Some aspects of radiation effects in ionic systems

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Some Aspects of Radiation Effects in Ionic Systems

BY
Lanchakorn Kittiratanawasin

A Doctoral Thesis

Submitted in partial fulfillment of the requirements for the award of
Doctor of Philosophy of Loughborough University

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Abstract

Molecular dynamics simulations were performed to examine different aspects of radiation damage in materials having the bixbyite and NaCl structures. The displacement threshold energy, $E_d$, and the Frenkel pair formation energy, $E_{FP}$, were investigated. The $E_d$ values show a significant dependence on the Primary Knock-on Atom (PKA) direction and some correlation between $E_d$ values in the different materials can be observed. No functional relation between $E_d$ and $E_{FP}$ for materials with the same structures was found other than the obvious one that a higher value of $E_d$ corresponds to a higher $E_{FP}$.

Low and high energy cascades in Er$_2$O$_3$ were performed. The Er PKA, which is much heavier than the O PKA, produces more sub-cascades which spread over a shorter distance. The resulting collisional damage was investigated and analysed. Temperature accelerated dynamics and kinetic Monte Carlo methods were used to examine diffusion of point defects in Er$_2$O$_3$. Some of the transitions were found to be rank 2 saddles and a strategy for determining the exponential prefactors was introduced for these cases. The most mobile defect is the oxygen vacancy with lowest energy transition barrier for diffusion of 1 eV. Other defects have very high energy barriers but the energy barrier for recombination between the vacancy and interstitial is found to be dramatically reduced for closely separated Er defects.

Radiation damage was examined close to twist grain boundaries in MgO and in nanocrystalline MgO. Grain boundaries were shown to be sinks for interstitial defects with a build up of vacancies in the crystal grains away from the boundaries. The transition barriers for both defects to a grain boundary showed a reduction within 3 layers from the boundary. However there is no net reduction in system energy for a vacancy in the grain boundary compared to a vacancy in the bulk whereas a significant energy reduction is observed for the interstitial in the grain boundary compared with
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Chapter 1

Introduction

Nowadays, the computer is an important tool which affects all aspects of human life. It has a very fast speed of calculation which cannot be reached by human reckoning, so scientists can use this power to solve many multivariable problems which help to give insight and understanding that cannot in many cases be achieved using theory and experiment alone. In materials science computer modelling is almost a branch in itself and can be used to optimise industrial processes as well as giving insight into fundamental research problems [1].

Multiscale modelling of materials may be classified as shown in Fig. 1.1 where different techniques are used for the difference system sizes and time scales. The smallest scale is Quantum Mechanics which plays on the interaction between electrons and nuclei governed by the Schrödinger equation. The simulation in this model proceeds by calculating the energy and interaction forces between atoms using an ab-initio method such as density function theory (DFT) while the dynamical motion is determined by the Newtonian mechanics [2]. The current ab-initio molecular dynamics (MD) simulations are successful in calculation without the requirement to fit to experimental data. However, since the amount of time spent for the electronic structure calculation is very high, simulations are limited in size to only a few hundred atoms. On the molecular or atomistic scale, MD methods [3] using classical potentials can be currently carried out
with several million atoms by utilising parallel techniques. Classical MD simulations describe the atomic motion totally by Newtonian mechanics with forces determined from potential functions so they discard the calculation that involves the electronic degrees of freedom. These simulations can be much faster than ab-initio simulations. Nevertheless, the numerical integration time step which is used must be of the order of $10^{-15}$ seconds in an iteration loop to capture phonon vibrations and generally this confines the simulation to be run to the order of nanoseconds. The mesoscale model, often referred as the intermediate scale between microscopic and macroscopic level, is a coarse-graining which spans the range from nm to mm. The model removes further degrees of freedom implicit in a classical potential model based on atoms while still retaining some fundamental physical properties [4]. This type of simulation can be achieved by many different methods and is used to understand phenomena at the atomistic level without knowing about the fate of individual atoms. Examples of simulations on this level could be the modelling of protein or polymer materials [5, 6] or dislocation dynamics [7].

On the continuum level, the bulk of material will be considered rather than individual atoms. The finite element method is an example of such a model and requires the discretisation of the material into small sub-domains, call elements which are then used in a numerical solution of the continuum equations relating stress, strain and strain rate [8]. Sometimes these continuum models are linked to atomistics when a problem is governed by two disparate length scales [9].

In this work, MD simulations will be used to examine some aspects of radiation effects in ionic systems. MD simulations have been used for many years to study radiation damage from collision cascades over ns time scales [10]. This can reveal mechanisms of defect generation and the re-arrangement of atoms during the ballistic phase of a cascade. The study is a part of continuing work [11, 12, 13, 14, 15, 16] which has examined different ionic crystal structures for their radiation tolerance. The results
1.1 Motivation and outline of the work

To reveal the complex mechanisms involved in irradiation, computer MD simulations have been employed. Previous works in our group have examined the radiation damage that can occur in MgO [11, 12] and spinel, especially magnesium aluminate spinel, MgAl$_2$O$_4$ [13, 14, 15, 16]. In the latter case the material was found to have the ability to incorporate large numbers of cation antisite defects which is one of the reasons for its relative tolerance to radiation. In the former case the vacancies were found to be relatively immobile at room temperature but the isolated interstitial and di-interstitial defects can diffuse at room temperature and even some larger interstitial clusters were relatively mobile [12].
Figure 1.2: The structure of bixbyite and fluorite. Bixbyite has an arrangement like the fluorite structure where the oxygen position occupies three fourths of the positions in fluorite and leaves one fourth to be vacancies located at the opposite corners of the cube.

The study will concentrate on materials which have the lattice structure of NaCl and the bixbyite structure. These structures are shown in Fig. 1.2 and 1.3. The simpler crystal structure will be used to examine some basic phenomena that have not yet been considered while radiation damage in the more complex bixbyite structure will be considered as part of an on-going investigation into radiation effects in different metal oxide systems.

The study will be start with an investigation of displacement mechanisms in ionic systems with both the simple structure of NaCl and materials with the more complex structure of bixbyite. Threshold displacement energies ($E_d$), the lowest kinetic energy required by a primary knock-on atom (PKA) for generating point defects, will be determined for a range of different displacement directions. The value of $E_d$ is one measure of radiation tolerance and various models have been used with this parameter e.g. the Kinchin and Pease [17] or NRT [18] models used to estimate the number of Frenkel pair defects produced from PKA atoms. The defects generated when the kinetic energy given to the PKA exceeds $E_d$ will also be determined. Another measure of radiation tolerance is the Frenkel pair formation energy ($E_{Fp}$) and $E_{Fp}$ is also
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Figure 1.3: The NaCl structure with 4 anion and 4 cations in a unit cell. The anion and cations are individually arranged in the face centred cubic (FCC) structure.

computed and compared to $E_d$ in order to see if there is some functional relationship. For this study materials with the simple NaCl structure will be primarily examined.

After this, cascades in $\text{Er}_2\text{O}_3$ which has the bixbyite structure are examined. This material has recently been studied experimentally and found to have a tolerance to high energy irradiation but has not previously been examined by MD simulation work before. Unlike spinel, bixbyite does not have the antisite defect to absorb kinetic energy from collision cascades. In comparison to other ionic systems $\text{Er}_2\text{O}_3$ has a big mass difference between the anion and cation and a strong charge on the cation. This part of the study will concentrate on the types of defects generated in the ballistic phase of the cascade.

After collision cascades are studied, long time scale techniques will be employed for the analysis of defect evolution in $\text{Er}_2\text{O}_3$. Temperature accelerated dynamics (TAD) simulation will be the main tool used here. The data of energy barriers and time for diffusion will be used to evaluate on the diffusion process and time to recombine between vacancy and interstitial defects. Moreover, these data will be applied to con-
construct a Kinetic Monte Carlo (KMC) simulation for the computation of point defect diffusion coefficients.

Finally, radiation effects close to grain boundaries and in nanocrystalline MgO will be examined. A material with the simple NaCl structure is chosen because of its relatively simple lattice and as the preliminary material to study before the possible study of more complex nanocrystalline oxide materials.

1.2 Experimental work

The topic of radiation tolerance of materials, which could be possibly used to host nuclear waste or to contain an advanced nuclear fuel form, has attracted much interest over the last decades [19]. A wide range of materials has been chosen for testing and many ionic systems have the impressive property of irradiation tolerance [20]. Some A$_2$O$_3$ - BO$_2$ oxides related to the fluorite structure (CaF$_2$) are materials which can resist amorphisation from irradiation, such as ZrO$_2$, some of A$_2$B$_2$O$_7$ oxide compounds (pyrochlore and disordered fluorites) and A$_2$O$_3$ (bixbyite) while rutile (TiO$_2$) which shares the composition, AO$_2$ but not the fluorite structure, has less resistance and amorphises with an irradiation dose of 10 displacement per atom (dpa) [21]. The resistance to amorphisation is an important factor for determining radiation tolerant materials since amorphisation causes changes in volume and mechanical properties. Other criteria can also be used to measure radiation tolerance, such as resistance to interstitial point defect clustering, vacancy induced cavitation, precipitation or phase transformation [19].

Zirconia, ZrO$_2$, is a polymorphic crystalline with 3 forms of crystal structures at different temperatures; cubic-fluorite, (2950 - 2950 K), tetragonal (1440-2640 K) and monoclinic ($<1420$ K) [22]. Amorphisation of zirconia is not observed from many experiments up to a damage dose about 680 dpa [23] but the phase transformations from
monoclinic phase to higher symmetry structure phases (tetragonal- or cubic phases) are observed from irradiation between 2 and 20 dpa after exposed to heavy (Xe) ion irradiation. Cubic stabilised zirconia, made by doping with a trivalent (+3) ion has a cubic, disordered fluorite form, from room temperature to the melting point [22]. The cubic form of zirconia is interesting for nuclear fuel containment due to its similar structure to compounds such as urania (UO$_2$), plutonia (PuO$_2$), ceria (CeO$_2$) and thoria (ThO$_2$). Cubic stabilised zirconia has a large tolerance to irradiation [23]. Amorphisation is observed from irradiation by Cs ions but this is seemingly from a chemical effect [24] while generally amorphisation is not observed up to a dose of about 200 dpa [21].

The pyrochlore materials, A$_2$B$_3$O$_7$, with A$^{3+}$ and B$^{4+}$ are of interest on radiation tolerance because of their compatibility with a large number of radionuclide species e.g. Th, U, Pu [20]. The structure of pyrochlore is related to the fluorite structure in that the cations (A and B) are located on an fcc lattice whereas the oxygen ions occupy three fourths of the anion positions of the fluorite structure. Recent studies [20, 25, 26] show improvement of radiation tolerance when the radii of A and B are similar. For example, Er$_2$Ti$_2$O$_7$ and Er$_2$Zr$_2$O$_7$ : $r_A/r_B = 1.66$ and 1.39 have considerably different tolerances. Er$_2$Ti$_2$O$_7$ is observed to amorphise at a dose of about 3 dpa but Er$_2$Zr$_2$O$_7$ is not observed to amorphise until a dose of 190 dpa [20].

Magnesium aluminate spinel, MgAl$_2$O$_4$, is also a candidate nuclear application material due to its structural stability under irradiation[27]. Spinel shows resistance to swelling under neutron irradiation where the interstitial loops do not lead to a dislocation network [28, 29]. Sickafus et al. found it to be relatively stable under irradiation by neutrons at a fluence $> 5 \times 10^{26}$ n/m$^2$ with the formation of a large number of disordered cations rather than interstitial accumulation [30]. This occurs because of a high recombination rate of vacancy-interstitial pairs and the formation of stable cation
CHAPTER 1. INTRODUCTION

antisite defects which retain the lattice structure [27].

The accumulation of defects (interstitial or vacancy) from irradiation can induce unexpected properties to materials such as decomposition, disordering or amorphisation, which leads to volume change or cracking [20]. Besides the effect on the perfect crystal structure, enhanced radiation resistance was also observed in some nanocrystalline materials due to the sink property of defects at a grain boundary, as many more such boundaries exist with nanoscale grains [31, 32]. Many materials were tested for tolerance to irradiation and it was found that enhanced resistance occurred in nanocrystalline Au (grain size ∼23 nm) [32], MgGa₂O₄ (∼ 4-12 nm) [31], a TiNi alloy (23-31 nm) [33] and Gd₂(Ti₀.₆₅Zr₀.₃₅)₂O₇ (<20 nm) [34]. The latter case showed that the Gd₂(Ti₀.₆₅Zr₀.₃₅)₂O₇ could retain its crystal structure after irradiation to a dose of 2.05 dpa while the material with large grains (> 100 nm) is amorphised at a lower dose of 0.73 dpa. A lower density of defect accumulation in grains was also observed in some other nanocrystalline materials compared to the density of defects inside the polycrystalline form [31, 32].

To date little modelling work has been carried out on materials with the bixbyite structure. The materials, Dy₂O₃, Er₂O₃ and Lu₂O₃ not only have a different crystal structure but they also have a large mass difference between the metal and oxide atoms and so will behave much differently from the spinels or MgO. Experimental work has however been performed and work by Tang et al [35, 36, 37, 38, 39, 40] has reported these effects. Dy₂O₂ was studied by irradiation with 300 keV Kr⁺⁺ ions at a temperature of 120 K by using a dose rate of 2.8 × 10¹⁶ Kr⁺⁺/m²s to a fluence of 1×10²⁰ Kr/m². A phase transformation from the cubic phase (C-phase) to the monoclinic phase (B-phase) of Dy₂O₃ [35, 36] was observed near the irradiation surface. The B-phase of Dy₂O₃ is normally observed at high temperature [41, 42] or pressure [43, 44]. The phase transformation from the C phase to B phase makes the volume decrease by around 9% and the structure changes to a less symmetric structure. To
compare the result with phase transformations in Fig. 1.4, irradiation at different fluences have been tested on Dy$_2$O$_3$, Er$_2$O$_3$ and Lu$_2$O$_3$ [37]. At a fluence of $1 \times 10^{20}$ Kr/m$^2$, the transition of Dy$_2$O$_3$ from the C-phase to B-phase occurs while a partial transition is also observed for Er$_2$O$_3$. However, a phase change is not observed for Lu$_2$O$_3$. These results can be compared with the phase transformation diagram in Fig. 1.4 in which Dy$_2$O$_3$ can transformed to the B-phase at low temperature (as it can with low fluence) and Er$_2$O$_3$ changes at a higher temperature (higher fluence) whereas Lu$_2$O$_3$ has no B-phase transformation with temperature (or by irradiation). Moreover, when increasing irradiation fluence to $5 \times 10^{20}$ Kr/m$^2$, the Dy$_2$O$_3$ is transformed to a H-phase (hexagonal phase) [38]. The reason for this phase transformation for irradiation in bixbyite is not clear and still open to discussion. A discussion from the author for the phase transformation is that it might occur due to the thermal spike of irradiation heating the material to very high temperature during the collision phase. The heat transforms some parts of the material to the new phase since the quenching process could occur quickly after irradiation and the material could become frozen in the new form when cooled to cryogenic temperature ($\sim 120$K) [37].

At a low fluence of irradiation, the ordered bixbyite structure transformation to a disordered fluorite structure is observed. The bixbyite structure has twice the unit cell size of fluorite but when disordered can be thought of as having the same cell size. The disordered fluorite structure is where the structural (anion) vacancy sites are randomly filled by anions (leaving anion vacancies at other sites), see Fig. 1.2, while the cation atoms have the same positions as the cation positions in bixbyite. In the experiments involving 300 keV Kr$^{++}$ ions at a temperature 120 K using a fluence of $1 \times 10^{19}$ Kr$^{++}$/m$^2$ ($\sim 2.5$ dpa), of Dy$_2$O$_3$, the disordered fluorite structure appears near the surface. A temperature dependence is found for this transformation. At 300 K the disordered fluorite structure is observed at a much higher dose ($\sim 25$ dpa). This temperature dependence hints that the increasing mobility of atoms at high tempera-
CHAPTER 1. INTRODUCTION

Figure 1.4: The phase diagram of rare earth sesquioxides after Foex and Traverse [45]. The diagram shows the structure at different temperatures of rare earth sesquioxides which can be any of the A, B, C, H and X phase crystal formations. The letter L on the diagram refers to the liquid phase. The shaded area of the B phase on the top right represents the additional phase obtained from Lopato et al. [46] [Figure from ref. [37]]

Figure 1.5: The structures of A-phase (a), B-phase (b) and C-phase (c) of sesquioxides compared with fluorite structure (d). [Figure from ref. [47]]
tures will enhance the defect and damage recovery from irradiation [39, 40].

1.3 Crystal structures

1.3.1 Bixbyite structure

Bixbyite, named after the American Mineralogist Maynard Bixby (1853-1935), is a rare-earth oxide with the formula $(\text{Fe}^{+3},\text{Mn}^{+3})_2\text{O}_3$. Bixbyite is attractive and interesting for collectors because of its black colour lustre. Many specimens, usually smaller than 2 cm, are often in cube form modified with on octahedral or dodecahedral face on the corner. Bixbyite itself is not considered here but two materials which have the same for, $\text{Er}_2\text{O}_3$ and $\text{Dy}_2\text{O}_3$ are considered. Thus from now on the term bixbyite is used to refer to one of these two materials.

$\text{Er}_2\text{O}_3$ is commonly available as a pale pink powder (see Fig. 1.6). It is generally used for application in colouring glass and ceramics in industry, medicine or dentistry [48, 49, 50]. It is also used to dope for stabilising zirconia into its cubic form at room temperature [23]. The ceramic bixbyite can be made from the high purity powder by sintering at high temperature and then being cold pressed [37].

Crystals are materials arranged in a periodic form with the unit cell, the smallest structure representing the structure of the whole crystal. Each unit cell determines the overall crystal structure by axis the length, $a_0$, $b_0$, and $c_0$, the angle between the axes and the positions of atoms inside.

The bixbyite crystal structure is cubic and has the space group $\Gamma^7_h$ (Ia$\overline{3}$). The arrangement of the unit cell is complicated and composed of 16 molecules. Using the notation of W. G. Wyckoff from crystal structures vol.2 [52], the atoms have the po-
CHAPTER 1. INTRODUCTION

Figure 1.6: 
Er$_2$O$_3$ is found generally in a pale pink powder form [51].

...ions as following.

\[
[\text{Fe,Mn}](1): (8a) \quad \frac{111}{111} \cdot \frac{333}{333} \cdot \frac{333}{333} \cdot \frac{111}{111} \quad \text{B.C.}
\]

\[
[\text{Fe,Mn}](2): (24d) \quad u0\frac{1}{4} \cdot \frac{1}{4} \cdot \frac{1}{4} ; \quad \frac{1}{4} \cdot \frac{1}{4} \cdot \frac{1}{4} ; \quad \frac{1}{4} \cdot \frac{1}{4} \cdot \frac{1}{4} \quad \text{B.C.}
\]

O: (4e) \quad \pm (xyz; x, y, \frac{1}{2} - z; \frac{1}{2} - x, y, z; \frac{1}{2} - x, y, z; \frac{1}{2} - y, z, x; \frac{1}{2} - x, \frac{1}{2} - y, z, x)

In bixbyite, [Fe,Mn] occupies 2 equipoints at 8a and 24d with 32 atoms and oxygen occupies at 48e with 48 atoms. Total atoms combining to a unit cell are 80 atoms.

The structure of bixbyite is similar to that of fluorite (Fig. 1.2) with 6 oxygen atoms and 2 vacancies forming a cube with vacancies at opposite corners. When compared to calcium fluorite, oxygen in bixbyite occupies three of the four fluorite positions and leaves the fourth position as a tetrahedral vacancy, which we will call a...
structural vacancy (or oxygen vacancy in some case) in this thesis.

Er$_2$O$_3$ and Dy$_2$O$_3$ have the bixbyite structure. The unit cell of bixbyite has $a_0(=b_0=c_0)$ with the parameters with $u=-0.033$, $x=0.394$, $y=0.149$, and $z=0.38$. The unit cell values are shown in the Table 1.1.

Table 1.1: Lattice constant for Bixbyite structure.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$a_0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er$_2$O$_3$</td>
<td>10.547</td>
</tr>
<tr>
<td>Dy$_2$O$_3$</td>
<td>10.667</td>
</tr>
</tbody>
</table>

1.3.2 The NaCl structure

The NaCl structure (RX) is cubic with 8 atoms per unit cell composed of 4 cations and 4 anions arranged in the face-centred cubic (FCC) formation. The positions of atoms by using the notation of W. G. Wyckoff from crystal structures vol.1 [53] are given by

R: (4a) 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; or 000; FCC.

X: (4b) $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}00$; $0\frac{1}{2}\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$; or $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; FCC

NaCl, MgO and SrO which all have this structure will be used in the study of chapter 2 concerned with displacement threshold energies and only MgO will be studied in chapter 5 concerned with grain boundaries and nanocrystalline materials. The unit cell dimensions used in the study are shown in Table 1.2
CHAPTER 1. INTRODUCTION

Table 1.2: Lattice constants for the NaCl-like structure.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$a_0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>4.21</td>
</tr>
<tr>
<td>SrO</td>
<td>5.16</td>
</tr>
<tr>
<td>NaCl</td>
<td>5.64</td>
</tr>
</tbody>
</table>

1.4 Final introductory remarks

Radiation tolerance of some materials which are related to the fluorite structure, zirconia, pyrochole or bixbyite are observed from experimental works. Some of these materials have been the subject of investigation by MD but materials with the bixbyite structure have not so far been studied. In addition, interest in nanostructured materials has shown that they also behave differently under irradiation than bulk crystals. Thus the thesis will concentrate on studying collision cascades and diffusion of simple point defects in materials with the bixbyite structure but will also examine some aspects of cascades in MgO which has a simpler structure. Especially here will consider the relationship between the displacement threshold energy and the Frenkel pair formation energy and the role of complex interfaces.
Chapter 2

The Classical Molecular Dynamics methodology

2.1 Introduction

Molecular Dynamics (MD) is a technique which is widely used for simulating the motion of an N-body system. Nowadays, MD simulations are rapidly growing in popularity in materials science and are used to simulate ionic systems, metals, covalent materials and molecular solids. They can also be used to model interfaces between materials such as grain boundaries or thin films. MD can also be applied to biochemistry such as for modelling of proteins. The general idea of a classical MD simulation is based on a potential function which are usually created by fitting with experimental data or data obtained from quantum theory. Classical MD simulation uses Newton’s 2\textsuperscript{nd} law for calculating the interaction force. If the potential of a system of atoms is given by \( V \), the interaction force on the atom \( i \) can be expressed by the gradient of the potential function;

\[
-\nabla_{\mathbf{r}_i} V(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n) = \mathbf{F} = m_i \mathbf{a}_i. \tag{2.1}
\]

where \( \{\mathbf{r}_j : j = 1...n\} \) are the vector positions of the atoms. \( m_i \) and \( \mathbf{a}_i \) are mass and acceleration of atom \( i \) respectively. These equations cannot be solved analytically so
are solved numerically so that the force from the evaluation at time step \( t \) will be used to forward positions and velocities of the atoms in the system by integrating to the new time step at \( t + \Delta t \). By repeating this procedure, the motion of the atoms can be followed as time advances. The simulation is terminated when the points of interest to the user have been reached such as at a time when the number of defects produced in a collision cascade no longer changes. The procedure of the classical MD simulation is shown in Fig. 2.1. If the potential function has been accurately approximated, the simulation can model phenomena which are observed in a real material. Many additional techniques can be applied in the MD simulations to enhance the understanding or to simplify the calculations. This chapter will briefly discuss these techniques, which are widely used in MD simulations.

Figure 2.1: Diagram describing the general idea of an MD simulation. The MD simulation is started from an initial position \( x_0 \). Forces are calculated and the accelerations of the particles are obtained. All atoms are moved to their new positions by the integration algorithm and time is incremented. This scheme is repeated until the simulation time exceeds a predefined stopping time or until some other user-specified criterion.
CHAPTER 2. THE CLASSICAL MOLECULAR DYNAMICS METHODOLOGY

2.2 Potential function

Various forms of potential functions are proposed to suit each material. The simple form of potential function may be represented by the combination of functions of individual atoms, pairs, triples, etc., given by

\[ V = \sum_i V_1(r_i) + \sum_i \sum_{j>i} V_2(r_i, r_j) + \sum_i \sum_{j>i} \sum_{k>j>i} V_3(r_i, r_j, r_k) + ... \]  

2.2

The first potential term represents the potential from the external effect, such as an electric field. The second term is the pair potential which usually depends on the separation distance, \( r_{ij} = |r_i - r_j| \), between atoms. The third term, the triple body potential, is the potential that is commonly used with the covalent bonds when bond angles are important. The later terms in the equation are generally not calculated since they contribute less that the first three terms and take longer to compute [65].

