

Energy Minimization Method In Alkali Halides

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Abstract:

In the present research work an attempt has been made to model and simulate the polarization mechanism around a complex defect lattice of ionic lattice -type by considering various parameters that constitute and describe the defect lattice. The present investigation reveals the polarization and its influence on binding energy of the ground state of a Rare Earth impurity Ba^{2+} and cat ion vacancy defect complex in some ionic solids. For modeling and simulation the three body interaction potential and static simulation technique is used. The computed binding energy reveals that the phenomena of polarization around the defect complex is a responsible factor and governs the stability and ground state configuration of the defect complex. Also, many body interactions are found responsible to enhance the polarization of the complex and in turn to the larger binding energy of the defect complex, in comparison with the general two body potentials. Thus the present works stresses the significance of computer simulations for the study of defect crystal systems where the experimental investigations are difficult.

Keywords-Micro Computer simulation, modeling, three body interactions, Polarization, Impurity- Cation vacancy. complex.

I. INTRODUCTION

The Computer Simulation and Modeling of various types solids that include conductors, semi-conductors, insulators, alloys, mixed crystals, solid solutions, non-stoichiometric compounds, surfaces, interfaces, nano-materials etc., plays a significant role in understanding the properties of point defects, defect complexes and clusters, F-centre aggregates and their influence over the rest of the solid continuum.[1-21]. Ruiz-Mejia etal [21, 23] have extended the initial work of Reitz and Gammal [24] and Bassani and Fumi [25], to calculate the binding energy alkali halide crystals, with different impurities for both the ground and excited states. In their investigations they have considered a two-body inters ionic potential with arbitrary parameters for the first neighbor ion-ion interactions. Also they have neglected the van der Waals and many body forces. In addition at this, the ionic polarizabilities considered by them are arbitrary and hence predict inaccurate description of the polarization energy around the defect complex. In the present work we model the Divalent impurity-Cation vacancy complex defect in some ionic crystals by considering a divalent impurity like Ba^{2+} and cat ion vacancy in $\langle 100 \rangle$ direction. In section -2, we model the mechanism of the divalent impurities cation vacancy defect configuration in ionic crystal lattice. In section - 3 we present the formulation of charge transfer effects around the defect complex. Section-4 deals with method of computations and simulations.

II. THREE BODY INTERACTION POTENTIAL

The three body interaction potential can be expressed as

$$W(r) = \frac{1}{2} \sum_{kk^1} \frac{z_k z_{k^1} e^2}{|\vec{r}_{kk^1}|} + \frac{1}{2} \sum_{kk^1 k^{11}} \frac{z_k z_{k^1} e^2}{|\vec{r}_{kk^1}|} f(r_{kk^{11}}) + \sum_{kk^{11}} c_{kk^{11}} r_{kk^{11}}^{-6}$$

$$+ \sum_{kk^1} D_{kk^{11}} r_{kk^{11}}^{-8} + \sum_{kk^1} b \beta_{kk^1} \exp [r_k + r_{k^1} - r_{kk^1} / \delta_{kk^1}] \tag{1}$$

Here, the primary term is that the usual long- range coulomb interaction energy. The second term is the long-range 3 body inter action energy. The third and fourth terms are the energies, severally as a result of van der Wall dipole –dipole and dipole –Quadra pole interactions. The last term is that the Hafemeister and Flygare type short range overlap repulsive potential. This potential has three parameters b, ρ and f (r). The three –body interaction parameter f (r) has the functional form f (r) – f₀ exp [-r/ ρ] and is considered to be effective up to the first neighbors only. The higher order derivatives of f (r) can be evaluated by the above functional form. The short range parameters ρ and f (r) can be obtained from overlap integrals [20].

