# Chapter 1

# Introduction

## 1.1 Disorder in Crystalline Materials

### 1.1.1 Crystal Structures

This thesis is concerned with crystalline materials and primarily with disorder in those materials. Crystalline materials are characterised by their regular repeating structures. As early as 1848 Bravais showed that there are fourteen symmetrical ways of arranging points in a 3 dimensional Euclidian geometry, these are known as the Bravais lattices [1]. The Bravais lattices belong to one of seven systems of crystal symmetry [1]. All possible crystal structures may be formed from these lattices, which define the long-range symmetry. Around each lattice point there are a series of atoms known as the basis or motif (each lattice point accommodates an identical basis). The symmetry associated with the basis is called the point group symmetry and includes short-range elements such as rotation and reflection. Translational symmetry adds additional symmetry possibilities which combine with the Bravais lattices to create 230 distinct space groups. All crystals (except quasi-crystals) belong to one of these space groups.

This description, of course, is of a perfect lattice. In this thesis defects are discussed as departures from the perfect lattice.

### 1.1.2 Point Defects and the Dilute Limit

#### Intrinsic Disorder Reactions

Disorder in crystalline materials occurs when atoms are displaced from their crystal structure sites. Intrinsic disorder is so called because it is a thermally activated process, requiring the addition of no impurities. In this respect it is distinct from extrinsic disorder which arises through the presence of impurity/dopant ions. Much of the work in this thesis is concerned with intrinsic disorder in oxides. This intrinsic disorder can arise through three processes. Frenkel disorder [2] (see figure 1.1) happens when an atom is displaced from it's lattice site onto an interstitial site, leaving behind a vacancy. Both anions and cations undergo this type of disorder. For a binary metal oxide, MO the defect reaction associated with this process is:

$$\mathrm{M}_{\mathrm{M}}^{\times} + \mathrm{V}_{\mathrm{i}}^{\times} \rightarrow \mathrm{M}_{\mathrm{i}}^{\cdot\cdot} + \mathrm{V}_{\mathrm{M}}^{\prime\prime} \tag{1.1}$$

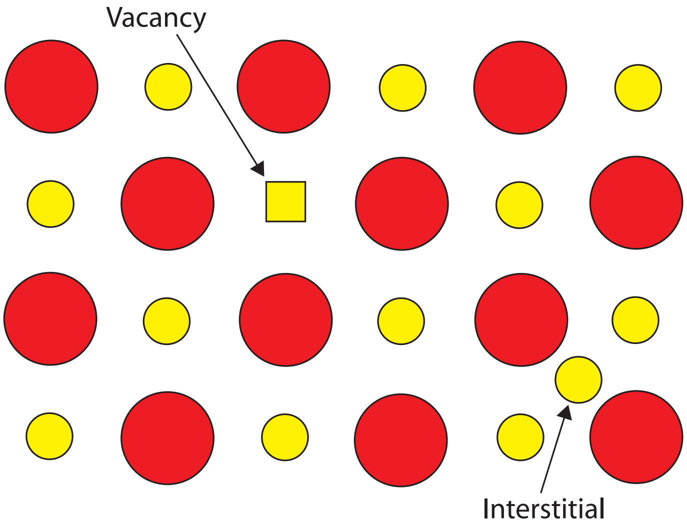

Figure 1.1: Schematic diagram showing Frenkel disorder.

Schottky disorder [3, 4] (see figure 1.2) involves the creation of vacancies in the lattice in a stoichiometric ratio. For example, for the same binary metal oxide, MO, (such as that shown in figure 1.2) one vacancy of each type (M and O) is created. The Schottky defect reaction for this material is thus:

$$\mathrm{M}_{\mathrm{M}}^{\times} + \mathrm{O}_{\mathrm{O}}^{\times} \rightarrow \mathrm{V}_{\mathrm{M}}^{\prime\prime} + \mathrm{V}_{\mathrm{O}}^{\cdot\cdot} + \mathrm{MO} \tag{1.2}$$

In a crystalline material with more than one type of ion, each species occupies its own sublattice. If one atom of each species exchanges lattice sites then an antisite pair is formed (see figure 1.3) The defect reaction for the antisite process in MO is therefore:

$$\mathrm{M}_{\mathrm{M}}^{\times} + \mathrm{O}_{\mathrm{O}}^{\times} \rightarrow \mathrm{O}_{\mathrm{M}}^{\prime\prime\prime\prime} + \mathrm{M}_{\mathrm{O}}^{\cdot\cdot\cdot\cdot} + \mathrm{MO} \tag{1.3}$$

