

A three-body force shell model calculation of Schottky defect formation energies of ionic crystals with CsCl structure

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Abstract. A three-body force shell model (TSM) for the calculation of Schottky defect formation energies in solids with cesium chloride structure has been developed by incorporating the effects of long-range three-body interactions (TBI) in the shell model. These TBI in the defect lattice arise from the deformation of electron shells when the nearest neighbour ions get relaxed from their equilibrium position. This model has been used to calculate the cation and anion extraction and Schottky defect formation energies of CsCl, CsBr, CsI, TlCl, TlBr and NH_4Cl crystals. The calculated values of these defect properties agree reasonably well with their measured values.

Keywords. Schottky defect energy; rigid shell model; polarizable point ion model; three-body force shell model.

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1. Introduction

In an earlier paper (Mishra *et al* 1986) (referred to as I), we have reported a modified polarizable point ion (PPI) model which includes the effects of long-range three-body interactions (TBI) for the calculation of point defect formation energies of solids with CsCl structure. As pointed out in I, the PPI model neglects the dependence of the short-range forces on the electronic polarization of ions and predicts substantially higher values of static and dielectric constants. In the presence of an electric field, the electrons get displaced and consequently, the short-range forces between the ions also change. Since the PPI model considers the ions to be point charges, it fails to account for the electronic polarization and hence fails to predict the Cauchy violation in the elastic constants, phonon dispersion curves, dielectric and optical properties of ionic solids.

A satisfactory prediction of the polarization effects in ionic solids has been achieved from the rigid shell model (RSM) developed by Woods *et al* (1960). The ionic charges (Z_e) in RSM consists of core (X_e) and shell (Y_e) charges such that $Z_e = X_e + Y_e$. Its shell can move bodily with respect to its core and this mechanism gives rise to electronic polarization. The corresponding cation (α_+) and anion (α_-) polarizabilities have been defined in terms of the core-shell force constant (K_{\pm}) as (Woods *et al* 1960):

$$\alpha_{\pm} = (Y_{\pm} e)^2 / (K_{\pm} + R_0), \quad (1)$$

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with R_0 as the short-range force constant. In RSM, the short-range forces are regarded as acting between the shells only and arise from overlap and exchange interactions between the shell-electrons. The basic principles of this model for diatomic crystals are schematically illustrated in figure 1.

In recent years, the Schottky defect formation energies of ionic crystals have been extensively studied by several workers (Faux and Lidiard 1971; Boswarva and Simpson 1973; Catlow *et al* 1976; Murty and Usha 1978) following the semi-discrete approximation of Mott and Littleton (1938). Similar calculations for alkaline earth fluorides (Franklin 1968; Chakravorty 1971; Norgett 1971; Keeton and Wilson 1973; Catlow and Norgett 1973; Catlow *et al* 1977) and oxides (Catlow *et al* 1976; Mackrodt and Stewart 1979; Sangster and Rowell 1981; Vempati and Jacobs 1983) have also been made in the framework of RSM using HADES programme developed by Norgett (1974). The RSM calculations of Schottky defect formation energies in cesium halides have been reported by Uppal *et al* (1978). No such calculation has yet been reported for other crystals with CsCl structure.

It is also obvious that studies have been made only on two-body potentials which generally consist of long-range Coulomb and short-range repulsive and/or, van der Waals interactions. The major limitation of these potentials is that they fail to reproduce the elastic and dielectric constants of ionic crystals (Singh 1982). This is true because the electronic polarizability introduced in RSM has no effect on the elastic constant and hence RSM does not go beyond the PPI model in this regard. In order to overcome these common weaknesses, a three-body force shell model (TSM) was developed by Singh and Verma (1969) for successful description of lattice dynamical, dielectric and elastic properties of ionic solids (Singh 1982).

Recently, it has been emphasized by several workers (Catlow and Mackrodt 1982; Lidiard and Norgett 1972) that the effects of long-range three-body forces in the defect structure and properties of ionic solids should be explored. Motivated from this remark, we have employed the TSM formalism for calculating the Schottky defect formation energies in cesium, thallium and ammonium halide crystals. The essential theory for these calculations will be described in § 2 indicating the modifications introduced by three-body interactions (TBI) in the ionic charges in the defect formation energy when they are incorporated through the TSM framework. The Schottky defect formation energy has been calculated by us using the method of minimization of defect energy (Norgett 1974; Silvarajan 1978; Catlow and Mackrodt 1982). A brief account of this is presented in § 3. Section 4 collects the computed results, and the results discussed in § 5.