III. MODELING OF DEFECT COMPLEX

According to crystallography, a perfect lattice consists of regular, periodic and geometrical arrangement of points (atoms/ions). But in real crystals deviations occur from this perfect geometrical arrangement due to various reasons. The deviations influence various properties of the crystal. In the present model a divalent impurity and a cation vacancy cited at regular lattice positions considered as a defect lattice. It is evident that in ionic-type crystals the crystal structure is constituted by alternative positive and negative ions at regular lattice points. In the presence of a point defect the neighboring ions displace towards or away from the defect and causes polarization. At the same time the virtual and real charges (at displaced ion positions) also cause polarization. In addition to this, the overlapping of electrons shells of both virtual and real charges (due to lattice vibrations) also lead to polarization. All these polarizations contribute to the total polarization around the defect lattice. In turn this polarization influence the other properties of the crystal like defect formation and binding energies. The displacement patterns and dipole moments of each ion up to first neighbor of the defect complex are depicted in fig.1 In the absence of the vacancy, the nearest neighbor of the divalent impurity will be displaced two wards the impurity. The ions at distance of $\sqrt{2} r$ and 2r will be displaced at x_2 and x_1 respectively. Similarly in the absence of the impurity , the nearest neighbors of the are displaced away from the vacancy. The second and third neighbors of the vacancy will be displaced bt x_4 and x_3 respectively. In the presence of the both the defects simultaneously, the resultant displacements of the first neighbor of the defect complex will be $\xi_1 r_0$ and $\xi_2 r_0$. Since the divalent impurity and cation vacancy is a neutral defect, the displacements of the second neighbors of both impurity and vacancy will not be affected much and remain same as in the individual cases. For calculation of modified charge on the ions around the defect complex the presence of the both the real and virtual charges at each ion sets is considered, and thereby calculate the three- body interaction energy [20].

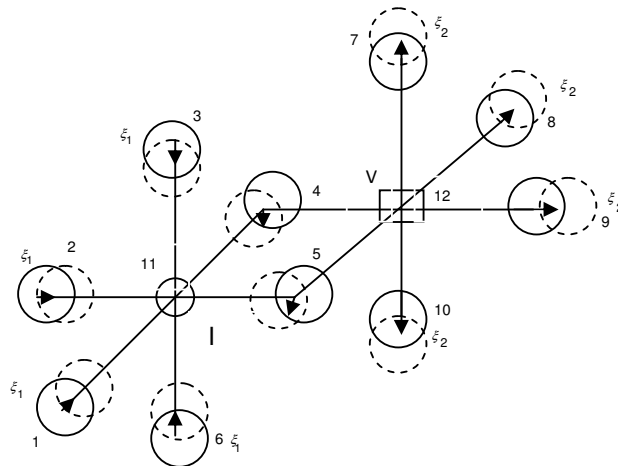


Fig. 1. Distorted lattice configuration due to the divalent impurity-cation vacancy complex defect in NaCl-type crystal. (I) denotes for divalent impurity and (v) denotes the cation vacancy.

Accordingly the modified charge of the impurity and vacancy due to overlap of virtual charges with these defects can be written as

$$Z_m e = Ze (1+ 6 f (r)) \tag{2}$$

In the absence of the vacancy, the real charges at positions 1 – 6 each being displaced by $\eta_1 r_0$ (not shown in fig.1) from the original position due to the effective charge of the impurity, will have an amount of overlap with impurity sets can be expressed as

$$f_d^{(a)} (r) = f_0 \exp [- (1- \eta_1) r_0 / \rho] \tag{3}$$

The corresponding modified charge is

$$Z_{ma}^{(a)} e (r) = ze [1+ 6f_d^{(a)} (r)] \tag{4}$$

The other type of overlapping charges result from the interactions between the ions 1 to 6 with their respective neighbors. The amount of overlap between the ions and their six nearest neighbors (including impurity) can be writes as

$$f_{dd}^{(a)} = f_0 [\exp (-(1-\eta_1) r_0 / \rho) + \exp (-(1+ \eta_1 + 2x_1) r_0 / \rho)] + 4 \exp (-((1+x^2) + (x_2 + \eta_1)^2 + (x^2 + \eta_1)^2)^{1/2} r_0 / \rho) \tag{5}$$