While, for binary oxides either Schottky or Frenkel process' might dominate, the antisite reaction would not be expected to occur as exchanging ions of opposite charge ions will have a much greater distorting effect on the lattice

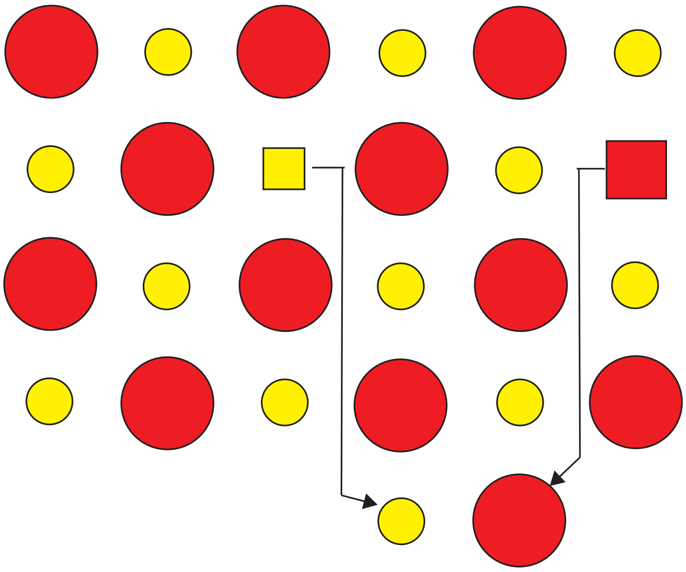

Figure 1.2: Schematic diagram showing Schottky disorder.

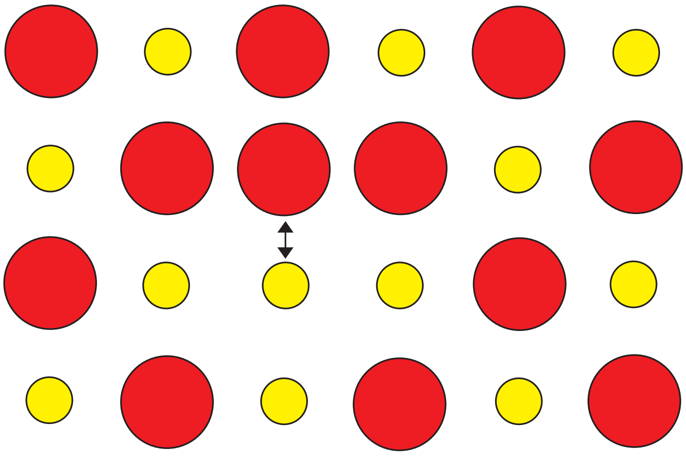

Figure 1.3: Schematic diagram showing antisite disorder.

than the creation of vacancies or interstitial defects. In more complex oxides, with multiple cations, such as $MgAl_2O_4$ spinel the antisite reaction is much more commonplace as the distortion resulting from exchanging the sites of $Mg^{2+}$ and $Al^{3+}$ i.e. two positively charged ions is less (than exchanging the places of oppositely charged ions).

### Intrinsic Defect Concentrations

As temperature is raised, increasing numbers of atoms have sufficient enthalpy to move off their lattice sites, however in doing so they increase the internal energy of the system. This increase is mediated by an increase in the configurational entropy (the vibrational entropy may in contrast increase, decrease or remain constant).

If the enthalpy of formation of $n$ Schottky pairs in the material MO is $n\Delta h$ and the vibrational entropy is $T\Delta s$, then $n\Delta g = n\Delta h - T\Delta s$ and if the change in configurational entropy associated with this reaction is $\Delta S_c$, the change in the free energy, $\Delta G$ of the system is:

$$\Delta G = G - G_0 = n\Delta g - T\Delta S_c \tag{1.4}$$

where $G$ is the free energy of the disordered system and $G_0$ is the free energy of the perfect crystal. The configurational entropy may be expressed as:

$$\Delta S_c = k\ln\Omega \tag{1.5}$$

where $k$ is Boltzmann's constant and here, $\Omega$ is the number of ways of arranging $n$ Schottky pairs in the crystal. If, in the lattice, there are $N$ 'M' lattice sites the number of ways of arranging $n$ M site vacancies, $\Omega_M$ is

$$\Omega_M = \frac{N!}{n!(N-n)!} \tag{1.6}$$

An identical expression can be obtained for $\Omega_O$ so that:

$$\begin{aligned} \Delta S_c &= k \ln \left(\Omega_M \Omega_O\right) && (1.7) \\ &= k \ln \left( \frac{N!}{n!(N-n)!} . \frac{N!}{n!(N-n)!} \right) && (1.8) \\ &= 2k\{\ln(N!) - \ln[(N-n)! - n!]\} && (1.9) \end{aligned}$$

