Theory of point defect energetics: A review

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The energetics of point defects provide the controlling factor in determining the atomistic mechanisms in a wide range of solid state processes. We present here a pedagogical overview of the development of the continuum, quasi-lattice and lattice theories for different classes of point defects and materials. Varied approaches were followed in the past in modelling the relevant perfect crystals for interatomic forces for nonionic solids and model potentials for ionic materials. The earliest continuum approaches are those of Eshelby and Jost for treating point defects as elastic and dielectric singularities. These were followed by semicontinuum Mott-Littleton techniques and the Kanazaki defect force techniques in application to charged and neutral defect species. However the importance of a correct assessment of the dielectric polarization and the anharmonicity of the forces in the evaluation of the enthalpies and volumes have been well documented. Numerical computations of the enthalpies are seen to be sensitive to the choice of potential parameters and polarization models to varying degrees. While the theoretical picture is relatively clear in the case of the simpler materials with a near-ideal pure disorder, materials with mixed type of point defect disorders call for a more challenging simulation of defect environments which among other things should take into account the strong inhomogeneities of defect fields. The paper gives an overview of the evolution covering the highlights of these developments.

1 Introduction

The fundamental physical, chemical and engineering properties of crystalline materials are invariably influenced by the state of lattice disorder. While the mechanical and metallurgical behaviour is affected primarily by dislocations, with an important role played by point defects, there are a number of processes - both microscopic and macroscopic in which point defects act as the essential driving force. The prominent of these properties are broadly classified in Tables 1 and 2. Besides these properties, the mechanical behaviour of materials - notably the inelastic and an elastic response are sensitively dependent on the nature and content of the point defects.

<table>
<thead>
<tr>
<th>Process</th>
<th>Property</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass transport</td>
<td>Diffusion</td>
<td>D</td>
</tr>
<tr>
<td>Charge transport</td>
<td>Electrical conductivity</td>
<td>( \sigma )</td>
</tr>
<tr>
<td>Energy transport</td>
<td>Thermal conductivity</td>
<td>( \kappa )</td>
</tr>
<tr>
<td>Momentum transport</td>
<td>Internal friction</td>
<td>( Q^{-1} )</td>
</tr>
</tbody>
</table>

Table 1 -- Ionic processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Property</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical Transitions</td>
<td>Optical absorption or emission</td>
<td>( \alpha )</td>
</tr>
<tr>
<td>Dielectric response</td>
<td>Dielectric constant</td>
<td>( \varepsilon )</td>
</tr>
<tr>
<td>Magnetic response</td>
<td>Static / dynamic susceptibility</td>
<td>( \chi )</td>
</tr>
</tbody>
</table>

Table 2 -- Electronic processes

The role of point defects in transport properties are perhaps among the best atomistically modelled so far. To understand this role, it is necessary to introduce the concepts of the thermodynamic parameters of point defects. When a point defect such as a vacancy is added to the lattice, many changes in the thermodynamic extensive variables will occur. Each defect increases the internal energy of the crystal by a certain amount called the energy of formation of the defect, \( u' \). The unbalance in force equilibrium will bring about a relocation of the atoms in the neighbourhood and beyond, depending on the extent of unbalance. These atomic relaxations will lead to a change in the volume of the crystal, by an
amount $v^{rel}$. In the case of Schottky defects, there will be an additional change in volume due to the extra volume ($\Omega$) occupied on the surfaces where the vacancies originate from. These two contributions add to give the volume of formation of a defect, $v^f = v^{rel} + \Omega$. For Frenkel defects, for e.g., the second contribution does not exist.

When the atoms in the proximate region of the defect have relaxed into new equilibrium sites with a different potential curvature, the frequencies of lattice vibrational modes are altered. The phonon entropy of the lattice is changed by $s^f$, the entropy of formation of a point defect.

$$s^f = k_B \sum_i \ln \left( \frac{\omega_i}{\omega'_i} \right)$$  \hspace{1cm} (1)

where $\omega_i$ is the frequency of a normal mode $i$ in the perfect crystal and the primed symbol refers to the frequency of the same mode in the presence of the point defect. $k_B$ is the Boltzmann constant.