Since ionic systems are the main focus in this thesis, only pair potentials will be treated. This will be done by dividing into a combination of a long range potential, \( V_{\text{Coulomb}} \), and a short range potential \( V_{\text{SR}} \) term:

\[ V_{ij} = V_{\text{Coulomb}} + V_{\text{SR}} \]  

2.3

The \( V_{\text{Coulomb}} \) is the Coulomb potential which varies inversely with the separation distance, \( r_{ij} \). Since this term only slowly reduces with increasing separation distance it is called a long range interaction. The short range interaction, \( V_{\text{SR}} \), rapidly decays with increasing separation distance and has negligible value at long distances. Therefore, this potential is often included only for atoms which are closer to atom \( i \) less than a cut-off distance, \( r_0 \). \( V_{\text{SR}} \) generally accounts for the effects of the interaction between atomic nuclei and overlapping electron shells.
CHAPTER 2. THE CLASSICAL MOLECULAR DYNAMICS METHODOLOGY

2.2.1 Coulomb interaction

The Coulomb interaction is the well known property in physics discovered and published by Charles Augustin de Coulomb (1783). The original study investigated the interaction force between charged particles as a function of the separation distance and the magnitude of charges. In modern notation the law can be written:

$$V_{Coulomb} = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$$  \hspace{1cm} (2.4)

where $q_i$ and $q_j$ are charges of ions $i$ and $j$ respectively and $\epsilon_0$ is the electrical permittivity of free space and has value of $8.854 \times 10^{-12}$ C²N⁻¹m². For numerical calculation in an MD code, the Coulomb potential is not suitable for calculation by direct summation since it is too time consuming for reasonable convergence. As a result many techniques, such as Ewald summation [54], the fast multipole method [55], the Wolf method [56] etc., are proposed for solving the problem. In this work, the fast multipole method and Ewald summation are used to compute the Coulomb interaction.

2.2.2 Short range potential

Buckingham potential

The Buckingham potential is a potential function often used in conjunction with the ionic systems [57]. It is simply composed of the two functions; a Born-Mayer and Van Der Waals potential function. The Born-Mayer function ($A_{ij} e^{-r_{ij}/\rho_{ij}}$) is used to describe the repulsive energy between atomic nuclei and the Pauli exclusion principle for preventing the overlap between electron clouds. The Van Der Waals potential ($C_{ij} r_{ij}^{-6}$) is added to the function for the attractive dipole energy of the model. Therefore, the Buckingham potential is expressed by

$$V_{SR} = A_{ij} e^{-r_{ij}/\rho_{ij}} + C_{ij} r_{ij}^{-6}$$ \hspace{1cm} (2.5)

where $r_{ij}$ is the separation distance between two atomic cores and $A_{ij}$, $\rho_{ij}$ and $C_{ij}$
are the function parameters. The function can be used in different ionic materials by adjusting the function parameters. The values are chosen to fit values as close as possible to important experimental data, such as the cell dimension, atomic coordinates, elastic properties and the dielectric constant [57]. The Buckingham potentials mostly used in this thesis are for the potential functions of Er$_2$O$_3$, Dy$_2$O$_3$, MgO and SrO. The parameter values are shown in table 2.1 and 2.2.

**Potentials for alkali halides**

The potential for the alkali halides proposed by Catlow, Diller and Norgett are modified from their original form in order better to fit experimental data [58]. The new model is similar to the Buckingham potential and uses the Born- Mayer and Van der Waals potential for accounting for the repulsive and dipole energy in the model. However, the regions of validity are separated and the potential function is divided into four regions smoothly joined at, $r_B$, $r_m$ and $r_A$ (see Fig. 2.2).

In Fig 2.2, the potential in region (i) is calculated by the Van Der Waals interaction ($-C/r^6$) while in the region (ii), the potential between $r_A$ and $r_m$ is represented by a 3$^{rd}$ order polynomial function. The three coefficients of the polynomial function can be obtained by the requirement of continuity of the functions and its derivatives at the joining point $r_A$. The last coefficient can be calculated by a requirement of minimum point at $r_m$. For the region (iii), the potential function is expressed by a 5$^{th}$ order polynomial function. The coefficients of the function can be obtained from the requirement of continuity of the functions and its derivatives at the joining points, $r_m$ and $r_B$. In region (iv), the potential is described by the Born-Mayer potential. This potential can be adjusted by fitting potential parameters, $A_{ij}$, $p_{ij}$, $C_{ij}$, $r_A$, $r_m$ and $r_B$ with the experimental data. This model will be implemented only on the anion-anion interaction while the potential between cation-cation and cation-anion will be employed using the pure Buckingham potential.

**Ziegler-Biersack-Littmark potential**
Figure 2.2: Plot of the alkali halide potential function. Region(i) and region(iv) are calculated by using the Van Der Waals potential \((-C/r^6)\) and Born-Mayer model \((A \exp(-r/\rho))\) respectively. For region(ii) and region(iii), the third and fifth order polynomials are applied respectively with the smooth continuity between the functions at \(r_A, r_B\) and \(r_m\). (This figure was adapted from [58])
The Ziegler-Biersack-Littmark (ZBL) potential is used for calculating the potential between atoms at very short separation distance. This is different from the above-mentioned short range potential since it is calculated from the screened Coulomb interaction between the atomic cores of the atoms. The idea is that for high energy collisions, the interaction of the nuclei between 2 atomic cores will play an important role. Thus, the ZBL potential is calculated by the multiplication of the Coulomb potential between the charges on each nucleus and a screening function. This screening function is used for reducing the potential when the separation distance is large but approaches 1 as the distance tends to 0. The equation is given by

\[ V_{ZBL} = \frac{1}{4\pi\varepsilon_0} \frac{Z_i Z_j}{r_{ij}} \phi\left(\frac{r_{ij}}{a_{ij}}\right) \]

(2.6)

where \(Z_i\) and \(Z_j\) are atomic numbers of atom \(i\) and \(j\) and \(a_{ij}\) is the screening length for the interaction. The screening function for ZBL potential has a form

\[ \phi(x) = 0.1818e^{-3.2x} + 0.5099e^{-0.9423x} + 0.2802e^{-0.4029x} + 0.02817e^{-0.2016x}, \]

(2.7)

where \(x = \frac{r_{ij}}{a_{ij}}\) and \(a_{ij}\) is given by

\[ a_{ij} = \frac{0.8854a_0}{Z_i^{0.23} + Z_j^{0.23}} \]

(2.8)

where \(a_0 = 0.529\) Å, the Bohr radius. The ZBL potential is widely used and is chosen for use in this work since it has good agreement with many experimental results such as implantation profiles [59]. As a result a further inner region is added to the above potentials which again must be smoothly joined.

### 2.2.3 Potentials and parameters setting

In this section, the parameter values used in the later MD simulation are discussed. As given in Eq. 2.3, the potentials used in this project are pair potentials described by short range and long range interactions where the long range interaction is always...
the Coulomb potential. However, different potentials are used for the short range interactions. For the closest separation region, the ZBL potential is used. For the larger distances where the potential is effected mainly by the Pauli repulsion, the Buckingham potential or the alkali halide potential mentioned above is used. For continuous connection between the ZBL and the Buckingham potential or the potential of alkali halide, a spline function, \( g(r_{ij}) \), is applied to make the potential functions smooth and continuous at the joining points. Moreover, a smooth cut-off function, \( h(r_{ij}) \), is also employed for reducing the short range potential to zero at the cut-off distance \( r_0 \). Eqs. 2.9 and 2.10 give the full pair potential functions representing the short range potentials for the Buckingham potential and the potential of the alkali halide respectively.

\[
V(r_{ij}) = \begin{cases} 
V_{ZBL}(r_{ij}) & r_{ij} < r_a \\
g(r_{ij}) & r_a \leq r_{ij} < r_b \\
A_{ij}e^{-\frac{r_{ij}}{r_{ij}}} - \frac{C_{ij}}{r_{ij}^6} + V_{coul}(r_{ij}) & r_b \leq r_{ij} < r_c \\
h(r_{ij}) \times \left( A_{ij}e^{-\frac{r_{ij}}{r_{ij}}} - \frac{C_{ij}}{r_{ij}^6} \right) + V_{coul}(r_{ij}) & r_c \leq r_{ij} < r_0 \\
V_{coul}(r_{ij}) & r_{ij} \geq r_0 
\end{cases} 
\] (2.9)
\[ V(r_{ij}) = \begin{cases} V_{ZBL}(r_{ij}) & r_{ij} < r_a \\ g(r_{ij}) & r_a \leq r_{ij} < r_b \\ A_{ij} e^{-r_{ij}^{6/r_{ij}}} + V_{\text{coul}}(r_{ij}) & r_b \leq r_{ij} < r_B \\ 5\text{th order polynomial} + V_{\text{coul}}(r_{ij}) & r_B \leq r_{ij} < r_m \\ 3\text{th order polynomial} + V_{\text{coul}}(r_{ij}) & r_m \leq r_{ij} < r_A \\ -\frac{C_{ij}}{r_{ij}} + V_{\text{coul}}(r_{ij}) & r_A \leq r_{ij} < r_c \\ h(r_{ij}) \times (-\frac{C_{ij}}{r_{ij}}) + V_{\text{coul}}(r_{ij}) & r_c \leq r_{ij} < r_0 \\ V_{\text{coul}}(r_{ij}) & r_{ij} \geq r_0 \end{cases} \] (2.10)

The spline function, \( g(r_{ij}) \), connecting the ZBL and the Buckingham potential or the potential for alkali halide is chosen as an exponential of a 5th order polynomial function;

\[ g(r_{ij}) = e^{(f_1 + f_2 r_{ij} + f_3 r_{ij}^2 + f_4 r_{ij}^3 + f_5 r_{ij}^4 + f_6 r_{ij}^5)} \] (2.11)

and the cut-off function, \( h(r_{ij}) \), which gradually reduces the short range function to zero at cutoff, \( r_0 \), is give by

\[ h(r_{ij}) = 0.5(1 + \cos(\pi \frac{r_{ij} - r_0}{r_c - r_0})) \quad \text{where} \quad r_c \leq r_{ij} \leq r_0. \] (2.12)

Eq. 2.10 is used only for interaction of Cl\(^-\) - Cl\(^-\) in NaCl. The parameters of the potential and the spline function for NaCl, MgO and SrO are shown in Table 2.1. The parameters for MgO and SrO are obtained from Lewis and Catlow [60]. The O\(^{-2}\) - O\(^{-2}\) interaction are taken to be the same value for both MgO and SrO. The cation-cation interaction used is a pure Coulomb interaction by setting \( A_{ij} \) and \( C_{ij} \) to zero and the cation-anion is taken to be only the Born-Mayer part (\( C_{ij} = 0 \)). For NaCl
the procedure is the same as with the previous set using only the purely Coulomb interaction for the Na\(^+\)-Na\(^+\) interaction. The Na\(^+\)-Cl\(^-\) interaction is described by the Buckingham potential in Eq. 2.9 while the Cl\(^-\)-Cl\(^-\) interaction uses the potential in Eq. 2.10. For Er\(_2\)O\(_3\) and Dy\(_2\)O\(_3\), the parameter values are obtained from the Imperial College group [61, 62] by a ‘multistructure-fitting procedure’ [63] and are shown in table 2.2. The separation distance parameters, \(r_a, r_b, r_c\) and \(r_0\) have different values for the different materials to obtain a smooth connection at each joining point. For the splining of the ZBL function the potential, its first derivative and the second derivative are made continuous at the joining points. Figs. 2.3 and 2.4 illustrate the potential functions between the cation-anion and the anion-anion for NaCl and bixbyite structures respectively.

### 2.3 Integration Algorithm

The integration algorithm is used to forward the position and velocity of an atom to the next time step through numerical solution of Newton’s equation in Eq. 2.1. The Velocity Verlet algorithm is an algorithm which is broadly used in MD simulations. The velocity Verlet algorithm, is similar to the Verlet algorithm proposed by Loup Verlet for the simulation of liquid argon [64]. The Verlet algorithm updates the position \(\mathbf{r}_i\) and velocity \(\mathbf{v}_i\) according to the following:

\[
\mathbf{r}_i(t + \delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \delta t) + \mathbf{a}_i(t)\delta t^2
\]  
\[
\mathbf{v}_i(t) = \frac{\mathbf{r}_i(t + \delta t) - \mathbf{r}_i(t - \delta t)}{2\delta t}
\]  

where \(\mathbf{v}_i\) is the velocity, \(\mathbf{a}_i\) is the atomic acceleration and \(\delta t\) the time step. The equation computes position \(\mathbf{r}_i(t + \delta t)\) by using the acceleration \(\mathbf{a}_i\), position \(\mathbf{r}_i(t)\), and position \(\mathbf{r}_i(t - \delta t)\) with local error of order \(\delta t^4\). The velocity is not required for the calculation of position and is used only in calculating the kinetic energy with an accuracy of order \(\delta t^2\). The velocity can be estimated after the \(\mathbf{r}_i(t + \delta t)\) is calculated. Then, the velocity
Table 2.1: Potential parameters for NaCl SrO and MgO. The units of $r_1$ and $r_2$ are Å. $A_{ij}$ and $offset$ are in eV, $\rho_{ij}$ is in Å, $C_{ij}$ has units of eV Å$^6$. The units of $f_n$ are Å$^{-1}$. For Cl$^-$-Cl$^-$, $r_A$, $r_B$ and $r_{AB}$ are 4.103, 3.551 and 2.69 Å respectively.

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<th>Sr-Sr</th>
<th>Sr-O</th>
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Table 2.2: Potential parameters for Dy$_2$O$_3$ and Er$_2$O$_3$. The units of $r_1$ and $r_2$ are Å. $A_{ij}$ and $offset$ are in eV, $\rho_{ij}$ is in Å, $C_{ij}$ has units of eV Å$^6$. The units of $f_n$ are Å$^{-1}$.

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Figure 2.3: Plot of the pair potential functions between the cation-anion interaction of Sr-O (A), Mg-O (B) and Na-Cl (C) and anion-anion interaction of O-O (D) and Cl-Cl (E). These plots show the continuity between the functions at the joining points using parameters from table 2.1. The insets show the complete smoothly-joined potential function.
Figure 2.4: Plot of the pair potential functions (top to bottom) of Er-O, Dy-O and O-O interactions. These plots show the continuity between functions at the joining points using parameters from table 2.2. The insets show the complete smoothly-joined potential function.
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calculation is delayed one time step from that of the position. The Verlet algorithm is accurate and simple to programme with only 3 variables stored. The energy is well conserved using this method and the algorithm is (in theory) time reversible.

Some equivalent or similar schemes to the Verlet algorithm are also proposed in the literature, e.g. the Leapfrog algorithm which uses the half time step for calculation and includes the velocity for updating the positions [65]. The velocity Verlet algorithm, also an equivalent algorithm, is proposed by Swope et al. [66]. The scheme for updating position at time $t + \delta t$ is the same but now the velocity is calculated at the same time step:

\[
\mathbf{r}_i(t + \delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\delta t \frac{a_i(t)}{2} \delta t^2 \tag{2.15}
\]

\[
\mathbf{v}_i(t + \delta t) = \mathbf{v}_i(t) + \frac{a_i(t) + a_i(t + \delta t)}{2} \delta t \tag{2.16}
\]

The position is first updated. Then, the acceleration computed from force and velocity is updated. The velocity Verlet algorithm is an equivalent algorithm to the Verlet algorithm since Eq. 2.15 and 2.16 can be derived directly from Eq. 2.13 and 2.14 (see e.g.[3]). The velocity Verlet algorithm is chosen for the simulation code because it is simple and convenient as it updates position and velocity at the same time step. Moreover, it is a symplectic algorithm, which preserves energy from the numerical integration over a large number of time steps [59].

2.4 Optimisation techniques.

Minimisation is an important technique frequently employed in atomic systems to find local (possibly metastable) equilibria. In the simulations of collision cascades, the system’s particles are usually in a local minimum energy state before initialising the collision cascade or heating the system to desired temperature. Moreover, in
the analysis of defect formation or the transition energy barrier between states, the potential energy of the two end states needs to be accurately determined. Many optimisation techniques, i.e. the steepest descent, Newton methods etc, have been proposed but for atomic systems conjugate gradient of Quasi-Newton methods are more efficient. In the following, two techniques, conjugate gradient and the damped MD method, which are applied in this thesis, will be discussed.

2.4.1 Conjugate gradient

The conjugate gradient is a method developed to find the optimum or local minimum point in the quadratic function given by

$$f(x) = \frac{1}{2}x^T A x - b^T x + c$$

where $A$, $b$ and $c$ are a matrix, vector, and scalar constant respectively. If $A$ is symmetric ($A^T = A$) and positive-definite ($x^T A x > 0$ for every $x$ where $x \neq 0$), $f(x)$ can be minimised by solving $A x = b$. To find a minimum we proceed iteratively and for a quadratic, the exact solution to $A x = b$ is found in $n$ steps.

For a quadratic function of $n$ variables, the negative gradient direction, $-\nabla f(x)$, is used as the initial direction. The steepest descent and conjugate gradient methods therefore use the same initial scheme. However, they differ in the condition for choosing the next direction. The steepest descent uses a vector which is orthogonal to a current direction vector ($d_{(i+1)}^T d_{(i)} = 0$) as new search direction while the the conjugate gradient use the $A$ - orthogonal or conjugate ($d_{(i+1)}^T A d_{(i)} = 0$) as the new search direction.

For a non-quadratic function, the conjugate gradient method can be applied by approximating a function, $f(x)$, by a quadratic function. This can be done by expanding
$f(x)$ as a second order Taylor series:

$$f(x) \approx \frac{1}{2} x^T A x - b^T x + c$$  \hspace{1cm} (2.18)

where $A$ is the Hessian matrix and $b$ is the gradient vector of the quadratic approximation. The algorithm for minimisation is similar to the original method. The algorithm is computed by:

- initialise the search direction, $d_0$, at a starting point, $x_0$, by using the negative gradient vector: $d_0 = -\nabla f(x_0)$.

- determine $\lambda_i$ the minimum point of the function $f(x_i + \lambda_i d_i)$, which is calculated by one-dimensional optimisation.

- move $x_i$ to a new position, $x_{i+1}$ by: $x_{i+1} = x_i + \lambda_i d_i$.

- calculate the gradient vector at the new position, $\nabla f(x_{i+1})$, and determine a new search direction by:

$$d_{i+1} = -\nabla f(x_{i+1}) + \beta_i d_i$$  \hspace{1cm} (2.19)

where $\beta_i$ is scalar which makes the $d_{i+1}$ satisfy the conjugacy condition, $d_k^T A d_i = 0$ for all $k < i$.

- and iterate the procedures until reaching the termination criterion which is set to stop when infinity norm of the force or the change of total energy between steps are smaller than a given tolerance, $\varepsilon$.

The scalar $\beta_i$ in Eq. 2.19 can be determined by several schemes, e.g. the Hestenes-Stiefel formula, Polak-Ribière formula or Fletcher-Reeves formula. Here, the Polak-Ribière scheme, which is frequently used for atomistic problem [69], is applied and $\beta_i$ is given by

$$\beta_i = \frac{\nabla f(x_{i+1})^T (\nabla f(x_{i+1}) - \nabla f(x_i))}{\nabla f(x_i)^T \nabla f(x_i)}$$  \hspace{1cm} (2.20)
Chapter 2. The Classical Molecular Dynamics Methodology

The tolerance for the force criterion, $\varepsilon_F$, is normally set at $10^{-4}$ eV/Å and the tolerance for the total energy criteria, $\varepsilon_E$, is usually used at $10^{-8}$ eV in this thesis.

2.4.2 Minimisation by damping

Minimisation by damping is based on a quenching method. It starts from computing the velocity at an initial point then rescaling every time step by

$$
\mathbf{r}_i = \mathbf{r}_i - \alpha \mathbf{v}_i \quad (2.21)
$$

$$
\mathbf{v}_i = \beta \mathbf{v}_i \quad (2.22)
$$

where parameters, $\alpha$ and $\beta$, are determined in our implementation by using the Lindhard-Scharff and Schiøtt inelastic energy loss model [67]. Eqs. 2.21 and 2.22 can be implemented in the velocity Verlet integration by

$$
\mathbf{r}_i(t + \delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\delta t + \frac{\mathbf{a}_i(t)}{2}\delta t^2 - \alpha \mathbf{v}_i(t) \quad (2.23)
$$

$$
\mathbf{v}_i(t + \delta t) = \beta \mathbf{v}_i(t) + \frac{\mathbf{a}_i(t) + \mathbf{a}_i(t + \delta t)}{2}\delta t \quad (2.24)
$$

The system dynamics continues until reaching a stopping time which is chosen to be sufficiently large for the method to find the minimum energy point, i.e when the kinetic energy of the system is sufficiently small. Damped MD is slower than the conjugate gradient method but can find more stable minima for a system where the initial position is a long way from the final minimum position, such as in interface relaxation [69].
2.5 Temperature control

In the microcanonical ensemble, the average temperature, $T$, can be obtained from kinetic energy $U_K$ by the equation:

$$T = \frac{2U_K}{3Nk_B}.$$  \hspace{1cm} (2.25)

where $k_B = 1.38065 \times 10^{-5}$ eV K$^{-1}$ is Boltzmann’s constant and $N$ is the number of atoms. In the simulation of materials, temperature control of the system is a useful tool for increasing or decreasing the temperature of a system to a desired temperature or by controlling the temperature when energy is input into the system (e.g. in modelling nanoindentation). Many researchers often initialise the temperature of a system to be at a constant room temperature as this is the temperature at which many experiments are carried out. Present temperatures are also applied in the temperature accelerated dynamics technique for study on diffusions over longer time scales. This section will discuss some temperature control techniques which have been used in the thesis.

2.5.1 Berendsen thermostat

The Berendsen thermostat was proposed by Berendsen et al. [68]. The method controls the temperature by scaling the velocity at each time step. If changing temperature is given by multiplication of the velocity by a constant, $\lambda$, at each time step, the change in temperature will be expressed by

$$\Delta T = \sum_{i=1} m_i (\lambda v_i)^2 - \sum_{i=1} m_i v_i^2$$

$$= \frac{m_i (\lambda v_i)^2}{3Nk_B} - \frac{m_i v_i^2}{3Nk_B}$$

$$= (\lambda^2 - 1)T(t)$$  \hspace{1cm} (2.26)

From the above equation, the temperature can be increased or decreased by giving different values to the factor $\lambda$. To approach a desired temperature, $T_0$, the changing
temperature is defined by

$$\Delta T = \frac{\delta t}{\tau} (T_0 - T(t))$$  \hspace{1cm} (2.28)

where $\delta t$ is the integration time step and $\tau$ is a coupling parameter between the heat bath and the system. By replacing Eq. 2.28 by Eq. 2.27, $\lambda$ is given by

$$\lambda^2 = 1 + \frac{\delta t}{\tau} \left( \frac{T_0}{T(t)} - 1 \right)$$  \hspace{1cm} (2.29)

The method can be implemented in a simulation as a thermal layer as shown in Fig. 2.6 by applying the thermostat to the several layer of atoms at the boundary. Free atoms, which are not in the thermal layer, move normally. The thermal layer controls the temperature by giving or reducing energy to those atoms near the boundary which then collide with free atoms, thus gradually reducing the temperature of the entire system. The parameter $\tau$ controls the rate at which the temperature is reduced or increased.

Figure 2.5: The coloured region represents the thermal layer used in the MD simulation. When the temperature of system is lower than a desired temperature, $T_0$, the thermal layer will give some kinetic energy to the system (left figure). However, when energy in the system is higher than desired temperature, energy will be absorbed (right figure).
2.5.2 Nosé - Hoover thermostat

The Nosé - Hoover method [70] controls the temperature to be constant by modifying the equation of motion by

\[ m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i - \zeta m_i \frac{d\mathbf{r}_i}{dt} \]  \hspace{1cm} (2.30)

where \( \zeta \) is the ‘friction coefficient’, used for constraining the temperature. Hoover developed the original analysis of Nosé to a slightly different form of friction coefficient and the equation is given by

\[ \frac{d\zeta}{dt} = \frac{1}{Q} \left( \sum_i v_i^2 - 3Nk_B T_0 \right). \]  \hspace{1cm} (2.31)

Here, the parameter \( Q \) is the strength of coupling between the heat bath and the system and \( T_0 \) is the desired temperature. The Nosé - Hoover thermostat is employed in the MD simulation through the velocity Verlet algorithm in Eq. 2.15 and 2.16 by changing to the force in Eq. 2.30 and the new equations are given by

\[ \mathbf{r}_i(t + \delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\delta t + \left[ \mathbf{f}_i(t)/m_i - \zeta(t)\mathbf{v}_i(t) \right] \frac{\delta t^2}{2} \]  \hspace{1cm} (2.32)

\[ \mathbf{v}_i(t + \delta t) = \mathbf{v}_i(t) + \left[ \mathbf{f}_i(t + \delta t)/m_i - \zeta(t + \delta t)\mathbf{v}_i(t + \delta t) + \mathbf{f}_i(t)/m_i - \zeta(t)\mathbf{v}_i(t) \right] \frac{\delta t^2}{2} \]  \hspace{1cm} (2.33)

The implementation of the Nosé - Hoover thermostat to the simulation is the same as with the Berendsen thermostat by applying the thermostat to the atoms in a thermal layer as in Fig. 2.5. These atoms will control the temperature by increasing or decreasing the velocity of system to accord with \( T_0 \) by Eq. 2.31.

2.6 Boundary condition

Normally, the boundary atoms in the system have to be treated differently than the bulk atoms and three separate conditions; free, fixed or periodic boundary conditions
are usually applied. In this work, only fixed and periodic boundary are used due to the study concentrating only inside bulk materials. The free boundary condition is frequently used with simulations which are related with the surfaces, such as the thin film growth, nano-indentation, impact of radiation in the surface etc.

2.6.1 Periodic boundary conditions

The periodic boundary condition is a common technique used in the MD simulation. When the lattice containing $N$ atoms is constructed, the image of the lattice will be infinitely repeated on the boundary (see Fig. 2.6). During the simulation, if an atom in the lattice moves past the boundary, another atom will move into the lattice across the opposite boundary. This condition ensures that the number of atoms in the system is constant.

