

Schottky Defect Formation Energy in Transition Metal Oxide

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Abstract —

In the current paper an attempt has been made to review briefly the research carried out so far in the study and investigate of the defect properties of various solids using different computer simulation techniques. The significance of Transition Metal Oxides (TMO) (on which the present work is focused) in the field of science and technology has also been outlined. The Origin and significance of the Three Body Interactions (TBI) and their inclusion in inter ionic potentials that are used to compute various physical properties of wide range ionic solids have also been discussed. Finally the results of PC reproduction investigation of impacts of three-body interactions (TBI) on Schottky imperfection properties of some transition metal oxides (TMO) have been reported. The computations have been done in the structure of polarizable point ion (PPI) show utilizing the three-body interaction potential (TBP) executing static simulation system and contrasted and accessible other hypothetical and trial investigations. The processed strong and Schottky formation energies are in great concurrence with the test information and thus, bolster the inclusion of three-body interactions in computations of imperfection properties of ionic solids.

Keyword: Three-Body interactions, Inter ionic potential, Schottky formation energy, cohesive energy, and Polarization.

I. Introduction

The review of the literature reveals that the computer simulation and modeling of various types of solids that include conductors, semi-conductors, insulators, alloys, solid solutions, non-stoichiometric compounds, surfaces, interfaces etc. have been playing a prominent role in understanding the properties of point defects, complex defects, defect clusters, F-centre aggregates, color centers, electron traps and their influence over the rest of the solid continuum [1-5]. The presence of these defects in solids leads to anomalous behavior with respect to some of their physical properties such as electrical conductivity, ionic conductivity, specific heat, thermal expansion, dielectric properties, optical properties etc. The common point defects are vacancies, interstitials and substitution impurities. These defects are known to influence transport properties like diffusion, electrical conduction, creep etc. The Schottky defects influence the ionic conductivity, thermal conductivity, migration and diffusion properties of ionic solids like alkali halides, metal oxides etc.

Since 1930, the defect properties of the crystalline solids have been studying extensively both theoretically and experimentally. The experimental techniques like diffusion measurements ionic thermo current techniques, dielectric loss measurements produce an indirect prediction of the defect properties and sometimes cannot be correlated to each other. The other experimental techniques available are measurement of X-ray lattice parameter or density changes or the combination of both. The resonance methods like NMR and EPR monitor the time dependent local fields experienced by moving particles [5-10]. Hayes and Stoneham reviewed that none of these experimental techniques can reveal the interaction mechanism, polarization and relaxation phenomena, elastic energy, formation energy and binding energies of complex defect aggregates accurately.

The theoretical methods use computer simulation techniques like static simulation, abinitio computations, Monte- Carlo simulations, molecular dynamics simulations etc. The static simulation and abinitio computations are generally used for simple ionic solid structures where the dynamic simulations are suitable for complex defect structures, covalent crystals, metals, minerals, alloys and other amorphous solids. The hypothetical investigations of a few sorts of migration and restricting energies in ionic solids have been done by a few specialists for as long as eight decades. The greater part of these calculations utilize the semi-discrete cross section approximation proposed by Mott and Littleton for the simulation of the imperfection properties of the wide assortments of solids. The discrete lattice approximation proposed

by Kanzaki and the Green Function technique have also been used to study the defect induced vibrational transport properties of the several systems of the solids. An alternative approach was initiated by Hardy and his coworkers by adapting the lattice static method proposed by Kanzaki and used the deformation dipole model to study the defect properties of alkali halides. Though this approach was found quite satisfactory in predicting the dielectric properties, the computed Schottky and Frenkel defect formation energies in ionic solids are considerably lower than the experimental results. The defect properties have also been studied using rigid shell model which takes the electronic polarization into account. In addition to these static simulation strategies, the atomistic displaying systems are currently being utilized widely for the investigation of properties and conduct of ionic materials. The abinitio and Density Functional Theories (DFT) are also used to determine defect formation energies, surface chemical reactivity etc. which are in good agreement with the spectroscopic measurements. However when contrasted with the basic static simulation procedure these abinitio and dynamic simulations are costlier for expansive scale simulations, particularly for the frameworks containing more than several molecules or ions [11-12]. This thusly high light the application of between ionic potentials which permit quick static simulations for expansive ionic frameworks.

The transition metal oxides (TMO) are a class of non-metallic solids that address a model of a broad grouping of non-metallic solids yet tend to grow because of their non-stoichiometric lead. The non-stoichiometric structure of the metal oxides prompts point defects in these solids and assume a major part in deciding the physical and compound properties of these inorganic materials. The abinitio and Density Functional Theories (DFT) are utilized to decide imperfection formation energies, surface reactivity and so on., Atomistic and Density Functional Theory approaches are valuable for the investigation of imperfection formation energies, surface substance reactivity and so on which are in great concurrence with spectroscopic estimations. The imperfection properties of transition metal oxides have been contemplated by utilizing the idea of polarizable point ion and the shell display and the HADES program created by Norgett [13] with various arrangements of bury ionic potentials. Catlow et al [14] have considered the imperfection energies by utilizing the summed up Born-Mayer potential comprising of six flexible parameters got from the versatile, dielectric and phonon properties. Vempati and Jacobs have revealed the deformity formation energies of TMO ascertained from various arrangements of potential parameters and shell show. All the above investigations utilized two-body potentials, which don't consider the many – body impacts, which are observed to be dependable in clarifying the dynamical properties.