All these changes taken together can be used to define the Gibb's free energy $g^f$ for the formation of a point defect as follows:

$$g^f = u^f + Pv^f - Ts^f$$  \hspace{1cm} (2)

at any temperature $T$ and pressure $P$.

When $n$ such defects are formed, independently of one another, true for dilute defect densities, the Gibb's free energy of the crystal as a whole is increased by $ng^f$. In addition, there is a further contribution coming from the configurational entropy, which depends statistically on the thermodynamic probability of arranging the $n$ defects on $N$ sites. The importance of $g^f$ is the fact that it governs the thermal equilibrium concentration of the point defects according to an Arrhenius law. For Schottky defects in a binary crystal, this has the form

$$\frac{n}{N} = \exp \left( - \frac{g^f_S}{2k_B T} \right)$$  \hspace{1cm} (3)

Here $g^f_S$ is the combined free energy of formation for a Schottky pair. Similar thermodynamic quantities are also defined for other defect processes such as migration ($g^m$) or binding ($g^h$) between defects. Table 3 lists some of these different parameters.

A physical property such as ionic conductivity can be modelled to yield a defect dependent electrical conductivity ($\sigma$) as a function of temperature, impurity density, pressure and other relevant physical parameters. The model may then be subjected to a detailed comparison with experimental data. It is expected that the experimentation is carried out under controlled conditions of sample preparation, treatment and measurement. It may then be possible to obtain good values of all the thermodynamic parameters of the defects. In a similar manner, measured self-diffusion coefficients ($D$) can also lead to the defect parameters. Normally, the enthalpy of formation, $h^f$, is extracted from the temperature dependence of the property, while the volumes can only be obtained if the experiments are done under different hydrostatic pressures. It thus turns out that the thermodynamic parameters of point defects are obtainable from experiment no doubt but the process involves quite a significant amount of care and thoroughness in measurement and analysis. It is in this context that the theoretical evaluation of point defect enthalpies assumes importance.

### Table 3 -- Thermodynamic parameters of point defects

<table>
<thead>
<tr>
<th>Process</th>
<th>Formation</th>
<th>Migration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>$u^f$</td>
<td>$u^m$</td>
</tr>
<tr>
<td>Volume</td>
<td>$v^f$</td>
<td>$v^m$</td>
</tr>
<tr>
<td>Entropy</td>
<td>$s^f$</td>
<td>$s^m$</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>$h^f$</td>
<td>$h^m$</td>
</tr>
<tr>
<td>Free energy</td>
<td>$g^f$</td>
<td>$g^m$</td>
</tr>
</tbody>
</table>

What are the different theoretical techniques available towards this purpose? Table 4 lists these techniques and physical models. Even though we are covering the ground with techniques applicable to all point defect types, the Schottky defect in ionic materials is used as an example.
2 Continuum Models

2.1 Dielectric continuum

Jost was the first to show that on account of the vacancy bearing an effective charge, the induced polarization reduces the formation energy drastically. This reduction is estimated readily by treating the crystal as a dielectric continuum subjected to the field of the defect charge \( q_d \). The static dielectric constant \( \varepsilon_0 \) of the crystal is the relevant response parameter. The displacement \( \tilde{D} \), polarization \( \tilde{P} \) are related to the electric field \( \tilde{E} \) by

\[
\tilde{D} = \varepsilon_0 \tilde{E} + \tilde{P} \quad \ldots(4)
\]

\[
\tilde{P} = (\varepsilon_0 - 1) \varepsilon_0 \tilde{E} \quad \ldots(5)
\]

\[
\tilde{E} = \frac{q_d}{4\pi \varepsilon_0 |\tilde{r}|^3} \quad \ldots(6)
\]

\[
\tilde{P} = \frac{\varepsilon_0 - 1}{\varepsilon_0} \frac{q_d}{4\pi |\tilde{r}|^3} \quad \ldots(7)
\]