This can in turn be written:

$$\Delta S_c = 2k[N \ln(N) - (N-n)\ln(N-n) - n\ln(n)] \tag{1.10}$$

if Stirling's formula [5] for large numbers is employed:

$$\ln(m!) \simeq m \ln(m) - m \tag{1.11}$$

Therefore,

$$\Delta G = n\Delta g - 2kT[N\ln(N) - (N-n)\ln(N-n) - n\ln(n)] \tag{1.12}$$

At thermodynamic equilibrium the free energy is at a minimum with respect to $n$, i.e. $\left(\frac{\partial \Delta G}{\partial n}\right)_{T,p} = 0$. Thus, differentiating equation 1.12,

$$\left(\frac{\partial \Delta G}{\partial n}\right)_{T,p} = 0 = \Delta g - 2kT \ln\left(\frac{N-n}{n}\right) \tag{1.13}$$

Now, if $N \gg n$ then the approximation $N - n = N$ is valid and equation 1.14 becomes:

$$\frac{N}{n} = e^{\left(\frac{\Delta g}{2kT}\right)} \tag{1.14}$$

or

$$\frac{n}{N} = e^{-\left(\frac{\Delta g}{2kT}\right)} = e^{-\left(\frac{\Delta h}{2kt}\right)} e^{\left(\frac{\Delta s}{2k}\right)} \tag{1.15}$$

The quantity $\frac{n}{N}$ is defined as the concentration. $\Delta s$ is the change in vibrational entropy arising from the disorder, often this is assumed to be zero though this is not always the case [6]. An analagous derivation for each type of intrinsic disorder discussed in section 1.1.2 exists for any, arbitrary lattice structure. Nevertheless, implicit within the model is the assumption that defect concentrations are small. Furthermore, if the enthalpy of formation of a defect is calculated at the dilute limit then the quantity $n\Delta h$ is the enthalpy of formation of $n$ *noninteracting* defects.

### 1.1.3 Defect Association

While it is not immediately obvious under what conditions the approximations made in the previous section are valid, it is clear that as defect concentrations increase they will begin to interact, in particular oppositely charged defects will become associated. Previously when discussing Schottky disorder it was assumed that the defects involved were isolated from one another. If, instead they are next neighbours as in figure 1.4 it might be expected that their enthalpy of formation is reduced. Association can be written as a defect reaction, for the case discussed above:

$$\mathrm{V}_{\mathrm{M}}'' + \mathrm{V}_{\mathrm{O}}^{\cdot\cdot} \rightarrow \{\mathrm{V}_{\mathrm{M}}'' : \mathrm{V}_{\mathrm{O}}^{\cdot\cdot}\}^{\times} \tag{1.16}$$

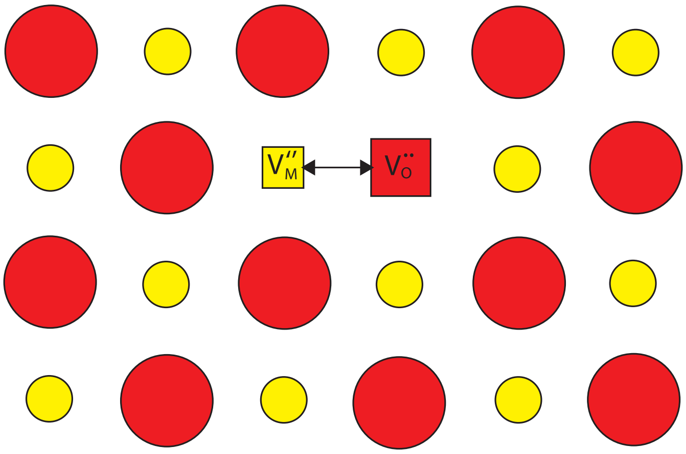

Figure 1.4: Schematic diagram showing a nearest neighbour Schottky pair.