A point by point survey of significance and outcomes of the impacts of the TBI on the ideal precious stone properties has been made by Singh. Singh and his colleagues have utilized the numerous body interaction potential to consider the imperfection properties of salt halides. These investigations have demonstrated that long-range TBI altogether impacts the relaxation and polarization system of ionic gems. The point of the present investigation is to think about the impacts of TBI on the imperfection formation energies of some transition metal oxides of shake salt structure in the system of PPI show utilizing static simulation strategy. In this paper, we influenced an endeavor to introduce a PC simulation to an investigation of impacts of three-body interactions (TBI) on Schottky imperfection properties of some transition metal oxides (TMO). The calculations have been done in the structure of polarizable point ion (PPI) model and utilizing the three-body interaction potential (TBP). The figured durable and Schottky formation energies are in great concurrence with the test information.

II. Three – Body Interaction Potential

2. 1. Coulomb Potential

The electrostatic or coulomb interaction occurs between charged point ions, which possess integral electronic charge. In ionic crystal lattice the nearest neighbors are of opposite polarity and hence they are attracted by strong attractive coulomb potential. The coulomb energy is long range in nature and represents

the energy due interaction between these spherically symmetric (point - like) charges $Z_K e$ and $Z_{K'} e$ of the ions designed by $(1 k)$ and $(1' k')$ with 1 as the unit cell index and k as the basis index denoting their type.

The coulomb energy per ion-pair with separation $|\vec{r}(1k, 1'k')|$ is written as

$$W_C = \frac{Z_k Z_{k'} e^2}{|\vec{r}(1k, 1'k')|} \quad 2.1$$

This energy per molecule can be expressed as

$$W_C = \frac{1}{2N} \sum'_{1k, 1'k'} \frac{Z_k Z_{k'} e^2}{|\vec{r}(1k, 1'k')|} \quad 2.2$$

Where, N is the number of molecules per unit cell. The prime over the summation indicates that the sum should be excluded for $k = k'$. Introducing the concept of Madelung constant (α_M), the above equation can be written as

$$W_C = \frac{\alpha_M e^2 Z^2}{r} \quad 2.3$$

Here r is the nearest neighbor separation and Z is the largest common factor of Z_K and $Z_{K'}$. The Madelung constant, α_M depends on the structure of the crystal. Various methods for determination of Madelung constant have been excellently reviewed by Tosi [15].

2.2. Three-Body Interaction

The ions amid grid vibrations endure a considerable cover and therefore, their electron-shells experience deformation. This system causes an exchange of charge between the overlapping ions. These exchanged charges interface by means of Coulomb law with every other charge and offer ascent to the long-run many-body interactions whose most critical segment is the three-body interactions(TBI).

The relevant expression for TBI potential used by us is given by

$$W_T = \sum_{kk'k''} \frac{Z_k Z_{k'} e^2}{r_{kk'}} f(r_{kk''}) \quad 2.4$$

Where, $f(r_{kk''})$ is the three-body interaction parameter and depends on the overlap integrals. The essential reason for choosing this form of TBI potential due to Lowdin [16] and Lundqvist [17] in the present investigation can be traced from the fact that the existence of this TBI in ionic crystals is well established. Also, extensive studies carried out by Singh and his co-workers [12] for lattice vibration properties of ionic solids show that these interactions have significant influence on the dynamical, elastic, photo elastic and anharmonic properties of these solids. On the other hand, the SR TBI introduced by The expression for TBI potential energy mentioned above, cab be derived from both quantum and classical mechanical considerations. A brief account of these methods is given below.

2.2.1 Quantum Theory of TBI

In the Heitler-London approximation, the nuclear wave functions are dealt with inflexibly associated with their cores and are assumed not to change because of a deformation of the ions. In any case, when the ions are placed in a cross section, their electron wave functions cover and this causes their deformation. The nonorthogonality came about because of such deformation makes the charge distribution contrast from the aggregate of the densities with the expectation of complimentary ions and this distinction is more articulated in the regions of apparent cover of the nuclear wave functions. This adjustment in the electron charge thickness causes a charge depletion which relies upon the intra atomic separation and interfaces with every single other charge through coulomb law and offers ascend to the long-go TBI as presented by Lowdin [18] and Lundqvist [17]. An expand numerical treatment of this hypothesis has been given somewhere else[18].

2.2.2. Classical theory of TBI

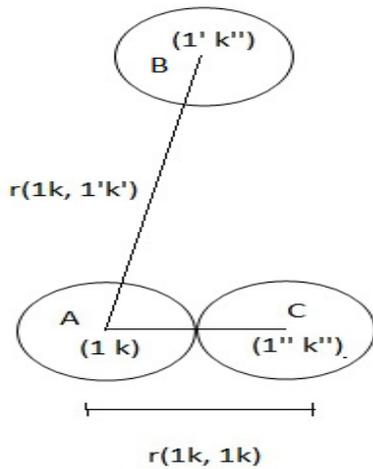


Fig.1 Three body interaction due to electron shell overlap.

For a proper understanding of the existence of TBI from the charge transfer mechanism, we consider the ions A,B and C as designated by (1 k), (1' k') and (1'' k'') in an ionic crystal as shown in Fig.1. C is the nearest neighbor (nn) of A separated by a distance $|\vec{r}(1k, 1''k'')|$ while B is any ion at a distance $|\vec{r}(1k, 1'k')|$ apart from A. The electron shells of ions A and C overlap during lattice vibrations and give rise to the transfer of a charge by an amount

$$dq_k = \pm Z_k f_k(r(1k, 1''k'')) = \pm Z_k f_k(r) \quad 2.5$$

This clearly shows that the amount of transferred charge depends on the degree of overlap, i.e., inter atomic separation (r). Here $f_k(r)$ is a function which is significant only between nn ions. The occurrence of the above transferred charge leads to a modification in the ionic charge of ion A, as

$$Z_m(K)e = \pm Z_k e \left(1 + \frac{2n}{Z} f(r(1k, 1''k''))\right)^{1/2} \quad 2.6$$

Here, n represents the number of nearest neighbor (nn) ions and $\left(1 + \frac{n}{Z} f(r)\right)^2$ has been approximated as $\left(1 + \frac{2n}{Z} f(r)\right)^{1/2}$. 2.7

$$\text{Similarly, we can write the total charge on B as } Z_m(K')e = \pm Z_k' e \left(1 + \frac{2n}{Z} f(r(1'k', 1''k''))\right)^{1/2} \quad 2.8$$

Where, (1'' k'') is the nn ion of B (not shown in Fig.1).