The polarization energy is equal to

\[
U_p = \frac{1}{2} \phi(-q_d) \quad \ldots(8)
\]

where \( \phi \) is the potential of the polarized crystal at the defect site and the above is simply the work done by the dipoles in extracting the ion of charge \(-q_d\) from the lattice site. In the spirit of the continuum concept, he potential \( \phi \) is calculated as

\[
\phi = \int_{R_0}^{\infty} \frac{P^2}{4\pi \varepsilon_0 |\tilde{r}|^2} \, d\tilde{r} \quad \ldots(9)
\]

\( R_0 \) is the lower limit of integration, a quantity hard to define for a vacancy. On substitution of \( q_d \) with the negative of the ion charge \((-Ze)\), the expression for the polarization energy becomes

\[
U_p = -\frac{1}{2} \left( \frac{1}{\varepsilon_0} \right) Z^2 e^2 \quad \ldots(10)
\]

Taking \( R_0 \) to be \((r/2)\), where \( r_0 \) is the nearest anion-cation separation, a working formula for this energy (in eV), may be written as

\[
U_p = -1.44 \frac{Z^2 e^2}{r_0} \left( \frac{1}{\varepsilon_0} \right) \quad \ldots(11)
\]

with \( r_0 \) in units of nm. Estimates of this quantity are given in Table 5 for a few typical crystals. The polarization energy is as large as the the defect formation energy (for e.g. the energy of formation of a cation vacancy, \( u_c^\prime \)) and thus it is clear that this quantity plays an important part in any defect formation process and requires careful assessment.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>( u_c )</th>
<th>( U_p )</th>
<th>( u_c^\prime )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>7.93</td>
<td>4.15</td>
<td>5.20</td>
</tr>
<tr>
<td>AgCl</td>
<td>9.46</td>
<td>4.75</td>
<td>5.41</td>
</tr>
<tr>
<td>AgBr</td>
<td>9.33</td>
<td>4.54</td>
<td>5.04</td>
</tr>
<tr>
<td>MgO</td>
<td>42.2</td>
<td>24.53</td>
<td>26.4</td>
</tr>
<tr>
<td>CaO</td>
<td>36.7</td>
<td>21.75</td>
<td>22.3</td>
</tr>
</tbody>
</table>

2.2 Elastic continuum

While the Jost model is meant for charged point defects, point defects with or without charge may also be regarded as singularities in an elastic continuum. The equilibrium equation for the displacement field \( \tilde{u}(\tilde{r}) \), of an elastic solid with rigidity modulus \( \mu \), Poisson ratio \( \nu \), and under the action of a body force density \( \tilde{f} \), is given by
\[
\mu \nabla^2 \bar{u} + (\lambda + \mu) \nabla \nabla \cdot \bar{u} + \vec{f} = 0 \quad \text{...(12)}
\]

where the Lame constant \( \lambda \) is defined by
\[
\lambda = \frac{2\mu\nu}{1 - 2\nu} \quad \text{...(13)}
\]

If the point defect preserves the spherical symmetry of the continuum, with the realistic constraint of a displacement field decreasing with increasing distance from the defect centre, and with no body forces present, the solution of the above equation takes the form\(^5\)
\[
\bar{u} = \frac{\vec{r}}{|\vec{r}|} c \quad \text{...(14)}
\]

where \( c \) is an unknown quantity termed the elastic strength of the point defect. Recourse to other input information is taken to arrive at a plausible estimate of this quantity. This strength parameter is essentially a measure of the size misfit of the singularity. For example, for an impurity of radius \( R_j \) replacing an atom of radius \( R_a \), the displacement \( u(r_0) \) is taken to be equal to \( (R_j - R_a) \). It then follows that \( c \) is given by
\[
c = r_0^2 (R_j - R_a) \quad \text{...(15)}
\]

It is noteworthy that the displacement field is long-ranged with the elastic misfit displacement \(|\bar{u}|\) decreasing with distance \( r \) as \( 1/r^2 \). In section 4, we will give a better definition of \( c \). Eshelby's theory also leads to the relaxation volume of formation of the defect in terms of \( c \):
\[
v^{\text{ref}} = c \kappa \quad \text{...(16)}
\]

where \( \kappa \) is the isothermal compressibility of the crystal.