![Figure 2.6: The periodic boundary condition. The image of the region of interest is infinitely repeated and if an atom passes the boundary during the simulation another atom from the opposite boundary will move into the region as shown by the arrows in the diagram.](image)

The periodic boundary condition stabilises atoms near the edge or surface which have lower number of surrounding atoms compared to an atom in the bulk. In this thesis, the periodic boundary is mainly used in the temperature accelerated dynamics
simulations for study the diffusion and in the main LBOMD code for the study of energy barriers since it requires fewer atoms in the system to get good convergence.

2.6.2 Fixed boundary condition

The fixed boundary condition is used by fixing the atomic positions in several layers close to the boundary. Atoms in the fixed layers are not moved in the simulation but their force interaction with the free atoms inside the system is considered. In this case the boundary effects are felt further from the boundary than in the case of the periodic boundary conditions. However it is necessary to implement fixed boundaries when the long range forces are summed using DPTMA which also does not use periodic boundaries. In this thesis, the fixed boundary is used for studies of collision cascades which are simulated around centre of the lattice and the distance of the boundary chosen so that atoms displaced from their lattice sites do not move closer than 10 Å to the fixed layers.

2.7 Potential calculation techniques

2.7.1 Neighbour list and cell index

Since the short range potentials, which are discussed in section 2.2.2, are zero at small separation distances, (usually \(< 10 \text{ Å}\)), then, calculation of the short range potential need not be computed for all atoms in the system, but only for atoms, closer than the cut off radius, \(r_0\). In this case, Verlet [72] suggested a technique for reducing computational time by constructing a neighbour list. This list is reconstructed when an atoms moves a distance greater than \(r_1 - r_0\), (see Fig. 2.7a). The value of \(r_1\) must be bigger than the cut off distance, \(r_0\). After the neighbour list is constructed, the short range potential for each atom can be computed by using atoms from the list. The distance between \(r_0\) and \(r_1\) is a skin with thickness \(r_1 - r_0\). In the simulations, atoms can move in or out the neighbour list radius, \(r_1\). Therefore, the thickness of skin must be sufficiently large to ensure that atom outside neighbour list will not pass
into the cut off radius before the neighbour list is updated. The updating is commonly done around every 10 - 20 time steps. For guaranteeing that no atom outside the list can move past the skin into the cutoff radius, Fincham and Ralston [73] suggest an automatic update by using displacement vectors between atom positions at the current time and the last updating list time. Thus, the vectors will be zero, when the list is updated. The list automatically updates when the largest displacement vector is larger than the skin, \( r_1 - r_0 \).

![Verlet neighbour list](image)

Figure 2.7: Verlet neighbour list (a) and cell index (b). The Verlet neighbour list is constructed by making a list of atoms that lie closer to atom 1 than \( r_1 (r_1 > r_0) \). Only atoms in the list will be used to compute the short range potential and force until the list is updated. Some atoms outside the list can move into the skin \( (r_1 - r_0) \) but not pass to the cutoff radius \( (r_0) \). The cell index (b) is similarly used for computing the short range potential and the force in the bigger system by using only atoms in the same and neighbouring boxes. In (b), after the simulation box is divided into small cells, only atoms in cells 1-9 will be used for computing of the potential and force of atom 1.

When the number of atoms \( N \) in the system is more than a few thousand atoms, the Verlet neighbour list alone becomes less efficient. In this case, the cell index method [75] which scales as \( O(N) \) is an alternative technique for bigger lattice sizes. The cell index is carried out by dividing the simulation box into small boxes of \( M \times M \times M \) cells. Each cell is chosen to be bigger than the cutoff \( r_0 \). When computing the potential, only atoms in the same cell and neighbour cell will be used (see Fig. 2.7b).
2.7.2 Long range interaction techniques.

The long range interaction, the Coulomb potential, is a problem in the simulations since it leads to conditionally convergent series for the potential energy [65]. In this section, we will briefly discuss the fast multipole method (FMM) and Ewald summation method, which are used to solve this problem in the present work.

Ewald summation

The Ewald summation is a method which was developed for a system composed of positive and negative ions in a cubic box with periodic boundaries [54]. The total Coulomb energy of \( N \) particles in the cubic box of size \( L \) is given by

\[
U = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} Z_i Z_j \left| \mathbf{r}_{ij} + \mathbf{n}L \right| \quad (2.34)
\]

where \( q_i \) is charge of particle \( i \) and \( \mathbf{n} \) is cell-coordinate vector defined by \( \mathbf{n} = n_1L\mathbf{x} + n_2L\mathbf{y} + n_3L\mathbf{z} \) where \( n_1, n_2, n_3, \) are scalars used for counting lattice in periodic boundary condition in the \( x, y \) and \( z \) coordinates respectively. The original lattice is \( \mathbf{n} = (0,0,0) \). The prime on the first sum indicates that the terms where \( i = j \) will not be included.

Figure 2.8: The Ewald summation in 2 dimensions. The potential of point charges on the left graph can be calculated by dividing into 2 parts; real space and reciprocal space, which leads to rapid convergence [adopted from [71]].
Ewald summation transforms the poorly convergent series of point charges into two rapidly convergent series as shown in Fig. 2.8. The general idea is that the point charges on the left graph will be clouded by charge distributions, which have the same total charge values with the point charges but opposite signs. Since all point charges are screened by opposite charge distributions, the potential will be rapidly convergent in real space and can be calculated by direct summation (the middle graph). However, this potential is not the potential that we need. The potentials added to the point charges have to be subtracted by the same screening distributions with opposite charges (the right graph). The distributions, which are the smooth varying and periodic function, will be represented by Fourier series which rapidly decay in the reciprocal space. The charge distribution in the Ewald summation is represented by a Gaussian with width of $\sqrt{2/\alpha}$:

$$\rho_{\text{Gauss}} = -q_i \frac{1}{\pi} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}} \exp(-\alpha r_{ij}^2)$$  \hspace{1cm} (2.35)$$

Explicit details for deriving the Ewald summation can be found in [71] and the final equation is given by

$$U = U_r + U_k + U_c$$  \hspace{1cm} (2.36)$$

$$U_r = \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}} \text{erfc}(\sqrt{\alpha r_{ij}})$$

$$U_c = \frac{\alpha^{1/2}}{\pi} \sum_{i=1}^{N} q_i^2$$

$$U_k = \frac{1}{2\pi} \sum_{k \neq 0} \frac{4\pi}{k^2} |\rho(k)|^2 e^{-k^2/4\alpha}$$

where

$$\rho(k) = \sum_{i=1}^{N} q_i e^{ikr}$$

$V$ is the volume of the system, $k = (i, j, k)$ is the reciprocal space vector, $\alpha$ is a Gaussian parameter and erfc is the error function, defined by $\text{erfc}(x) = (2/\sqrt{\pi}) \int_0^x \exp(-u^2)du$. The $U_r$ and $U_k$ are the potentials calculated from the real space and reciprocal space.
part respectively. The $U_c$ term is a correction term from the self interaction between the Gaussian charge clouds and point charges at their centre.

**Fast multipole method and DPMTA**

The fast multipole method (FMM) is another technique which is used here to evaluate $N$-body interactions. The basic idea of the FMM is a separation of the potential into two components: the close particle part which can be computed directly and the long range part which can be approximated by the multipole expansion (ME).

For $m$ particles with $q_1, ..., q_m$ charges at position $z_1, ..., z_m$ where $z_i < r$, the $p$-term multipole expansion of the potential at the point $z$, with $z > r$ can be expressed by

$$\Phi_{ME}(z) = a_0 \log(z) + \sum_{k=1}^{p} \frac{a_k}{z^k}$$  \hspace{1cm} (2.37)

where $\sum_{k=1}^{m} q_i$ and $a_k = \sum_{k=1}^{m} -\frac{q_i z_i^k}{k}$. Furthermore, the error is estimated by

$$|\Phi(z) - \Phi_{ME}(z)| \leq \left( \frac{A}{c - 1} \right) \left( \frac{1}{c} \right)^p$$  \hspace{1cm} (2.38)

where, $c = |\frac{z}{r}|$ and $A = \sum_{k=1}^{m} |q_i|$

For the fast multipole algorithm by algorithm of Greengard and Rokhlin [55], the simulation cells will be divided into 4 small boxes (8 cells in 3D) in each level of division (Fig. 2.10a). At the finest level, the multipole expansions (MEs) of every box are computed from representing effect of group of ions in the cell. The ME of child cells will be shifted to the centre of their parent cell for representing the effect of the higher groups (Fig. 2.10b). This process will be repeated until the MEs are shifted to the highest level in which the MEs of all cells in every level are obtained. From this point, the MEs of cells, which are well separated from the parent cell, will be
Figure 2.9: The fast multipole algorithm. The MEs of atoms in each child’s cell are computed and accumulated to the parent cell. The ME on parent A, a well separated cell from parent B, translates to a local expansion at the centre of parent B. The local expansion is shifted to the centre of the child cells for calculating potential and force. [adopted from [74]].

converted to a local expansion (LE) at the centre of parent cell (Fig. 2.10c) and will be downward passed to be LEs at the centre of child cells (Fig. 2.10d). Then, the effect of atoms which reside in the same cell or neighbour cells of parent cells, which are not well separated from the parent cell, will be computed by a direct summation if they are in the neighbour cells of a child cells or by evaluation to be LEs if the cells are not the neighbour cells of the child cell. Finally, the potential and force can be obtained from the LEs adding in the direct summation.

The FMM can be used to calculate the Coulomb potential by reducing the computation from an \( O(N^2) \) method to \( O(N) \). The speed and accuracy of the FMM can be set from the parameters of the \( p \)-term multipole expansion and the number of levels. The Distributed Parallel Multipole Tree Algorithm or DPMTA [74] is a hybrid version of the FMM which can be usefully applied in MD. It was developed by the scientific research group at Duke University. The parallel version of the DPMTA is used in LBOMD to calculate the Coulomb potential. This works well for big systems
containing many millions of atoms when non-periodic boundary conditions are applied [27].

2.8 Visualisation Tool

In running the MD simulations, results can be stored with the position and energy data of atoms in a sequence of times. For analysing data, pictures of results are a great advantage. A visualisation tool, known as LBOVIS written by Marc Robinson, is generally used for analysing and visualising the data results. The main data analysis for this visualiser are the displacements, energy, point defects, slip, Q4 parameter [76] and pressure. In this thesis, only point defects and Q4 parameter filters will be used.

Figure 2.10: Screen images from the LBOVIS visualiser. (a) The point defects filter shows interstitials and vacancies represented by spheres and cubes respectively. (b) The Q4 parameter filter is used to distinguish between atoms in a nanocrystalline structure. The light green colour shows atoms in the bulk whereas the dark green represents atoms in the grain boundary.

The Q4 parameter filter is a tool used to analyse the local phase. The Q4 parameter can identify each atom $i$ as belonging to a known structure such as simple cubic, face centred cubic, hexagonal close packed and body centred cubic by employing spherical harmonics [76]; The general $Q_l$ parameter is given by
\[ Q_l = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |q_{lm}(i)|^2} \]  
(2.39)

where

\[ q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(r_{ij}). \]  
(2.40)

Here, \( N_b(i) \) is the number of nearest neighbours of atom \( i \), \( l \) is a free parameter and \( m \) is an integer, which takes the value from \(-l\) to \(+l\). \( Y_{lm}(r_{ij}) \) is a spherical harmonic function and \( r_{ij} \) is the vector from atom \( i \) to atom \( j \). \( l \) is chosen to take the value 4 as this is applicable for cubic material [77]. The Q4 filter will calculate a value between 0 and 1 to identify the local structure. If two atoms have the same arrangement of neighbours, they will have the same Q4 parameter values. The Q4 parameter filter will be employed later in the nanocrystalline section to identify grain boundaries.

### 2.9 Parallel Molecular Dynamic

To perform MD simulations for large systems containing millions of atoms, parallel techniques are necessary. In the early MD models, only a few hundred atoms were used. Fortunately, due to the fast development in computer technology and simulation techniques, the number of atoms in the systems has rapidly increased. However, it still be computationally expensive to simulate large systems with millions of atoms. In the last decades, parallel computing techniques have been developed. Nowadays, parallel techniques are extensively employed in the MD simulations and billion atom simulations have been reported [78, 79].

Parallel techniques used in MD simulations may be implemented in terms of atom, force or spatial decompositions. However for the short range force calculations spatial decomposition is the most efficient for simulation of very large system size [80]. Spatial
decomposition is implemented in the LBOMD code and used for the work in this thesis. Spatial decomposition works by dividing the simulation region into smaller boxes. Each small box will be assigned to a processor. During the simulation, communication between processors occurs since information about neighbouring atoms may be held on an adjacent processor. Communication occurs using the Message Passing Interface (MPI) transfers the data between adjacent boxes.
Chapter 3

Displacement Energies in Ionic Systems

3.1 Introduction

In order for a permanent displacement to occur in an initially perfect crystal lattice, an atom in the lattice must be given a certain amount of kinetic energy. The minimum energy that needs to be imparted to produce this displacement is called the displacement energy threshold $E_d$. One of the main uses of $E_d$ is that it can give an estimation of the damage in a material due to a radiation event. Kinchin and Pease [17] proposed a simple model by hard sphere binary collisions to estimate number of displaced atoms, $N_d$, by equation

$$N_d = \begin{cases} 
0 & 0 < E < E_d \\
1 & E_d < E < 2E_d \\
E/2E_d & E_d < E < E_1 \\
E_1/2E_d & E_1 < E < \infty
\end{cases}$$

where $E$ is the kinetic energy of the primary knock-on atom (PKA). At energies above
CHAPTER 3. DISPLACEMENT ENERGIES IN IONIC SYSTEMS

$E_1$, the PKA loses energy mainly due to electron excitation while at a lower energy than $E_1$, the collision is assumed to be only pure elastic. This model was also refined by Nelson [81], who included inelastic collisions and some other factors for a more realistic model. Norgett, Robinson and Torrens [18] proposed later an equation, known as the NRT model, by calculation and comparison with previous work of Torrens and Robinson [84, 85]. This equation is given by

$$N_d = 0.8 \hat{E}/2E_d$$

(3.2)

where the $E_d$ is threshold energy averaged over all directions and $\hat{E}$ is the energy available for the elastic collision. $\hat{E}$ is calculated from $E$ by including the inelastic energy loss by method of Lindhard et al [67]. Although, this equation does not account for diffusional recombination of damage and electronic stopping, it is a useful formula often used by experimentalists to assess radiation damage.

$E_d$ is larger than the formation energy of a Frenkel pair $E_{Fp}$, usually 4 or 5 times larger. This is because a small collision cascade needs to be initiated in order to create the defect and a number of energy barriers have to be overcome to form the defect. In some cases also atoms are displaced and change sites without a permanent defect occurring in the lattice. Each crystal direction has also its own threshold displacement energy which can also vary considerably. An additional complication is that the threshold displacement energy for a given direction varies with temperature due to the random displacements of the atoms and the chaotic nature of atomic motion. $E_d$ is also not necessarily a well-defined quantity even for an initial lattice temperature of 0 K. One can define a lower threshold $E_{dl}$ where a displacement event first occurs and an upper one $E_{du}$ where such an event will always occur [82]. For a given direction, these two values are not necessarily the same as will be demonstrated later.
Although there have been a number of previous studies calculating $E_d$ in ionic systems, see for example [83, 86], there has been no systematic study which has determined a statistically significant set of values of $E_d$ over all possible crystal directions nor one that examines the relationship between $E_d$ and $E_{FP}$. Here we evaluate $E_d$ and $E_{FP}$ in 2 lattice types, the NaCl and bixbyite structures, using classical molecular dynamics (MD) and fixed charge potentials. For the NaCl structure, the materials considered are MgO, SrO and NaCl which all have the same relatively simple structure. In the case of MgO the masses of the atoms are fairly similar whereas in SrO they differ by a factor of 5, the atoms having a nominal charge of ±2 in the perfect crystal structure. The masses of the atoms considered for the threshold calculations are given in Table 3.1. In the case of NaCl the nominal charge on the atoms is ±1. For the bixbyite structure, Er$_2$O$_3$ and Dy$_2$O$_3$ are chosen for comparison between materials of the same structure which have similar atomic mass and nominal charges. The nominal charge of bixbyite is +3 for the cation and -2 for the anion and the atomic masses are 162.5 and 167.26 amu for Dy and Er respectively. The aim of the investigation is therefore a detailed investigation of $E_d$ over all crystallographic directions and to see if there is any correlation with $E_{FP}$.

Table 3.1: Atomic weights of atoms considered in this study.

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Atomic weight (amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>O</td>
<td>15.9994</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na</td>
<td>22.9898</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg</td>
<td>24.3051</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl</td>
<td>35.4528</td>
</tr>
<tr>
<td>Strontium</td>
<td>Sr</td>
<td>87.62</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>Dy</td>
<td>162.500</td>
</tr>
<tr>
<td>Erbium</td>
<td>Er</td>
<td>167.26</td>
</tr>
</tbody>
</table>
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Figure 3.1: The lowest energy positions of a Frenkel pair defect in (a) the NaCl structure and (b) the bixbyite structure. In bixbyite, the cation interstitial has the lowest energy when it forms as a split interstitial.

3.2 Methodology

3.2.1 Frenkel Pair formation energy ($E_{Fp}$)

The Frenkel pair formation energies ($E_{Fp}$) is defined as the excess energy of a Frenkel pair defect compared to the perfect lattice. In this work, $E_{Fp}$ is calculated directly by the equation

$$E_{Fp} = E_{\text{perfect}} - E_{\text{Frenkel pair}}$$

(3.3)

where $E_{\text{perfect}}$ and $E_{\text{Frenkel pair}}$ are the total energies of a perfect lattice and a lattice containing the Frenkel pair defect respectively. The conjugate gradient method is used for minimising the system’s energy in which the criterion to stop is when energy changes less than $10^{-8}$ eV in a conjugate gradient step. The Frenkel pair is made by moving an atom from the centre of a perfect lattice to an interstitial stable site far from the vacancy. The distance between the vacancy and interstitial is called the separation distance of the Frenkel pair. The lowest energy position of the Frenkel pair
is chosen for calculating $E_{\text{Frenkel pair}}$. In the NaCl structure, the stable interstitial atom position is at the centre of a cubic cell (see Fig. 3.1(a)) and in the bixbyite structure, the interstitial is a split interstitial at the corner of an oxygen cube (see Fig. 3.1(b)). Both Ewald summation [54] and the fast multipole method (FMM) [55] are used to calculate the electrostatic part of the potential. The former uses periodic boundary conditions whereas the latter does not, is faster and scales linearly with the number of particles in the system. For the short range potential part a standard Buckingham potential, based on Lewis and Catlow [60] is implemented in MgO, SrO, Er$_2$O$_3$ and Dy$_2$O$_3$. For NaCl, the short range potential is a model given by Catlow, Diller and Norgett [58] which is a better model for alkali halides. The distances between the interstitial and vacancy of a Frenkel pair are increased until the value of $E_{Fp}$ converged. If $E_{Fp}$ is calculated by the FMM, the interstitial is always kept at least 1.7 nm from the boundary in order to avoid the effect of the fixed boundary condition while if $E_{Fp}$ is calculated by Ewald summation, the separation distance was never greater than a half of the lattice size due to the periodic boundary condition.

3.2.2 Displacement energy threshold ($E_d$)

We calculate the displacement energy threshold as the minimum kinetic energy, $E_{dl}$, given to an atom in order to produce permanently displaced atoms in the lattice, not $E_{du}$ at which a displacement event will always occur. The displacement directions are chosen to cover an irreducible symmetry zone of the crystal as shown in Fig. 3.3. To determine $E_d$, we impart a kinetic energy to the primary knock-on atom (PKA), starting with a low value, increasing in stages of 10 eV until displaced atoms are detected. When this occurs we start again from the last highest kinetic energy at which displaced atoms are not found, increasing in steps of 1 eV. PKA’s are chosen from near the centre of lattice and the defects are assumed to be found for a given PKA energy, if displaced atoms are found in the lattice after 2.5 ps after which time defects are expected to be immobile. For NaCl, this time is required to be longer at 4.5 ps due to the weaker interaction energy. An interstitial atom is defined as an atom lying further.
from a lattice site than one-third of the first nearest neighbour distance. Conversely, a 
vacancy is defined as an original lattice position which has no atom as neighbour closer 
than one-third of the first nearest neighbour distance (See Fig. 3.2). All simulations 
are run with the temperature originally at 0 K.

![Figure 3.2](image)

For NaCl, MgO and SrO, the irreducible symmetry zone, towards which the PKA 
is projected, is the triangular area as shown in Fig. 3.3. 91 trajectories were investi-
gated, uniformly spread over this area for both cation and anion atoms. A lattice 
containing 13,824 atoms was chosen for the calculations, except for the \(<100>\) and 
\(<111>\) directions, where the value of \(E_d\) was found to be very high producing a Frenkel 
pair which was well-separated. For these directions the lattice was increased to contain 
46,656 atoms. For Er\(_2\)O\(_3\) and Dy\(_2\)O\(_3\), only the cation at the 8a position is used for 
examining \(E_d\). The irreducible symmetry zone is the square area (see Fig.3.3). 169 
trajectories were examined in the area in a lattice containing 10,300 atoms.
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Figure 3.3: The PKA directions used to calculate threshold displacement energy for (a) the NaCl structure and (b) the bixbyite structure. For anion PKA’s, in the NaCl structure the directions used are the same as with cation PKA’s.

3.3 Results and Discussion

3.3.1 Threshold energy

NaCl structure

Figs. 3.4(a-f) shows the $E_d$ values of MgO, SrO and NaCl in different directions. Table 3.2 gives the average values. Some correlation between the values of $E_d$ are observed for certain given directions in different materials, especially peak and low $E_d$ values are often found in similar directions for the different materials. The values of $E_d$ often change with the same trend, but not in the same proportion as the directions change. The peak $E_d$ values are found in directions $<100>$, $<111>$ and in the region close to $<641>$ while low $E_d$ values are found close to $<211>$ and $<110>$, along the bottom line of the triangle (see Fig. 3.4(a-f)). The reason for the peak $E_d$ values in the $<100>$ and $<111>$ directions is because the PKA collides directly with a first nearest neighbour atom, of a different species (see Fig. 3.6(a,b)). Thus sufficient energy must be imparted to cause the PKA to set up a focused collision sequence which will allow
the PKA to move through a larger distance than in the <110> direction where the line of atoms are all of the same type. Thus a smaller value of $E_d$ is required in this direction. In the region of the <641> direction, the PKA transfers most kinetic energy to two neighbouring atoms (Fig. 3.6(c,e)) making two small sub-cascades. This then requires more energy and results in a three-way atom exchange or a Frenkel pair defect. The average values of $E_d$ given in Table 3.2 show no dependence on the mass of the atoms. Sr has a mass five times that of O but a smaller average value of $E_d$ whereas Cl has a higher mass than Na by 50% but a higher $E_d$ value than Na.

Figure 3.4: The threshold displacement energies of MgO, NaCl and SrO as a function of direction. The energies are in eV shown in the key next to each figure. (a) and (b) show $E_d$ for Mg and O PKA’s in MgO, (c) and (d) show $E_d$ for Sr and O PKA’s in SrO, and (e) and (f) show $E_d$ for Na and Cl PKA’s in NaCl. The $a$ distance given in (a-f) is the separation distance between the PKA and the first nearest neighbour atom and the values are 2.105 Å, 2.815 Å and 2.58 Å for MgO, NaCl and SrO respectively.

Fig. 3.5 shows the effect on the lattice when the threshold energy is first exceeded. In MgO and SrO, the most common feature is the Frenkel pair defect. When this forms...
Figure 3.5: The types of damage interstitials formed after $E_d$ is exceeded. (a) and (b) are for Mg and O PKA’s in MgO, (c) and (d) for Sr and O PKA’s in SrO and (e) and (f) for Na and Cl PKA’s in NaCl. In the case labelled ‘exchange’ no defects are created and atoms only exchange sites.

Table 3.2: Average threshold displacement energy for MgO, NaCl and SrO

<table>
<thead>
<tr>
<th></th>
<th>Average $E_d$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation</td>
<td>Anion</td>
</tr>
<tr>
<td>MgO</td>
<td>87.7</td>
</tr>
<tr>
<td>SrO</td>
<td>48.7</td>
</tr>
<tr>
<td>NaCl</td>
<td>28.1</td>
</tr>
</tbody>
</table>

53
it is also the case that a number of other atoms may have exchanged sites. The other common situation is where atoms merely exchange sites and no defect remains. There are a small number of other defects formed, close to major crystallographic directions, when a large value of $E_d$ is necessary. For NaCl, the situation is reversed with more displaced atoms than those that just exchange lattice sites. In the case of MgO and SrO the cation PKA almost always produces one of these two cases and these are also the dominant cases in NaCl. For the anion PKA the situation is different. Cation Frenkel pairs are formed near the $<100>$ directions in both MgO and SrO whereas for NaCl there are very few cases of single anion Frenkel Pairs.

The results in Figs. 3.4 and 3.5 show that there is much more similarity between MgO and SrO both in the type of defect and the energy threshold trends compared to NaCl. One reason for this is that the Cl ions have a low energy threshold for motion in the lattice and are also able to recombine easily over MD timescales. For the Cl PKA we therefore see that there are a large number of trajectories where the ions merely exchange sites or produce more extended defect structures other than simple Frenkel pairs. If the frequency distribution of the values of $E_d$ are also compared then we can see from Fig. 3.7 that these are also more similar for MgO and SrO with a hint of a two-peaked distribution for these two materials whereas the distribution for NaCl appears to have a single peak.