In view of the above descriptions, the coulomb interaction energy between ion pairs A and B is given by

$$W_C = \frac{\sum_{k'k''} e^2 \left(Z_k + n f_k(r(1k, 1''k'')) \right) \left(Z_{k'} + n f_k(r(1'k', 1''k'')) \right)}{|r(1k, 1'k')|}$$

$$= \frac{Z_k Z_{k'} e^2}{|r(1k, 1'k')|} + \frac{n e^2}{|r(1k, 1'k')|} (Z_k f_k(r(1'k'), (1''k'')) + Z_{k'} f_{k'}(r(1k, 1''k''))) + \frac{n^2 e^2}{|\vec{r}(1k, 1''k'')|} (f_k(r(1k, 1''k'')) \times r(1'k', 1''k''))$$

2.9

Here, the principal term is notable two-body Coulomb potential; the second term contains two sections indicating the contributions of the focal kind whose size relies upon the directions of three atoms and subsequently they might be alluded to as TBI. The last term is clearly a contribution because of four-body interactions and is dismissed in perspective of its littleness, being a result of two little amounts. Since the ion sets are indistinguishable all through the gem, in this manner, a similar function can be utilized to speak to the charge exchange between every ion sets.

The expression for altered coulomb potential, along these lines, can be composed as

$$W_C^m = W_C + W_T$$

2.10

Where,

$$W_C = \sum_{1k, 1'k'} \frac{Z_k Z_{k'} e^2}{|r(1k, 1'k')|}$$

2.11

and

$$W_T = \sum_{1k, 1'k', 1''k''} Z_k f_k(r(1k, 1''k'')) \frac{Z_{k'} e^2}{|r(1k, 1'k')|} \quad 2.12$$

Here, W_C is the usual coulomb potential, while W_T is purely TBI potential.

2.2.2. Three – Body Interactions in a defect lattice

The subtle elements of the incorporation of the three-body interactions in the calculation of imperfection properties have been talked about by our gathering in our prior papers [11-14]. The schematic chart of the nearness of a Schottky deformity in an ionic precious stone is as appeared in fig.2. Because of the creation of a deformity at 1 (0, 0, 0) (+ve ion opening), all the main neighbor ions (2-7) make tracks in an opposite direction from the opportunity by a separation of x . The ions 8 to 12 which are considered as the neighbors of 2 likewise endure dislodging. The ion 8, being at a separation of $2r$ from the opportunity will be uprooted by x_1 and the ions 9 to 12 is at remove from the opening, will be dislodged by x_2 . In the region - I of the deformity grid (i.e. 2 to 7 in fig.1) there exist two kinds of cover charges called genuine and virtual.

A consideration of a virtual charge at the first position and a genuine charge at the dislodged position of an ion around the deformity is a legitimate approximation [2] for the calculation of the Coulomb vitality. A similar approximation has been embraced for the calculation of the long-go TBI vitality [4]. In like manner, it has been accepted that there will be exchanged charges (like those in consummate cross sections) because of the cover between the opening and virtual charges (positioned at 2 to 7) and the measure of this cover is proportional to $f(x)$. Subsequently, the interaction between the opening (at 1) and the virtual charges (at 2 to 7) will prompt adjusted ionic charges of the opportunity as

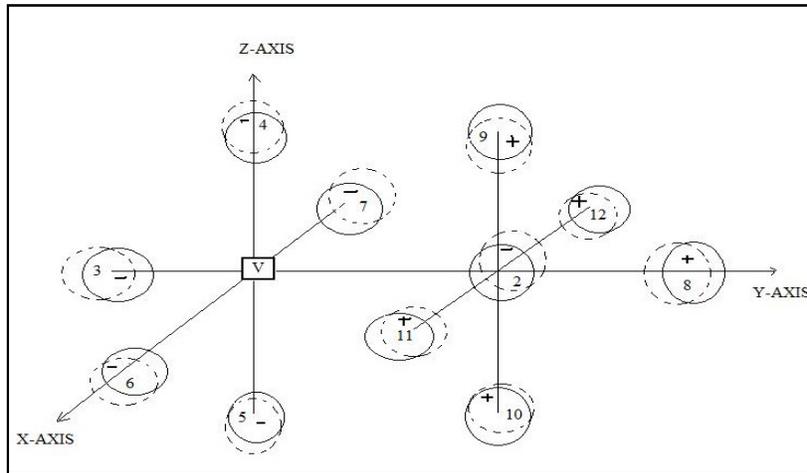


Fig.2. Polarization around the Schottky Vacancy Defect Lattice Configuration

$$Z_m e = Ze (1+6 f (r)) = \pm Ze \left(1 + \left(\frac{12}{2}\right) f (r)\right)^{1/2} \quad 2.13$$