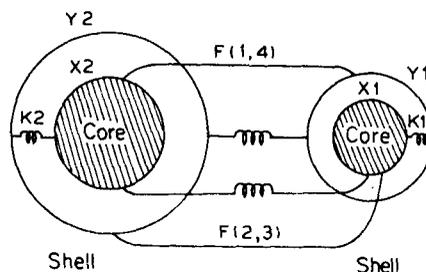


Figure 1. Schematic diagram representing the shell model for ionic crystals.

2. Theory

2.1 Three-body interaction potential

The development of the three-body force shell model (Singh and Verma 1969) basically rests on the fact that the ions during lattice vibrations suffer an appreciable overlap and consequently their electron shells undergo deformation. This mechanism causes a transfer of charge between the overlapping ions. In turn, these transferred charges interact with all other charges of the lattice via Coulomb field and give rise to the long-range many body interactions (Singh 1982). The TSM formalism can be derived from the three-body potential written as

$$E_L(r) = \sum'_{ij} \frac{Z_i Z_j e^2}{r_{ij}} + \sum'_{ijk} \frac{Z_i Z_j e^2}{r_{ij}} f(r_{ik}) + \sum_{ij} c_{ij} r_{ij}^{-6} + \sum_{ij} d_{ij} r_{ij}^{-8} + \sum_{ij} \beta_{ij} b \exp((r_i + r_j - r_{ij})/p), \quad (2)$$

where the first and second terms are the long-range Coulomb and three-body interactions respectively. The third and fourth terms correspond to van der Waals interactions. The last term is the overlap repulsion operative upto the second neighbour ions. Here, the short-range potential has only two parameters (b and p) and the TBI potential has one parameter $f(r)$, which is the measure of overlap between adjacent ions. The physical concept underlying the mechanism of charge transfer is reviewed by Singh (1982). Accordingly, the transferred charge between the adjacent ions i and k can be written as

$$\Delta q_i = Z_i e f(r_{ik}), \quad (3)$$

which consequently modifies the ionic charge ($Z_i e$) of the i th ion as

$$Z_{mi} e = \pm Z_i e [1 + n f(r_{ik})]^{\frac{1}{2}}, \quad (4)$$

with $f(r_{ik})$ as a TBI function (Singh 1982) and n as the number of nearest neighbour ions. This modification in ionic charge corresponds to a change in core and shell charges from ($X_i e$, $Y_i e$) such that

$$Z_{mi} e = (X_{mi} + Y_{mi}) e = (x_i Z_{mi} + y_i Z_{mi}) e, \quad (5)$$

with $x_i + y_i = 1$. The corresponding modification in the core-shell spring constants (K_m) is given by (Singh 1982)

$$K_{mi} = ((Y_{mi} e)^2 / \alpha_{mi}) - R_0, \quad (6)$$

where α_{mi} is the modified polarizability and R_0 is the short-range force constant between cation and anion as defined by Singh (1982).

2.2 Effective charge in defect region

In TSM formalism, we define Q_{mv} , Q_{mc} , Q_{ms} and Q_{md} as the modified virtual, core, shell and defect charges of the ions, respectively, in region I which consists of vacancy and its surrounding neighbours. Also, X_c , X_s and X_T are the core, relative core-shell and total

fractional displacements of the ions in this region. In defect lattice, due to creation of a point defect, the overlap effect between the ions increases significantly with the displacements of nearest neighbours of the vacancy from their original position. A schematic representation of this effect has been shown in figure 2. The creation of a point defect at $(0, 0, 0)$ will lead to the displacements of shells of the nearest neighbour ions (2 to 9) from their original positions. Let these displacements (away from the vacancy) be X_T which will change the amount of overlap between the vacancy and the nearest neighbour ions. Accordingly, this change can be defined as

$$f_d(r) = f_0 \exp(-r_0(1 + X_T)/p). \quad (7)$$

This modifies the defect charge as

$$Q_{m(d)}e = Ze(1 + 8f_d(r)). \quad (8)$$

Also, the second neighbour ions get displaced due to the creation of the vacancy. Let X_1 be the displacement of an ion at a distance $\pm a$ from the vacancy. Similarly, X_2 and X_3 be the displacements of the ions at distances $\pm \sqrt{2}a$ and $\pm \sqrt{3}a$ from the vacancy. These displacements change the ionic charges of the first neighbours of the vacancy such that (Singh *et al* 1984)