Fig. 3.8 highlights the point that as the value of $E_d$ is increased it is not always the case that damage to the lattice continues to be formed. In both (a) and (b) we have calculated the value of $E_d$ as 56 and 75 eV respectively where damage is first observed. However we might also have taken the value as 95 and 129 eV where damage to the lattice always occurs if this energy is exceeded. These values are also very sensitive to both the accuracy of the numerical calculations and temperature. An important point of this is not only the discussion that different $E_d$ values could be used ($E_{dl}$ or $E_{du}$) but also the searching algorithms used evaluating $E_d$ have to be carefully chosen. If a
bisection algorithm is used and if the middle point of the searching algorithm is a no

defect point lying between $E_{dl}$ and $E_{du}$ (orange colour in Fig. 3.8) the next point will

be chosen with an energy higher than $E_{dl}$ and as a result the algorithm will not find $E_{dl}$.

In experimental works, the $E_d$ values for MgO are generally found to be about 50 -

55 eV for both Mg and O PKA and approximately constant in the temperature range

between 75 K and 400 K [87]. These values are lower than our simulations with 88
eV for Mg and 92 eV for O. The similarity of $E_d$ values between the Mg and O PKA

are agreement with experiments. However, the overestimated $E_d$ values from simu-
lations are possible because the simulations are calculated at 0 K and the $E_d$ value

will increase if the temperature is decreased. Moreover, the atoms in lattice at 0 K in

some directions, such as $<100>$ or $<111>$ have a linear arrangements with the PKA
direction. Then, they can have very high $E_d$ for example 218 eV in $<100>$ direction

and 313 eV in $<111>$ direction while in nature, atom will not be frozen on the perfect
lattice position because of temperature fluctuations. If we average values by excluding

the $<100>$ and $<111>$ directions, then $E_d$ will be reduced to 83.8 eV for Mg PKA

and 87.4 eV for O PKA.

Bixbyite structure

Fig. 3.9 shows the $E_d$ values of Er$_2$O$_3$ and Dy$_2$O$_3$ for cation PKA (Er and Dy)
located at 8a equipoint and average values are given in table 3.3. The irreducible
symmetry zone is a square area as shown in the figure 3.3b. The $E_d$ values are very
similar for many directions. The peak and low $E_d$ values are mostly found for the
same trajectorries. 42 from 120 trajectories have the same $E_d$ values between Er$_2$O$_3$
and Dy$_2$O$_3$ while 78% of directions have differences in $E_d$ values less than 5 eV. The
largest difference in $E_d$ value is found in the $<321>$ direction with 87 eV for Dy$_2$O$_3$
and 111 eV for Er$_2$O$_3$. The minimum values are found in areas close to $<111>$ and
$<100>$ while the peak $E_d$ values are found in the region close to direction $<110>$
Figure 3.6: Snapshots of collision cascades in MgO for cation PKA energies of $E_d$. Blue represents Mg atoms and red O. The squares are the vacancies and the spheres are the atoms that have moved during the collision. (a) and (b) show the collision by Mg in $<100>$ and $<111>$ directions. In (a) a di-interstitial defect forms separated from the di-vacancy by 3.7 Å. In (b) an anion Frenkel pair forms with a separation of 5.2 Å and two cations exchange places. (c), (d) and (e) show the collision cascade by Mg in the $<12\overline{7} 1>$, $<12\overline{7} 0>$ and $<6\overline{4} 1>$ directions. In (c) only atomic rearrangements take place with three cations exchanging places. In (d) a cation Frenkel pair forms separated by 10.4 Å as a result of a focused collision sequence with atoms knocked-on along a chain. In (e) only a cation Frenkel pair forms separated by 3.7 Å.
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Figure 3.7: The frequency distribution of $E_d$ for MgO (a), SrO (b) and NaCl (c). The $E_d$s in the $<111>$ and $<100>$ directions are not included in these graphs since the $E_d$s are significantly higher than other directions.

Figure 3.8: The formation of damage as a function of increasing PKA energy in MgO. (a) Mg atom projected in the $<210>$ direction and (b) an Mg projected along $<441>$.

Figure 3.9: The threshold displacement energies of Er$_2$O$_3$ and Dy$_2$O$_3$ as a function of direction. The energies are in eV shown in the key next to each figure. (a) and (b) show $E_d$ for the Dy and Er PKA’s in Er$_2$O$_3$ and Dy$_2$O$_3$ respectively. The symbol ‘a’ is a quarter of the unit cell given by 2.66 Å, and 2.63Å for Dy$_2$O$_3$ and Er$_2$O$_3$ respectively.
and $<101>$. The reason for the peak and low $E_d$ values found in these directions can be explained by the structural arrangement of atoms which are shown in Fig. 3.10. For the $<11\bar{1}>$ direction, the PKA atom moves out of the oxygen cube through the structural vacancy (see number 3 in Fig. 3.10) to the next oxygen cube and forming as a split interstitial which is a stable defect formation in bixbyite. In the $<100>$, $<1\bar{1}0>$ and $<101>$ directions, the PKAs directly collide with the first nearest neighbour cation atoms. Although in these directions, the PKA first collides with the same species atom, they have significantly different $E_d$ values. The reason is because in the $<100>$ direction, the PKA collides with Er (number 1 in Fig. 3.10) occupying the $8a$ equipoint. At this position, the cations are located at the centre of an oxygen cube. After collision with the PKA, it is pushed to a structural vacancy at a corner of the oxygen cube while the PKA moves back to an opposite vacancy (number 4 in Fig. 3.10) and both of them form as split interstitials. However, In direction $<1\bar{1}0>$ and $<101>$, the PKA collides directly with a cation atoms (number 2 in Fig. 3.10) located at the $24d$ equipoints. At this point, the cation has not as stable a formation as at the $8a$ equipoint (result from chapter 5). Therefore, to displace an atom, the PKA needs sufficient kinetic energy to move this cation or make a small cascade to damage the structure and leave displaced atoms far from PKA initial position.

![Figure 3.10: The atomic arrangement of the PKA in Er$_2$O$_3$ and Dy$_2$O$_3$. The $E_d$ values are low when the PKA is directed towards atom number 1 and the structural vacancy number 3. However, the collision with atom number 2 has a high $E_d$ value.](image-url)
Fig. ?? shows the residual defect formation after the kinetic energy first exceeds the threshold energy. For around half of directions, the residual defects are often found as single Frenkel pair defects. These defects are found when the threshold energies have low values such as in the $<11\bar{1}>$ and $<100>$ directions. The reason is the same as discussed before. These directions point to the structural vacancy (number 3 in Fig. 3.10) or to the Er atom located at the 8a equipoint (number 1 in Fig. 3.10). Therefore they can easily form either as a single interstitial or a split interstitial. In addition, sometimes the split interstitial around direction $<100>$ can move back to the original PKA site (number 2 in Fig. 3.10) to replace the Er vacancy at the 24 equipoint formed by the PKA. This process make a site exchange mechanisms. In comparison, the high $E_d$ values occur around direction $<1\bar{1}0>$ and $<101>$ where much energy is required to displace the blocking Er atoms. These energies are sufficient to form a small collision cascade. Thus the types of residual defect can vary and these are shown in Fig. ?? categorised as exchange position, di-interstitial (1 cation & 1 oxygen interstitials), O-square formation (2 O interstitials) and 1 cation & 2 oxygen interstitials. The $E_d$ values for bixbyite also found the relation, similar to MgO and SrO, that the higher mass of the cation PKA has a lower $E_d$ values.

Table 3.3: The average threshold displacement energy of the cation for Dy$_2$O$_3$ and Er$_2$O$_3$

<table>
<thead>
<tr>
<th></th>
<th>average $E_d$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy PKA</td>
<td>72.1</td>
</tr>
<tr>
<td>Er PKA</td>
<td>71.1</td>
</tr>
</tbody>
</table>

3.3.2 Frenkel pair formation energy

The $E_{Fp}$ values are calculated from the energy difference between a perfect lattice and a lattice containing the Frenkel pair. Graphs of $E_{Fp}$ as a function of separation distance between the vacancy and interstitial are shown in Figs. 3.12 and 3.13 and table 3.4. For NaCl, the separation distances are varied in the $<100>$ and $<111>$ di-
Figure 3.11: The types of damage first formed after $E_d$ is exceeded for (a) $\text{Er}_2\text{O}_3$ and (b) $\text{Dy}_2\text{O}_3$.

Directions for different lattice sizes which contain 1,000, 1,728, 4,096, 10,648, 54,872 and 97,336 atoms. For the first three lattice sizes, Ewald summation is used to calculate the electrostatic potential and the last three lattices are calculated by FMM. For the bixbyite structure, the $E_{Fp}$s are calculated for separations in the $<100>$ and $<111>$ directions. The lattice sizes contain 5,120, 10,000, 17,712, 41,728 and 81,200 atoms where the first 2 lattice sizes are calculated by Ewald summation and the last three are calculated by FMM. Ewald summation is much slower than FMM so the lattice sizes calculated by the Ewald summation are chosen smaller than the sizes calculated by FMM as the periodicity allowed for better convergence as a function of lattice size.

The $E_{Fp}$ values calculated by Ewald summation are found to be a little smaller than those calculated by FMM. In the NaCl structure, when the lattice sizes are increased, the $E_{Fp}$ values are increased when calculated by Ewald summation and decreased when calculated by FMM. At the biggest lattice size in both methods, (97,336 atoms for FMM and 4,096 atoms for Ewald summation) $E_{Fp}$ values tend to be the same with a small difference in values of around 0.1 eV at separation distance around 2.5 nm. This suggests convergence when the lattice sizes are big enough. For a separation distance of around 2.5 nm in the $<111>$ direction the $E_{Fp}$ value were different less
than 0.1 eV. Table 3.4 gives some of there values for the first nearest neighbour separation and a separation of 3 nm which was the furthest separation considered and some previous works calculated by empirical potentials and one calculated by DFT \cite{90}. In the NaCl structure, the calculations use a lattice containing 54,872 atoms for FMM and 4,096 atoms for Ewald summation and in the bixbyite structure, the calculations use lattices containing 81,200 atoms for FMM and 10,000 atoms for Ewald summation.

Table 3.4: Frenkel Pair formation energies. The columns show the values of $E_{Fp}$ for both the first nearest neighbour separation and a separation of 3 nm. The last column gives values from some previous works calculated by empirical potentials \cite{88, 89, 91} and one calculated by DFT \cite{90}

<table>
<thead>
<tr>
<th></th>
<th>1st nn FMM</th>
<th>1st nn Ewald</th>
<th>3 nm FMM</th>
<th>3 nm Ewald</th>
<th>Other works</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>11.8</td>
<td>11.8</td>
<td>13.5</td>
<td>13.3</td>
<td>12.43\cite{88}, 11.9\cite{89}, 10.35\cite{90}</td>
</tr>
<tr>
<td>O</td>
<td>11.9</td>
<td>11.9</td>
<td>13.1</td>
<td>12.8</td>
<td>12.33 \cite{88}, 15.2 \cite{89}, 12.17\cite{90}</td>
</tr>
<tr>
<td>Sr</td>
<td>9.0</td>
<td>8.9</td>
<td>10.1</td>
<td>10.0</td>
<td>9.21\cite{88}, 9.3\cite{89}</td>
</tr>
<tr>
<td>O</td>
<td>8.8</td>
<td>8.8</td>
<td>10.1</td>
<td>9.9</td>
<td>8.97\cite{88}, 11.0\cite{89}</td>
</tr>
<tr>
<td>Na</td>
<td>3.1</td>
<td>3.0</td>
<td>3.7</td>
<td>3.5</td>
<td>2.88\cite{91}, 1.36, 2.63</td>
</tr>
<tr>
<td>Cl</td>
<td>3.6</td>
<td>3.5</td>
<td>4.2</td>
<td>4.0</td>
<td>4.6\cite{91}, 4.6, 6.38</td>
</tr>
<tr>
<td>Er</td>
<td>12.8</td>
<td>12.6</td>
<td>16.8</td>
<td>16.4</td>
<td>-</td>
</tr>
<tr>
<td>Dy</td>
<td>13.0</td>
<td>13.2</td>
<td>17.4</td>
<td>16.9</td>
<td>-</td>
</tr>
</tbody>
</table>

3.3.3 The relation between $E_d$ and $E_{Fp}$

One of the original purposes of this work was an investigation to see if there was any correlation between $E_d$ and $E_{Fp}$. Tables 3.2, 3.3, 3.4 and 3.5 show that $E_d$ and $E_{Fp}$ values and some relations between them. Table 3.5 shows that $E_d$ values are greater than $E_{Fp}$ values by between 4 and 10 time with average values around 6 times. These values do not have any relation in terms of proportion between $E_p$ and $E_{Fp}$ but a relation which can be observed is that high $E_{Fp}$ values correspond to the high $E_d$
Figure 3.12: $E_{FP}$ energy as a function of separation distance in Er$_2$O$_3$ and Dy$_2$O$_3$. The graphs show the convergence of $E_{FP}$ as the lattice size increases for different calculation methods of the Coulomb sum (DPMTA and Ewald). The lattices contained 17,715, 41,728 and 81,200 atoms for DPMTA but only 5,120 and 10,000 atoms for the Ewald summation method.

values. For example, we observed that the $E_{FP}$ values for Mg are higher than those of Sr and we also found that the $E_d$ values for Mg is higher than those for Sr.

Table 3.5: The ratio between the average threshold displacement energy and the Frenkel Pair formation energies (Ewald summation).

<table>
<thead>
<tr>
<th></th>
<th>MgO</th>
<th>NaCl</th>
<th>SrO</th>
<th>DyO</th>
<th>ErO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation</td>
<td>6.6</td>
<td>8.0</td>
<td>4.9</td>
<td>4.3</td>
<td>4.3</td>
</tr>
<tr>
<td>Anion</td>
<td>7.2</td>
<td>10.3</td>
<td>6.7</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 3.5 and Fig. ?? show that there are many cases where different type of damage remain in the lattice for an atom projected in the same direction. In order to try to compare like with like, we consider in MgO and SrO only directions which have same residual Frenkel pair defects. 32 directions are used and we have an average value of $E_d$ for Mg of 80 eV, for O in MgO of 81 eV. For Sr, we have 44 eV and for O in SrO 56.
Figure 3.13: $E_{FP}$ as a function of separation distance in MgO, NaCl and SrO. The first column shows the potential energy when the interstitial is located in the <100> direction with respect to the vacancy. The <111> direction results are shown in the second column. The graphs show the convergence of $E_{FP}$ as the lattice size increases for different calculation methods of the Coulomb sum (DPMTA and Ewald). The lattices contained 10,648, 54,872 and 97,336 atoms for DPMTA but only 1,000, 1,728 and 4,096 atoms for the Ewald summation method.
eV. The difference in the values between Mg and Sr is 36 eV, whereas the difference in the Frenkel pair formation energy is \( \approx 3.4 \) eV. For O, in the two structures the difference in the \( E_d \) values are 25 eV whereas the differences in \( E_{Fp} \) are \( \approx 3.0 \) eV. The only conclusion therefore to be drawn from this is that the displacement energy thresholds are between 4.5 and 6.5 times greater than the Frenkel pair formation energies and that this factor is not the same even when there is a similar lattice structure. The differences between the \( E_d \) values are also between 8 and 10 times the differences in the values of \( E_{Fp} \). This is not different from the previous conclusion regarding all trajectories. The only observation is that the average energies are a bit smaller than those averaged over all directions. This indicates that the directions which have exchange site or other defect formations often have higher values than the average values.

A factor that is not taken into account in the above calculations are the energy barriers for defect recombination. We have previously calculated these for MgO [12]. These show that the isolated anion and cation interstitial have energy barriers for diffusion of 0.32 and 0.4 eV respectively and 0.75 eV for the di-interstitial. It is therefore interesting to speculate if the difference in these barriers is also related to \( E_d \). The interstitial diffusion barriers for the isolated point defects are so small that it is possible for closely separated Frenkel pairs to recombine within nanosecond timescales and therefore within the time frame of the MD simulations. In our case we did not carry out the simulations for longer than 4 ps. However the exact role of the diffusion barriers is unclear because in NaCl, for example the Cl atoms have a low energy barrier for diffusion but the ions when displaced do not move back to their original sites. Instead they exchange position which is our definition of a displacement and it means that \( E_d \) is exceeded.
3.4 Conclusions

In this chapter, we have undertaken MD simulations to study the threshold displacement energy, $E_d$, and the Frenkel pair formation energy, $E_{Fp}$, and attempted to find out the relation between them when they are calculated the same structures. We considered 5 ionic materials, MgO, SrO, NaCl, Er$_2$O$_3$ and Dy$_2$O$_3$.

$E_d$ values are investigated systematically using trajectories projected onto an irreducible symmetry zone. We also calculate the average value over all directions. The results show that $E_d$s are significantly dependent on the directions of the PKA. In the NaCl structure, some correlation between the $E_d$ values can be found in similar directions for the different materials, especially peak and low $E_d$ values are often found in similar directions. The peak values are often found in directions $<100>$, $<111>$ and $<641>$ and the low values are found in a region close to the $<211>$ and $<110>$ directions. For average $E_d$ values over all directions, MgO has a values of 88 eV for Mg and 92 eV for O. These values are higher than that of experimental work in which the $E_d$ values are approximately about 50 - 55 eV for both Mg and O PKA. However, since the simulation is done at 0 K then these values can be higher than that of experiments. For SrO, the $E_d$ values are 49 eV for Sr and 67 eV for O. These are lower than the values for MgO for both the Sr and O PKA and indicate that when the weight of cation PKA is increased, the $E_d$ values are reduced. For NaCl, the $E_d$ values are 28 eV for Na and 41 eV for Cl. These values are lowest since this materials has the weakest interaction potential. The average values between Na and Cl are in contrast to the previous 2 materials in which the higher weight PKA should have lower $E_d$ but Cl’s weight is higher than that of Na around 64% while it has the higher $E_d$ value. This is because the Cl interstitials are observed from MD simulations to be very mobile and easy recombine to lattice sites over MD timescale. Therefore, for NaCl the simulation time was increased to 4.5 ps instead of 2.5 ps in MgO and SrO. The formation of defects after the PKA energy first exceeds $E_d$ shows that in MgO and SrO the defects
often form as a single Frenkel pair defect. Oppositely, NaCl often found exchanged positions as the main indication of atomic displacements. For the bixbyite structure, because of only a small difference in the masses and the interatomic energy function between Er and Dy, these materials behave very similarity. The peak $E_d$ is often found when the PKA collides with the Er atoms at the 24 equipoint in the $<10\bar{1}>$ and $<110>$ directions whereas the lower $E_d$ values are found around direction $<1\bar{1}1>$, where the trajectory of PKA points to a structural vacancy, and $<100>$ where the trajectory points to the Er at equipoint 8a. The average $E_d$ values are 71 eV for the Er PKA and 72 eV for the Dy PKA. In these materials, the lower mass cation PKA has the higher $E_d$ value.

Both $E_{dl}$ and $E_{du}$ are discussed in this chapter since there is a difference between them found in some directions, such as in direction $<210>$ and $<441>$ in MgO. At energies between $E_{du}$ and $E_{dl}$, we observe some interval of energy in which defects can not be observed. These intervals can be found using appropriate searching algorithms.

The Frenkel pair formation energies were examined in different size of lattices and methods (Ewald summation and FMM). Increasing the distance between the interstitial and vacancy led to a convergence in the value of $E_{Fp}$ when the separation distance was $\sim 3$ nm. The $E_d$ values using different methods converged to similar values when the lattice sizes were increased. In the NaCl structure, MgO has the highest $E_{Fp}$ values for both cation and anion Frenkel pairs whereas NaCl has the lowest Frenkel pair formation energy. The $E_{Fp}$ values between cation and anion are similar with differences of less than 0.5 eV.

We found that the $E_d$ values are greater than $E_{Fp}$ values between 4 and 10 times larger with an average value of around 6 times. We also found no relation between differences in $E_d$ and $E_{Fp}$ values for materials with the same structure but a relation
which we found is high $E_d$ corresponds to high $E_{Fp}$. 

Chapter 4

MD simulation of radiation damage in \( \text{Er}_2\text{O}_3 \)

4.1 Introduction

In this chapter, MD simulations are performed in \( \text{Er}_2\text{O}_3 \) to determine the ballistic effects of a primary knock-on atom (PKA) over short time scales (a few picoseconds). These MD simulations were successful in previous studies of radiation effects on MgO and spinel: \( \text{MgAl}_2\text{O}_4 \), \( \text{MgGa}_2\text{O}_4 \) and \( \text{MgIn}_2\text{O}_4 \) [12, 13, 14, 15, 16]. The studies are carried out by giving the PKA a prescribed energy and direction at time \( t = 0 \), inside a crystal lattice. The PKA will form a collision cascade and generate the displaced atoms, which are mostly immobile after a few picoseconds. The collisions are assumed to be purely elastic and the atoms have fixed charges so that electronic structure is not explicitly considered. The defects, which are generated from collision cascades, i.e. the initial data of defects induced from ballistic collisions will be used to analyse the initial effects of radiation, which cannot be observed in experimental works. Some of the point defects, observed from this chapter, will be used in long time scale simulations discussed in chapter 5.
4.2 Methodology

Similar to the study of threshold energy in the last chapter, the interatomic potential is based on fixed charges with a pairwise additive potential energy function, composed of a standard Buckingham potential and an electrostatic potential. The details of the standard Buckingham potential parameters are given in [57]. These parameters give an equilibrium lattice constant of 1.052 nm, compared to experimental values of 1.055 nm. The elastic properties of the potential have not been tested. The simulations were carried out using fixed boundaries (3 cation and 2 anion layers) and the fast multipole method was used to calculate the Coulomb sums [55]. The system was minimised to equilibrium before the start of simulation.

We investigate PKAs with initial energies of 0.4, 2.0 and 10 keV. The system sizes for running the collision cascades varied between 10,300 atoms to 1,112,832 atoms in cubic box whose size was chosen so that the defects which formed were well separated from boundaries, i.e. by at least 10 Å. At 0.4 keV, 42 different trajectories were run in a lattice containing 10,300 atoms; at 2 keV, 20 separate PKAs were considered but for the 10 keV data (due to computing constraints) only Er PKAs from 10 separate cascades were analysed. This is because the lattice containing 1,112,832 atoms could not contain the 10 keV collision cascade from an O PKA. No thermostat was used so the initial temperature of the lattice was 0 K. For analysis, interstitials and vacancies are defined the same as in the previous chapter. The interstitial is defined as an atom that resides at a site which is further than 0.86 Å from any lattice site in the original system. Conversely, a vacancy is defined as a site in the original lattice which does not have an atom lying closer than 0.86 Å.
4.3 Collision Cascade results

4.3.1 Low energy cascades (0.4 keV)

The low energy cascades were run with 21 trajectories of the Er PKA and the O PKA. The maximum number of defects occurred at a time of around 300 fs and the main recombination processes of displaced atoms from an original lattice site generally happens in a time around 1.5 picoseconds. After 1.5 ps, the displaced atoms only vibrate in their positions and there are only few defects which have sufficient energy for diffusion. The simulations were run until a stopping time of 4.5 ps for guaranteeing that the ballistic phase was over. A graph of number of defects as a function of time is shown in Fig 4.1. These graphs indicate that Er PKAs produce more displaced atoms than O PKAs both for peak damage and at the end of the cascades. The Er PKA can generate both Er and O interstitials while collision cascades by O PKAs mostly have only oxygen interstitials. Snapshots of typical cascades from an Er PKA (a) and an O PKA (b) are shown in Fig. 4.2. The figure shows that the Er PKA produces a di-vacancy and a split Er interstitial next to an O interstitial, whereas the O PKA leaves two isolated O vacancies and interstitials.

![Figure 4.1](image)

Figure 4.1: The evolution of defects as a function of time in 0.4 keV collision cascades for (a) Er PKA and (b) O PKA, each averaged over 21 separate PKA directions.

Average numbers of defects left at the end of cascades in table 4.1 illustrate that the collision cascade made by the O PKA mostly found oxygen Frenkel pairs in which the oxygen interstitial comes from the O PKA. Half of the directions generate 2 oxy-
Figure 4.2: Snapshots from typical 400 eV collision cascades for an Er PKA ((a)-(d)) and an O PKA ((e)-(h)) at times of 200, 400, 800 and 1600 fs.

Table 4.1: The average number of defects left at the end of the ballistic part of the collision cascade, per cascade averaged over 21 individual cascades for the 400 eV simulations and 10 individual cascades for the others.

<table>
<thead>
<tr>
<th>PKA energy</th>
<th>0.4 keV O</th>
<th>0.4 keV Er</th>
<th>2 keV O</th>
<th>2 keV Er</th>
<th>10 keV Er</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average number of Er vacancies per PKA</td>
<td>0.2</td>
<td>1.4</td>
<td>4</td>
<td>7</td>
<td>25</td>
</tr>
<tr>
<td>Average number of O vacancies per PKA</td>
<td>1.5</td>
<td>2.2</td>
<td>11</td>
<td>15</td>
<td>77</td>
</tr>
</tbody>
</table>
gen interstitials at the end of the cascade. A few rare directions, where O PKAs move towards the neighbouring Er atoms, can generate an Er interstitial. For the Er PKA, around 2 oxygen vacancies (also interstitials) and 1.4 Er vacancies (interstitials) are generated on average by the Er PKA. However, the Er interstitials are sometimes found as split interstitials and these are counted as 2 Er interstitials in our scheme so the 1.4 value comes from a combination of split and isolated interstitials. From these data, we can conclude that low energy cascades of 0.4 keV are too small to create much damage on Er sub-lattices.

