00409	-0.00415
NaBr	-0.597	-0.598	0.0537	0.05413	-0.00446	-0.00453
NaI	-0.551	-0.552	0.04441	0.0448	-0.00405	-0.00411
KF	-0.661	-0.669	0.06444	0.0650	-0.00364	-0.00368
KCl	-0.567	-0.568	0.05533	0.0558	-0.00465	-0.00470
KBr	-0.541	-0.542	0.05408	0.5450	-0.00492	-0.00498
KI	-0.505	-0.506	0.0473	0.4770	-0.00471	-0.00477

RbF	-0.631	-0.632	0.0621	0.626	-0.00425	-0.00430
RbCl	-0.542	-0.543	0.0551	0.556	-0.00520	-0.00526
RbBr	-0.518	-0.519	0.0531	0.536	-0.00501	-0.00506
RbI	-0.486	-0.487	0.0484	0.487	-0.00528	-0.00534

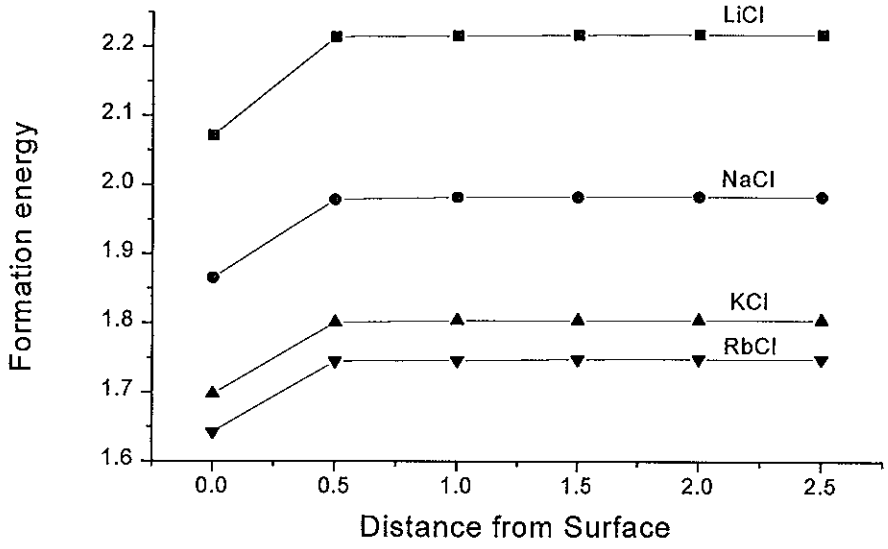


Fig 3.Schottky formation energy (10^{-18}J) for different distance from the surface for different alkali Chlorides.

The Schottky formation energy decreases as we go from the bulk to the surface of the cluster and this shows that Schottky-like defect arise with relatively small energy at the surface and become stabilized in the bulk as the energy larger and constant in the interior of the crystal. The energy expended during the first few jumps can be considered as the formation energy of Schottky-like

defects in this mechanism. Once the vacancies are separated from their sources by several lattice constants, the potential energy of the crystal becomes essentially independent of the lattice site occupied by the vacancies i.e. the surface effect on the vacancies becomes negligible. This effect will be significant when relaxation cases are considered.

There appears to be a greater concentration of vacant sites on and near the surface of alkali halide than the interior. These considerations are particularly useful in the making of extrinsic defects for a particular requirement and determination of the distribution of defects at a given thermodynamic equilibrium.

4.4 Diffusion of cation and anion vacancies to opposite direction: The conductivity of alkali halides can be considered in terms of the motion of cation and anion vacancies in opposite direction. Therefore the electrical conductivity requires separation of the Schottky defects and the Schottky pairs with different configuration will have different activation energies for conductivity. In this part the activation energy is calculated from Schottky pair separation energies of different configuration of defects.

To do this five different Schottky-like defect clusters are made for each alkali halide by increasing the one-dimensional distance of the ions to be removed sequentially by one lattice constant. The first defect clusters were made by removing the nearest neighbor ions from the center of the cluster to infinity. The second types of Schottky like defect were made by removing ion pairs with one-dimensional separation distance of 1.5a, to infinity. The third type of Schottky

like defects is created by a similar method with a separation distance of 2.5a and so on. The crystallographic coordinates of Schottky like defects, their separation distances, R and calculated Schottky formation energies are listed bellow.

Crystallographic coordinates and separation distance R between Schottky vacancies.