$$\begin{aligned} Z_{m(dd)}e = Ze \left\{ 1 + f_0 \left[3 \exp\left(-\left(2\left(\frac{1}{2} + \frac{1}{2}X_T\right)^2 + \left(\frac{1}{2} + X_1 - \frac{1}{2}X_T\right)^2\right)^{1/2} \frac{2r_0}{\sqrt{3p}}\right) \right. \right. \\ + 3 \exp\left(-\left(\left(\frac{1}{2} + \frac{1}{2}X_T\right)^2 + 2\left(1 + X_2 - \frac{1}{2}X_T\right)^2\right)^{1/2} \frac{2r_0}{\sqrt{3p}}\right) \\ + \exp\left(-\left(3\left(\frac{1}{2} + X_3 - \frac{1}{2}X_T\right)^2\right)^{1/2} \frac{2r_0}{\sqrt{3p}}\right) \\ \left. \left. + \exp(-r_0(1 + X_T)/p) \right] \right\}. \quad (9) \end{aligned}$$

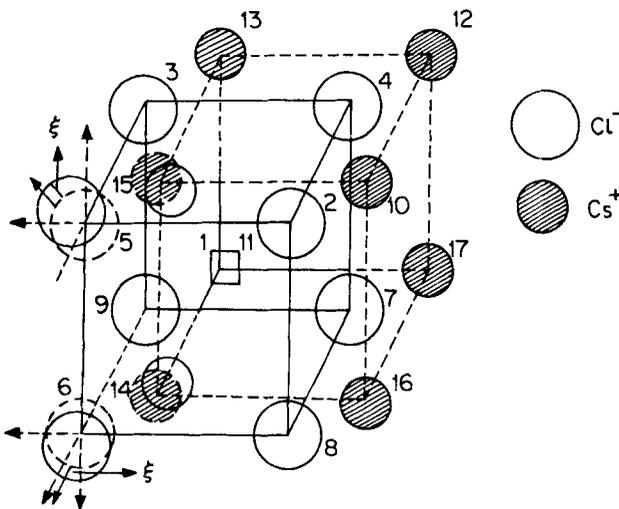


Figure 2. Description of a defect lattice with CsCl structure. The ions shown with circles of full and dotted lines are the virtual and real charges respectively.

This modified ionic charge due to the creation of a defect will change the original shell charges from Y_m to $Y_{m(dd)}$ such that

$$Z_{m(dd)}e = (X_m + Y_{m(dd)})e = (Q_{mc} + Q_{ms(dd)})e, \quad (10)$$

of each ion at their displaced positions. However, the virtual charge $Q_{mv}e (= Z_{mv}e)$ remains the same. These modified ionic and shell charges can be used to minimize the energy of the defect lattice. Besides these modifications, the TBI introduces modifications in the polarization mechanism in the defect lattice. These modifications have been discussed in detail in I.

3. Method of calculation

For the calculation of formation energy of Schottky defect, we have followed the semi-discrete approximation (Mott and Littleton 1938) and the general formulation for treating the defect lattice developed by Lidiard and Norgett (1972) and Norgett (1974). Accordingly, the defect crystal is divided into two regions; region I consists of the defect and its nearest neighbours, while rest of the lattice is considered as region II. Each ion in the defect lattice can be described by its displacement from its original position in a perfect lattice and by its electronic dipole moment. Since these displacements and moments of the ions in region II are small, they are treated in the harmonic approximation (Catlow and Mackrodt 1982). The displacements and dipole moments of the ions in region II are derived using Mott and Littleton (ML) method, while those for ions in region I are obtained by minimizing the energy of the defect lattice with respect to these parameters. The details of the method of defect energy minimization have been reviewed by Norgett (1974), Lidiard and Norgett (1972) and Catlow and Mackrodt (1982).