After running the collision cascades until reaching a time of 4.5 ps, typical defects from the cascades were categorised and described in Fig. 4.3. From the figures, the residual defects were found to be of the type tri-interstitial, di-interstitial, split Er interstitial, split O interstitial, split O vacancy, tri-vacancy, di-vacancy and O-square defect. The numbers of each type of defect observed from the simulations are shown in table 4.2. The most common defects observed from low energy cascades simulations are the isolated oxygen interstitial and vacancy. The split Er interstitial is the second most common defect found whereas the di-interstitial and di-vacancy are the cluster defects, which are most commonly seen. In the following we will describe and analyse details of each defect formation. These data can then provide information that will be used in the study of long time scale dynamic simulations in chapter 5.

Figure 4.3: Typical defects from 0.4 keV collision cascades. (a) shows a tri-interstitial (red circle), a split Er interstitial (yellow circle), a tri-vacancy (black circle) and a di-vacancy (green circle). (b) shows a split O vacancy (pink circle) and a split O interstitial (brown circle). An O-square (grey circle) and a di-interstitial (violet circle) are shown in (c)
Table 4.2: The main types of defect that remain 4.5 ps after the start of the 400 eV PKA cascades for the 42 trajectories considered. A few other more extended defects were also formed.

<table>
<thead>
<tr>
<th>defect type</th>
<th>Er- PKA</th>
<th>O PKA</th>
</tr>
</thead>
<tbody>
<tr>
<td>split Er interstitial</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>split O interstitial</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>O interstitial at structural vacancy</td>
<td>19</td>
<td>26</td>
</tr>
<tr>
<td>Er interstitial at structural vacancy</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>O split vacancy</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Er-O di-interstitial(^a)</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>O- square(^b)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>isolated Er vacancy</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>isolated O vacancy</td>
<td>10</td>
<td>26</td>
</tr>
<tr>
<td>Er-O di-vacancy</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>O-Er-O tri-vacancy</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>O-Er-O tri-interstitial</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^a\) The di-interstitials were a mixture of first and second nearest neighbour types.
\(^b\) This defect consists of a symmetric interchange of two O atoms with their neighbouring structural vacancies so that the interstitial and vacancy complex takes the shape of a square, see Fig. 4.3(c).

4.3.2 Typical defect from low energy cascades

- isolated Er and O interstitial.

Figure 4.4: Isolated O interstitial (a) and isolated Er interstitial (b). The Isolated O and Er interstitial are mostly found at the structural vacancy (tetrahedral interstice) at the corner of an oxygen sub-cube.

Isolated Er and O interstitials are classified as the O or Er interstitials which reside far from other defects and cannot be categorised as part of some other defect structure. The oxygen interstitial is the most common defect found from the low energy cascade in table 4.2. They are generally found in the tetrahedral interstice (structural vacancy)
at the corner of the oxygen sub-cube. However, they are a few cases where the Er interstitial and O interstitial can be seen at a site between the oxygen sub-cubes (octahedral interstice), such as the di-interstitial or split O vacancy. These positions will be discussed again later.

- **Isolated Er and O vacancy.**

![Figure 4.5: The isolated Er and O vacancy. The O vacancy is generally found at the 48e equipoint and the Er vacancy can be seen only at the 8a equipoint. No Er vacancy is observed in Er sites of the 24d equipoint](image)

The isolated Er or O vacancy is a vacancy defect which is isolated far from other defects and cannot be categorised as part of another defect configuration. The positions of the Er and O vacancies are shown in Fig. 4.5. The O vacancy occurs in the equivalent oxygen position at 48e equipoint while Er vacancy is found on the Er position at 8a equipoint. No Er vacancy is observed on the Er site at 24d equipoint. The positions of Er at 8a and 24d are shown in the Fig. 4.5.

- **Split Er interstitial.**

A split Er interstitial is a defect formed in a dumbbell shape by having vacancy at the centre and two Er interstitials at the opposite side of the vacancy. This formation is related to a single Er interstitial and both of them can revert to each other depending on the surrounding defects. If the Er interstitials live far from the other defects, they
are most often found as the split Er interstitials. However, if they live close to any oxygen interstitials, they are often be observed as an Er interstitial or a di-interstitial. The angle subtended by the split Er interstitial, checked by local minimisation after the end of the simulations, varied between $162^\circ$ and $179^\circ$ degrees whereas the distances between the Er vacancy and Er interstitial lie between 0.9 Å and 2.12 Å. The variations come from the effects of environmental defects surrounding them. When we check the split Er interstitial, which lies far from other defects, the angle and length between Er interstitial and vacancy are found to be around $178^\circ$ and 1.7 Å respectively. The position of a split Er interstitial shows that the Er atoms of the split Er interstitial reside close to a structural vacancy site and the Er vacancy is the position of the Er atom at the 8a equipoint (see Fig. 4.6). The Er interstitial can transform to be a split Er interstitial by pushing the Er atom at the 8a equipoint to a nearby structural vacancy.

$$0.9 \, \text{Å} < r_1, r_2 < 2.12 \, \text{Å}$$

$$162^\circ < \theta < 179^\circ$$

Figure 4.6: The split Er interstitial (a) They have a shape like dumbbell with an angle that varies between $160^\circ$ and $179^\circ$ and distances that vary from 0.9 to 2.12 Å, depending on the local environment and surrounding defects. (b) Two Er interstitials from a split Er interstitial live near the structural vacancy and share the Er vacancy site at the centre of the cube.

- Di-interstitial.

The di-interstitials occur from the attractive force between opposite charges of the Er and O interstitials. They are one of the most observed defects from irradiation and they can be separated into 3 types: The first nearest neighbour di-interstitial (type 1),
the second nearest neighbour di-interstitial (type 2) and the third nearest neighbour di-interstitial (type 3) depending on the positions of Er and O interstitials and separation distance between them (see Fig. 4.7). The type 1 di-interstitial (Fig. 4.7a) is the most common di-interstitial found from the simulations. The separation distance between the O and Er interstitial is 2.1 Å, which is the closest separation distance among the 3 types. The position of the O interstitial is located on a structural vacancy site on a corner of oxygen sub-cube whereas the Er interstitial resides at the site between 2 oxygen sub-cubes. This Er position is not the regular place where the interstitial is found as mentioned above. The type 2 di-interstitial is formed further apart from type 1 by moving the Er interstitial to a structural vacancy site (see Fig. 4.7b). This position has a separation distance of 3.75 Å. The type 3 di-interstitial is where the Er and O interstitials are found at the structural vacancies as shown in Fig. 4.7(c). In this position, the O interstices lie on a corner of the oxygen sub-cube while the Er interstitial is placed at the third nearest neighbour structural vacancy with the separation distance of 4.45 Å.

- **Tri-interstitial.**

Similar to the di-interstitial, the tri-interstitial is formed by the attractive force between opposite charges of the Er and O interstitial and since Er has a higher charge than that of the O interstitial, it can attract more than one O interstitial. The formation of the tri-interstitial obtained from the simulation is shown in Fig. 4.8. These positions of Er and O interstitials are similar to the two di-interstitials (type 2 and 3 di-interstitial) sharing an Er interstitial. The separation distances between the Er and O interstitials are the same with the separation distances of type 2 and 3 di-interstitial at 3.75 and 4.45 Å respectively.

- **O-square defect.**
CHAPTER 4. MD SIMULATION OF RADIATION DAMAGE IN \textit{Er}_2\textit{O}_3

Figure 4.7: The di-interstitial structure seen in the cascades. (a) the first nearest neighbour di-interstitial (type 1); (b) the second nearest neighbour di-interstitial (type 2); (c) the third nearest neighbour di-interstitial (type 3).

Figure 4.8: A tri-interstitial formed from 2 di-interstitials (type 2 and 3 di-interstitials) sharing an Er interstitial.
The O-square formation is so-called since the configuration looks like a square. The positions of O interstitials and vacancies of O-square defect are shown in Fig. 4.9. The O-square formation occurs by two oxygen atoms swapping with the two structural vacancies between adjacent oxygen sub-cubes. This formation has not only an interesting symmetric configuration but it also looks like the formation of a disordered fluorite structure which might be observed as initial transformation before the structure is change from phase C to phase B which is found at higher doses (see experimental review in chapter 1). The O-square defect is a similar defect to the ‘ring defect’ in spinel whereby the three Al ions on octahedral sites move to nearby tetrahedral sites.

Figure 4.9: O-square defect. Two oxygen atoms in adjacent cubes swap their positions to reside at structural vacancies leaving oxygen vacancies. The positions of these interstitials and vacancies look like a square so we name it the ‘O-square’ defect.

- Split O vacancy.

The split O vacancy is formed when two oxygen vacancies share an interstitial as shown in Fig. 4.10. This is a rare defect seen from simulations and they are found only 3 times from 42 simulations. The defects are found in 2 formations shown in Fig. 4.10(a) and (b). In (a), two oxygen vacancies are located at the corners of the two nearest neighbour oxygen sub-cubes and the oxygen interstitial lives at the structural vacancy site between them. For (b) the oxygen vacancies are found in the first nearest neighbour oxygen sub-cube while the oxygen interstitial is sited between the vacancies. The position of the oxygen interstitial in (b) is another special
case where the interstitial does not reside in the structural vacancy position at the
tetrahedral interstice.

![Figure 4.10](image)

Figure 4.10: The two types of split O vacancy structure seen from simulations. (a) is the
first type where O vacancies reside as third nearest neighbours and the O interstitial is found
between. (b) Another form of the split O vacancy. The oxygen interstitial of this type is in
an unusual position compared to other defects.

- Split O interstitial.

The formation of the split O interstitial is shown in Fig. 4.11. This configuration,
similar to the O-square defect, arises when the oxygen interstitial moves to a structural
vacancy between two oxygen vacancies on the corners of adjacent oxygen sub-cube.

![Figure 4.11](image)

Figure 4.11: The split oxygen interstitial where structural vacancies on adjacent oxygen
sub-cubes are filled.

- Di- vacancy and Tri - vacancy
Di-vacancy and tri-vacancies are Schottky defects. The di-vacancy and tri-vacancy observed from simulations are shown in Fig. 4.12. The Er vacancy for di- and tri-vacancy is found only at the 8a equipoint of the Er atom and the oxygen vacancies surrounding the Er vacancy occur at the oxygen atom sites at the corners of the oxygen sub-cubes.

Figure 4.12: Di-vacancy (a) and tri-vacancy (b). The Er vacancy is found only at the 8a equipoint of Er atom. No Er vacancies are found at the 24d equipoint.

### 4.3.3 High energy cascades (2 keV and 10 keV)

In the following section, high energy cascades will be studied by increasing the kinetic energy of the PKA to 2 keV and 10 keV. Although the simulations may be more realistic than low energy cascades since most nuclear radiation events result in higher energy cascades, experience with other ionic materials has shown that similar defects can also arise at higher energy. In what follows, parallel computing techniques were implemented to reduce computing time. The numbers of processors was varied between 16 and 32.

- **2 keV**

For 2 keV cascade simulations, different lattice sizes are chosen for different PKAs. The lattice for the Er PKA contains 59,292 atoms whereas the O PKA needs a bigger lattice size containing 1,112,832 atoms. The reason for the bigger lattice size is because the O PKA (being much lighter than Er) is easily scattered by Er and O transferring
less energy during collisions. As a result, it can move for a long distance before stopping. 10 trajectories for different PKA orientations were run for both the Er and O PKAs. The main differences observed between the Er and O PKA are in the number of retained defects and distance over which the cascade spreads. Graphs in Fig. 4.13 show that Er PKAs cause more damage than O PKAs and the spatial spread of the Er PKA collision cascades is less. The displaced atoms shown are mostly stable after 3 ps. However the simulations are run until the stopping time of 6.5 ps for the Er PKA and 7.5 ps for the O PKA before the defects remaining after collision cascade are analysed.

![Graphs showing the evolution of defects as a function of time in 2 keV collision cascades for the (a) Er PKA and (b) O PKA, each averaged over 10 separate PKA directions. The error bars on the graphs are standard deviations.](image)

Figure 4.13: The evolution of defects as a function of time in 2 keV collision cascades for the (a) Er PKA and (b) O PKA, each averaged over 10 separate PKA directions. The error bars on the graphs are standard deviations.

![Snapshots of 2 keV collision cascades initiated by the O and Er PKA along the <123> and <253> directions, respectively. (a) and (c) show the damage after 0.3 ps for the O and Er PKA, respectively. (b) and (d) show the damage for the O and Er PKAs after the ballistic phase of the cascade (4.5 ps). The dotted region outlined in (a) is shown in (b).](image)

Figure 4.14: Snapshots of 2 keV collision cascades initiated by the O and Er PKA along the <123> and <253> directions, respectively. (a) and (c) show the damage after 0.3 ps for the O and Er PKA, respectively. (b) and (d) show the damage for the O and Er PKAs after the ballistic phase of the cascade (4.5 ps). The dotted region outlined in (a) is shown in (b).

Fig. 4.14 shows samples of the 2 keV collision cascades by the O PKA (a,b) and
the Er PKA (c,d) at the peak damage and the defects formation after the collision cascade finishes. The numbers of O and Er vacancies from the O and Er PKAs are shown in the table 4.2. The O PKA can cause damage averaging around 4 Er interstitials and 11 O interstitials in each simulation whereas the Er PKA averages approximate 7 Er interstitials and 15 O interstitials as residual defects from each simulation. The number of O interstitials is several times that of Er from both Er and O PKAs. Fig. 4.15 gives insight into the collision processes by connecting atoms that have moved with their original positions by lines, showing how sub-cascades can form. These Er atoms which produce the small sub-cascades remain as interstitials at the end of the ballistic phase. Therefore, Er and O interstitials are often found far from the central damage core. At the same time, at the centre of the cascades the vacancies will be observed as well as O interstitials. For the O PKA, similar processes occur with the O PKA transferring energy to make small sub-cascades but these are smaller. In Fig 4.15(b), the O PKA transfers energy to two O atoms to make small sub-cascades but they do not cause any damage, just two of them move to be two O interstitials.

Figure 4.15: The residual defects after collision cascades by Er (a) and O (b) PKAs showing the process over small time frames. (a) shows how an Er PKA can transfer energy to form 5 small sub-cascades while the O PKA in (b) transfers much less energy and the damage occurs close to the PKA path.
The residual defects after collision cascades are in part similar to the defects found after low energy cascades. However, the defects at the core of the higher energy collisions can be in the form of clusters of vacancies and interstitials. Fig. 4.16(a) and (b) show the complex formation of a group of O vacancies and O interstitials, which reside in relatively stable sites at structural vacancies rather than move back to occupy the adjacent O vacancies. This provides further evidence for a disordered fluorite structure in which the vacancies are randomly arranged on the corners of oxygen sub-cubes. Moreover, groups of 2 Er vacancies and 3 O vacancies (c) and a split Er vacancy((a) (middle left circle)) which are not found at low energy cascades, are observed here.

Figure 4.16: The residual defects after 2 keV collision cascades in the \textless 343\textgreater{} (a), \textless 513\textgreater{} (b) and \textless 245\textgreater{} (c) directions. (a) shows the complex defects on the oxygen sub-lattice (in the circle) and a split Er vacancy (in the rectangle). (b) shows disordering on the oxygen sub-lattice with some Er vacancies observed inside the group and (c) shows a group of Er and O vacancies.

- 10 keV

As for the 2 keV cascades, the collision cascades formed by the Er PKAs produce more damage than O PKAs since they can transfer kinetic energy more efficiently to surrounding atoms. For 10 keV collision cascades, the simulations were performed only with Er PKAs on the lattice containing 1,112,832 atoms. From Fig. 4.17, the peak damage occurs between 0.5 and 0.6 ps after the start of cascade, somewhat later than at 2 keV, and defects are mostly stable after a time of around 4 ps. The simulations were run until 7.5 ps to guarantee that the defects stop moving. 10 simulations are
run in different directions and average numbers of interstitials are shown in table 4.1. 25 Er interstitials and 77 O interstitials are approximately found in each simulation and Fig. 4.18 shows the relation between the number of vacancies and energy. The number of defects varies approximately linearly with the PKA energy.

Figure 4.17: The evolution of defects as a function of time in 10 keV collision cascades for Er PKA, averaged over 10 PKA directions. The error bars on the graph are standard deviations.

Figure 4.18: The number of vacancies as a function of the PKA kinetic energy for an Er PKA (solid line) and O PKA (dashed lines). There is a linear relation between number of vacancies and PKA energy for the Er PKA.

A sample of a simulation in the <474> direction is shown in Fig. 4.19.
(a) and (b) show the peak damage at 0.5 ps and the defects remaining after the ballistic phase at 7.5 ps. The defects are located in the region of the crystal that roughly follows the initial path of PKA. It can be seen that the Er interstitials and some of the O interstitials tend to be isolated from the core of collision path. This is again because of small sub-cascades formed from the PKA along its trajectory (see Figs. 4.19 (c)). There is also some disordering of the O sub-lattice along the path of the most energetic recoil. This disordering occurs because of the oxygen interstitials and vacancies clusters with short separation distances between interstitial and vacancy. Er vacancies and split Er vacancies are also widely found inside the groups. These clusters of disorder on the oxygen sub-lattice are different from the defects observed in low energy cascades but similar to the defects of the 2 keV cascades in Fig 4.16. However, disordering of the O sub-lattice after 10 keV cascades is significantly bigger.

Some snapshots of defects remaining from 10 keV collision cascades are shown in Fig. 4.20. The figures show that disordering on the O sub-lattice is composed of groups of closely separated oxygen vacancies and interstitials. Er vacancies and split Er interstitials are widely seen inside the groups of disordering on the O sub-lattice. The positions of O interstitials and vacancies are similar with the positions observed for the O-square defect, split O vacancy and split O interstitials however we cannot categorise them in terms of single defects. The disordering on the O sub-lattice is very similar to the disordered fluorite structure consistent with experimental works [39, 40].

4.3.4 Discussion and Conclusion

The study has shown that the number of displaced atoms and the PKA energies are linearly related. In the low energy cascades, the damage often occurred on the oxygen sub-lattice. The 0.4 keV energy is generally too small for an O PKA to displace Er atoms while the Er PKA also produces mainly damage on the oxygen sub-lattice. The defects remaining after the ballistic phase are categorised in terms of various point defects, which provide data for the study of diffusion over long time scales in chapter.
Figure 4.19: Snapshots of a 10 keV collision cascade initiated by an Er PKA. (a) The defects near the time of peak damage, 0.5 ps and (b) the defects after the end of the ballistic phase, 7.5 ps. (c) shows the line figure which illustrates the connections between atoms moved in (b) and their initial points. (1) - (4) are zoomed images from (b). Considerable damages on the oxygen sub-lattice is observed at the core of the cascade.

Figure 4.20: The defects remaining after 10 keV Er PKA collision cascades in the <474>(a), <216>(b) and <513>(c) directions. The figures shows the complex defects of disordering on the oxygen sub-lattice.
5. For 2 keV and 10 keV cascades, damage is observed on both the Er and O atom sub-lattices. The collision cascades form when the main PKA transfers its kinetic energies to atoms on its paths causing branching into smaller sub-cascades. The heavier Er atoms, as expected, cause larger sub-cascades and leave more defects remaining after the cascade than the lighter O atoms. After the collision cascades, the Er and O interstitials found far from the core of the energetic recoiling collision are similar to those found in low energy cascades. However, disordering of the oxygen sub-lattice is observed at the centre of the high energetic recoiling path of the PKA. The disordering on the oxygen sub-lattice is complex with clusters composed of oxygen interstitials and vacancies. These defects are not observed in low energy cascades.

The disordering on the oxygen sub-lattice is evidence of the disordered fluorite structure observed experimentally after low doses of radiation. After increasing the PKA kinetic energy, the number of disordered O atoms is significantly increased. However, the inequality between the numbers of O interstitials and vacancies compared to Er inside these cluster defects, found in simulations, are not observed in experiments. Diffusion and aggregation between vacancies and interstitials will occur over longer time scales which would probably significantly reduce the disorder.

The phase transformation between the C-phase and B-phase (see Fig. 1.5) after irradiation in bixbyite is not observed in these simulations. This is because single atom events do not model the high dose (fluence) situation where the phase changes are observed experimentally. However, some clues to this phase transformation are observed from the simulations. For example, the oxygen interstitials which fill in the structural vacancies increase the coordination of Er from 6 neighbouring O atoms to 7 or 8, similar to the coordination of the cation in the B-phase, with 7 coordinations. Secondly, the split Er vacancy in a group of O vacancies and interstitials may represent the start of a phase transformation since the cation positions between the C-phase and
B-phase are different.
Chapter 5

Long time scale dynamics of point defects

5.1 Introduction

In the previous chapter, radiation damage in bixbyite, $Er_2O_3$, was examined by MD simulation for both high (5 keV+) and low energy (<1 keV) collision cascades. The damage data, generated from the simulations, were used for understanding of the radiation tolerance of bixbyite and to compare with the experimental work. However, the analysis of damage induced by ballistic collisions over the MD simulation scale is not sufficient to give a full insight. The motion of point defects or clusters of defects found after the ballistic phase occur as infrequent events but many of these may occur before the next radiation event. For diffusion, the system must evolve from one local minimum state to another and millions of thermal vibrations can occur before a jump to the next basin on the potential energy hypersurface can happen. This depends on the energy barriers of the dividing surface between basins and the temperatures involved. To examine these events, normal MD simulations are not possible because the time scales involved are inaccessible. To evolve the infrequent events, long time scale techniques simulations are used. In this chapter, the long time scale techniques, temperature accelerated dynamics (TAD) method [92], the Vineyard method [93] and the
Kinetic Monte Carlo (KMC) method [94], are employed to examine the point defects, categorised from the previous section. Some issues arising from the implementation of these methods are also discussed.

5.2 Simulation Methodology

5.2.1 The TAD method

TAD, introduced by Sørensen and Voter et al [92], is a method to reach longer time scales than is possible with MD for system characterised by rare events. The basic concept involves reducing the waiting time between events by raising the temperature to some temperature, $T_{\text{high}}$, higher than the temperature of interest, $T_{\text{low}}$. However, doing this directly disrupts the relative probability of the system following one pathway versus another. Therefore, correcting the bias from temperature is performed and transitions are filtered out so that only transitions that should occur at low temperatures are considered. The method works well when the energy barriers between transitions are relatively high which is the case for many ionic systems but the speed up is less good when the potential energy surface is dominated by lots of small energy barriers.

For an infrequent event, the waiting time, $t$, which is spent in a state before transiting to next state, $i$, is exponentially distributed by a probability distribution

$$f_i(t)dt = k_i e^{-k_i t} dt$$

(5.1)

where $k_i$ is the rate constant for transition to state $i$. By applying harmonic Transition State Theory (hTST), [93], $k_i$ in Eq. 5.1 can be calculated by the Arrhenius expression

$$k_i = \nu_i e^{-E_i/k_B T}$$

(5.2)
where, $\nu_i$ is the attempt frequency (prefactor), $k_B$ is Boltzmann constant, $E_i$ is the transition energy barrier, which is a minimum energy requirement for a transition to state $i$, and $T$ is the temperature of material. These equations are assumptions required for TAD method.

The TAD method performs a special kind of MD, called basin-constrained MD (BCMD) when a dynamical system is constrained in a potential energy basin. The system is heated thus accelerating the probability of a transition to move to the next basin. When a transition is detected at $T_{\text{high}}$, a waiting time, $t_{i,\text{high}}$, is recorded and the energy barrier, $E_i$, is calculated by using the climbing image nudged elastic band method (cNEB) [95]. The transition time, $t_{i,\text{high}}$, is extrapolated to the transition time, $t_{i,\text{low}}$, at $T_{\text{low}}$ by simple equation derived from 5.2 assuming a constant prefactor.

$$t_{i,\text{low}} = t_{i,\text{high}} e^{E_i / (k_B T_{\text{low}} - k_B T_{\text{high}})}.$$  (5.3)

After that, the system is moved back to the initial position to explore the next transition again. The simulations will be run repeatedly to find a large number of possible transition paths and transition times until reaching a stopping time, $t_{\text{high,stop}}$, given by the equation

$$t_{\text{high,stop}} = \frac{\ln(1/\delta) \nu_{\text{min}} t_{\text{low,short}}}{\nu_{\text{min}}} \left( \frac{1}{k_B T_{\text{low}}} - \frac{1}{k_B T_{\text{high}}} \right).$$  (5.4)

where $t_{\text{low,short}}$ is the shortest extrapolated time for all events at $T_{\text{low}}$, $\nu_{\text{min}}$ is an assumed minimum prefactor of system ($\sim$ normally chosen $10^{12} - 10^{13}$), and $\delta$ is an uncertainty parameter or probability that, if the high temperature MD were continued, some other event could extrapolate to an even shorter time at $T_{\text{low}}$. Once $T_{\text{high,stop}}$ is reached at high temperature, the event with the shortest time, $t_{\text{low,short}}$, is accepted, the system is moved to the corresponding state and the clock advanced by $t_{\text{low,short}}$. The procedure is then repeated for the new state.
Each transition time which is recorded at $T_{\text{high}}$ need not keep the same ordering when extrapolated to $T_{\text{low}}$. For example, two transitions are detected at $T_{\text{high}}$ and $t_{1,\text{high}} > t_{2,\text{high}}$ but it may be found that $t_{1,\text{low}} < t_{2,\text{low}}$, when they are extrapolated to $T_{\text{low}}$. This changing order comes from the difference of energy barriers which determine the slope of extrapolation in the Arrhenius plot of Eq. 5.3. This is described schematically in Fig. 5.1.