Cation vacancy	Anion vacancy	R
3,3,3	3,2.5,3	0.5a
3,2,3	3,3.5,3	1.5a
3,4,3	3,1.5,3	2.5a
3,1,3	3,4.5,3	3.5a
3,5,3	3,0.5,3	4.5a

Taking NaCl as a typical example the contribution of each part of the interionic interaction to the total is listed bellow for comparison.

Table 12. a) Contribution of each part at different vacancy separation distances.

R	Coulomb part(10^{-18}J)	Born part (10^{-18}J)	van der Waals part(10^{-18}J)
0.5a	-1208.7	109.654	-74.2056
1.5a	-1208.2	109.631	-74.2003
2.5a	-1208.0	109.632	-74.2005
3.5a	-1207.9	109.631	-74.2054
4.5a	-1208.0	109.630	-74.2012

The van der Waals and Born repulsion once again show non consistent behavior as they are not sensitive to distant interactions.

Table 12.b) Formation energies of the different vacancy configurations (10^{-18}J).

Halide	0.5a	1.5a	2.5a	3.5a	4.5a
LiF	2.536	3.269	3.420	3.520	3.484
LiCl	2.218	2.795	2.915	2.989	2.965
LiBr	2.187	2.671	2.782	2.850	2.828
LiI	1.983	2.481	2.583	2.646	2.626
NaF	2.270	2.909	3.043	3.131	3.099
NaCl	1.983	2.511	2.620	2.690	2.666
NaBr	1.909	2.408	2.511	2.575	2.553
NaI	1.902	2.216	2.433	2.498	2.500
KF	2.038	2.599	2.714	2.790	2.762
KCl	1.975	2.282	2.380	2.443	2.418
KBr	1.739	2.195	2.289	2.348	2.327
KI	1.698	2.065	2.106	2.216	2.299
RbF	1.961	2.470	2.602	2.673	2.647
RbCl	1.748	2.208	2.302	2.361	2.340
RbBr	1.690	2.088	2.192	2.212	2.289
RbI	1.654	1.890	2.016	2.186	2.234

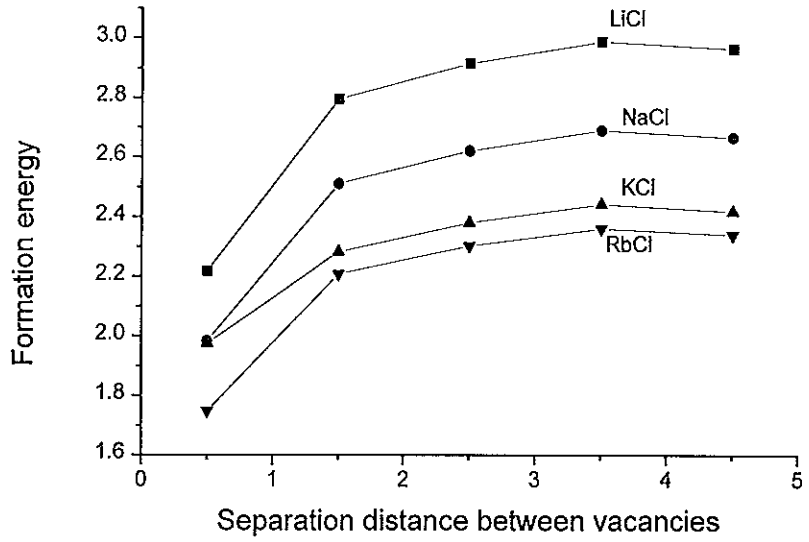


Fig 4. Schottky formation energy (10^{-18}J) for different separation distance of alkali chlorides.

Calculated values of Schottky formation energies show that the formation energy decreases as the separation distance of the vacancies decreases. The value of the relative extra energy released increases with decreasing the separation distance of the vacancies of the Schottky like defects. The value needed for separation of the nearest neighbor vacancy pairs can be considered as the activation for ionic conduction. This activation energy needed for conduction is greater for associated defects and decreases for isolated or free vacancies.

5. Conclusion

The effect of surface structure on the formation energies of Schottky defects have been assessed by using three different models of surface structure including the plane surface. The Schottky formation energies calculated for the different surface structure show that the surface structure significantly affect the formation energies.

The values obtained from the contribution of the each interionic interactions show that the near neighbor interactions do not play a significant role after the vacancies are separated form each other. The van der Waals contribution increases when the difference between the ionic radius of the cation and anion or more generally when both ionic radii increase i.e. when the possibility of polarizability of electron cloud is greater.