Hence the modified ionic charge of the nearest neighbours of the impurity can be expressed as

$$z_{md}^{(a)} e = ze [1+ f_{dd}^{(a)} (r)] \tag{6}$$

Similarly , the modified ionic charges for the ions around the vacancy can be calculated. The corresponding modified charges are $z_{md}^{(b)}$ and $z_{mdd}^{(b)}$ for the nearest and next-nearest neighbors respectively. These modified charges include different displacement terms corresponding to the nearest

(η_2, x_3) and next nearest neighbor (x_4) displacements. But in the presence of the divalent impurity-cation vacancy pair, the impurity and the vacancy influence the displacements each other neighboring ions. Hence the displacements around the impurity and vacancy will changed. As shown in fig.1, the displacements of the nearest neighbors (nn) of impurity will be ξ_1, r_0 due to the influence of the vacancy and the same for the nn of the vacancy will be ξ_2, r_0 due to the influence of the impurity on them. Hence, in the presence of both impurity and vacancy, the modified charge of atom at 1 due to its nearest neighbors (including the impurity) can be written as

$$Z_{md}^{(1)} e = Ze [1+ f_0 (\exp (-1- \xi_1) r_0 / \rho + 3 \exp (- ((\xi_1 + x_2)^2 + (1+x_2)^2)^{1/2} r_0 / \rho + \exp (-(1+ \xi_1 2x_1) r_0 / \rho + \exp (- ((\xi_1 + x_2 - 2x_3)^2 + (1+x_2)^2)^{1/2} r_0 / \rho) \tag{7}$$

Which is same for ion at 2 , as it situated at a symmetrical position with respect to the defect complex. In the similarly way, the modified charge on the ions at 3 and 6 will be

$$Z_{md}^{(2)} e = Ze [1+ f_0 (\exp (-1- \xi_1) r_0 / \rho + 2 \exp (- ((\xi_1 + x_2)^2 + (1+x_2)^2)^{1/2} r_0 / \rho + \exp (-(1+ \xi_1 2x_1) r_0 / \rho + 2 \exp (-(1+ x_2)^2 + x_4^2 + x_2 - x_4 + \xi_1)^2)^{1/2} r_0 / \rho) \tag{8}$$

The modified charges on the ion at 4 and 5 will be

$$Z_{md}^{(3)} e = ze [1+ f_0 (\exp (- ((1- \xi_1)^2 + \xi_2^2)^{1/2} r_0 / \rho + \exp (- ((1+ \xi_2)^2 + \xi_1^2)^{1/2} r_0 / \rho + 2 \exp (- ((\xi_2 + x_4)^2 + (\xi_1 + x_2)^2 + (1+ x_2 - x_4))^{1/2} r_0 / \rho) + \exp (- ((\xi_2 + x_4)^2 + (1+ \xi_1 + 2x_1 - x_4)^2)^{1/2} r_0 / \rho + \exp (- ((1+x_2 - 2x_3 - \xi_2)^2 + (\xi_1 + x^2)^{1/2} r_0 / \rho)] \tag{9}$$

The modified charges on the ions at 7 and 10 due to defect complex is

$$Z_{md}^{(4)} e = Ze [1+f_0 (\exp (- (1+ \xi_2) r_0 / \rho) + 2 \exp (- (x_2^2 + (1-x_4)^2 + (\xi_2 - x_2 + x_4)^2) \frac{1}{2} r_0 / \rho)) + \exp (- (1- \xi_2 - 2x_3) r_0 / \rho) + 2 \exp (- ((1-x_4)^2 + (\xi_2 + x_4)^2) \frac{1}{2} r_0 / \rho))] \quad (10)$$