With $f (r)$ as the TBI parameter expressed as [20]

$$f (r) = f_0 \exp \left(\frac{-r}{\rho} \right) \quad 2.14$$

Here f_0 is a consistent. The genuine charges at 2 to 7 each being uprooted by x from their unique position because of the creation of the imperfection (opportunity), will have an alternate level of cover with the opening site than the virtual charges. Scientifically the level of this cover is proportional to the function [11-14]

$$f (r) = f_0 \exp \left(\frac{-r (1+x)}{\rho} \right) \quad 2.15$$

Which, implies that due to the interactions between the real charges and the vacancy, the charge of the defect ion (or vacancy) gets modified to a value

$$Z_{md} e = Ze (1+ 6 f_d (r)) \quad 2.16$$

In this way, the principal kind of overlapping charges between the virtual and opportunity charges and the genuine opening charges prompts the changed opportunity charge, which thusly, offers ascent to the TBI (I). Alternate kinds of exchanged charges, which offer ascent to TBI (II), emerge because of the cover between the ions 2 to 7 and their separate neighbors. The measure of exchanged charge on the ion 2, because of its six neighbors will be proportional to the function [11-14]

$$f_{dd} (r) = f_0 \left[\exp (-1+x) r_0 / \rho + \exp (- (1+2x_1 -x) r_0 / \rho + 4 \exp [-((x_2-x)^2 + (1+x_2)^2)^{1/2} r_0 / \rho] \right] \quad 2.17$$

The corresponding modified ionic charge at the immediate neighbors of the vacancy due to their respective neighbors will become

$$Z_{mdd} e = Z_c (1 + f_{dd}(r)) = \pm Z_c (1 + \frac{2}{2} f_{dd}(r))^{1/2}$$

2.18

In this manner the incorporation of the TBI impacts in deformity grid adjusts the ionic charge of the ions in region 1. Since whatever remains of the gem is considered in ceaseless approximation [7], the TBI impacts in the region II are the same as those on account of impeccable grid.

2.3 TBI Effects on dielectric properties

The nearness of point absconds in an ionic precious stone irritates the grid harmony and offers ascend to the electric fields at the ions. Therefore, the electronic shells of the ions get distorted, prompting an electronic polarization. Every ion is the deformity precious stone is portrayed by its dislodging dipole and electronic dipole minutes. The polarization in region II can be because of the uprooting of the positive and negative charges in inverse directions because of the outer field and furthermore because of the electronic polarizabilities of ions. The consideration of dipolar approximation prompts the expression for the powerful electric field [14].

$$\vec{E}_{eff} = \vec{E} + \frac{4\pi}{3} \vec{p}$$

2.19

following up on an ion. Here is a naturally visible field and is the polarization created by the uprooting of the ions. The presence of long range three-body powers together with coulomb field alters the above expression [14] as

$$\vec{E}_{eff} = \vec{E} + \frac{4\pi}{3} \vec{p} + \lambda \vec{p}$$

2.20

The last term in the above expression is due to three-body coupling coefficients [3]. The abbreviation λ stands [14]

$$\lambda = \frac{16\pi Z r_0 f_0^1}{3Z_m^2} \tag{2.21}$$

Now, using the polarizabilities relations

$$\vec{p} = \frac{\alpha}{V} E_{eff} \text{ and } \frac{\vec{p}}{E} = \frac{\epsilon - 1}{4\pi}$$

2.22

The modified Lorenz and Clausius - Mossotti (CM) relations can be expressed as

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{\alpha_m}{V} \left[\frac{4\pi}{3} + \lambda \right] \left[1 + \frac{\lambda \alpha_m}{V} \right]^{-1} \tag{2.23}$$

and

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} = \left(\frac{\alpha_m + \alpha_{mD}}{V} \right) \left[\frac{4\pi}{3} + \lambda \right] \left[1 + \frac{\lambda}{V} (\alpha_m + \alpha_{mD}) \right] \tag{2.24}$$

Where, ϵ_0 and ϵ_∞ are the static and electronic dielectric constants respectively. α_m and α_{mD} are respectively, the electronic and ionic polarizabilities modified due to TBI.

III. FORMULATION OF DEFECT ENERGY CALCULATION

The nearness of point imperfection in an ionic gem irritates the grid harmony and offers ascend to the electrical fields at the ions. Thusly, the electronic shells of the ions get disfigured, prompting an electronic polarization. Every ion in the deformity precious stone is portrayed by its uprooting dipole and electronic dipole minutes.

For the calculation of Schottky imperfection formation vitality, we have utilized the Mott and Littleton [7] approximation, as indicated by which the dislodging of ions in region II is adequately little and thus they can be dealt with inside normal continuum approximation [7]. The polarization in region II can be because of the uprooting of the positive and negative charges in inverse directions because of the outside field and furthermore because of the electronic polarizabilities of ions.

If the external field is due to the modified ionic charge $Z_m e$ then the polarizabilities \vec{P} and \vec{r} away will be given by

$$\vec{P} = \frac{1}{4\pi} \left(1 - \frac{1}{\epsilon_0} \right) Z_m e / r^3 \vec{r} \tag{3.1}$$

Where, ϵ_0 is the static dielectric constant. The dipole moment on a volume ($=2r_0^3$) of the primitive unit cell is therefore equal to $P (2r_0^3)$. This is divided in the ratio of the electronic polarizabilities (α_{m+}, α_{m-}) of the ions in the unit cell to give the electronic dipole moment (m_{\pm}^{II}) per ion such that

$$m_{\pm}^{II} = M_{\pm} r_0^3 \left(Z_m e / r^3 \right) \vec{r} \tag{3.2}$$

with

$$m_{\pm} = \frac{\alpha_{m\pm}}{\left(\alpha_{m\pm} + \frac{\alpha_m}{2} \right)} \frac{1}{4\pi} \left(1 - \frac{1}{\epsilon_0} \right) \tag{3.3}$$