This system is at equilibrium when:

$$K = \frac{[\{\mathrm{V}_{\mathrm{M}}'' : \mathrm{V}_{\mathrm{O}}^{\cdot\cdot}\}]^{\times}}{[\mathrm{V}_{\mathrm{M}}''][\mathrm{V}_{\mathrm{O}}^{\cdot\cdot}]} = Ze^{-\left(\frac{\Delta h_a}{2kt}\right)} \tag{1.17}$$

where $K$ is the reaction constant, Z is the number of ways of placing this cluster in the lattice (6 in this case assuming that MO takes the rocksalt structure as in figure 1.4) and it has been assumed that $\frac{\Delta s}{2k} \simeq 0$. The quantity $\Delta h_a$ is the association (or binding) enthalpy. Its value is calculated for explicit clusters as the difference between the enthalpy of formation of the cluster and of the equivalent isolated defects, i.e.:

$$\Delta h_a = \Delta h_c - \sum_i \Delta h_i \tag{1.18}$$

where $\Delta h_c$ is the formation enthalpy of the cluster in question and the $\Delta h_i$'s are the formation enthalpies of the $i$ isolated component defects. Some of the work presented in this thesis considers ways to calculate such binding enthalpies.

For a large ensemble of interacting defects explicit calculations are not feasible and so an approximation is required. The most simple approximation is to equate the enthalpy of association with the coulombic interaction between defects:

$$\Delta h_a = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \tag{1.19}$$

where $q_i$ and $q_j$ are the charges on defects $i$ and $j$, $\epsilon_0$ is the permittivity of free space and $r_{ij}$ the interdefect separation. Taking the effect of the medium into account, assuming it to be a dielectric continuum;

$$\Delta h_a = \frac{q_i q_j}{4\pi\epsilon_r\epsilon_0 r_{ij}} \tag{1.20}$$

where $\epsilon_r$ is the relative dielectric constant.

As concentrations increase there is a tendency for defects to become surrounded by oppositely charged ions. This process screens ions from one another, lessening the strength of their interaction. Debye-Hückel theory [7,8] provides a means of correcting for this screening process. The change in energy arising from the screening, per pair of point defects, is given by:

$$\Delta h_{DH} = -\frac{q_i^2 l}{\epsilon_r\epsilon_0(1+Rl)} \tag{1.21}$$

where $q_i$ is the defect charge, $\epsilon_r\epsilon_0$ is the static dielectric constant and $R$ is the smallest distance at which associates will not form. The distance $\frac{1}{l}$ is the Debye length (screening length), where $l$ is given by the expression:

$$l = \sqrt{\frac{8\pi}{\epsilon_r\epsilon_0 kT}\sum_i n_i q_i^2} \tag{1.22}$$

where $n_i$ is the number of defects per cm$^3$. From the form of this equation it is clear that the screening length increases with a decrease in defect concentrations.

Debye-Hückel theory has been used to calculate defect concentrations in crystalline materials, primarily the alkalide halides(for example [9–11]) where it reduces the degree of association; the differences becoming larger with increased temperature and defect concentration. It is, however, not a panacea: the distance $R$ is not easily defined, as even distant pairs may be loosely bound. Furthermore, the method relies (as does the corrected coulombic approximation, equation 1.20) on a dielectric continuum model, i.e. it assumes that lattice relaxations are isotropic and a linear function of the interdefect separation. At intermediate distances these assumptions are valid (see section 6.2.1). However, at larger concentrations defects will tend to cluster closely meaning that the association energy can differ based on the local lattice structure.

In systems with very high defect concentrations different approaches are required. Sometimes it is feasible to assume that a particular cluster will dominate the defect distribution, such as in work on disorder fluorite/pyrochlore transition in which ions in the material become ordered/ disordered as a function of temperature [13, 14]. In other cases a statistical approach is required in which the partition function is estimated through intelligent sampling of the different possible defect states, for example Al-Fe disorder in $Ca_2FeAl\ O_5$ brownmillerite [12] and in MnO-MgO solid solutions [15].