Finally, the modified charges on the ions at 8 and 9 can be written as

$$Z_{md}^{(5)} e = Ze [1+f_0 (\exp (- (1+ \xi_2) r_0 / \rho) + \exp (- ((1-x_4)^2 + (\xi_2 - 2x_1 + x_4)^2) \frac{1}{2} r_0 / \rho)) + 3 \exp (- ((1-x_4)^2 + (\xi_2 + x_4)^2) \frac{1}{2} r_0 / \rho) + \exp (- ((1- \xi_2 - 3x_3) r_0 / \rho))] \quad (11)$$

The above modified charges are incorporated in various energy terms appropriately to calculate the binding energy of the defect complex.

IV. FORMULATION BINDING ENERGY OF DEFECT COMPLEX

For the formulation of binding energies of the complex defects in alkali halides, we adopted the semi-discrete lattice approximation. In this approximation we treat the lattice relaxations of regions I explicitly but calculate them for region II using Mott and Littleton approximation [26]. The binding energy (h_B) of a divalent impurity cation vacancy complex defect is expressed as

$$h_B = W_0 - W_1 \quad (12)$$

Where W_0 is the energy required to remove an ion from a real crystal and W_1 is the energy necessary to create a vacancy along $\langle 000 \rangle$ direction in the presence of the divalent impurity at (11).

The energy term W_0 can be written as

$$W_0 = -\frac{1}{2} (E_1^2 + E_2^2) \quad (13)$$

Here E_1^2 and E_2^2 are the potential energies at the position of the ion before (E_1^V) and after (E_2^V) its removal. The potential energies E_1^2 and E_2^2 can be expressed as

$$E_1^2 = \phi_1^{CV} + \phi_1^{TV} + \phi_1^{RV} + \phi_1^{VV} \quad (14)$$

Here ϕ_1^{CV} and ϕ_1^{TV} are the long- range coulomb and three body inter action energies. ϕ_1^{RV} I the short range repulsive energy and ϕ_1^{VV} denotes the van der Waal inter action energy. The details of explicit expressions for the above energy terms have been discussed elsewhere [27].

Now, the energy W_1 can be written as

$$W_1 = -\frac{1}{2} (E_1^C + E_2^C) \quad (15)$$

Here E_1^C and E_2^C represent the energies at the position of the cation (in the presence of impurity) before and after its removal respectively. As in the case W_0 , we can express E_1^C and E_2^C as follows

$$E_1^C = E_1^{CC} + E_1^{CT} + E_1^{CR} + E_1^{CP} + E_1^{CD} + E_1^{CV} \quad (16)$$

E_1^{CC} and E_1^{CT} are coulomb and TBI contributions to the undistorted lattice energy. The term E_1^{CR} is the short-range repulsive energy. The term E_1^{CP} represents the polarization energy due to induced dipoles at the nearest neighbours of the divalent impurity as well as the dipoles of the rest of the lattice. The last two terms represent correct to the energy due tot the Ionic displacements in the lattice and the van der Waal interaction energy. In a similar fashion E_2^C can be expressed as

$$E_2^C = E_2^{CC} + E_2^{CT} + E_2^{CR} + E_2^{CP} + E_2^{CD} + E_2^{CV} \quad (17)$$

$$\text{Where } E_2^{CC} + E_2^{CT} = E_1^{CC} + E_1^{CT} \quad (18)$$

The field \vec{E}_k is calculated taking into account of the charges and the displacements of the ten neighbours of the complex. α_k are the polarizabilities of the anion impurity

V. COMPUTATIONS AND SIMULATION

The simulation of the polarization around the defect lattice can be done by computing the displacements and dipole moments of the real and virtual charges of region I. We have used the energy minimization method under the framework of static simulation technique. In the present investigation, we have computed the displacements and dipole moments and hence polarization due to divalent metal impurity – cation vacancy complex defect in six alkali halide crystals, namely NaCl, Na Br, KCl, KBr, RbCl and RbBr for Ba^{2+} impurity by using energy minimization method. For that we have developed a computer program CPCDL. The input data has been taken from elsewhere [27]. The computed displacements and dipole moments in alkali halides have been given Table I and Table II . The Various energy contributions leading to the formation of the defect complex have been presented in Table III and IV respectively. The corresponding binding energy of the defect complex and its contributions has been shown in Table V.