In the framework of TSM, the total energy of the defect configuration can be minimized with respect to the relaxations of the cores and shells of each ion surrounding the defect. Thus, the total energy of the defect configuration can be written as (Silvarajan 1978)

$$E_f = E_1(x) + E_2(x, X) + E_3(X). \quad (11)$$

Here, $E_1(x)$ is the energy of the defect region, $E_3(X)$ is the energy of the outer region and $E_2(x, X)$ is the interaction energy between the two regions with x and X as the displacements of defect and outer region ions, respectively. $E_3(X)$ is a quadratic function of X and can be expressed as (Catlow and Mackrodt 1982)

$$E_3(X) = -\frac{1}{2} \left(\frac{dE_2(x, X)}{dX} \right)_{x=\bar{x}} \cdot \bar{X}, \quad (12)$$

and hence the total energy of the defect configuration, E_f , will be

$$E_f = E_1(x) + E_2(x, X) - \frac{1}{2} \left(\frac{dE_2(x, X)}{dX} \right)_{x=\bar{x}} \cdot \bar{X}, \quad (13)$$

where \bar{X} is the equilibrium value of X . If we make an assumption on the equilibrium displacements of region II ions (Mott and Littleton 1938), then the revised expression

for E_f is a function of only region I variables with respect to which E_f can be minimized to get the final equilibrium configuration of region I and also the energy of formation of the defect. The details of the formulation developed for these calculations are given in Appendix A.

4. Results and discussion

The Schottky defect formation energy (h_s) has been computed for the solids with CsCl structure (CsCl, CsBr, CsI, TlCl, TlBr and NH_4Cl) by employing the TSM for defect lattice (Mishra 1985). The values of r_0 and the calculated values of potential and shell model parameters have been listed in table 1. The calculated values of equilibrium relaxations of core and relative core-shell of first neighbour ions surrounding a cation and an anion vacancy with their corresponding extraction energies (E_+ and E_-) are given in table 2. The calculated values of Schottky defect energies (h_s) are also presented in the same table.

In the present study, the calculations of defect energies have been performed by restricting the defect region to contain the first neighbour ions (first shell) only. The calculations carried out for CsCl, by enhancing the defect region to contain next nearest neighbours of the vacancy (second shell) have, however, shown insignificant difference

Table 1. Values of constant used for calculation of defect energies.

Parameters	CsCl	CsBr	CsI	TlCl	TlBr	NH_4Cl
r_0 (Å) [†]	3.591	3.750	3.990	3.310	3.440	3.348
b (10^{12} ergs)	0.244	0.268	0.378	0.502	0.430	0.259
ρ (Å)	0.307	0.350	0.430	0.385	0.387	0.313
$f(r)$ ($\times 10^{-3}$)	-3.15	-1.73	2.37	-11.45	-12.14	-3.88
Y_{m+}	-10.87	-10.47	-6.48	-3.30	-3.01	-4.29
Y_{m-}	-5.05	-1.80	-1.17	-1.85	-1.60	-1.89
Km_+ (10^4 dyn/cm ²)	969.00	1007.31	280.95	60.03	45.66	236.93
Km_- (10^4 dyn/cm ²)	217.20	22.06	2.47	28.90	11.81	27.47

[†] Values correspond to 300 K.

Table 2. Equilibrium values of relaxations of nearest neighbour cores (X_c) and shells (X_s) (in units of r_0), extraction energies of cation (E_+) and anions (E_-) (in units of eV) and Schottky defect formation energies (h_s) (in eV) of solids with CsCl structure.

Solids	Cation vacancy			Anion vacancy			h_s
	X_c	X_s	E_+	X_c	X_s	E_-	
CsCl	0.062	0.006	4.359	0.065	-0.004	4.284	1.952
CsBr	0.055	0.012	4.346	0.071	-0.004	4.196	2.079
CsI	0.052	0.018	4.330	0.082	-0.006	3.725	1.941
TlCl	0.045	0.014	5.468	0.095	-0.016	3.271	1.227
TlBr	0.032	0.021	5.294	0.095	-0.018	3.154	1.109
NH_4Cl	0.055	0.012	4.614	0.085	-0.008	3.954	1.528

between the values of Schottky defect energies ($h_s = 1.952$ and 1.953 eV for region I consisting of 8 ions (first shell) and 20 ions (second shell), respectively). This fact is in agreement with previous calculations carried out by Boswarva and Simpson (1973) and Murty and Usha (1978) who have shown that the relaxations and defect energies converge rapidly as the region I is expanded.