### 1.1.4 Defect Transport

In chapter 5 the migration of intrinsic defects in $\mathrm{MgAl_2O_4}$ is investigated. Assuming that the system is at equilibrium, defects are able to diffuse through the lattice under the action of Fick's first law [6, 16, 17]:

$$J = \mathrm{D}\frac{d\mathrm{C}}{dx} \tag{1.23}$$

where $J$ is the transport flux of a species in moles per unit area time unit, D is the diffusion coefficient and $\frac{d\mathrm{C}}{dx}$ is the concentration gradient. The diffusion coefficient is composed of several parts [6]: a geometric term, $\gamma$; the jump distance, $\lambda$ and the jump frequency, $\Gamma$ and can be written:

$$\mathrm{D} = \gamma\lambda^2\Gamma \tag{1.24}$$

It is found experimentally that ln(D) exhibits a straight line when plotted against $\frac{1}{T}$, implying that the diffusion coefficient can be expressed as,

$$\mathrm{D} = \mathrm{D}_0 e^{-\frac{(Q_f+Q_a)}{kT}} \tag{1.25}$$

where $\mathrm{D}_0$ is a constant; $Q_f$ and $Q_a$ are, respectively the formation energy of the migrating species and the activation energy for the migration mechanism and $k$ is Boltzmann's constant. This relation suggests that atomic diffusion is a thermally activated process and the jump frequency, $\Gamma$, may therefore be written in the form:

$$\Gamma = \nu e^{-\frac{\Delta G_m}{kT}} \tag{1.26}$$

where $\nu$ is the vibrational attempt frequency and $\Delta G_m$ is the activation energy of migration, equal to $\Delta H_m - T\Delta S_m$, where $\Delta H_m$ is the enthalpy of migration and $\Delta S_m$ is the entropy change associated with the migration process. Substituting for $\Gamma$ in equation 1.24 results in:

$$\mathrm{D} = \gamma \lambda^2 \nu e^{-\frac{\Delta G_m}{kT}} \tag{1.27}$$

Comparing equation 1.25 and 1.27 leads to a new expression for D:

$$\mathrm{D} = \gamma \lambda^2 \nu e^{-\frac{(Q_f + Q_a)}{kT}} \tag{1.28}$$

Assuming the exponential term to be dominant then the diffusion coefficient depends strongly on the activation energy for migration, especially if this number is comparable in size with the formation energy of the defect species in question.

Care should be taken in assuming the validity of Fick's first law as it is applicable only in steady state conditions, when $J$ is time independent. If the defect concentration, $C$ varies with time, then the rate of change of concentration must equal the negative flux:

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x} \tag{1.29}$$

this may then be substituted into equation 1.23 to give Fick's second law:

$$\frac{\partial C}{\partial t} = \mathrm{D}\frac{\partial^2 C}{\partial x^2} \tag{1.30}$$

a discussion of the solutions to this equation may be found in [17].

## 1.2 $MgAl_2O_4$ spinel

The mineral spinel was first characterised by Bragg [18] and Nishikawa [19]. This class of compounds, to which $MgAl_2O_4$ belongs, have a face centred cubic pseudo close packed oxygen sublattice within which the 64 tetrahedral and 32 octahedral interstices are partially occupied by 8 $A^{2+}$ and 16 $B^{3+}$ cations respectively. Oxygen ions are displaced from the ideal fcc sites to positions described by the anion positional parameter, $u$. This displacement results in bond lengths, angles and interstice volumes. In $MgAl_2O_4$ the shift is away the tetrahedral interstices meaning that the A site becomes larger at the expense of the B site when compared to the idealised positions.

Barth and Posjnak [20–22] were the first to note that many materials having the spinel structure could accommodate much disorder on the cation sublattices. The disorder process involved is an antisite reaction in which an A and a B cation exchange sublatttices. Verwey and Heilmann [23] introduced the terms 'normal' and 'inverse' to describe the end members in the series of all possible configurations. In a 'normal' spinel the A cations (Mg) occupy the tetrahedral sites whereas the B cations (Al) occupy the octahedral sites. An 'inverse' spinel is then one in which the tetrahedral lattice sites are occupied by B cations with the octahedral lattice sites being occupied with equal numbers of A and B cations. Cation order between the extremes of normal and inverse spinel can be expressed as $(Mg_{1-i}Al_i)[Mg_iAl_{2-i}]O_4$ where parentheses refers to the tetrahedral sites and square brackets to the octahedral sites and $i$ is the *inversion parameter*.

The degree of inversion in $MgAl_2O_4$ has been measured in numerous experimental studies using nuclear magnetic resonance (NMR) [24, 25], magic-angle-spinning NMR [26, 27], infrared absorption [28, 29], neutron diffraction [30–32] and electron spin resonance [33,34].