The suffix II appearing with m_{\pm}^{II} denotes that it belongs to a region II ion. $\alpha_m D$ and $\alpha_m (= \alpha_{m+} + \alpha_{m-})$ are respectively the displacement and electronic polarizabilities modified due to TBI [12]. These polarizabilities have been determined from the modified LL and CM relations given by equations 2.23 and 2.24. In the light of these modifications, the displacement dipoles are given

$$\vec{d}_{\pm}^{II} = M_{D\pm} r_0^3 \frac{Z_m e}{r^3} \vec{r} \tag{3.4}$$

with

$$m_{\pm} = \frac{\alpha_{m\pm}}{\left(\alpha_{m\pm} + \frac{\alpha_m}{2} \right)} \frac{1}{4\pi} \left(1 - \frac{1}{\epsilon_0} \right) \tag{3.5}$$

The corresponding displacement of the region II ions is expressed as

$$\vec{X}_{\pm}^{II} = \frac{Z_m e}{\vec{d}_{\pm}^{II}} \tag{3.6}$$

The above equations totally characterize the relocations and dipole snapshots of region II ions.

The aggregate vitality of the imperfection configuration would now be able to be composed as [19].

$$E = E_0 + E^I (X^I, m^I) + E^{I,II} (X^I, m^I; X^{II}, m^{II}) + E^{II} (X^{II}, m^{II}) \quad 3.7$$

Where E_0 is the vitality required to make the deformity. Whatever is left of the terms basically speak to the grain in vitality because of the distortion and polarization E^I and E^{II} are the vitality contributions from region I and II separately. $E^{I,II}$ is the interaction vitality between the regions I and II. A substitution of the vitality expressions in the balance conditions [20]

$$\frac{\partial \vec{E}}{\partial \vec{m}^I} = 0, \quad \frac{\partial \vec{E}}{\partial \vec{m}^{II}} = 0 \quad \text{and} \quad \frac{\partial \vec{E}}{\partial \vec{X}_i^{II}} = 0 \quad 3.8$$

Given us

$$E^I = E_0^I + E_1^I (X^I, 0) - 1/2 \sum_i \vec{m}_i^I \cdot \vec{F}_i^{(I)} - 1/2 \sum_j (\vec{m}_j^{II} + \vec{d}_j^{II}) \cdot \vec{F}_j^{(I)} + E_{SR}^{I,II} (\vec{X}^I, 0; \vec{X}^{II}, 0) - 1/2 \sum_j \vec{X}_j^{II} \frac{\partial}{\partial \vec{X}_j^{II}} E_{SR}^{I,II} (\vec{X}^I, 0; \vec{X}^{II}, 0) \cdot \vec{X}_j^{II} \quad 3.9$$

With $\vec{F}_i^{(I)}$ as the field at ion (i) due to all the monopoles region I. \vec{m}_j^{II} and \vec{d}_j^{II} are obtained by ML method[12]. Once they have been evaluated, the total energy can be minimized with respect to \vec{X}^{II} and \vec{m}^I .

The above energy expression can also be written as [69].

$$E = W_1 + W_{2,LR} + W_{3,SR} + W_{4,SR} - 1/2 \sum_j \vec{X}_j^{II} \frac{\partial}{\partial \vec{X}_j^{II}} W_{3,SR} \cdot \vec{X}_j^{II} + W_4 + W_5 \quad 3.10$$

Here, W_1 is precisely same as E_0 characterized in equation 3.3. $W_{2,LR}$ is the change in long-go coulomb and TBI energies because of the relaxation of the region I ions. $W_{3,SR}$ is the vitality of relaxation of the short-extend powers inside the region I. $W_{4,SR}$ is the short-run interaction term between the ions of the region I and their closest and next-closest neighbors which frame regions II. W_4 is the polarization vitality of region II and is basically the interaction between the dipoles of region II with the field of the

region I monopoles. It is communicated as

$$W_4 = - 1/2 \sum_j (\vec{m}_j^{II} + \vec{d}_j^{II}) \cdot \vec{F}_j^{(I)} \quad 3.11$$

W_5 is the polarization energy of region I, defined as [20]

$$W_5^1 = - \frac{1}{2} \sum_i \frac{1}{m_i^2} F_i \quad (1)$$

3.12

The TBI effects on these energy terms have been explicitly demonstrated in the following section.

IV. TBI EFFECTS ON VARIOUS ENERGY TERMS

The three-body interactions are long-run in nature and present modifications in ionic charge, versatile and dielectric constants and polarizabilities along these lines, the vitality terms contributed by the polarization marvels will likewise get altered as examined underneath. The vitality W_1 which is expected to extricate the cation (anion) from an inflexible grid is communicated as

$$W_{1\pm} = \frac{\alpha_m Z_m e^2}{r_o} - 6 B_{+-} \exp(-r_o/\rho) - 12 B_{+-} \exp(-\sqrt{2} r_o/\rho) + \frac{6.5952 C_{+-}}{r_o^6} + \frac{6.1457 d_{+-}}{r_o^8} + \frac{1.8067 C_{\pm\pm}}{r_o^6} + \frac{0.8 d_{\pm\pm}}{r_o^8}$$

4.1

Where $\alpha_m (=1.74756)$ is the Madelung constant and the remaining abbreviations stand for

$$B_{+-} = b_{+-} \beta_{+-} \exp((r_{+} + r_{-})/\rho) \quad 4.2$$

$$B_{\pm\pm} = b_{\pm\pm} \beta_{\pm\pm} \exp(2r_{\pm}/\rho) \quad 4.3$$

Where β_{ij} are the Pauling coefficients. All other symbols have their usual meaning [20].

