

Modeling and Simulation of A Defect Complex in Alkali Halides

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Abstract: In the present paper we present the investigation result of the binding energy of the ground state of a Rare Earth impurity and cat ion vacancy complex in some ionic solids, using a many body interaction potential using computer simulation. The calculated binding energy reveals that the phenomena of polarization due to the charged impurity is a responsible factor and governs the stability and ground state configuration of the defect complex. 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.

Keywords: Computer simulation, many body interactions, Polarization, Impurity, cat ion Vacancy, Defect Complex.

1. 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., play 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.[1-20]. Ruiz-Mejia et al [21, 22] have extended the initial work of Reitz and Gammal [23] and Bassani and Fumi [24], to calculate the bonding energy alkali halide crystals, with different impurities for both the ground and excited status. In their investigations they have considered a two-body 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 discretization of the polarization energy around the defect complex. In the present work we calculate the binding energies of divalent impurity-cat ion vacancy complex defect in some alkali halide crystals by considering divalent impurity like Eu^{2+} . In section- 2 we briefly explain the present three-body potential. In section -3, we outline the mechanism of the divalent impurity- cat ion vacancy defect configuration in ionic crystals. In section – 4 we present the charge transfer effects around the defect complex. Section-5 and Section-6 deal with method calculation and the results respectively.

2. THREE BODY INTERACTION POTENTIAL

The three body interaction potential can be expressed as

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

$$\frac{z_k z_{k^1} e^2}{|\vec{r}_{kk^1}|} f(r_{kk^{11}}) + \sum_{kk^1} c_{kk^{11}} r_{kk^{11}}^{-6} + \sum_{kk^1} D_{kk^{11}} r_{kk^{11}}^{-8} + \sum_{kk^1} b \beta_{kk^1} \exp [r_k + r_{k^1} - r_{kk^1} / \rho_{kk^1}] \quad (1)$$

Here, the first term is the usual long-range Coulomb interaction energy. The second term is the long-range three-body interaction energy. The third and fourth terms are the energies, respectively due to van der Waals dipole-dipole and dipole-Quadrupole interactions. The last term is 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 $f(r) = f_0 \exp[-r/\rho]$ 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].

3. DIVALENT IMPURITY- CAT ION VACANCY DEFECT COMPLEX CONFIGURATION

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 vacancy are displaced away from the vacancy. The second and third neighbors of the vacancy will be displaced at x_4 and x_3 respectively. In the presence of 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 Cat ion 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].

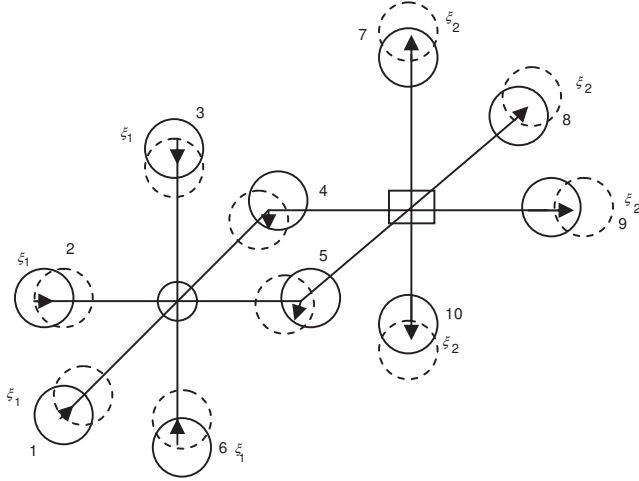


Fig. 1. Distorted lattice configuration due to the divalent impurity-cation vacancy complex defect in NaCl-type crystal. (I) denotes for divalent impurity and (v) denotes the cat ion vacancy.

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

$$Z_{m}e = Ze (1+ 6 f (r)) \quad (2)$$

In the absence of the vacancy, the real charges at positions 1 – 6 each being displaced by $\eta_1 r_0$ 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

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

The corresponding modified charge is

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

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

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

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

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

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-cat ion vacancy pair, the impurity and the vacancy influence the displacements each other neighboring ions. Hence the displacements around the impurity and vacancy will change. As shown in fig.1, the displacements of the nearest neighbors (nn) of impurity will be $\xi_1 r_0$ due to the influence of the vacancy and the same for the nn of the vacancy will be $\xi_2 r_0$ 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

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

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

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

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

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

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

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

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

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

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

4. 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 [25]. The binding energy (h_B) of a divalent impurity cat ion vacancy complex defect is expressed as

$$h_B = W_0 - W_1 \tag{12}$$

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 (110).