Studies of naturally occurring spinel have been performed, finding inversion in the range $0.025 \leq i \leq 0.12$ [26,33,34]. The same samples annealed at elevated temperatures for a few minutes show values a high as $i = 0.3$ [33]. Synthetic $MgAl_2O_4$ has been found to have inversion in the range $0.1 \leq i \leq 0.6$ [30,34].

$MgAl_2O_4$ has previously been shown to retain crystallinity under irradiation by fast neutrons up to a high damage level [35–37] (as much as 250 displacements per atom, dpa [39]). Sickafus *et al.* [40] suggest that this radiation resistance is largely due to three factors, namely: (i) Complex chemistry ensuring that the critical size of a dislocation loop is large. (ii) The complex structure which prohibits dislocation loops from easily unfaulting. (This is significant because faulted interstitial loops are relatively poor sinks for interstitial absorption). (iii) The ease with which $MgAl_2O_4$ is able to accommodate disorder. In fact the cation sublattices of spinel can be completely disordered ($i \approx 2/3$) [39].

This resistance to neutron irradiation has resulted in $MgAl_2O_4$ being considered a candidate material for use as an electrical insulator in future fusion reactors [41]

## 1.3 Ceria

Cerium dioxide (Ceria) takes the fluorite crystal structure. The lattice is a face centred cubic cation sublattice with oxygen ions filling all the tetrahedral interstices. Ceria is able to accommodate significant non-stoichiometry in the form of oxygen deficiency, this gives rise to oxygen vacancies [42]. As a consequence of these $V_O^{\cdot\cdot}$ the material allows for ionic conduction via oxygen vacancy migration, an effect which can be enhanced through the addition of trivalent dopants [43–49].

High ionic conductivity has led to widespread study of ceria as a potential solid electrolyte for fuel cells. Of the trivalent dopants (e.g., $Y^{3+}$, $La^{3+}$, $Gd^{3+}$ and $Sm^{3+}$) gadolinium is favoured for this application because dopant cation has a small association enthalpy with oxygen vacancy defects [50, 51]. Wang *et al.* [52] showed that at in $Ce_{1-2x}Y_{2x}O_{2-x}$, at low dopant concentration (x < 0.02) charged dimers form. They found the association enthalpy to vary as a function of dopant concentration, attributed to the interaction of vacancies with the dopant ions. This association is important because it acts so as to trap oxygen vacancies and so reduce ionic conduction. Gerhardt-Anderson and Nowick [50] investigated conduction in $CeO_2$:$M_2O_3$ where M = (Sc, Y, Gd, La) finding the conductivity to vary over three orders of magnitude across this range of compound and reaching a maximum for $Gd^{3+}$ doping. Kilner and Brook [51] investigated the effect of host cation type on migration enthalpies and of dopant cation size on association enthalpies concluding that the contribution to the elastic strain energy due to the size mismatch between host and dopant cations is more significant than the electrostatic energy between the dopant cation and oxygen vacancy.

## 1.4 Kröger-Vink Notation

Kröger and Vink proposed a useful notation to describe point defect reactions [53]. The point defects are assumed to be dilute species, with the solid being the solvent. The nomenclature consists of three parts; the body, the superscript and the subscript. Using the example of the MO crystal, the body represents the defect itself, ie. $V$ for a vacancy or $M$ for a M ion. The superscript represents the effective charge of the defect i.e. a M vacancy has an effective charge of $-2$. A positive charge is represented by a dot ($^{\bullet}$) and a negative charge by a prime ($'$) and neutral by ($^{\times}$). The subscript represents the site of the defect or if it is an interstitial, ($_i$), ($_M$) would represent a M lattice site. Several examples follow:

### M Vacancy

$\mathrm{V}_M''$

A M ion has a charge of $^{2+}$ therefore its absence implies a net charge in the lattice of $^{2-}$.

## M Interstitial

$\mathrm{M}_i^{\bullet\bullet}$

As the previous example except this time there is an extra M ion in the lattice so the effective charge is $^{2+}$

## $\mathbf{B^{2+}}$ substitutional on M site

$\mathrm{B}_M^{\times}$

$\mathrm{B}^{2+}$ has the same charge as $\mathrm{M}^{2+}$ so the lattice remains neutral.