Figure 5.1: The plot of the extrapolation of transition times from high temperature to low temperature. The orders of transition times at high and low temperature may be changed since the difference in the energy barriers of transitions determine the slope of each line. The MD simulation at high temperature is run until $t_{\text{high,stop}}$ is reached. (See also [92] and [27])

The boost factor in TAD, is defined by $t_{\text{low,shortest}} / (\sum t_{i,\text{high}})$ and can attain dramatically large values when choosing $T_{\text{high}}$ to be much larger than $T_{\text{low}}$. However, the anharmonic effect at $T_{\text{high}}$ can cause an error in the time at $T_{\text{low}}$ [98]. This anharmonicity error can be controlled by choosing $T_{\text{high}}$ and $T_{\text{low}}$ as close as possible consistent with computational limitations. In comparison with other accelerated dynamic techniques, parallel replica [96] and hyperdynamics [97] methods, TAD is relatively easy to implement and from numerical experiment, TAD also gives the best boost factor.
Because the energy barriers for diffusion in Er₂O₃ are relatively high, $T_{\text{high}}$ was set to be 3,000 K and $T_{\text{low}}$ was varied between 300 and 2,000 K depending on the rate of movement and the amount of computer time consumed in performing the calculation. $v_{\text{min}}$ and $\delta$ were chosen at $10^{12} \text{s}^{-1}$ and 0.05, respectively. Only isolated point defects typically observed in the collision cascade were analysed. The chosen lattice contained 640 atoms and periodic boundary conditions were used.

5.2.2 Energy barrier determination

In the TAD method, the energy barrier is an important parameter required for extrapolation from the time $t_{i,\text{high}}$ to $t_{i,\text{low}}$ (see Eq. 5.3). Determination of the saddle point on the potential energy surface is important since the diffusion event occurs by passing over the saddle between two states whose height is the energy barrier (see Eq. 5.2). Many different methods have been proposed for finding the saddle point and the associated Minimum Energy Path (MEP) on the potential-energy surface [99]. The MEP is the minimum energy path which connects two minimum energy points on the potential-energy surface. The MEP is frequently used to determined the reaction coordinate [100] for transitions and it can also be important for describing anharmonic effects or even quantum corrections [101]. Henkelman, Johannesson and Jónsson [99] review and compare some common methods, used in condensed matter studies of transitions. These methods include the Drag method, the NEB method [102], the Climbing Image NEB (cNEB) method [95], the Conjugate Peak Refinement (CPR) method [103], the Ridge method [104], the DHS method [105] and the Dimer method [106]. They suggest that cNEB is the most efficient method for finding saddle points and also show the shape of whole MEP. However many other methods exist such as the string method [107], the ART method [108] and the RAT method, developed at Loughborough [109]. In the following section, we will discuss the methodology and
theory of the NEB and cNEB which along with TAD are the main methods used in this work.

The Regular NEB Method

The NEB algorithm starts from constructing a string of images connecting two minimum points (usually constructed from linear interpolation). The string of \(N+1\) images can be represented by the position vectors \([R_0, R_1, ..., R_N]\), where \(R_0\) and \(R_N\) are vectors of the initial and final points respectively. The vector positions between \(R_0\) and \(R_{N-1}\) are given by

\[
R_i = R_0 + \frac{i}{N}(R_N - R_0).
\] (5.5)

The intermediate points, \(R_1, ..., R_{N-1}\), between the initial and final points are controlled by an adjusted force, which is composed of a spring force along tangent of elastic band, \(\tau\), and the perpendicular component of the real force derived from the potential \(V\):

\[
F_i = F_i^{spr}|| - F_i|_\perp.
\] (5.6)

The spring force is introduced to keep equal distances between the images along the tangent vector and equation is given by

\[
F_i^{spr}|| = k[(|R_{i+1} - R_i| - |R_i - R_{i-1}|) \cdot \hat{\tau}_i] \hat{\tau}_i
\] (5.7)

where \(k\) is the spring constant and the force perpendicular to elastic band is given by

\[
F_i|_\perp = \nabla V(R_i) - \nabla V(R_i) \cdot \hat{\tau}_i \hat{\tau}_i
\] (5.8)

The tangent vector estimation of image \(i\) used is that proposed from Henkelman and Jónsson [110];
\[ \tau_i = \begin{cases} \tau_i^+ & V_{i+1} > V_i > V_{i-1} \\ \tau_i^- & V_{i+1} < V_i < V_{i-1} \end{cases} \] (5.9)

where \( \hat{\tau}_i = \tau/|\tau| \), \( \tau_i^+ = R_{i+1} - R_i \) and \( \tau_i^- = R_i - R_{i-1} \).

At a maximum point or a minimum point, the tangent vector is estimated by

\[ \tau_i = \begin{cases} \tau_i^+ \Delta V_{i}^{\text{max}} + \tau_i^- \Delta V_{i}^{\text{min}} & V_{i+1} > V_{i-1} \\ \tau_i^+ \Delta V_{i}^{\text{min}} + \tau_i^- \Delta V_{i}^{\text{max}} & V_{i+1} < V_{i-1} \end{cases} \] (5.10)

where \( \Delta V_{i}^{\text{max}} = \max(|V_{i+1} - V_i|, |V_{i-1} - V_i|) \) and \( \Delta V_{i}^{\text{min}} = \min(|V_{i+1} - V_i|, |V_{i-1} - V_i|) \).

When all forces have been calculated, all images are moved following the force vector by using the velocity Verlet algorithm [66] or by relaxation using the conjugate gradient method. Normally only a small number of points are chosen, typically \( N \approx 10 \) and thus no image would lie directly on the saddle. The saddle point can be determined by interpolation or by using an adaptation of the NEB method described in the next section.

- Climbing Image NEB Method (cNEB)

Generally, the images from the regular NEB method do not lie on the saddle point and need interpolation to estimate it. This can lead to an over or under estimate of the energy barrier. To solve this, the modification, cNEB, is developed for more accurate energy barrier calculation. cNEB performs a few step of the regular NEB. Then the highest energy image is identified and the force of this image is modified to

\[ F_i = -\nabla V(R_i) + [2\nabla V(R_i) \cdot \hat{\tau}_i] \hat{\tau}_i \] (5.11)
Following this force, the images will climb up the elastic band to the maximum energy and but be minimised to the lowest energy perpendicular to the band.

5.2.3 The Vineyard method for the prefactor

The accelerated dynamics methods are nearly all based on Transition State theory (TST), directly or indirectly. TST works on the approximation of rate constant to escape from state $A$ to state $B$ by calculating the equilibrium flux through the dividing surface from $A$ to $B$. The primary assumption of TST is that there is no correlation event with state $B$ (even though it can be found in some cases, such as the double jump of an adatom in surface diffusion [92]). However, in many solid-state diffusion problems, TST is a very good approximation and in systems which have correlation events, the TST rate is an upper bound for the exact rate [98].

The Vineyard theory or hTST [93] is a modification of TST to a more simple form which is commonly used for approximating the real TST rate. In traditional TST, before computing the TST rate, the dividing surface between states must be determined while with hTST, the method requires one only to identify the two minima and the saddle points.

To simplify, the potential energy $U$ at the saddle point and the minimum point is expanded in a second-order Taylor series by changing all of co-ordinates to normal co-ordinates of vibration weighted by mass (Vibration mode) [111]:

$$U \approx U(A) + \sum_{j=1}^{N} \frac{1}{2} (2\pi \nu_j)^2 q_j^2 \quad (around \ the \ minimum \ point)$$  \hspace{1cm} (5.12)

$$U \approx U(P) + \sum_{j=1}^{N-1} \frac{1}{2} (2\pi \nu_j^*)^2 q_j'^2 \quad (constrained \ on \ the \ saddle \ line)$$  \hspace{1cm} (5.13)

where $A$ and $P$ represent the minimum and saddle points respectively. The $q_1...q_N$ and $q_1'...q_{N-1}'$ are normal co-ordinates of vibration around the minimum and saddle points.
points and $\nu_i...\nu_N$ and $\nu^*_i...\nu^*_N$ are normal frequencies of vibration around $A$ and $P$. Here it is assumed that there is only one negative eigenvalue of the Hessian matrix at the saddle point (a rank 1 saddle) so that on the saddle line, the co-ordinate, which has the negative eigenvalue is not included and the Taylor expansion has only $N - 1$ values. In practice, the normal frequencies of vibration are obtained by constructing the Hessian matrix, $K$, numerically. Thus although the method has been known for some years it is only recently that it has become practical numerically to implement since the system sizes normally require a few hundred atoms for good convergence and calculating the eigenvalues of a matrix with thousands of entries is a time consuming process.

$$K = \left[ \frac{1}{\sqrt{m_im_j}} \frac{\partial^2 U}{\partial r_i \partial r_j} \right]_{N \times N}$$

(5.14)

where $m_i$ is the mass of atom $i$. The positive eigenvalues, $\lambda_i$, from the Hessian matrix are used to evaluate the normal frequencies of vibration in Eq 5.12 by equation,

$$\lambda_i = (2\pi \nu_i)^2.$$

(5.15)

Finally, the prefactor can be obtained by

$$\nu_0 = \frac{\prod_{j=1}^{N-1} \nu_j}{\prod_{j=1}^{N-1} \nu_j^*}.$$

(5.16)

This is referred to as the Vineyard method although some similar expressions were proposed by others earlier [98]. Since this expression arises from a second-order energy expansion, (Eq. 5.12) the vibration modes are harmonic so we refer to this as harmonic Transition State Theory (hTST). The Vineyard method is normally good to
approximate the exact rate constants which often lies in the range of $10^{12} - 10^{13} \text{s}^{-1}$. These values can then be used in a KMC simulation [94].

5.2.4 Rank 2 saddles

In calculating the prefactor by the Vineyard method, the eigenvalues at the saddle and the minimum point need to be determined. However, in the transition of the oxygen vacancy in $Er_2O_3$, which will be discussed in more detail later in this chapter, we found two negative eigenvalues at the saddle point determined by the NEB method. Use of the string method also found this rank 2 saddle and no numerical method that we implemented was able directly to find a rank-1 saddle between the two states. Further investigation revealed that such saddle points exist when the potential energy surface is very flat, almost ridge-like near the transition point and when the rank-2 saddle lies on a symmetric pathway. When this occurs, the normal frequencies of vibration at the saddle point provide only $N-2$ values. However, if we calculate the transition rate by the Vineyard method in Eq. 5.16, the normal frequency of vibration $N-1$ values are required.

The saddle point, which has two negative eigenvalues, is normally called a rank-2 saddle point while the normal saddle point which has a negative eigenvalue is the rank-1 saddle point. The total energy of the system will be decreased when moving following a negative eigenvalue co-ordinate whereas moving the system along positive eigenvalues co-ordinate will increase the total energy.

J. N. Murrell and K. J. Laidler [112] give an example of a saddle point that has more than one negative eigenvalues from the calculation of the rate constant in a chemical reaction. They found a transition state of some reactant, $H + XH \rightarrow H_2X$, where the symmetry of the transitions gives a saddle point between the reactant and product which is not a rank-1 saddle point. The symmetry comes from the identical atoms. For example in $H + XH \rightarrow H_2X$, if two hydrogen atoms are labelled as different and
labelled by $H^1$ and $H^2$, the transition from product to reactant can be $H^1X + H^2$ or $H^2X + H^1$. They suggest in this case to multiply the rate expressed by the statistical factor, $l^\dagger$, defined as the number of equivalent activated complexes that can be formed from the identical atom. The rate expression is given by

$$k = l^\dagger \frac{kT}{h} \frac{Q_1}{Q_A Q_B} \exp\left(-\frac{E}{kT}\right)$$

(5.17)

where $Q$ is partition function. They also show that between any two minima joined by a path that passes through a rank-2 saddle there will be a lower energy path passing through a rank-1 saddle.

D. E. Jiang and Emily A. Carter [113] also found a rank-2 saddle on their study of diffusion of hydrogen interstitial through bcc Fe. Even though this point is a symmetric transition pathway but they point out that the transition of hydrogen interstitial from tetrahedral site to a neighbouring tetrahedral site through the octahedral site gives a rank-2 saddle point is at the octahedral site. They just conclude that this transition is not a true transition and did not consider it further in their study. This is also supported by Chao Jiang, S.A. Maloy and S.G. Srinivasan [114], who found that the bcc structure has a rank-2 saddle point at the octahedral site.

In this chapter, the rank-2 saddle point of an oxygen vacancy transition in $\text{Er}_2\text{O}_3$ will be studied in detail as we need to know the rate constant of the transition to implement in the KMC simulation. The Vineyard method at rank-1 saddles, the TAD method and the normal MD method are methods which we utilise for calculating the rate constant and the results of them will be discussed and compared. The methodologies of these methods are following.

- The Vineyard method at a rank-2 saddle
Since Vineyard method can be used at the rank-1 saddle point, then we will try to find out the rank-1 saddle between the two states in a straightforward way by moving the system from the rank-2 saddle point along the eigenvector direction of the negative eigenvalues. Generally the two negative eigenvalues have a large difference in size, typically around a factor of 10 so we call them the large negative eigenvalue and the small negative eigenvalue. The system will be moved following only the small negative eigenvalue since the eigenvector of the large negative eigenvalues has the same direction with the reaction coordinate. The system will be moved until finding the minimum point and at that point where the Hessian matrix has only one negative eigenvalue. Then, the prefactor and rate constant are calculated by Eq. 5.16 and 5.2.

**- TAD method**

The TAD method is used to determine transition pathways with no pre-knowledge of the likely transition. Having determined the pathway the energy barrier is determined by the cNEB method. The number of transitions in each pathway in a given time, can be counted. Therefore, we will use a straightforward way to calculate the rate of transition, \( k \), by using the ratio between the number of transitions and the time of simulation. The rate of transition is thus given by

\[
k = \frac{\text{Number of transitions}}{\text{Number of symmetry} \times \text{Total running time}}
\]  

(5.18)

The number of symmetry (equivalent pathway) is included in the equation for averaging the number of transitions in the equivalent pathways. The number of symmetry pathways for oxygen interstitial and vacancy transitions in \( \text{Er}_2\text{O}_3 \) are shown in table 5.1. In this work, the \( T_{\text{high}} \) is set to equal \( T_{\text{low}} \) and the uncertainty parameter, \( \delta \), is set to be 1. With this setting, TAD simulates transitions similar to MD simulation by moving to next state after a transition is found without searching other transitions.
However, there are some differences between TAD and MD as TAD will not recognise correlation between states, which may cause the system to be given a faster transition.

- **MD simulation**

The MD simulation is used to calculate the rate of transition directly by using a methodology similar to that described by Gillan, Harding and Tarento [115]. Defects in this method will be limited to hop only between 2 neighbouring states. The transitions will be detected by using a normalised reaction co-ordinate. This is determined from the dot product of the reaction coordinate vector and the vector of state, defined as the difference between the current position and saddle point. The dot product between these vectors will be zero when the system crosses the saddle line and transition occurs. The reaction coordinate is normalised by giving the dot product a value of 1 when the system is at minimum point. Fig. 5.2 shows an MD simulation of the oxygen vacancy at a temperature 1,500 K. When the ordinate is zero, a transition occurs. 14 transitions are detected from the graph in a duration of 0.2 ns. This method can be used here since the oxygen vacancy jumps only between 2 neighbouring states and is easy to implement in an MD simulation. The simulation will be stopped once the oxygen vacancy hops out from these 2 states through a higher energy barrier pathway. However this did not occur at this temperature over a time of 2 ns. The rate of transition is calculated by Eq. 5.18.

5.2.5 **Kinetic Monte Carlo (KMC) simulation**

The Kinetic Monte Carlo method is a powerful tool for extending the simulation time. It can be used to track the motion of the defects in materials over longer times scales than those accessible with MD and can also determine the diffusion constants. In traditional KMC, all possible transition pathways and the rate constants are required to be known in advance. If there are $n$ possible transitions for a point defect to move
Figure 5.2: Graph of an MD simulation of the oxygen vacancy motion at 1,500 K. The defect hops between 2 neighbouring states and when the ordinate (normalised reaction co-ordinate) equals zero, the defect jumps to next state. The * on the figure shows the correlation between states of the transition in which the oxygen vacancy can move back after a transition occurs in very short times, akin to a quick rebound back to the original state. TAD misses these events since once a transition is detected the system is moved back to the original state.

From state \( i \), the relative probability for a transition to state \( j \) is given by

\[
\rho_{ij} = \frac{k_{ij}}{\sum_{j=1}^{n} k_{ij}}
\]

(5.19)

where \( k_{ij} \) is rate constant for moving from state \( i \) to state \( j \) and \( n \) is the total number of transitions. A random number \( R_0 \in (0,1) \) is chosen and the system will move to state \( m \) (\( m \leq n \)), if \( \sum_{j=1}^{m-1} \rho_{ij} < R_0 < \sum_{j=1}^{m+1} \rho_{ij} \) (see Fig. 5.3). By this method, the transition will be chosen dependent on the probability of each transition pathway.

The KMC simulation time for the movements can be obtained by generating another uniformly random number \( R \in (0,1) \) (or \( (0,1] \) ) and advancing the simulation time clock by a time \( \Delta t \) given by

\[
\Delta t = -\frac{\log R}{\sum_{j=1}^{n} r_{ij}}
\]

(5.20)
Figure 5.3: The pathway for movement to new state can be chosen by using a uniformly random number $R_0 \in (0,1)$. From the figure, the transition will move to state $m$ if $\sum_{j=1}^{m-1} k_{ij} < R_0 \times \sum_{j=1}^{n} k_{ij}$ (left image) or $\sum_{j=1}^{m-1} \rho_{ij} < R_0 < \sum_{j=1}^{m+1} \rho_{ij}$ (right image), where $k_{ij}$ is rate of transition and $\rho_{ij}$ is the probability to move to state $j$ in Eq. 5.19. (Adapted from [94]).

The system is then moved to the next step by the chosen pathway with simulation time $\Delta t$ and the procedure is then repeated for the next state. When KMC is repeatedly run, the diffusion constant, $D$, can be obtained by the Einstein - Smoluchowski relation (in 3 -dimensions):

$$D = \frac{<|r|^2>}{6t_{\text{sample}}}$$

(5.21)

where $r$ is the displacement of the defect during the $t_{\text{sample}}$ interval time. Typically, the $t_{\text{sample}}$s are varied at each step. Therefore, millions of KMC steps are performed for a time $t_{\text{run}} = mt_{\text{sample}}$ and the values of $t_{\text{sample}}$ are varied with the values of the number of time intervals $m$ until good convergence for average values of $D$ is achieved.
5.3 Results

5.3.1 TAD simulations

Kinetics of point defects in $\text{Er}_2\text{O}_3$.

In order to have a greater understanding of long time evolution of radiation damage in $\text{Er}_2\text{O}_3$ we examine the point defect movements by using temperature accelerated dynamics (TAD). For this investigation, a lattice size containing 640 atoms is used with $T_{\text{high}}$ at 3,000 K and $T_{\text{low}}$ varying between 300 and 2,000 K, depending on the type of defect and magnitude of the energy barrier.

A. Oxygen Vacancy

Of all the point defects investigated, the oxygen vacancy has the smallest energy barrier for diffusion. The possible transition pathways and energy barriers of the oxygen vacancy are shown in Fig. 5.4. The transitions of energy barriers of 0.8, 1.0 and 1.36 eV (see Fig. 5.4(a-c)) occur via a direct exchange of the oxygen vacancy with a neighbouring oxygen atom. These are the dominant transitions and almost all transitions of oxygen vacancy at the temperatures studied here involved one of these transitions. The last three energy barriers are rarer events with higher energy barriers of 1.94, 1.97 and 2.31 eV (see Fig 5.4(d-f)). Rather than a direct exchange mechanism, these movements use the lattice structural vacancy (16c) as an intermediate site to which the replacing oxygen first moves. These latter transitions are rarer events, which are obtained from transition searching by TAD and observed at high temperatures.

In each transition, equivalent pathways can be observed. If the two transitions are symmetry transitions, they have similar transitions and the same energy barrier. For example in Fig 5.4(b), the transitions in the same direction of arrows are the symmetry transitions with an energy barrier of 1 eV. The number of symmetry transitions of the oxygen vacancy transition are shown in table 5.1. From simulations by TAD, the
Table 5.1: Transition energy barriers and symmetry pathways for the oxygen vacancy and oxygen interstitial.

<table>
<thead>
<tr>
<th>Energy barrier (eV)</th>
<th>Number of different pathways</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td>1.0</td>
<td>2</td>
</tr>
<tr>
<td>1.37</td>
<td>2</td>
</tr>
<tr>
<td>1.94</td>
<td>2</td>
</tr>
<tr>
<td>1.97</td>
<td>2</td>
</tr>
<tr>
<td>2.31</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 5.1: Transition energy barriers and symmetry pathways for the oxygen vacancy and oxygen interstitial.

<table>
<thead>
<tr>
<th>Energy barrier (eV)</th>
<th>Number of different pathways</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>1</td>
</tr>
<tr>
<td>2.2</td>
<td>6</td>
</tr>
<tr>
<td>2.3</td>
<td>3</td>
</tr>
</tbody>
</table>

lowest energy barrier results in the oxygen vacancy moving in the lattice as a repeating movement between two neighbouring states. When the oxygen vacancy moves through this 0.8 eV energy barrier, it will move back to the original site by the same energy barrier and transition pathway, but, in the opposite direction. Therefore, in order for the oxygen vacancy to diffuse through the lattice, a barrier greater than 0.8 eV needs to be overcome and the minimum diffusion barrier is the second lowest energy barrier of 1.0 eV.

B. Oxygen interstitial

The oxygen interstitial is a common point defect observed from the collision cascade results and has the second lowest energy barrier for diffusion. The minimum energy oxygen interstitial is found at a structural vacancy site (16c). From TAD simulations, the oxygen interstitial movements are similar to the oxygen vacancy by hopping repeatedly between 2 sites and diffusing by other transition paths. From checking the transition pathways and energy barriers, there are three possible transition pathways for the oxygen interstitial to move, with energy barriers of 1.4, 2.2 and 2.3 eV. The transitions pathways are shown in Fig. 5.5 and the number of symmetry transitions are shown in the table 5.1. The smallest energy barrier of 1.44 eV (Fig. 5.5(a)) shows that the oxygen interstitial can move directly to the structural vacancy along the diagonal in the oxygen sub- cube with only one symmetry pathway. Fig. 5.5(b) and 5.5(c)
Figure 5.4: Motion of the oxygen vacancy can occur via multiple pathways. (a) - (c) are the most dominant transitions with energy barriers of 0.8, 1.0 and 1.37 eV. (e) - (f) are rare transitions which have higher energy barriers of 1.94, 1.97 and 2.31 eV respectively.
show pathways which have higher energy barriers of 2.2 and 2.3 eV. These transitions require two atoms to move. First the oxygen atom labelled 1 moves to occupy the structural vacancy and then the oxygen interstitial moves to site 1. An additional point noticed from the transition barrier of 2.2 eV in Fig. 5.5(b) is that two oxygen atoms labelled 1 can be chosen for the transition. Although both of them produce the same final state of transition, the transitions are categorised to be different transitions since they come from the different processes and have different saddle points. The barrier of 2.2 eV has then 6 equivalent pathways even if it has only 3 end points. As for the transitions of the oxygen vacancy, since the smallest energy barrier is only an exchange mechanism between similar sites, net diffusion through the lattice requires the second lowest barrier to be overcome.

![Figure 5.5: Motion of the oxygen interstitial can occur via 3 pathways. (a) has the smallest energy barrier of 1.4 eV. Here the oxygen interstitial moves to a nearby vacancy structural site directly. (b) and (c) are transition pathways which have energy barriers of 2.2 and 2.3 eV where the oxygen atom labelled 1 moves to a structural vacancy site and oxygen interstitial moves to replace its site. For the transition pathways in (b), 2 oxygen atoms labelled 1 can be chosen for the same transition. They will be categorised as different transitions even though they have the same final state. Therefore, the symmetry pathway for energy barrier of 2.2 eV will have 6 symmetry transitions while the final states are only 3.](image)

The barrier for diffusion of 2.2 eV for the oxygen interstitial is too high a barrier for diffusion at low temperatures. The oxygen interstitial will be stuck in a repeating movement at room temperature whereas the oxygen vacancy can possibly move. If diffusion is limited by the 1 eV barrier, this gives a hop time of less than 2 hours assuming an attempt frequency of $10^{13}$. This is different from the work in MgO [116]
and spinel [16] in which the most mobile defect is the interstitial with much lower barriers but consistent with studies in UO$_2$ [117] and may be a general feature of fluorites and their derivatives.