The experimental values of h_s in cesium halides have been derived by Harvey and Hoodless (1967) and Lynch (1960) from the results of conductivity and diffusion studies. Lynch (1960) has, however, concluded from the self-diffusion measurements in CsBr and CsI that both cations and anions take part significantly in the mass transport processes. For TlCl, experimental values of Schottky energy have been derived from thermoelectric power measurements (Christy and Dobbs 1967) and conductivity studies (Friauf 1961). More recently, the Schottky energy in thallos halides has been predicted by Samara (1979) from conductivity measurements. All these investigations have provided evidences suggesting the predominance of Schottky defects in cesium and thallos halides. On the other hand, experimental studies on defect properties in the case of ammonium halides are less numerous. Harrington and Staveley (1964) reported the values of h_s to be 0.81 eV in the case of NH_4Cl , corresponding to low activation energy of the order of 0.75 eV.

The earlier defect properties of solids with CsCl structure have been studied by Boswarva (1967), Murthy and Murty (1971) and Shukla *et al* (1972) using polarizable point ion (PPI) model and by Uppal *et al* (1978) using the shell model. Boswarva (1967) made extensive calculations of defect energies of cesium halides by varying the description of the polarization and displacement fields and also by describing the short-range potential in different forms. However, he has obtained negative values of equilibrium relaxations which obviously indicate the hardness of the short-range potential. Moreover, the reported values of h_s are substantially lower than their measured values. This might be due to the incorrect prediction of dielectric properties by PPI model. The increased hardness inherent in the potentials of Boswarva (1967) results in higher values of the energy required to create cation and anion vacancies, leading to smaller values of h_s . This situation has been considerably improved by Murthy and Murty (1971) who used a softer potential to represent the short-range interactions and obtained fairly reasonable values of h_s in the case of CsCl. Their results in the case of other members of this family of solids have, however, shown poor agreement with experimental results. Subsequently, shell model calculations of h_s in alkali halides with NaCl and CsCl structures have been carried out by Uppal *et al* (1978) using the potential devised by Sangster and Atwood (1978). In particular, the defect formation energies reported by Uppal *et al* (1978) for cesium halides, referred to in table 3, are at the lower side of the experimental values.

Table 2 shows that the extraction energies of cation (E_+) and anion (E_-) in cesium and thallos halides obtained from the present calculations show a systematic variation and the cation extraction energy is higher in comparison to that of anion. However, as the polarizability of anion increases from Cl^- to I^- , the anion extraction energy reduces considerably. This fact is consistent with other theoretical results, like oxides (Mackrodt and Stewart 1979; Sangster and Rowell 1981) in which a similar trend is observed.

A comparison between the results obtained from the two models (modified PPI and TSM), as presented in table 3, reveals that no substantial change in the Schottky defect formation energy is observed in the case of cesium halides. One, however, notes a

Table 3. Comparison of Schottky defect energies (in eV) in solids with CsCl structure.

Solids	Present			Other theoretical results		
	PPI	TSM	Expt.	(Boswarva 1967)	(Murthy and Murty 1971)	
CsCl	2.024	1.952	1.86 ^a	1.648	1.986	1.79 ^g
CsBr	2.019	2.079	2.0 ^b	1.521	1.878	1.86 ^g
CsI	2.094	1.941	1.9 ^b	1.490	1.517	1.82 ^g
TlCl	0.851	1.227	0.84–1.3 ^{c,d} 1.03 ^e	—	1.349	0.79 ^h
TlBr	0.810	1.109	—	—	1.322	0.69 ^h
NH ₄ Cl	1.890	1.528	0.81	—	1.387	

^a Harvey and Hoodless (1967); ^b Lynch (1960); ^c Christy and Doobs (1967); ^d Friauf (1961); ^e Samara (1979); ^f Harrington and Staveley (1964); ^g Uppal *et al* (1978); ^h Shukla *et al* (1972).

marked enhancement in the value of h_s in thallos halides obtained from TSM. This fact, thus, clearly emphasizes that the modified PPI model fails to predict the dielectric behaviour of some solids where the static dielectric constant is too large. A more consistent value of h_s has been obtained from TSM in the case of NH₄Cl. Moreover, it has recently been pointed out by Catlow *et al* (1981) that to avoid misleading situations of comparing static lattice defect energies calculated at constant volume with an experimental enthalpy at constant pressure, one must carry out such defect energy calculations over a range of lattice parameters. In view of this, we have calculated the values of Schottky defect energies of all the solids under consideration, over a range of $\pm 0.15 \text{ \AA}$ of the respective lattice parameters corresponding to 300 K. The calculated values of h_s from this procedure do not, however, go beyond the experimental uncertainties in the present system of solids. Referring to the uncertainties involved in the measurements of these defect properties, the agreement achieved from TSM seems to be good. Moreover, the theoretical estimates of defect energies emphasize the need for further detailed experimental efforts to reveal the defect structure and properties in this family of solids.