The energy $W_{2,LR}^1$ in equation 3.10 is the change in long-range coulomb and TBI energies due to the relaxation of the ions in region I. The coulomb energy term due to such relaxation (X), is expressed as [20]

$$W_{2C}^1 = \frac{6Z^2 e^2}{r_o} \left[\frac{\sqrt{2} + 5/4}{(1+X)} - \frac{1}{(2+X)} - \frac{4}{(1+(1+X)^2)^{1/2}} + (\sqrt{2} - 3/4) \right]$$

4.4

The long-go TBI in imperfection has been gotten from the exchanged charges on opening because of the interaction of each virtual and genuine accuse of all other virtual and genuine charges in region I. The TBI contributions to this vitality is given by

$$W_{2T}^1 = \frac{6Z e^2}{r_o} \left[\frac{1}{(1+X)} - 1 \right] (\delta f(r) + \delta f_d(r))$$

4.5

The transferred charge on the nearest neighbors of the vacancy will also interact with all virtual and real charges in region I to give

$$W_{2T}^2 = \frac{\delta Z e^2}{r_0} \left[\frac{2\sqrt{2} + 1/2}{(1+X)} f_{dd}(r) - \left(\frac{1}{(2+X)} + \frac{4}{(1+(1+X)^2)^{1/2}} \right) (6f(r) + 6f_d(r)) + 6f(r)(2\sqrt{2} + 1/2) \right]$$

4.6

Thus the total long-range energy of the region I

$$W_{2,LR}^I = W_{2C}^1 + W_{2T}^1 + W_{2T}^2$$

4.7

Since the introduction of TBI in the defect energy modifies the long-range part only, it will not have any direct effect on the short-range energy. Therefore, the short-range interaction energy involved in $W_{2,SR}^I$ and $W_{3,SR}^{II}$ can be expressed as [20]

$$W_{2,LR}^I = 12 \left[(W_{+-}(R_1) - (W_{+-}(R_1^0)) \right]$$

and

4.8

$$W_{3,SR} = 6 \left[(W_{+-}(R_2) - W_{+-}(R_2^0)) \right] + 24 \left[(W_{++}(R_3) - W_{++}(R_3^0)) \right] + 24 \left[(W_{--}(R_4) - W_{--}(R_4^0)) \right] + 24 \left[(W_{+-}(R_5) - W_{+-}(R_5^0)) \right]$$

4.9

Where

$$W_{+-}(R_i) = B_{+-} \exp(-R_i/\rho) - \frac{C_{+-}}{R_i^6} - \frac{d_{+-}}{R_i^8}$$

4.10

$$W_{++}(R_i) = B_{++} \exp(-R_i/\rho) - \frac{C_{++}}{R_i^6} - \frac{d_{++}}{R_i^8}$$

4.11

With

$$R_1 = \sqrt{2} r_0 (1+x)$$

$$R_2 = r_0 (1+x_1-x)$$

4.12

$$R_3 = r_0 \left[\left(1 + \frac{x_2}{\sqrt{2}} \right)^2 + \left(x - \frac{x_2}{\sqrt{2}} \right)^2 \right]^{1/2}$$

$$R_4 = r_0 \left[2 \left(1 + \frac{x_3}{\sqrt{3}} \right)^2 + \left(x - \frac{x_3}{\sqrt{3}} \right)^2 \right]^{1/2}$$

$$R_5 = r_0 \left[\left(1 + \frac{x_4}{\sqrt{5}} \right)^2 + \left(1 - x + \frac{x_4}{\sqrt{5}} \right)^2 \right]^{1/2}$$

4.13

Where X_1 , X_2 , X_3 and X_4 are the displacements (in units of r_0) of the (200), (110), (111) and (210) type ions respectively, and are defined as,

$$X_1 = -\frac{M}{4} D_{\pm} \quad X_3 = -\frac{M}{3} D_{\pm}$$

$$X_2 = -\frac{M}{2} D_{\pm} \quad X_4 = -\frac{M}{5} D_{\pm}$$

4.14

in terms of constant $M_{D_{\pm}}$, defined in equation 3.5. The terms with zero suffix in equation 4.9 are obtained from the corresponding expression by putting $X = 0$.

The fifth term in equation 3.10 represents the derivative of short-range energy which can be simplified by differentiating $W_{3,SR}^{III}$ with respect to X_1 , X_2 , X_3 and X_4 , respectively.

The energy W_4^{II} , is given by both the relaxation and polarization energy of region II due to coulomb and TBI potentials such that

$$w_{4\pm}^II = -\frac{Z_m^2 e^2}{2 r_0} (4.1977 M_{+} + 6.3346 M_{-}) + \frac{3 Z_{md}^2 e^2 X}{r_0} (0.388 M_{+} + 1.965 M_{-})$$

4.15

The first term in it is contributed by the energy due to the interaction of the vacancy with dipoles of region II and the second term is contributed by the energy due to interaction of the displacement dipoles of region I with the field of region II dipoles

The energy W_5^I expressed by equation 3.12 is the polarization energy of region I.