The Schottky formation energies are also dependent on the configuration of the Schottky vacancies. The calculated values of formation energy decrease with decreasing separation distance of vacancies. This shows that equilibrium configuration of vacancies is an associated pair. Schottky formation energy calculated for the different vacancy configuration relative to the surface suggest that the surface is the source and sink of most of the vacancies.

The formation energy of Schottky like defects calculated shows that there is a wide range of possibility of formation energy for the same size of cluster due to different surface structure and configuration of vacancies. Further improvement of the above values can be made by using

larger size of cluster and considering surfaces other than the (100). But the values obtained are even greater with out relaxation. The improvement of the obtained values therefore requires modification in either the near neighbor parameters or the interatomic potential model used.

The values obtained from variation of surface structure shows that the surface structure effect, which was not possible to consider with earlier theoretical methods, plays significant role in Schottky defect formation energies. The comparison shows that the simple numerical summation method is an easy and efficient method to treat defects and particularly their configuration and surface effects.

6. REFERENCES

1. Gellings, P. J. and Bouwmeester, H. M. J., The CRC handbook of solid state electrochemistry, CRC press, 1997.
2. Smart, L. and Moore E. Solid state chemistry, Chapman and Hall 1996.
3. Mott, N.F. and Littleton, M.J., *Trans. Faraday Soc.*, **1938**, 34, 485.
4. Tamiru Ayana, MSc-Thesis, Addis Ababa University, **1996**.
5. Marx, V., *Z. Naturforsch.* **1997**, 56b, 895.
6. Azaroff V. L. Introduction to solids, McGraw-Hill, 1981.
7. Barr, L. W. and Lidiard, A. B. Physical chemistry-an advanced treatise, Vol. X, Academic Press, N.Y. 1970.
8. Henderson, B. Defects in crystalline solids, Pitman press, 1972.
9. Anthony, R. W. Basic solid state chemistry, John Wiley & Sons Ltd., 1984.
10. Catlow, C. R. A., Corish, J., Millers, K. M., Jacobs, P. W. and Norget, M. J., *J. Phys. C.* **1979**, 12, 541.
11. Chadwick, A.V. and Terenzi, M. NATO ASI Series B: physics, **1986** v.147.
12. Catlow, C.R.A. and Norget, M. J., *J. Phys. C.* **1973**, 6, 1325.
13. Maril, P. T., *J. Phys. C.* **1964,** 16, 1.
14. Roy, G. G. and Yung, S. K., *J. Chem. Phys.* **1972**,56,3122.
15. Simpson, J.H., *Canadian J. Phys.*, **1972**, 50, 729.
16. Scholz, A.H., *Phys. Stat. Sol.***1968**, 25, 285.
17. Boswarva, I.M. and Simpson, J.H., *Can. J. Phys.*, **1973**, 51,1923.
18. Jaswal, S.S. and Sharma, T.P., *J. Phys. Chem.* **1973**,34, 509.

19. Fumi, F. G., and Tosi, M. P., J. *phys. Chem. Solids*, **1964**, 25, 31.

20. Faux, I.D. and Lidiard, A.B., *Z. Naturf.* a **1971**, 26, 62.

21. Boswarva, I.M., *J. Phys. C.*, **1972**, 5. L-5.

22. Dick B. G. and Overhauser A. W., *Phys. Rev.* **1958**, 90, 112.

23. Marx, V., Phys. Stat. Solidi. in press.

24. O'Brien, M.h., Akinc, M., *J. Solid State Chem.* **1990,** 84, 130.

25. Catlow, C.R.A., Diller, K.M., Norget, M.J., *J. Phys. C.* **1977**, 10, 1395.

26. CRC handbook of chemistry and Physics, 74th ed. CRC Press, 1993.

27. Slater, J. C., and Kirkwood, J. G., *Phys. Rev.* **1931,** 37, 682.

28. Catlow, C.R.A. and Norget, M. J., *J. Phys. C.* **1973**, 6, 1325.

29. Kittel, C., *Introduction to solid state Physics, 5th ed.,* Wiley, New York **1976.**

30. Wedpohl, P. T., *J. Phys. C.* **1976**, 10, 1858.

31. Allnatt, A.R., and Yuen, P. S., *J. Phys. C.* **1975,** 8, 2199.