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Appendix A. TSM formulation for defect energy

The energy of region I consists of various combinations of contributions from core, shell, virtual and defect charges. The Schottky defect formation energy (h_s) is given by

$$h_s = E_+ + E_- - E_L \quad (\text{A1})$$

in terms of the energy (E_+ and E_-) required to extract an ion (cation and anion) from the lattice and the lattice energy (E_l) given by (1). The energy E_+ (or E_-) consists of several contributions such that

$$E_{\pm} = \sum_{j=1}^8 E_{j\pm}. \quad (\text{A2})$$

The evaluation of these contributions from E_1 to E_8 is made from the following expressions.

(i) *Rigid unpolarizable lattice energy*

The energy required to extract an ion from the rigid unpolarized lattice E_1 is given by

$$\begin{aligned} E_1 = & \alpha_m e^2 Z m^2 r_0^{-1} - 8B_{+-} \exp(-r_0/p) - 6B_{++} \exp(-2r_0/\sqrt{3}p) \\ & + 8c_{+-} r_0^{-6} + 8d_{+-} r_0^{-8} + 6c_{++} (2/\sqrt{3})^{-6} r_0^{-6} \\ & + 6d_{++} (2/\sqrt{3})^{-8} r_0^{-8} \end{aligned} \quad (\text{A3})$$

with $B_{+-} = b\beta_{+-} \exp((r_+ + r_-)/p)$

and $B_{++} = b\beta_{++} \exp(2r_+/p)$.

(ii) *Long range attractive energy*

The long-range (LR) attractive energy, E_2 of region I is contributed by various combinations of the charges as expressed below:

(a) W_1 is the energy due to interactions between core-core, shell-shell and virtual-virtual expressed as

$$W_1 = 2(1 + 3\sqrt{3} + 3\sqrt{3}/2)[Q_{mc}(1 + X_c)^{-1} + (Q_{ms(dd)}^2 + Q_{mv}^2)(1 + X_T)^{-1}]. \quad (\text{A4})$$

(b) W_2 is the energy due to the interaction between core and shell charges given by

$$\begin{aligned} W_2 = & Q_{mc} Q_{ms(dd)} \{ 12\sqrt{3} [2(\frac{1}{2}X_c - \frac{1}{2}X_T)^2 + (1 + \frac{1}{2}X_c + \frac{1}{2}X_T)^2]^{-1/2} \\ & + 12\sqrt{3} [(\frac{1}{2}X_c - \frac{1}{2}X_T)^2 + 2(1 + \frac{1}{2}X_c + \frac{1}{2}X_T)^2]^{-1/2} \\ & + 4(1 + \frac{1}{2}X_c + X_T)^{-1} \} \end{aligned} \quad (\text{A5})$$

(c) W_3 is the LR interaction energy between core and virtual charges given by

$$\begin{aligned} W_3 = & Q_{mc} Q_{mv} \{ 12\sqrt{3} [\frac{1}{2}X_c^2 + (1 + \frac{1}{2}X_c)^2]^{-1/2} \\ & + 12\sqrt{3} [\frac{1}{4}X_c^2 + 2(1 + \frac{1}{2}X_c)^2]^{-1/2} + 4(1 + \frac{1}{2}X_c)^{-1} \}. \end{aligned} \quad (\text{A6})$$

(d) W_4 is the LR interaction energy between shell and virtual charges expressed as

$$\begin{aligned} W_4 = & Q_{ms(dd)} Q_{mv} \{ 12\sqrt{3} [\frac{1}{2}X_T^2 + (1 + \frac{1}{2}X_T)^2]^{-1/2} \\ & + 12\sqrt{3} [\frac{1}{4}X_T^2 + 2(1 + \frac{1}{2}X_T)^2]^{-1/2} + 4(1 + \frac{1}{2}X_T)^{-1} \}. \end{aligned} \quad (\text{A7})$$