C. Er interstitial and Split Er interstitials

The split Er interstitial and the isolated Er interstitial prefer to reside at the structural vacancy. This is shown schematically in Fig. 5.6(a) and (b). The split Er interstitial has a formation energy lower than Er interstitial by 0.18 eV and the energy barrier for converting from the split Er interstitial to the non-split form is 0.21 eV whereas the reverse barrier is 0.02 eV. These energy barriers show that Er interstitial prefers the formation as a split interstitial rather than the isolated Er interstitial form. Both of these defects are apparent in the cascade simulations. However, when the Er interstitial is found close to the other defects, it generally forms as a non-split Er interstitial or together with oxygen interstitials to form a di-interstitial or tri-interstitial which will be discussed in detail later. Diffusion processes which are observed for $T_{\text{low}} = 2,000 \, K$ are shown in Fig 5.6(c). The split Er interstitial (Fig 5.6(c1)) can diffuse to reside as a non-split Er interstitial (Fig 5.6(c2)) at the structural vacancy in the next sub-cube if it can overcome an energy barrier of 2.46 eV and the non-split Er interstitial can then move to form a split Er interstitial (Fig 5.6(c3)) with an energy barrier of 0.023 eV.

The minimum energy barrier for diffusion is 2.46 eV and is similar to the oxygen interstitial which has a minimum energy barrier for diffusion of 2.2 eV (the second lowest energy barrier). These barriers, 2.2 and 2.46 eV, are very high for diffusion times of (> a hundred years at room temperature) and we can consider that both of these are effectively immobile defects.

D. Er vacancy

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Figure 5.6: Diffusion of the Er interstitial and the split Er interstitial. The split Er interstitial is shown in (a) and the isolated Er interstitial is shown in (b). The diffusion of the split Er interstitial (c1) to be an isolated Er interstitial (c2) in the next sub-cube has an energy barrier of 2.46 eV. The isolated Er interstitial is moved to become a split Er in the same sub-cube overcoming an energy barrier of 0.023 eV, while the reverse barrier is 0.21 eV.
The Er vacancy is another type of defect which we can observe in the collision cascades. However, it is mostly found in the form of a tri-vacancy or di-vacancy with one or two oxygen vacancies. As discussed in the section on the bixbyite structure, Er atoms have two non-equivalent positions at 8a and 24d sites, which are differentiated only by the relative positions of the 2 nearby structural vacancies (see Fig. 5.7(a)). For the Er vacancy at the 24d site in contrast to the oxygen vacancy, which often oscillates and returns back to its original position, the Er atom in Fig. 5.7(b1) moves to reside at the structural vacancy in Fig. 5.7(b2) overcoming an energy barrier of 2.65 eV whereas the reverse energy barrier is 0.13 eV. Later, the Er interstitial in Fig. 5.7(b2) replaces the Er vacancy in Fig. 5.7(b3) overcoming an energy barrier of 0.02 eV with the reverse energy barrier being 3.43 eV.

From Fig. 5.7, we can see that 8a position has a lower formation energy than 24d
CHAPTER 5. LONG TIME SCALE DYNAMICS OF POINT DEFECTS

site by 0.9 eV. This is in agreement with the cascade results where the Er vacancy is always found in the 8a position. Moreover, If we track the processes from Fig 5.7(b3) to (b1), we will see the diffusion of the Er vacancy from 8a to 24d positions has an energy barrier of 3.43 eV.

E. Er-O di-interstitials

The di-interstitial is a common type of defect observed from cascades simulations. The defect arises during the recrystallisation state after peak damage in which interactions between different charged ions mean that Er and O wish to reside together forming di- or tri-interstitials. The motivation for checking diffusion of the di-interstitials comes from a similar study of defect clusters in MgO in which some clusters of point defects have low energy barriers for diffusion and can move as a group [12]. The di-interstitials in Er₂O₃ can be classified to be first (type 1) and second nearest neighbour (type 2) di-interstitials (see Fig. 5.8(a-b)). For type 1, Er atoms find a site in the lattice between 2 oxygen sub-cubes, which is not regular position of Er interstitial, while in type 2 the Er interstitial sits on a structural vacancy. In TAD, complex movements of the oxygen interstitial around the Er interstitial are observed. The diffusion of di-interstitials occurs when the oxygen interstitial forms an intermediate state as in Fig. 5.8(C2). The intermediate state can transform to be di-interstitial type 1 or type 2. Some transitions observed in the simulations are shown in Fig. 5.8(C1-4). The type 2 di-interstitials in Fig. 5.8(C1) move to an intermediate state as in Fig. 5.8(C2) overcoming an energy barrier of 2.15 eV with the reverse energy barrier of 0.51 eV. After that, the intermediate state transform to a type 1 di-interstitial as in Fig 5.8(C3) with an energy barrier and reverse energy barrier of 0.7 and 1.5 eV respectively. Finally, type 1 di-interstitials can change to be type 2 di-interstitials overcoming an energy barrier of 1.22 eV with a reverse energy barrier of 2.06 eV.
Figure 5.8: Diffusion of di-interstitials. The di-interstitials is observed in 2 forms, type 1 (a) and type 2 (b). The diffusions of di-interstitials from type 2 (c1) to the type 1 (c3) in adjacent oxygen sub-cubes, passing the intermediate state (c2) have energy barriers of 2.15 and 0.7 eV respectively. Type 1 (c3) can move to type (2) with an energy barrier of 1.22 eV.
The transitions from type 1 in Fig. 5.8(C1) to form type 1 in Fig. 5.8(C4) have the highest energy barrier at 2.15 eV. The intermediate state is required for connecting the transition. The energy barriers for moving from the intermediate state to be a type 1 and type 2 interstitial are 0.51 and 0.7 eV respectively. This shows that in the intermediate state, they often move back to form a type 1 structure which has a lower energy and it requires several vibrations between the intermediate state and type 1 before they can move to form type 2. Moreover, transitions from Fig. 5.8(C3) to (C4) shows that type 2 di-interstitials have lower total energy than type 1 at 0.83 eV. It means that di-interstitials prefers type 2 formation than type 1. However, since the energy barriers to move between them are high they will require a long time before they can move to be the more stable type, 2 formation.

The diffusion of the di-interstitial requires an intermediate state before it can move. However, before the di-interstitial finds the intermediate state, a complex movement of the oxygen interstitial surrounding Er interstitial is also required. The movement of the oxygen interstitial has energy barriers between 2 and 2.5 eV. Therefore, we can conclude that the diffusion of di-interstitial involves with 2 processes. The first is the movement of oxygen interstitial which has energy barrier around 2 eV or more until it finds the intermediate state. Secondly, the intermediate state can move to be a type 1 or type 2 di-interstitial with energy barriers of 0.7 and 0.51 eV respectively.

F. Er-O-O tri-interstitials

Tri-interstitials can be observed from the collision cascade. Since Er has the charge +3, it can attract more than one oxygen atom, which has charge -2. In TAD simulations, if we initiate the tri-interstitial position as we observed from the cascade results in a relatively short time scale the oxygen moves to find the minimum position as shown in Fig. 5.9(a). The diffusion processes of the tri-interstitial are shown in the Fig. 5.9(a) to (d). From (a) to (b), the oxygen interstitial moves to a next structural
vacancy by replacing the oxygen atom labelled 1 overcoming a maximum energy barrier of 2.21 eV. In the figures, we show only maximum energy barriers although there are intermediate states, which have small energy barriers, less that 1 eV. After that, the Er interstitial (c) can move to the next structural vacancy by replacing the Er atom, labelled 2. The energy barrier for this transition is 0.53 eV. This is a considerably lower energy barrier than that isolated Er interstitial (split Er interstitials) used for the transition around 2.46 eV. Finally, the last oxygen interstitial (d) can move with maximum energy barrier of 0.63 eV by replacing the oxygen atom labelled 3. We can also see that states (a) and (d) are equivalent states.

Figure 5.9: Diffusion of tri-interstitials. The diffusion of the tri-interstitials from (a) to (d) has the maximum energy barrier of 2.21 eV. The reverse energy barrier shows the movement from (d) to (a) has the same transitions as the energy barriers from (a) to (d).

**G. Di - and Tri - vacancies**
Di-vacancies are defects composed of an Er vacancy and an oxygen vacancy and, similarly, tri-vacancies are comprised of 2 oxygen vacancies and an Er vacancy. Both of these defects are frequently observed from residual defect after collision cascades. From simulations using TAD, it was not possible to detect any motion of these defects with only the movement of the oxygen vacancy surrounding Er vacancies. However, the energy barriers and simulations show that an isolated Er vacancy has the ability to attract a nearby oxygen vacancy to form a di-vacancy. The energy barrier is only 0.31 eV while the minimum energy barrier for diffusion of an isolated oxygen vacancy is 1.0 eV. Moreover, when a di-vacancy is formed, the oxygen vacancy moves towards the Er vacancy with an energy barrier for moving out to the adjacent sub-oxygen cube of 1.3 eV while the reverse energy is 0.2 eV.

![Di-vacancies and Tri-vacancies](image)

Figure 5.10: Di-vacancies (a) and Tri-vacancies (b). The TAD simulations show that these are very stable defects with no net diffusion observed. The oxygen vacancies can move around the Er vacancy on the oxygen sub-lattice but the Er vacancy remains fixed.

**H. The O-square defect**

The O-square is the last defect, considered using the TAD simulations. The O-square, is so called because O atoms exchange positions symmetrically where there were previously structural vacancies (Fig. 5.11(a)). The O-square is interesting since it is often found from high energy cascades and experimental works where a disordered fluorite structure is observed. From investigation by TAD simulations, the O-square can move back to a perfect crystal structure by 2 different pathways. The first way is
where the two oxygen interstitials move following pathway 1 in Fig. 5.11(b) with an energy barrier of 0.78 eV while the reverse energy barrier is 5.3 eV. The second path is shown in Fig. 5.11(c). The oxygen interstitials cross into the adjacent sub-cubes in opposite directions. The energy barrier is 0.54 eV with the reverse energy barrier of 5.1 eV. The formation energy of the O - square formation is 4.6 eV. This reveals that the O-square formation can help to absorb energy from a collision cascade through the high value of its formation energy. It can release energy back to a perfect crystal structure over longer time scales.

Figure 5.11: The O- square defect (a). Oxygen atoms can move back to their original lattice sites in two ways. The first way (b) follows arrow 1 with an energy barrier of 0.78 eV. The second path is by following the arrow 2 with energy barrier 0.54 eV.

Table 5.2 summarises the smallest energy barriers for diffusion and the average hop times using the hTST method. The prefactor and temperature are fixed at $10^{13}$ and 300 K respectively. From the table, the only defect which is movable at room temperature is the oxygen vacancy which has escape time around 2 hours while other
Table 5.2: The smallest diffusion energy barrier and average time to escape by hTST of oxygen vacancy (O-V), oxygen interstitial (O-I), erbrium interstitial (Er-I), Di- interstitials (Di-I) and tri- interstitial (Tri-I). The prefactor is fixed at $10^{13}$ and the temperature is 300 K.

<table>
<thead>
<tr>
<th>Defect formations</th>
<th>O-V</th>
<th>O-I</th>
<th>Er-I</th>
<th>Di-I</th>
<th>Tri-I</th>
</tr>
</thead>
<tbody>
<tr>
<td>The smallest diffusion energy barrier (eV)</td>
<td>1.0</td>
<td>2.2</td>
<td>2.46</td>
<td>&gt; 2.0</td>
<td>2.21</td>
</tr>
<tr>
<td>escape time hTST</td>
<td>1.75 hours</td>
<td>$2.9 \times 10^{16}$ years</td>
<td>$6.7 \times 10^{20}$ years</td>
<td>$&gt; 1.3 \times 10^{13}$ years</td>
<td>$4.3 \times 10^{16}$ years</td>
</tr>
</tbody>
</table>

Defects require very long times for a transition.

For a more accurate determination of the transition time, the prefactor needs to be calculated. In the methodology section, the prefactor in the Vineyard method can be numerically calculated from the eigenvalues of Hessian matrix at saddle point and minimum point. However, the transition of oxygen vacancy, with the energy barrier of 0.8 eV, produced two negative eigenvalues at the saddle. The two negative eigenvalues cannot be used to calculate the prefactor by the Vineyard method. In the following section we will discuss the situation of the two negative eigenvalues and perform some comparisons with different methods used for determining the prefactor.

5.3.2 Two negative eigenvalues at saddle point

The two negative eigenvalues or rank-2 saddle points are found in the transition of the oxygen vacancy with an energy barrier of 0.8 eV (see Fig. 5.4(a)). This is a problem when we need to determine the rate of transition by the Vineyard method. Further calculations on other systems showed that the rank-2 saddle is not only found in the transition of oxygen vacancy in Er$_2$O$_3$ but also detected in transitions of the oxygen interstitial in spinel and MgO.
A. Movement of atoms following the eigenvector of negative eigenvalues.

We start the study of two negative eigenvalues by moving atoms from the saddle point following the eigenvectors corresponding to the negative eigenvalues. One of these directions should be in the same direction as the transition pathway whereas the other will lie along the ridge.

This calculation used a lattice containing 639 atoms with periodic boundary conditions. The second derivatives in the Hessian matrix (Eq. 5.14) are numerically constructed by performing small displacements of an atom equalling 0.0001 Å. The two negative eigenvalues obtained from the Hessian matrix are termed the small negative eigenvalue for smaller negative value and the large negative eigenvalue for the larger negative value.

Fig. 5.12 shows the movement of the atom which moves to the oxygen vacancy (labelled I) following eigenvectors of the large (a) and small (b) negative eigenvalue. The figures start from the saddle point (a2 and b2) and move following the directions of the eigenvectors. The movement along the eigenvector of the large negative eigenvalue shows that the oxygen atom has the same transition pathway with the oxygen vacancy transition observed from the simulation in Fig. 5.4(a) while the movement following eigenvector of the small negative eigenvalue makes another transition which has the same saddle point but the oxygen atom is moved perpendicular with the first transition to the structural vacancy.

B. Potential energy curve

From Eq. 5.12, if two negative eigenvalues occur at the saddle point, the movement following their eigenvectors will give a reduction in the total potential energy of the system. This section will examine this and give the potential energy graphs when they
Figure 5.12: The system moves following eigenvector corresponding two negative eigenvalues. Fig. (a1) - (a3) show movement following large negative eigenvalue. The movement is the same direction with reaction coordinate. Fig. (b1) - (b3) are the atoms’ movement following the small negative eigenvalue. In this direction, atoms move almost the same with the movement in Fig(a). However, the direction, oxygen atom I is lead to the structural vacancy (16c), which is not a stable position for defect. The red and yellow squares are the positions of the oxygen vacancy and structural vacancy respectively.
move along the negative eigenvalue directions.

Graphs (a) and (b) in Fig.5.13 shows the total energy of the system following the eigenvectors of small and large negative eigenvalues respectively. The total energy of both systems decreases when they are moved from saddle point. For the small negative eigenvalue, the energy is dropped by only 0.01 eV at a separation distance of 0.4 Å. For large negative eigenvalue, the energy is reduced 0.25 eV at minimum point with separation distance of 0.75 Å, however all this shows that the real minimum energy path deviates from that of the quadratic approximation as we move away from the
The figures and graphs confirm that the symmetric saddle point, determined by cNEB (and checked using other methods), has two negative eigenvalues. The minimum points of the small negative eigenvalue graph are expected to be the rank-1 saddles. We have calculated the Hessian matrix at the minimum points of graph 5.13(a) and the result is that indeed only one negative eigenvalue is found at these points which are symmetrically located close to the rank-2 saddle. We have also found a similar situation in other materials (e.g., one of the pathways for the diffusion of the Mg interstitial in MgO). In all cases the nearby rank 1 saddle could be determined, in this way, by following the direction of the eigenvector corresponding to the smallest negative eigenvalue from the rank-2 saddle. The two negative eigenvalues case always arose when there was a symmetric transition path and the potential energy surface near the rank-2 saddle was very flat. Tightening up the NEB method by adding more images to the string still did not find the close-by rank-1 saddles and so far we have not found a saddle point finding method that always determines these other than using the method described above.

C. Prefactor and Rate constant determination

In this section we use three different methods to calculate the rate constant for the lowest energy O vacancy transition. An MD simulation is performed using the LBOMD code with a lattice containing 5,311 atoms. 3 layers on boundary are fixed and the Fast Multipole method is utilised for calculating the electrostatic part. TAD is simulated on lattice size containing 639 atoms. The boundary has a periodic boundary condition and the Ewald summation is applied for calculating the electrostatic part. The rate constant by the Vineyard method is obtained from the Hessian matrix at the rank-1 saddle point. Table 5.3 presents the results for the rate constants by MD, TAD and Vineyard methods and an Arrhenius plot between the rate constant and
temperature is shown in Fig. 5.14.

Table 5.3: Rate constants using different methods for the oxygen vacancy transition in Er$_2$O$_3$ with the energy barrier of 0.8 eV. The values in the brackets for the TAD and MD methods are the numbers of transitions used to calculate the rate constant.

<table>
<thead>
<tr>
<th>Methods</th>
<th>1,500 K</th>
<th>1,750 K</th>
<th>2,000 K</th>
<th>3,000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vineyard method</td>
<td>5.5×10$^{10}$</td>
<td>1.4×10$^{11}$</td>
<td>2.6×10$^{11}$</td>
<td>1.2×10$^{12}$</td>
</tr>
<tr>
<td>TAD method</td>
<td>5.4×10$^{10}$ (116)</td>
<td>1.2×10$^{11}$ (236)</td>
<td>1.8×10$^{11}$ (118)</td>
<td>4.5×10$^{11}$ (360)</td>
</tr>
<tr>
<td>MD method</td>
<td>5.8×10$^{10}$ (64)</td>
<td>1.5×10$^{11}$ (45)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 5.14: Arrhenius plot of the rate constants as a function of temperature. The rate constants calculated from TAD are lower than MD and Vineyard at different temperatures and bend out from the Vineyard method at high temperatures while MD has slightly higher values than both methods.

At a temperature of 1,500 K, the rate constants from the 3 methods are very consistent. The MD method has a few higher value than the TAD and Vineyard methods. However, when the temperature is increased to 1,750, 2,000 and 3,000, the rate constant of the Vineyard method decreases by a factor of 4. The bending of the TAD method’s graph from the Arrhenius plot can be explained by the anharmonic
effect when the temperature is increased. However, for lower temperatures, the rate constants approach the same values. The Arrhenius plot between rate constant and time for other energy barriers of the oxygen vacancy are shown in Fig. 5.15. These plots show a similar but less pronounced anharmonic effect. For the MD simulations, the rate constants by MD are higher than that of TAD and Vineyard because of the correlation between states. The MD simulations found that when the vacancy moves to its next state, it can often move back to the first state in very short time, like a recoil motion, (see in Fig. 5.2).

The conclusion from this section is that the rank-2 saddle can be found in some transitions of defect in crystals. The Vineyard method can not be applied to determine the rate constant at the rank-2 saddle point since the two negative eigenvalues are obtained. However, we may use the rank-1 saddle, which can be obtained by moving the system along eigenvector of small negative eigenvalue to the local minimum point, to compute the rate constant instead. The comparison of the rate constants between the three methods gives good agreement at low temperatures. However, the anharmonic effect can be important at high temperatures. This also suggests that when we simulate using TAD, the $T_{\text{high}}$ should not be set too high in order to avoid the anharmonic effect. This has also been suggested by Sørensen and Voter [92].

5.3.3 KMC simulation

KMC simulations can study longer time scale evolution than TAD by passing through multiple crystal lattice sites and therefore better statistical sampling. The oxygen vacancy and interstitial are chosen for the diffusion study and the calculation of the diffusion constants since they are the most observed defects from collision cascades and have lowest energy barriers for diffusion. Since the KMC method requires us to know the rates of transitions and all transition pathways in advance, the TAD simulations results from last study were used for the KMC (see table 5.1). To calculate
Figure 5.15: Arrhenius plot of the rate constants as a function of temperature for the oxygen vacancy transition with energy barriers of 1.0 eV (a) and 1.37 eV (b). The red graphs represent rate constants calculated from TAD whereas the blue curves show the rate constants computed by the Vineyard method.
Table 5.4: Prefactor values used in the KMC simulation for each transition. The prefactor for the 2.2 eV barrier of the oxygen interstitial has 2 values since in the transition, the oxygen interstitial can move by 2 ways through different saddle points but with the same end point.

<table>
<thead>
<tr>
<th>Energy barrier (eV)</th>
<th>Prefactor ($s^{-1}$)</th>
<th>Energy barrier (eV)</th>
<th>Prefactor ($s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>$2.8 \times 10^{13}$</td>
<td>1.4</td>
<td>$2.6 \times 10^{13}$</td>
</tr>
<tr>
<td>1.0</td>
<td>$4.7 \times 10^{12}$</td>
<td>2.2</td>
<td>$3.1 \times 10^{13}$</td>
</tr>
<tr>
<td>1.37</td>
<td>$6.2 \times 10^{12}$</td>
<td>2.3</td>
<td>$1.1 \times 10^{14}$</td>
</tr>
<tr>
<td>1.94</td>
<td>$1.0 \times 10^{13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.97</td>
<td>$1.0 \times 10^{13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.31</td>
<td>$1.0 \times 10^{13}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

diffusion constants by Eq. 5.21, large enough values for the interval time $t_{sample}$ need to be chosen to ensure convergence. This is determined by trial and error since it depends on both the temperature of simulation as well as the particular defect under investigation. To ensure convergence, $t_{sample}$ was chosen until the average values for the diffusion constant in running time $t_{run}$, where $t_{run} = mt_{sample}$, did not change. Two significant figures are chosen for convergence.

For the calculation, the Vineyard theory was used to determine the rate constants. The prefactors used here are different for different transitions and are shown in table 5.4. The prefactor normally has values around $10^{12} - 10^{13}$ and can often be assumed to be constant (at $10^{13}$) to save computing time. The diffusion constants for both defects are given in the table 6.5. The diffusion constants for both defects follow exactly an Arrhenius relation (see Fig. 5.16).

During the diffusion process, the oxygen vacancy and interstitial must overcome the second-lowest energy barrier before they can move through the lattice. No preferred directions are observed for diffusion of the oxygen vacancy and oxygen interstitial (see Fig. 5.17). At 300 K, the oxygen vacancy moves through the minimum energy barrier, 0.8 eV, for 99.99 % for all attempts while it chooses the second minimum energy barrier for only 0.003 %. Thus, at room temperature, the oxygen vacancy will oscillate around
16 thousand times before moving to next state. The timescales for a hop with energy barrier higher than 0.8 eV is about 4 hours. At 1000 K, the probability of executing the minimum energy barrier is decreased to 97.56 % while the second minimum energy barrier is chosen in 1.2 % of cases. The oxygen interstitial at 300 K chooses the minimum energy barrier to move in more than 99.99% of all attempts with a very small probability to move via any other energy barrier. At 1000 K, the probability to move via the minimum energy barrier decreased to 99.87 % of all attempts. The oxygen interstitial is effectively immobile at room temperature. Although the minimum energy barrier is small enough for the possibility of diffusion at room temperature, the energy barrier for diffusion is the second lowest minimum barrier so the motion is just an oscillation between 2 adjacent states at room temperature.

Table 5.5: The diffusion constants obtained from KMC simulations for the O vacancy and O interstitial as a function of temperature.

<table>
<thead>
<tr>
<th>Temperature(K)</th>
<th>Oxygen vacancy $D(m^2s^{-1})$</th>
<th>Oxygen interstitial $D(m^2s^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000</td>
<td>$2.2 \times 10^{-8}$</td>
<td>4000</td>
</tr>
<tr>
<td>3000</td>
<td>$5.9 \times 10^{-9}$</td>
<td>3000</td>
</tr>
<tr>
<td>2000</td>
<td>$5.2 \times 10^{-10}$</td>
<td>2000</td>
</tr>
<tr>
<td>1000</td>
<td>$6.1 \times 10^{-13}$</td>
<td>1000</td>
</tr>
</tbody>
</table>

5.3.4  Recombination processes of point defects

In this section we are interested in the recombination process between interstitials and vacancies. The previous work indicates that the only isolated defect that can move at room temperature is the oxygen vacancy with a time of around 4 hours per transition. However, after irradiation, the vacancies and interstitial which are displaced from the core of a PKA path may lie close together. Then, the recombination between them could occur much more quickly.
Figure 5.16: Arrhenius plot of diffusion constants calculated by KMC simulation for the O vacancy and O interstitial as function of temperature.

The investigation is carried out by using the TAD code. The parameters are set the same as with the simulations of kinetic of point defects by TAD. The lattice contains 640 atoms and periodic boundary conditions are imposed. The $T_{\text{high}}$ and $T_{\text{low}}$ are set at 3,000 and 2,000 K respectively.

A. Oxygen interstitial and Oxygen vacancy

The oxygen vacancy and interstitial were tested in the recombination process by setting initial positions as in Fig. 5.18. The separation distance between the oxygen interstitial and the oxygen vacancy was 7.9 Å. From the figure, the oxygen vacancy moves to recombine with the oxygen interstitial with only a small energy barrier to overcome. The energy barriers for transitions from (a) to (b) and from (b) to (c) normally are 1.36 eV and 1.0 eV respectively for isolated oxygen vacancy. However, when it is located near to an interstitial, these barriers are reduced to be only 0.62 eV ((a) - (b)) and 0.005 eV ((b)-(c)) respectively. These processes show that the recombination between oxygen vacancy and interstitial can occur relatively quickly after a collision.
Figure 5.17: Diffusion of the oxygen interstitial and oxygen vacancy from the KMC simulations; (a) the oxygen interstitial diffusing at 4,000 K over a time of $2 \times 10^{-4}$ s; (b) the oxygen vacancy diffusing at 1,000 K over a time of $1.0 \times 10^{-1}$ s. The simulations start from the origin at (0,0,0). The simulation shows no directional dependence due to crystal structure.
cascade. The energy 0.62 eV is much lower than the barrier for diffusion of the isolated oxygen vacancy at 1 eV and can occur within a microsecond at room temperature.