The field $\vec{F}_i^{(1)}$ occurring in it is the long-range attractive field due to coulomb and TBI potentials generated by the actual and effective charges in region I. The electronic moment on first shell ions is expressed as

$$\vec{m}_\pm = \alpha_{m\pm} (\vec{F}_\pm^{(1)} + \vec{F}_\pm^{(2)})$$

4.16

Where $\vec{F}_i^{(1)}$ is the radial field at displaced (100) ion due to the vacancy charge and the other real and virtual charges of region I and $\vec{F}_i^{(2)}$ is the field due to all the dipoles of region I and II at a (100) ion. The contribution to these fields from the coulomb forces is given as

$$\vec{F}_{c\pm}^{(1)} = \frac{Z e}{r_o^2} \left[\frac{5/4 + \sqrt{2}}{(1+x)^2} - \frac{1}{(2+x)^2} - \frac{4(1+x)}{(1+(1+x)^{2/3})} \right] \hat{i}$$

4.17

And

$$\vec{F}_{c\pm}^{(2)} = \left[\frac{\alpha_{m\pm} (1+6\sqrt{2})}{4 r_o^3 (1+x)^3} (\vec{F}_c^{(1)} + \vec{F}_c^{(2)}) \pm \frac{Z e}{r_o^2} (0.388 M_\mp + 1.965 M_\mp) \right] \hat{i}$$

4.18

While the TBI contributions are,

$$\vec{F}_T^{(1)} = \pm \left[\frac{\delta f(r)}{r_o^2 (1+x)^2} - \frac{Z e}{r_o^2} \left(\frac{1/4 + \sqrt{2}}{(1+x)^2} \delta f_d(r) \right) \right. \\ \left. - \left(\frac{1}{(2+x)^2} + \frac{4(1+x)}{(1+(1+x)^{2/3})} (\delta f_d(r) + f_{dd}(r)) \right) \right] \hat{i}$$

4.19

$$\vec{F}_T^{(2)} = \left[\frac{\alpha_m (1+6\sqrt{2})}{4 r_o^3 (1+x)^3} (\vec{F}_T^{(1)} + \vec{F}_T^{(2)}) \pm \frac{Z e}{r_o^2} (0.388 M_\mp + 1.965 M_\pm) \delta f_d(r) \right] \hat{i}$$

4.20

The total field \vec{F} due to coulomb and three-body interactions is now given by the sum of equation 4.17 to equation 4.20 such that

$$\vec{F}^{(1)} = \vec{F}_c^{(1)} + \vec{F}_T^{(1)}$$

4.21

Utilizing three vitality expressions and the technique for calculation depicted before we have ascertained the Schottky deformity formation vitality of the transition metal oxide precious stones. The processed outcomes have been displayed and examined in the following section.

V. COMPUTATIONS

For the calculation of the schottky imperfection formation vitality of the TMO the Mott and Littleton approximation [6] has been considered. In this approximation the precious stone is separated into two regions; region I comprises of the imperfection and its closest neighbors, while whatever is left of the gem is considered as region II. The relocations of the ions of region II are adequately little and henceforth they

can be treated with in regular continuum approximation [6]. The polarization in region II can be because of the removal of the positive and negative charges in inverse directions because of the outer field and furthermore because of the electronic polarizabilities of ions. The uprooting and dipole snapshots of the ions in the region-I are computed expressly by limiting the aggregate vitality concerning the removals and dipole minutes. The aggregate vitality of the imperfection configuration can be communicated as [19]

$$W = W_1 + W_{2,LR}^1 + W_{3,SR}^1 - \frac{1}{2} \sum_J^{\text{II}} \frac{\partial}{\partial \bar{x}_J^{\text{II}}} W_{3,SR}^{I:II} \quad | \quad , \quad \bar{x}_J^{\text{II}} + W_4^{\text{II}} + W_5^{\text{I}} \tag{5.1}$$

Here W_1 is the vitality required to make the imperfection. $W_{2,LR}^1$ is the change in long-run coulomb and TBI energies because of the relaxation of the region I ions. $W_{3,SR}^1$ is the vitality of relaxation of the short-run powers inside region I. $W_{3,SR}^{I:II}$ is the short-go interaction term between the ions of region I and their closest and next closest neighbors, which shape region II. W_4^{II} is the polarization vitality of region II and is basically the interaction between the dipoles of the region II with the field of region-I monopoles. W_5^{I} is the polarization of region I. The TBI impacts that emerge because of charge exchange instrument, on these vitality terms have been expressly exhibited in our before works [12-14]. By utilizing these vitality terms or more talked about technique for calculation, the schottky deformity formation vitality of two transition metal oxide gems to be specific, CoO and NiO has been figured for which trial and other hypothetical outcomes are accessible for examination.

The present TBP show proposed for the deformity vitality calculation comprises of just five parameters b , ρ_{ij} , and $f(r)$, which can be resolved from the harmony, bury ionic separation (r_0). The estimations of ρ_{ij} that have been gotten from clementi wave functions [21]. The dielectric properties [22, 23], the altered electronic (α_{m+} and α_{m-}) and dislodging (α_{mD}) polarizabilities [24], ionic radii [25], and harmony cross section steady [26] have been given in Table-1. The estimations of different properties utilized as information and the model parameters for metal oxide precious stones [21] have been given Table-2. The van der Waals coefficients C_{ij} and D_{ij} are assessed from SKV [27] strategy and have been displayed in Table-3. The figured outcomes have introduced and examined in the following section.

Table-1:
Dielectric Properties, Ionic Radii And Equilibrium Lattice Constants For TMO.

Crystal	ϵ_o^1	ϵ_{oo}^2	$\alpha_{m+}^3(10^{-18}/m^3)$	$\alpha_{m-}^3(10^{-18}/m^3)$	$\alpha_{md}^3(10^{-18}/m^3)$	$r_{++}^4(A^o)$	$r^4(A^o)$	$r_o^5(A^o)$
CoO	12.9	5.30	1.095	1.765	0.925	0.74	1.40	2.133
NiO	12.7	5.70	1.049	1.623	0.790	0.70	1.40	2.084

Table-2:
Input Constants And Parameters For TMO.