(e) W_5 is the energy due to interaction of defect with core, shell and virtual charges, expressed as

$$W_5 = 8Q_{md(d)} [Q_{mv} + Q_{mc}(1 + X_c)^{-1} + Q_{ms(dd)}(1 + X_T)^{-1}]. \quad (\text{A8})$$

Thus, the modified LR energy of region I due to the Coulomb and TBI is given by

$$E_2 = \frac{e^2}{r_0} (W_1 + W_2 + W_3 + W_4 + W_5). \quad (\text{A9})$$

(iii) Polarization energy

In the framework of TSM, polarization of ions is accounted through K_m . In region I, the core and shell interaction of the same ion represents the linear spring energy (Silvarajan 1978)

$$E_3 = 8\left(\frac{1}{2}K_m X_s^2 r_0^2\right) \quad (\text{A10})$$

given in terms of the modified core-shell spring constant K_m . The polarization energy in region II arises from the interaction of region II dipoles with the effective charge of the vacancy, which is of $1/|\mathbf{R}|^4$ type, and is expressed as

$$E_4 = \frac{Q_{md(d)}^2 e^2}{2r_0} (5.3392 M_- + 9.2295 M_+). \quad (\text{A11})$$

An additional contribution to the polarization energy obtained from the dipole-dipole interaction between the two regions is given by

$$E_5 = \frac{4Q_{mv} e^2}{r_0} (Q_{mc} X_c + Q_{ms(dd)} X_T) [0.352 M_- + 5.333 M_+] \quad (\text{A12})$$

with M_- and M_+ as Mott and Littleton parameters.

(iv) Short range interaction energy

In region I (defect region), the short-range interaction energy is written as

$$E_6 = 12 \left\{ [B_{--} \exp(-2r_0(1 + X_T)/\sqrt{3}p) + B_{--} \exp(-2r_0/\sqrt{3}p)] \right. \\ \left. - \frac{c_{--}}{(2/\sqrt{3})^6 r_0^6} \left(\frac{1}{(1 + X_T)^6} - 1 \right) - \frac{d_{--}}{(2/\sqrt{3})^8 r_0^8} \left(\frac{1}{(1 + X_T)^8} - 1 \right) \right\}, \quad (\text{A13})$$

and for region II, this contribution is

$$E_7 = 8[\phi_{+-}(R_1) - \phi_{+-}(G_1)] + 24[\phi_{+-}(R_2) - \phi_{+-}(G_2)] \\ + 24[\phi_{+-}(R_3) - \phi_{+-}(G_3)] + 24[\phi_{--}(R_4) - \phi_{--}(G_4)], \quad (\text{A14})$$

where

$$\phi_{+-}(r) = B_{+-} \exp(-r_0/p) - c_{+-} r_0^{-6} - d_{+-} r_0^{-8}, \quad (\text{A15})$$

$$\phi_{--}(r) = B_{--} \exp(-2r_0/\sqrt{3}p) - c_{--} (2r_0/\sqrt{3})^{-6} - d_{--} (2r_0/\sqrt{3})^{-8}, \quad (\text{A16})$$

with

$$\begin{aligned} R_1 &= 3(\frac{1}{2} + X_3 - \frac{1}{2} X_T) (2/\sqrt{3}r_0), \\ R_2 &= [2(\frac{1}{2} + X_T)^2 + (\frac{1}{2} + X_1 - \frac{1}{2} X_T)^2]^{1/2} (2/\sqrt{3}r_0), \\ R_3 &= [(\frac{1}{2} + \frac{1}{2} X_T)^2 + (\frac{1}{2} + X_2 - \frac{1}{2} X_T)^2]^{1/2} (2/\sqrt{3}r_0), \\ R_4 &= [(1 + 3X_4 - \frac{1}{2} X_T)^2 + 2(X_4 - \frac{1}{2} X_T)^2]^{1/2} (2/\sqrt{3}r_0), \end{aligned} \quad (\text{A17})$$

G_i ($i = 1-4$), can be obtained by putting $X_T = 0$ in R_i ($i = 1-4$) in (A17).

The interaction energy between regions I and II (given by E_3 in (14)) also contributes to the short-range energy and it is expressed as

$$E_8 = - \sum_{i=1}^4 \left. \frac{dE_7}{dX} \right|_{X=X_i} \cdot \bar{X} \quad (\text{A18})$$

which can be evaluated from the knowledge of E_7 as defined earlier.

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