3 Mott-Littleton Model

The first successful lattice technique is that introduced by Mott and Littleton (ML) in their celebrated paper\(^6\). The technique is still the most used and yet to find a better replacement. The authors split the defect crystal into two regions 1 and 2. The defect and the neighbourhood to be chosen, represent Region 1. The remainder of the crystal constitutes Region 2. While the dipole moments and displacements of ions in Region 2 are deduced following essentially the Jost treatment of a continuum with some modifications, Region 1 is treated in a completely atomistic model. Thus the polarization \( \vec{P} \) as given by the equation in the Jost model is apportioned into two parts - the dipole moments \( \vec{P}_a \) for the anions and \( \vec{P}_c \) for the cations in a given cell in accordance with the polarizabilities. The displacement \( \eta \) of any ion in Region 2 is in proportion to the displacement polarizability. Thus for Region 2,
\[
\vec{P}_{c,a} = \frac{f_{c,a}}{f_{\text{cell}}} \Omega \vec{P} \quad \text{...(17)}
\]
\[
\eta = \frac{\alpha_d}{f_{\text{cell}}} \Omega \vec{P} \quad \text{...(18)}
\]
\[
f_{c,a} = \alpha_{c,a} + \alpha_d \quad \text{...(19)}
\]
\[
f_{\text{cell}} = \alpha + \alpha_a + 2\alpha_d \quad \text{...(20)}
\]

\( q_{c,a} \) are the charges of the cation or anion. \( \alpha_a \) and \( \alpha_c \) are the electronic polarizabilities of the anion and cation respectively. The interatomic potentials are commonly modelled by the Born-Mayer type of function:
\[
\phi_{ij}(|\vec{r}_{ij}|) = A_{ij} \exp(-\frac{|\vec{r}_{ij}|}{\rho_{ij}}) - \frac{q_{ij}}{4\pi \epsilon_{ij} |\vec{r}_{ij}|} - \frac{c_{ij}}{|\vec{r}_{ij}|^6} \quad \text{...(21)}
\]

The \( c_{ij} \) are the coefficients for dipole - dipole van der Waals potential. The first term is the energy of repulsion due to overlap of ions and the second term is the Coulomb energy.

Region 1 solutions were obtained by Mott and Littleton by balancing the forces, Coulombic \( \vec{F}_c \) and non-Coulombic \( \vec{F}_{NC} \):
\[
\vec{F}_c + \vec{F}_{NC} = 0 \quad \text{...(22)}
\]

The energy of the defect-distorted crystal is written as an additive sum of the rigid lattice energy \( U_{RL} \), the Coloumb energy \( U_C \), the short range contribution \( U_{SR} \) and the two polarization energies belonging to the Region 1 \( U_p^{(1)} \) and to the Region 2 \( U_p^{(2)} \).
\[
U = U_{c} + U_{SR} + U_p^{(1)} + U_p^{(2)} + U_{RL} \quad \text{...(23)}
\]

The Schottky formation energy follows as
\[
u_{s} = u_{c}^{T} + u_{m}^{T} - U_{s} \quad \text{...(24)}
\]
where $U_L$ is the lattice energy of the crystal per ion pair.