The energy term W_0 can be written as

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

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

$$E_1^2 = \phi_1^{CV} + \phi_1^{TV} + \phi_1^{RV} + \phi_1^{VV} \tag{14}$$

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 wall inter action energy.

The details of explicit expressions for the above energy terms have been discussed elsewhere. Now, the energy W_1 can be written as

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

Here E_1^C and E_2^C represent the energies at the position of the cat ion (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

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

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 neighbors 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 wall interaction energy. In a similar fashion E_1^C can be expressed as

$$E_1^C = E_2^{CC} + E_2^{CT} + E_2^{CR} + E_2^{CP} + E_2^{CD} + E_2^{CV} \tag{17}$$

$$\text{Where } E_2^{CC} + E_2^{CT} = E_1^{CC} + E_1^{CT} \tag{18}$$

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

5. METHOD OF CALCULATION AND RESULTS

In the present investigation, we have calculated the displacements and dipole moments and hence polarization due to divalent metal impurity – cat ion vacancy complex defect in six alkali halide crystals, namely NaCl, Na Br, KCl, KBr, RbCl and RbBr for Eu^{2+} impurity by using energy minimization method. For that we have developed a computer program. The calculated displacements and dipole moment coefficients to create a positive ion vacancy in the presence of impurities in alkali halides have been given Table. I(A) and I(B) respectively. Various energy contributions for the removal of a positive ion in the defect lattice for six alkali halides have been shown in Table-II (A) and II (B).

Table-I (A): Displacements, the perfect lattice for six alkali halides in the case of Eu^{2+} impurity

Crystal	η_1 (A°)	η_2 (A°)	ξ_1 (A°)	ξ_2 (A°)
NaCl	0.061	0.037	0.066	0.044
NaBr	0.069	0.040	0.077	0.048
KCl	0.063	0.098	0.072	0.104
KBr	0.072	0.092	0.081	0.100

RbCl	0.083	0.134	0.093	0.141
RbBr	0.075	0.125	0.085	0.133

Table-I (B): Dipole moments and the energy to remove a positive ion in the perfect lattice for six alkali halides in the case of Eu^{2+} impurity.

Crystal	m_1	m_2	m_3	m_4	W_o
(eV)					
NaCl	0.083	0.101	0.103	0.085	5.974
NaBr	0.070	0.088	0.090	0.071	5.746
KCl	0.054	0.062	0.063	0.054	5.679
KBr	0.064	0.075	0.077	0.064	5.398
RbCl	0.043	0.052	0.052	0.044	5.542
RbBr	0.056	0.063	0.066	0.057	5.256

Table II (A): Various energy contributions for the removal of a positive ion in the defect lattice for six alkali halides.

Crystal	E_1^C	E_1^R	E_1^D	E_1^P	E_1^V
NaCl	-5.49	1.42	-0.14	-1.06	-0.59
NaBr	-5.15	1.24	-0.14	-1.20	-0.54
KCl	-4.81	1.27	-0.30	-0.84	-1.03
KBr	-4.52	0.99	-0.26	-0.96	-1.00
RbCl	-4.57	0.89	-0.36	-0.86	-1.09
RbBr	-4.39	0.90	-0.32	-0.98	-1.08

Table II (B): Various energy contributions for the removal of a positive ion in the defect lattice for six alkali halides.

Crystal	E_2^C	E_2^R	E_2^D	E_2^P	E_2^V	W_i
NaCl	-5.50	0.90	1.76	-0.52	-0.38	4.80
NaBr	-5.15	0.75	1.92	-0.42	-0.32	4.50
KCl	-4.81	0.64	1.52	-0.25	-0.64	4.63
KBr	-4.52	0.46	1.65	-0.37	-0.59	4.57
RbCl	-4.57	0.35	1.82	-0.22	-0.60	4.61
RbBr	-4.39	0.38	1.62	-0.32	-0.63	4.60

6. CONCLUSION

In conclusion in the present paper we have presented our investigated result of the binding energy of the ground state of a Rare Earth impurity Eu^{2+} and cat ion vacancy complex in six ionic solids, using a many body interaction potential using computer simulation. The calculated binding energy reveals that the phenomena of polarization due to the charged impurity is a responsible factor and governs the stability and ground state configuration of the defect complex. Many body

interactions are found responsible to enhance the polarization of the complex and in turn to the larger bending energy of the defect complex, in comparison with the general two body potentials.

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