Table I:

The Computed Displacements In Alkali Halides

Crystal	η_1 (A°)	η_2 (A°)	ξ_1 (A°)	ξ_2 (A°)
NaCl	0.061	0.076	0.066	0.082
NaBr	0.069	0.072	0.077	0.080
KCl	0.063	0.132	0.072	0.139
KBr	0.072	0.121	0.081	0.128
RbCl	0.083	0.162	0.093	0.169
RbBr	0.075	0.144	0.085	0.152

Table II:

The Computed Dipole Moments In Alkali Halides

Crystal	m_1	m_2	m_3	m_4
NaCl	0.083	0.096	0.097	0.085
NaBr	0.070	0.085	0.086	0.071
KCl	0.054	0.058	0.059	0.054
KBr	0.064	0.070	0.072	0.064
RbCl	0.043	0.047	0.049	0.044
RbBr	0.056	0.061	0.063	0.057

Table III:

The Various Energy Contributions Of W_0 The Energy Required To Remove An Ion From A Real Crystal.

Crystal	E_1^C	E_1^R	E_1^D	E_1^P	E_1^V
NaCl	-5.50	1.42	-0.27	-1.00	-0.59
NaBr	-5.15	1.23	-0.24	-1.16	-0.53
KCl	-4.81	1.26	-0.38	-0.82	-1.03
KBr	-4.52	0.98	-0.33	-0.94	-1.00
RbCl	-4.57	0.88	-0.42	-0.85	-1.08
RbBr	-4.39	0.90	-0.37	-0.96	-1.07

Table IV:

The Various Energy Contributions Of W_1 The Energy Required To Remove An Ion From A Defect Crystal.

Crystal	E_2^C	E_2^R	E_2^D	E_2^P	E_2^V
NaCl	-5.50	0.89	1.64	-0.69	-0.38
NaBr	-5.15	0.75	1.82	-0.55	-0.32
KCl	-4.81	0.63	1.43	-0.36	-0.64
KBr	-4.52	0.46	1.58	-0.46	-0.59
RbCl	-4.57	0.34	1.76	-0.30	-0.60
RbBr	-4.39	0.38	1.56	-0.39	-0.62

Table V:

The Binding Energy Of The Defect Complex And Its Contributions.

Crystal	$W_0(eV)$	$W_1(eV)$	$h_B = W_0 - W_1$ (eV)
NaCl	5.974	4.93	0.083
NaBr	5.746	4.65	0.070
KCl	5.679	4.77	0.054
KBr	5.398	4.67	0.064
RbCl	5.542	4.71	0.043
RbBr	5.256	4.68	0.056

VI. CONCLUSION

The pattern of the above displacements and dipole moments is consistent in terms of their magnitudes. The influence of the polarization energy is clearly visible on W_1 when compared to W_0 . The present results are also accounting the three body interactions appropriately. The present investigation reveals the polarization and its influence on binding energy of the ground state of a Rare Earth impurity and cat ion vacancy defect complex in some ionic solids. For modeling and simulation the three body interaction potential and static simulation technique is used. The computed binding energy reveals that the phenomena of polarization around the defect complex is a responsible factor and governs the stability and ground state configuration of the defect complex. Also, many body interactions are found responsible to enhance the polarization of the complex and in turn to the larger binding energy of the defect complex, in comparison with the general two body potentials. Thus the present works stresses the significance of computer simulations for the study of defect crystal systems where the experimental investigations are difficult.

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