4 Lattice Statics

4.1 Kanzaki model

Kanzaki\textsuperscript{7} modelled the vacancy-distorted crystal in terms of virtual forces (Kanzaki forces) that reproduce the distortion and energy changes arising from a vacancy. Fig.1a shows a perfect undistorted crystal, Fig.1b the distorted crystal containing the vacancy while Fig.1c shows the Kanzaki lattice which has the same distortion as the defect lattice but without the vacancy. The problem reduces to finding the simulating force distribution of Fig.1c. For this purpose, Kanzaki used the harmonic approximation with the energy $U$ of the crystal under the action of a set of forces $F(\bar{r})$ expressed as

$$U = U_o - \sum_i \sum_{\alpha} F_\alpha (\bar{r}_i') \xi_\alpha (\bar{r}_i') + \frac{1}{2} \sum_{\alpha} \sum_{\beta \neq \alpha} A_{\alpha \beta} (\bar{l}_i') \xi_\alpha (\bar{r}_i') \xi_\beta (\bar{r}_i')$$

...(25)

$U_o$ is the energy of the perfect lattice. $\xi_\alpha (\bar{r}_i')$ are the Cartesian components of displacement of an ion at $\bar{r}_i'$. $I$ and $I'$ represent lattice cell labels. The elements of the force constant matrix $A$ are defined as spatial second derivatives of the energy.

$$A_{\alpha \beta} (\bar{l}_i') = \frac{\partial^2 U}{\partial \xi_\alpha (\bar{l}_i') \partial \xi_\beta (\bar{l}_i')}$$

...(26)

The element $A_{\alpha \beta} (\bar{l}_i')$ represents the $\alpha$ component of the force acting on the atom located at $\bar{r}_i'$ due to unit displacement in the $\beta$ direction of an atom located at $\bar{r}_i'$. The equilibrium equations are

$$\frac{\partial U}{\partial \xi_\alpha (\bar{r}_i')} = 0$$

...(27)

and they lead to

$$F_\alpha (\bar{r}_i') = \sum_i \sum_{\beta} A_{\alpha \beta} (\bar{l}_i') \xi_\beta (\bar{r}_i')$$

...(28)

giving $3N$ coupled equations - one each for the three Cartesian displacement components of each of the $N$ atoms in the crystal.

Kanzaki's technique consisted of Fourier transforming the real space quantities and the equilibrium equations using a normal coordinate expansion.

$$\xi_\alpha (\bar{r}_i') = \sum_{\beta} Q_\beta (\bar{q}) \exp(i\bar{q}.\bar{r}_i')$$

...(29)

where $Q_\beta$ are the Fourier amplitudes of displacements at any point $\bar{q}$ in the reciprocal space. The corresponding equilibrium equations are given by

$$N \sum_{\beta} V_{\alpha \beta} (-\bar{q}) Q_\beta (\bar{q}) = G_\alpha (-\bar{q})$$

...(30)

The matrix $V$ is the Fourier transform of $A$:

$$V_{\alpha \beta} (\bar{q}) = \sum_{I'} A_{\alpha \beta} (I') \exp(-i\bar{q}.(\bar{r}_i' - \bar{r}_i))$$

...(31)

The generalized forces $G$ are similarly the Fourier transforms of the real space forces:

$$G_\alpha (\bar{q}) = \sum_{I'} F_\alpha (I') \exp(i\bar{q}.\bar{r}_i')$$

...(32)

The three equilibrium equations in the Fourier space are now uncoupled - essentially a feature of the normal coordinates - and are solved for the amplitudes $Q_\alpha$ at each point $\bar{q}$. The $\bar{q}$ space to be covered is only the fundamental Brillouin zone. Further, in this zone we need only deal with the irreducible part as per the symmetry of the crystal. Thus in a cubic crystal with $O_h$ symmetry, this part is $1/48$ of the zone. Having obtained the $Q$'s, the real space displacements are calculated by the reverse transformation, involving summation over the $\bar{q}$ vectors. The convergence depends on the spatial
extent of the forces \( \tilde{F} \). The decoupling of the equations was possible because of the harmonic approximation. It follows that defects with relatively small distortion forces such as neutral defect species should be particularly amenable to treatment by this technique.