Crystal	$\rho_{+-} (A^\circ)$ [#]	$\rho_{++} (A^\circ)$ [#]	$\rho_{-} (A^\circ)$ [#]	$b (10^{19}j)$	$f (r) (x 10^{-2})$ [#]
CoO	0.280	0.211	0.37 0	2.582	2.51
NiO	0.275	0.211	0.37 0	2.468	5.28

Table-3:
Van Der Waals Coefficients For TMO

Crystal	C_{+-}	C_{++}	C_{-}	D_{+-}	D_{+}	D
CoO	57. 2	52.4	71. 1	33. 4	18.7	52.3
NiO	52. 6	45.4	71. 1	30. 4	15.1	52.3

IV. Results and Discussion

The computed displacements (ξ_{+} , ξ_{-}), the extraction energies (W_{+} , W_{-}) of cat ions and anions respectively and the cohesive energy W_L for the two transition metal oxides, CoO and NiO have been presented in Table -4. The calculated cohesive energies W_L and Schottky formation energies have been compared with the available experimental data [28, 29]. The comparison of the results reveal that the calculated values of schottky defect formation energies for CoO and NiO have a good agreement with the corresponding experimental values and they are better than the previous theoretical results. It is worth to point out that all these previous theoretical attempts [14,15, and 30] have used the pair wise two-body potentials and the parameters of their potentials have been fitted to some crystal properties in order to predict the fundamental point defect properties.

Table-4:
Displacements, Extraction Energies And Cohesive Energies.

Crystal	$\xi_{+} (A^\circ)$	$\xi_{-} (A^\circ)$	$W_{+} (eV)$	$W_{-} (eV)$	$W_L (eV)$	$W_L (eV)^*$
Co O	0 .061	0 .042	22. 483	2 3.873	40. 303	41. 400
Ni O	0 .064	0 .046	23. 364	2 4.852	41. 400	42. 300

Table-5:
Schottky Defect Formation Energies (Hs) CoO And Nio

Crystal	Present	Experiment [28]	other theoretical	Results	
			Ref.[15]	Ref.[30]	Ref.[14]
CoO	6.05	6.42	7.16	7.39	7.60
NiO	6.81	6.26	7.37	6.86	7.86

However, in the present investigation the potential parameters have not been derived using any of the crystal properties except equilibrium lattice constant. The effect of the three-body interactions on the formation energy of schottky defect is quiet significant as is revealed by the Table-5. Very large values of h_s predicted by other theories [59, 61, and 80] seem to originate from the inaccurate short-range potential and non-inclusion of long-range charge transfer effects in their potentials. Also, for a better understanding of the defect formation energy in these type of ionic crystals the variation of different energy contributions to the total energy of the defect configuration (W) of CoO and NiO have been shown in fig.3 and fig.4 respectively. The short range energy contribution (W_3), polarization energy contributions (W_4 and W_5) have been plotted as a function of nearest neighbor relaxation. It is noted that the non-polarization energy (W_3) is more sensitive to the relaxation than the polarization energies (W_4 and W_5) which vary very slowly. However, all the energy contributions do not follow a systematic variation may be due to nearly similar polarizabilities and ionic radii. Similar behavior of cation and anion extraction energies can also be observed from the depicted variations. In the figures the solid lines denote for cation vacancy and dashed lines denote for anion vacancy. In conclusion, the agreement achieved between the present theoretical results and available experimental data emphasizes the contribution of the TBI effect to the polarization in the defect region.

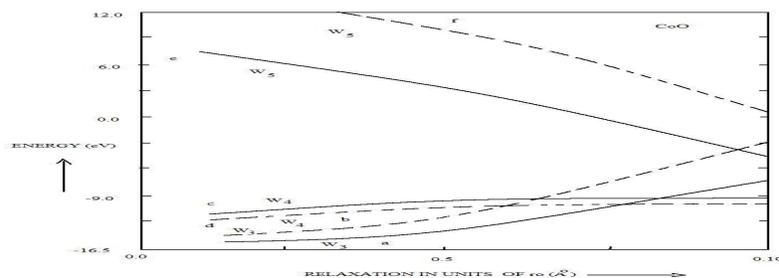


Fig.3 Variation of Energy contributions with nearest neighbor relaxation in CoO

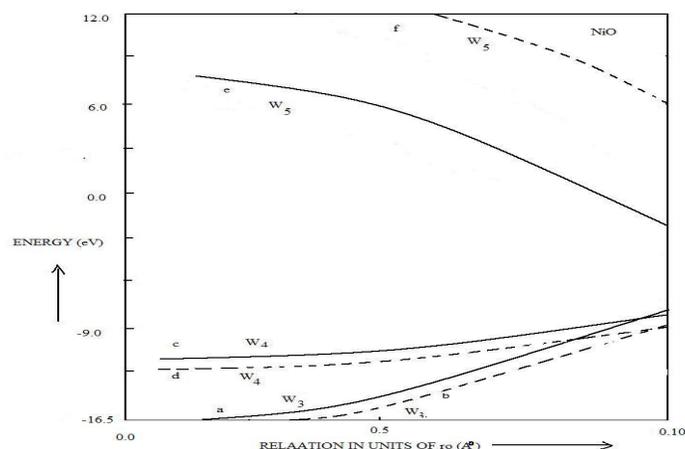


Fig.4. Variation of Energy contributions with nearest neighbor relaxation in NiO

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