### 4.2 Kanzaki forces

The Kanzaki forces can be obtained by writing the energy of the imperfect lattice relative to the perfect lattice in the following manner:

\[
U_c - U_a = U_c - U_h + U_h - U_a \quad \ldots (33)
\]

This leads to the expression for the energy of the defect lattice in terms of the change in the interaction potential energies as

\[
U_c - U_a = -\sum \phi(|r^t| + \tilde{\xi}(r^t))
\]

\[
+ \frac{1}{2} \sum \phi((r^t + \tilde{\xi}(r^t) - (r^t + \tilde{\xi}(r^t))) \quad \ldots (34)
\]

The energies \( U_a, U_h, U_c \) refer to the energies of the crystal depicted in Fig.1a,b,c respectively. Differentiation of the above energy difference with respect to the displacement component \( \xi_a \) leads to the formal expression of the Kanzaki forces.

\[
F_a^t(\mathbf{r}^t) = \frac{\partial}{\partial \xi_a^t}(\phi(|r^t + \tilde{\xi}(r^t)|)) \quad \ldots (35)
\]

The theory has been adopted with advantage in the treatment of vacancies in metals, strain field interaction of vacancy dimers, monovalent impurities and their dimers, as well as Φ centres. Tewary’s Greens function technique is also an equally good method. This approach is equivalent to the Kanzaki method but having other distinct advantages. Applying the Kanzaki theory to vacancy defects, Hardy and Lidiard obtained for the elastic strength of a vacancy, the following explicit expression:

\[
c = \sum R_{ij}^t \xi_j^t \phi(|\tilde{\mathbf{r}}^t + \tilde{\xi}^t|) \quad \ldots (36)
\]

### 5 Energy Method

Kurosawa was the first to adopt the energy approach in the treatment of the vacancy problem. Norgett and Lidiard generalized it to give a method that is generally followed in modern work. The basic principles of the method are recalled here for completeness. The total energy \( U_t \) of the imperfect crystal is composed of three parts: \( U_t(\beta) \) for Region 1, \( U_t(\beta,\gamma) \) - the energy of interaction between Region 1 and Region 2 and \( U_t(\gamma) \) - the energy of Region 2. Here \( \beta \) represents all the relaxations and dipole moments of ions in Region 1. \( \gamma \) represents these quantities for Region 2 ions (See Fig.2).

\[
U_t = U_t(\beta) + U_t(\beta,\gamma) + U_t(\gamma) \quad \ldots (37)
\]

It turns out that the \( ML \) approach is consistent with a harmonic treatment of Region 2. Accordingly the third energy term above can be written as

\[
U_t(\gamma) = \frac{1}{2} \sum H_{ij} \gamma_i \gamma_j \quad \ldots (38)
\]

Here \( H_{ij} \) is an appropriate force constant matrix for the Region 2. On using the equilibrium condition

\[
\frac{\partial U_t}{\partial \gamma_i} = 0 \quad \ldots (39)
\]

we effectively eliminate the third energy term. provided it is agreed that the equilibrium values of the relaxation variables of Region 2, viz., \( \gamma \), are taken to be those \( \gamma_{eq} \) given by the \( ML \) model.
While the above serves as the guiding equation for evaluating the energy of the imperfect crystal, more has to be developed before it is ready for application. If the pair-wise interatomic potential between two atoms $i$ and $j$ is represented by $\phi_{ij}$, the energy to be computed is

$$U_d = \sum_{i \neq j} \left[ \phi_{ij}(|\vec{r}_i - \vec{r}_j|) - \phi_{ij}(|\vec{R}_i - \vec{R}_j|) \right]$$

$$+ \sum_{i \neq j} \left[ \frac{\partial \phi_{ij}(|\vec{r}_i - \vec{r}_j|)}{\partial \vec{r}_j} \cdot \frac{\partial \phi_{ij}(|\vec{R}_i - \vec{R}_j|)}{\partial \vec{R}_j} \right] \phi_{ij}(|\vec{r}_i - \vec{r}_j|) \phi_{ij}(|\vec{R}_i - \vec{R}_j|)$$

(41)

Here $\vec{R}_i$ and $\vec{r}_i$ are respectively the unrelaxed and relaxed position vectors of the ion $i$. The partial derivatives are all evaluated at the equilibrium positions.

6 Physical Models

6.1 PPI

The energy changes depend on the details of interactions between the atoms, the effect of distorting the electron distributions of the ions, the effects of overlapping of the ions - both on account of long range forces as well as short range forces. The balanced configuration of the imperfect crystal will depend in a detailed way on all these factors. In the point polarizable ion (PPI) model, a model implicit in the ML work, each ion is represented as a point charge with a polarizability. The electronic polarizabilities of the ions can be related to the refractive indices $n$ using the Lorentz-Lorenz equation

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1}{3\varepsilon_o} N(\alpha_u + \alpha_v + 2\alpha_d)$$

(42)

In their widely cited paper, Tessman, Kahn and Shockley (TKS) use this equation to determine the electronic polarizabilities of a number of ions in cubic crystals in a self-consistent manner. It is to be noted that the validity of the use of the Lorentz factor $\frac{1}{3\varepsilon_o}$ is by no means definite. The local field is evaluated assuming point dipoles located inside the Lorentz cavity and assuming a cubic symmetry. The low frequency dielectric constant ($\varepsilon_r$) of the crystal is larger than the optical dielectric constant ($\varepsilon_{op}$) because of the additional contribution of the relative displacement of the sublattices. The polarizability ($\alpha_d$) for this displacement can be determined in terms of the short range force constant $K$ using

$$\alpha_d = \frac{Z^2e^2}{K}$$

(43)

$$K = \eta(\phi_{SR}(r_o) + \frac{2\phi_{SR}(r_o)}{r_o})$$

(44)

$\eta$ is 4 for the rocksalt structure and 16/3 for the CsCl structure. $\phi_{SR}$ above includes the van der Waals interaction potential besides the overlap repulsion potential, both for nearest neighbours. The second neighbours do not contribute to $\alpha_d$. The primes on the short range potential terms indicate spatial differentiation. Using TKS values of polarizabilities and this value of $\alpha_d$, we may calculate $\varepsilon_s$ from the Clausius-Mosotti equation.

$$\frac{\varepsilon_s - 1}{\varepsilon_s + 2} = \frac{1}{3\varepsilon_o} N(\alpha_u + \alpha_v + 2\alpha_d)$$

(45)

The calculated values of $\varepsilon_s$ come out to be too large for several crystals for which the Born-Mayer of cohesion works so satisfactorily. For e.g for NaCl, the calculated value is 12 compared to the measured value of 5.2. This is essentially a failure of the PPI model to account for the static polarization accurately. The field of the point dipoles is evaluated using the formula

$$\vec{F} = \frac{3(\vec{p}\cdot\vec{r})\vec{r} - |\vec{r}|^2 \vec{p}}{4\pi\varepsilon_o |\vec{r}|^3}$$

(46)

The PPI model overestimates the polarization because of the neglect of the finite sizes of the ions. Overlap reduces the magnitude of the dipole moments. Thus the values of $h^s$ based on PPI are underestimated. Besides, the formation enthalpy $h^f$ is unstable under expansion of Region 1. In order to overcome this problem, one should allow for a
coupling of the overlap forces and the induced dipole moments. This is achieved in three different ways:

- Deformation Dipole (DD) Model
- Shell Model (SM)
- Modified PPI Model (MPPI)

Hardy and Karo\textsuperscript{16} developed the Deformation Dipole (DD) Model for application in the dynamics of crystal lattices. The model allows for the reduction in polarization by adding a deformation dipole in opposition to the induced dipole. In the shell model (SM) first introduced by Dick and Overhauser\textsuperscript{17} each ion is represented by a core and a shell, the two being connected by springs. The shells of neighbouring ions are also connected by another spring. The force constants of these springs and the fractions of charges included in the shell or core of an ion etc., (the shell model parameters) are determined by matching the crystal properties such as the elastic constants, dielectric constant, refractive index and infrared resonance frequency. It was Faux and Lidiard\textsuperscript{18} who first used SM in defect modelling. It must be remarked that we have here not addressed the problem of obtaining the numerical values of the parameters of the potential corresponding to the overlap repulsion and the van der Waals dispersion effects. The overlap potential is given satisfactorily from a density functional approach based on a uniform electron gas model\textsuperscript{19}. The evaluation of the dispersion potential is less simple.

6.2 MPPI Model

Murti and Usha\textsuperscript{20} introduced the Modified Polarizable Point Ion (MPPI) model which while retaining the good features of PPI, remedied the deficiency in respect of the polarization. The model takes care of the elastic and dielectric response and is designed for application to situations in which electric fields of a static nature are present - as in the defect environment. New effective polarizabilities are introduced to account for the reduction in the polarization due to overlap. This model had met with success in a wide variety of defect environments. The MPPI model has the merit of being simple, physical, less parametric and computationally efficient. Another variant of PPI was suggested by Boswarva and Simpson\textsuperscript{21}.

6.3 EPPI Model

All the above models, PPI, DD, SM, MPPI treat the polarization of the dielectric in the dipole approximation. The electric field of the point defect is implicitly presumed to be spatially homogeneous - an assumption which can not be justified as the defect fields are indeed inhomogeneous. The Extended Polarizable Point Ion model (EPPI)\textsuperscript{22,24} was introduced to remove this inadequacy by including the effects of quadrupole moments interacting with the electric field gradients. Thus the dipole moments \( \vec{P} \) and quadrupole moments \( \vec{Q} \) of ions \( i \) in the Region 1, are given by

\[ \vec{P}_i = \alpha_d \vec{F}_i^{\text{loc}} \]  
\[ \vec{Q}_i = \alpha_q \vec{\nabla} \vec{F}_i^{\text{loc}} \]

Here \( \alpha_d \) is the dipole polarizability and \( \alpha_q \) is the quadrupole polarizability of the ions. The local field \( \vec{F}_i^{\text{loc}} \) and local field gradient \( \vec{\nabla} \vec{F}_i^{\text{loc}} \) are respectively given by

\[ \vec{F}_i^{\text{loc}} = \vec{F}_i^m + \vec{F}_i^d + \vec{F}_i^q \]  
\[ \vec{\nabla} \vec{F}_i^{\text{loc}} = \vec{\nabla} \vec{F}_i^m + \vec{\nabla} \vec{F}_i^d + \vec{\nabla} \vec{F}_i^q \]

The superscripts \( m, d, q \) refer to monopoles, dipoles and quadrupoles respectively. In the case of materials containing more polarizable ions, the quadrupolar deformations are large and assume significance. The quadrupole deformation does contribute very significantly to the defect formation process in two ways: Firstly there is an additional polarization energy due to the interaction of the induced quadrupoles with the electric field gradient.

\[ W_q = -\frac{3}{4} \frac{\nabla^2 \vec{F}_i}{\varepsilon^2} \]

The dipole moments are also modified because of the contribution of quadrupoles to the local field. Application of EPPI provided a conclusive demonstration\textsuperscript{25} of the reasons for the dominance of the Frenkel disorder on the cationic sublattice of AgCl and AgBr.
The model also led to insight into the cause of the perplexing anomalies that persisted in the transport behaviour in these materials. More recently, new findings have emerged from the application of EPPI to Schottky defects in the oxide system of alkaline earth metals. When we examine the values of defect energies deduced with and without including the quadrupolar contributions, it turns out that reliable values of the defect energies result only when the induced quadrupoles are included in the treatment, especially for crystals with largely polarizable ions. (Table 6). It has been seen that the quadrupole refinement is markedly effective and therefore can hardly be ignored in any defect modelling schemes.

7 MUDRA

A scientific software called MUDRA (Modelling Utility for Defects by Rapid Analysis) based on EPPI is being developed as a user-friendly tool for modelling defect energetics in ionic materials. The present version caters only to Schottky defects and rocksalt structure, with potentials of standard form. It is expected that MUDRA in the final form will be usable for other structures, many defect types and user-specified potentials.

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