![Figure 5.18: The recombination process. The oxygen vacancy moves to recombine with the oxygen interstitial overcoming an energy barrier of 0.62 eV. This barrier is lower than minimum barrier for isolated vacancy diffusion of 1 eV and it can occur in a microsecond at room temperature.](image)

A. Er interstitial and Er vacancy

The energy barriers for diffusion of Er vacancy and Er interstitial in the previous section show the immobility of isolated defects at room temperature since the energy barrier for transitions are 3.43 and 2.46 eV for the Er vacancy and interstitial respectively. The recombination processes for them were tested by setting atoms as the Figure 5.19 (a) and (b) with separation distance of 6.3 and 8.2 Å respectively. Hugely reduced energy barriers for the Er interstitial and vacancy are observed in Fig. 5.19, even more so than for the oxygen recombination. The energy for aggregation of the Er interstitial and vacancy show that they can be recombined at room temperature relatively quickly. The low energy comes from the high charge of Er interstitial (+3) and Er vacancy (-3), which produces a large attractive force between them.

From the data from the point defect diffusion, the barriers for an isolated Er or oxygen interstitial are too high to diffuse at 300 K. However, when the interstitials are located close to a vacancy, they can be recombined with a low energy barrier. In
Figure 5.19: Er aggregation. the Er interstitials move to recombine with Er vacancies with energy barrier of 0.08 eV in (a) and 0.43 eV in (b). These energy barriers show a considerable reduction from 2.46 eV for the isolated Er interstitial.

A situation of many collisions, the interstitial and vacancy can find quickly each other and recombine.

5.4 Discussion and Conclusion

Long time scale methods are used to examine the kinetics of point defects. The most mobile defect after irradiation is the oxygen vacancy with the minimum energy barrier for diffusion of 1.0 eV. This energy barrier for diffusion is the second lowest energy barrier. The minimum barrier does not cause the diffusion and only involves a hopping back and forth between equivalent adjacent states. The repeated movement depends on temperature and significantly reduces when the temperature is increased. For other point defects, the minimum energy barriers for diffusion are too high energy at over 2 eV, which have escape times of billions of years at room temperature.

Two negative eigenvalues are found at the saddle point determined by the NEB method for the transition of the oxygen vacancy. The rate constant by hTST cannot be determined at a rank-2 saddle point. The Murrel-Laidler theorem says that there
is always a rank-1 saddle point between two minima connected by a rank-2 saddle 
and this can be obtained by moving from the rank-2 saddle point along the direction 
of the small negative eigenvalue to a minimum point where only 1 negative eigen-
value occurs and this point can be used to calculate rate constant by the Vineyard 
method. This rate constant determined by the Vineyard method at the rank-1 saddle 
has good agreement with that calculated by TAD and MD. In comparison between 
the 3 methods, MD gives a higher rate than Vineyard and the TAD methods because 
of the correlation between states. For TAD, the rate constant has lower values than 
the Vineyard method and at higher temperatures. The difference between them is 
enhanced by the anharmonic effect at high temperature. This suggests in TAD that 
we could not set $T_{\text{high}}$ to be too high a value or the range between $T_{\text{high}}$ and $T_{\text{low}}$ to 
be much different values to avoid this anharmonic effect.

The KMC method is used to determine the diffusion constant and movement of 
the isolated oxygen interstitial and vacancy over long time scales. However, the infor-
mation of transition pathways, energy barriers and rates of transitions are provided 
by the TAD simulations. The diffusion constants at room temperature are $6.1 \times 10^{-13}$ 
for the oxygen vacancy and $2.8 \times 10^{-18} \text{ m}^2\text{s}^{-1}$ at 1000 K for the oxygen interstitial. 
The movement of the oxygen vacancy and interstitial is randomly moved with no di-
rectional effect observed.

The recombination energy barriers between neighbouring interstitials and vacan-
cies have also been studied. The energy barrier for recombination of the Er interstitial 
and vacancy is significantly reduced from the normally minimum energy barrier for 
diffusion to be only 0.43 eV for a separation distance 8.2 Å. The energy barrier for 
diffusion of the oxygen interstitial and vacancy to recombination is also reduced to be 
only 0.62 eV. Both of these barriers are small and can occur over microsecond time 
 scales at room temperature.
The experiments show that a disordered fluorite structure can be found from irradiation at a low dose of around 2.5 dpa [39, 40]. This structure has random positions of the structural vacancy in the oxygen sub-cube. Short time scale collisions by MD found formations of this form especially the swapping of oxygen atoms between the structural vacancies. This O-square defect is a simple form of a disordered fluorite and the investigations by TAD show that O-square has a high formation energy (∼4.5 eV) which can help to absorb PKA energy from collision cascades and can release energy out for going back to perfect lattice after longer times. Although the energy barriers for recombination of O interstitial and vacancies are reduced when they lie close to each other, the barriers are not as dramatically reduced as for the Er vacancies and interstitials which also have lower recombination barriers when existing close by. This could mean that over longer time scales the Er ions recombine more quickly than the O ions despite the lower barriers for O in the isolated defect cases leaving the main disorder on the O sub-lattice.
Chapter 6

Twist grain boundaries and nanocrystalline MgO

6.1 Introduction

In the last two chapters, radiation damage in a material having the bixbyite structure was examined in the crystal bulk, i.e. far away from any boundaries. The high energy barriers for the diffusion of point defects and the disordering of the oxygen interstitials to form the ‘O-square’ defects are interesting results that could be related with phase transformation and possibly, radiation tolerance of the bixbyite crystal. However, these defects are phenomena observed inside the bulk of the lattice crystals, far from any surfaces or grain boundaries. Real crystals, of course, are composed of crystal grains and radiation effects and defect production near or on a grain boundary are another aspect that it is important to study. In the experimental studies of radiation damage in the bixbyite crystal, discussed by modelling in the last 2 chapters, sample crystals with grain sizes around $\sim 2\, \mu m$ [35, 36, 37, 38] are often used. Moreover, some recent investigations of radiation tolerance found enhanced tolerance in some nanocrystalline materials, such as Au (grain size $\sim 23$ nm) [32], MgGa$_2$O$_4$ ($\sim 4$-$12$ nm) [31], TiNi alloy ($\sim 22$-$31$ nm) [33] and Gd$_2$(Ti$_{0.62}$Zr$_{0.35}$)$_2$O$_7$ ($<20$ nm) [34]. The expectation of radiation tolerance from these studies in a nanocrystalline
material comes from the sink property of defects near the grain boundary that can help to reduce the vacancy accumulation. Some preliminary studies of modelling in copper shows a self-healing property of an ingrain defect with an interstitial at a grain boundary moving to recombine with an ingrain vacancy with a low energy barrier [118]. Little work has been carried out to study this effect in oxide materials and rather than start the investigation in a material with the bixbyite structure, a material with the simpler rock salt structure is chosen for the study. In this chapter, grain boundaries (GBs) and nanocrystalline MgO will be modelled and used in a preliminary study of irradiation in a grain boundary region and in a nanocrystalline structure. We will consider primarily (001) twist grain boundaries as these are easier to model with fixed charge potentials since they are non-polar. Fig. 6.1 shows examples of nanocrystalline MgO.

Figure 6.1: HRTEM micrographs of nanocrystalline MgO at 823 K. (a) starting MgO-aerogel. (b) and (c) are MgO-aerogel after densifications. Grain areas are shown circled (Figure from ref [119]).

### 6.2 Methodology and Lattice construction

#### 6.2.1 Twist grain boundary

The twist grain boundary is a type of grain boundary produced from cleaving a crystal into two grains and twisting a grain around an axis perpendicular to the boundary plane. Using the coincident site lattice (CSL) scheme, the lattice will be
twisted with the 5 macroscopic degree of freedoms (DOFs) defined by
\[
\{DOFs\} = \{\hat{n}_{CSL}, \phi, \hat{n}_1\}
\]
where \(\hat{n}_{CSL}\) is the rotation axis, \(\hat{n}_1\) is grain boundary plane normal vector of the two grains and \(\phi\) is the rotational angle. In a pure twist grain boundary, \(\hat{n}_{CSL}\) and \(\hat{n}_1\) will be parallel. The rotation of a grain around \(\hat{n}_{CSL}\) will give coincident sites of atoms between the two grains at some rotation angle and generate a new common periodic supercell of two grain as shown in Fig. 6.2. The new periodic supercell will be dependent on the angle of twist. In this study, the angle of twist between the grains will be chosen to be consistent with the coincident site lattice (CSL) model. The CSL model is expected to be the lowest energy structure when the highest density of coincident atom sites are made. The inverse volume density \(\Sigma\), usually added as the sixth parameter, is used to indicate the values of coincident site density in the supercell. The lower \(\Sigma\) value mean the higher density of coincident sites. \(\Sigma\) can be calculated as illustrated in Fig. 6.2 and the \(\Sigma\) values and rotation angle are shown in the table 6.1.

Table 6.1: Parameters in MgO for (001) twist grain boundaries. \(\phi\) is the twist angle related to \(\Sigma\) and \(L_\Sigma\) is an length of new unit cell. \(N\) is the number of atoms in each grain of the unit cell (table adopted from [120]).

<table>
<thead>
<tr>
<th>(\phi)</th>
<th>(\Sigma)</th>
<th>(L_\Sigma) (Å)</th>
<th>(N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.87</td>
<td>5</td>
<td>6.65</td>
<td>10</td>
</tr>
<tr>
<td>22.62</td>
<td>13</td>
<td>10.7</td>
<td>26</td>
</tr>
<tr>
<td>16.26</td>
<td>25</td>
<td>14.9</td>
<td>50</td>
</tr>
<tr>
<td>12.68</td>
<td>41</td>
<td>19.1</td>
<td>82</td>
</tr>
<tr>
<td>10.39</td>
<td>61</td>
<td>23.3</td>
<td>122</td>
</tr>
<tr>
<td>61.92</td>
<td>17</td>
<td>12.3</td>
<td>34</td>
</tr>
<tr>
<td>46.40</td>
<td>29</td>
<td>16.0</td>
<td>58</td>
</tr>
<tr>
<td>30.52</td>
<td>65</td>
<td>24.0</td>
<td>130</td>
</tr>
<tr>
<td>71.08</td>
<td>37</td>
<td>18.1</td>
<td>74</td>
</tr>
<tr>
<td>58.11</td>
<td>53</td>
<td>21.7</td>
<td>106</td>
</tr>
</tbody>
</table>
Figure 6.2: The twist grain boundary of the cubic lattice structure. The red atoms are from the upper grain and blue atoms are from the lower grain. In the figure, the upper grain is twisted through an angle $\theta$ with respect to the lower to make coincident atom sites. The new periodic structure with the smallest area is highlighted by the yellow squares. The right figure shows how to calculate the inverse volume density, $\Sigma$ values, from the smallest periodic area.

(001) twist grain boundary in MgO

The twist grain boundaries will be constructed and tested for stability of the lattice by using a similar method previously described by Wolf [120]. Fig. 6.3 illustrates the method used for constructing the (001) twist grain boundary. The lattice is split into two and twisted in opposite directions through $\theta/2$ and $-\theta/2$ degrees respectively (Fig. 6.3 (a),(b)). Then the volume used in the simulation is cut to a new cube, (Fig. 6.3 (c),(d)). The angles applied at the twist grain boundary use the angle consistent with CSL method shown in table 6.1. In this study, only $\Sigma$ 5, 13, 17 and 25 are chosen to examine collision cascades near a grain boundary.

Grain boundary energy

The grain boundary energy is a value that can be used to determine the stability of the grain boundary as a lower grain boundary energy means a stabler grain boundary. The grain boundary energy can be computed from the different energy between atoms near the grain boundary and those inside bulk. However, before the grain boundary

\[\Sigma = \frac{|CSL\cdot N|}{V} = \frac{2}{10} = 0.2\]
Figure 6.3: Construction of a twist grain boundary. Atoms on different sides of the boundary are coloured red and blue. The two lattices are twisted by $\theta/2$ and $-\theta/2$ degrees respectively ((a) and (b)). Then, the twist grain boundary is cut to be a cube.
energy can be calculated, the width of the grain boundary (whose potential energy is affected) needs to be determined. In this work, the width is defined by the distance from the boundary that atoms have a potential energy that differs from the potential energy of atoms by less than 0.1%. The difference in the potential energy per atom between atoms far from the twist grain boundary and atoms in bulk is shown in Fig. 6.4. From the figure, the energy is mainly affected in the first layer of atoms from the boundary with a small oscillation at the larger distances. Therefore, only atoms in the 3 layers from the grain, \( \sim 10 \, \text{Å} \), will be used as a width for calculation of the grain boundary energy (see Fig. 6.4).

![Figure 6.4](image.png)

Figure 6.4: The difference in potential energy between an atom located near a grain boundary and an atom in bulk MgO. (a), (b), (c) and (d) show these energies for the \( \Sigma 5 \), 13, 17 and 25 twist grain boundaries respectively. The calculations show that the energies are different only in the first 2-3 layers from a grain boundary. Thus, the grain boundary region will be defined as that which covers 3 atom layers on either side of the boundary (light grey colour area).

After the width is determined, the grain boundary energy, \( E_\Sigma \), can be calculated
by using the equation,

\[ E_{\Sigma} = \frac{E_{gb} - nE_{bulk}}{A} \]  \hspace{1cm} (6.2)

where \( E_{gb} \) is energy of atoms in area \( A \). \( E_{bulk} \) is the energy per atom in the bulk and \( n \) is the number of atoms used. From this equation, when the area is sufficiently large, \( E_{\Sigma} \) will be converged to a certain value. Moreover, if we employ a width higher than the third layer from the grain boundary, the energy will be negligibly changed since the atom energies are mostly the same (see Fig. 6.5). Furthermore, Eq. 6.2 can be applied to calculate the surface energy of MgO. Without testing the width, but employing a sufficiently large area \( A \) and number of layers, the surface energy calculated in this work is shown in table 6.2 and compared with previous calculations.

Table 6.2: (001) surface energy of MgO compared with other studies (adopted from [121])

<table>
<thead>
<tr>
<th>Author</th>
<th>Values (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental Determinations</strong></td>
<td></td>
</tr>
<tr>
<td>Jura &amp; Garland [122]</td>
<td>1000(298 K⁰), 1040(0 K⁰)</td>
</tr>
<tr>
<td>Gilman [123]</td>
<td>1200 (77 K⁰)</td>
</tr>
<tr>
<td>Westwood &amp; Goldheim [121]</td>
<td>1150±80 (298 K⁰), 1230 (0 K⁰)</td>
</tr>
<tr>
<td>Kingery, Bowen &amp; Uhlmann [124]</td>
<td>1000</td>
</tr>
<tr>
<td><strong>Theoretical Estimates</strong></td>
<td></td>
</tr>
<tr>
<td>Born &amp; Stern [125]^a</td>
<td>1440 (0 K⁰)</td>
</tr>
<tr>
<td>Lennard-Jones &amp; Taylor [126]^b</td>
<td>1362 (0 K⁰)</td>
</tr>
<tr>
<td>Glauberman [127]^c</td>
<td>1450 (0 K⁰), 1230 (0 K⁰)</td>
</tr>
<tr>
<td>Wolf [120]^d</td>
<td>1116, 1226 (0 K⁰)</td>
</tr>
<tr>
<td>Evarestov &amp; Bandura [128]^e</td>
<td>1534 (0 K⁰)</td>
</tr>
<tr>
<td>Current work</td>
<td>1360 (0 K⁰)</td>
</tr>
</tbody>
</table>

\[^a,b,c\] elementary electrostatic approach  
\[^d\] empirical potential  
\[^e\] density function theory (DFT) method

**Rigid body translation**

In this section, grain boundary energy (eq. 6.2) will be optimised as a function of the microscopic variable \((T_x, T_y, T_z)\) where \( T_x \) and \( T_y \) are small displacements parallel to the grain plane with \( T_z \) being perpendicular to the grain plane. Increasing the distance \( T_z \) direction will expand the volume of the crystal, a property which is normally
observed in grain boundary studies. The volume expansion, $\delta V_\Sigma$, will be computed as a function of $d$ which is defined by

$$\delta V_\Sigma = \frac{d}{d_0} - 1$$

(6.3)

where $d_0$ (2.105 Å) is the distance between first neighbour atoms in MgO and $d$ is the distance between planes on either side of the grain boundary (see Fig. 6.5). The grain boundary will be first optimised in the direction of $T_z$ for getting the distance $d$ which has the minimum energy and then moved in the parallel direction of $T_x$ and $T_y$. Fig. 6.6 presents the unrelaxed grain boundary energy as a function of volume expansion. The lowest grain boundary energies were found for a volume expansion of 0.7 ($\sim$ 3.58 Å) for all $\Sigma$. At the minimum energy points, the grain boundary energies of all $\Sigma$ have lower energy than 2× the energies of the (001) surface energy of MgO (dotted line in the figure 6.6).

After fixing $T_z$ translations in the parallel plane are employed by moving in the $T_x$ and $T_y$ directions as shown in Fig. 6.5. The grain boundary energies as a function of the $T_x$ and $T_y$ translations are shown in Fig. 6.7. The repetition of the irreducible symmetry zone of the grain boundary energy when they are translated through $T_x$ and $T_y$ is observed. Finally, the minimum energy point thus evaluated is chosen to be the initial point for relaxing the crystal to minimum energy (using the conjugate gradient method) before use in the study of collision cascades. The summary of translation parameters of twist grain boundary using in this thesis is shown Table 6.3.

6.2.2 Nanocrystalline MgO

A nanocrystalline (NC) material is a construction of many small grains on the nanometre scale. Here we model a very simplified version of a NC material. The nanocrystal can be produced by employing the Voronoi construction [129] to divide the lattice space into small regions of grains. When the grains are produced, they
Figure 6.5: Rigid body translations of the twist grain boundary. The grain boundary region is shown in the light grey colour (left figure). This area includes three layers from the boundary into each grain. The right figure shows a top view of the twist grain boundary and the rigid body translations in the $T_x$ and $T_y$ directions.

Figure 6.6: The grain boundary energy as function of volume expansion $T_z$. The dotted line shows the $2 \times (001)$ surface energy of MgO. The $T_z$ translation values are found to be a minimum at a volume expansion of 0.7 for all $\Sigma$s tested.
Figure 6.7: The grain boundary energy as a function of $T_x$ and $T_y$ for the twist grain boundaries $\Sigma$ 5, 13, 17 and 25. The $T_z$ translation value is fixed at a volume expansion of 0.7.

Table 6.3: Summary of the parameters used in this thesis for the twist grain boundaries in MgO. The grain boundary energies represented in the table are the energies for crystals that have not been fully relaxed.

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$\Sigma$</th>
<th>$E_\Sigma$ (mJ/m$^2$)</th>
<th>width(A)</th>
<th>$T_x$</th>
<th>$T_y$</th>
<th>$T_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.87</td>
<td>5</td>
<td>1775.8</td>
<td>12</td>
<td>-0.05</td>
<td>-0.1</td>
<td>0.7</td>
</tr>
<tr>
<td>22.62</td>
<td>13</td>
<td>2321.1</td>
<td>12</td>
<td>0.05</td>
<td>-0.1</td>
<td>0.7</td>
</tr>
<tr>
<td>61.92</td>
<td>17</td>
<td>2641.9</td>
<td>12</td>
<td>0.0</td>
<td>0.15</td>
<td>0.7</td>
</tr>
<tr>
<td>16.26</td>
<td>25</td>
<td>2629.2</td>
<td>12</td>
<td>0.0</td>
<td>0.1</td>
<td>0.7</td>
</tr>
</tbody>
</table>
will be randomly orientated. The procedure of grain construction is shown in Fig. 6.8. First, the Voronoi points will be randomly chosen on the lattice as shown in Fig 6.8(a). Each Voronoi site represents a grain in the lattice and the number of Voronoi sites chosen means the number of grains which will be used on the study. Then, the Voronoi cell will be constructed around the Voronoi site as shown in Fig 6.8(b). For a Voronoi cell \( V \) which surrounds the Voronoi site \( s \), \( V(s) \) will consist of all atoms that lie closer to site \( s \) than to the other Voronoi sites in the lattice. Therefore, every site will be separated by a plane at the half distance between 2 such points (see Fig 6.8(b)). After the Voronoi cells are constructed, atoms will be filled in every cell with randomly orientation (see Fig 6.8(c)). Finally, grains will be embedded in outer layers of a perfect lattice as show in Fig. 6.8(d) so that the simulation region is cubic with non-polar edges.

![Figure 6.8](image.png)

Figure 6.8: A 2-D illustration of the procedure for constructing a nanocrystalline material. In (a), Voronoi sites are randomly chosen and then (b) shows the Voronoi cell obtained from Voronoi sites. (c) and (d) show that lattices that are filled in each Voronoi cell with randomly orientation and then embedded in a perfect lattice.
In this construction, the volume expansion between the grains of the nanocrystal will be used the same value that was found to be optimal for the twist grain boundary of 0.7 (3.58 Å). After the nanocrystal is completely built, the number of Mg and O atoms do not always match. The different number of anions and cations can lead to unphysical properties in the fixed charge model. To overcome this, atoms of the excess species that have the highest potential energy are deleted until an equal number of atoms is obtained. The nanocrystal from this construction can also have a very high stress from the arrangement of atoms near the grains. Thus, the lattice will be heated to 600 °K for 20 ps to allow atoms to move to the lower energy position before minimisation using, damped MD, for 10 ps. A figure of such a NC lattice after heating and minimising is shown in Fig. 6.9. The NC lattice is composed of 15 grains with an average diameter of around 10 nm. The Q4 parameter [76] is used to colour atoms dependent on their structure. Atoms in the red colour (Q4 parameter of around 0.8) occupying the simple cubic structure are the atoms inside the grains which maintain the original MgO structure. Atoms with the green colour are atoms in the grain boundary.

In the following section, MD simulations of collision cascades will be calculated both near to twist grain boundaries and also in a NC lattice. The simulation will be carried out in the same as in chapter 3 by imparting a kinetic energy to a PKA atom inside the lattice. The simulations will examine the effect near twist grain boundaries with Σ of 5, 13, 17 and 25 for 0.4 and 2 keV. For the nanocrystal, the simulation will consider 2 and 5 keV collision cascades in a lattice of dimension 21.4^3 nm, containing 961,124 atoms. The number of simulations and the lattice sizes are shown in Table 6.4.
Figure 6.9: NC lattice composed of 15 grains (size \(\sim 10\) nm). This lattice is heated to 600 \(K\) for 20 ps and minimised by damped MD for 10 ps. Atoms in the lattice are coloured by the Q4 parameter [76].

Table 6.4: The number of simulations for each PKA with lattice sizes and twist grain boundary types.

<table>
<thead>
<tr>
<th>Twist grain boundaries</th>
<th>0.4keV</th>
<th>2keV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. simulation</td>
<td>lattice size</td>
</tr>
</tbody>
</table>
| \(\Sigma 5\)           | 8      | 5.9\(
m\\times 5.9\times 7.5\ nm\) | 5      | 15.3\(
m\times 15.3\times 16.8\ nm\) |
| \(\Sigma 13\)          | 8      | 5.4\(
m\times 5.4\times 7.5\ nm\) | 5      | 16.1\(
m\times 16.1\times 16.8\ nm\) |
| \(\Sigma 17\)          | 8      | 6.1\(
m\times 6.1\times 7.5\ nm\) | 5      | 16.0\(
m\times 16.0\times 16.8\ nm\) |
| \(\Sigma 25\)          | 8      | 4.5\(
m\times 4.5\times 7.5\ nm\) | 5      | 13.4\(
m\times 13.4\times 16.8\ nm\) |

<table>
<thead>
<tr>
<th>Nanocrystalline</th>
<th>2keV</th>
<th>5keV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. simulation</td>
<td>lattice size</td>
</tr>
</tbody>
</table>
| NC (~10nm/grain) | 5    | 21.4\(
m\times 21.4\times 21.4\ nm\) | 4    | 21.4\(
m\times 21.4\times 21.4\ nm\) |
6.3 Simulation results

6.3.1 Twist grain boundary

0.4 keV cascades

The simulations of the low energy cascades were performed close to the twist grain boundaries with 8 simulations for each Mg and O PKAs. The orientations of the initial PKA were randomly chosen on both sides of the grain boundary and the simulations were performed for 4 ps. From the simulations, the first observed phenomena is the resistance of radiation to pierce into the next grain. Most defects from the cascades were found only on one side of grain which is the same side as the initial collision by the PKA and in only few cases can defects in the other grain be observed. This tends to confirm the attraction of the grain boundary to the displaced atoms. Fig. 6.10 shows snapshots of a 0.4 keV cascade for the $\Sigma_{13}$ twist grain boundary with the PKA projected in the $<135>$ direction. The width region, defined by 10 Å from the boundary and shown by the light grey colour in the figure, includes two atom layers from boundary in each grain. In our terminology changes in structure observed in the grey area will not be recognised as damage generated inside the bulk of lattice but will be considered as damage in the grain boundary region. The yellow and red lines in the figure highlight the boundary (the first layer) of each grain.

The collision cascade in Fig 6.10 (a) starts with an O PKA in the left grain. The displaced atoms from the collision cascade are observed on both sides at peak time damage. Later, in Fig 6.10 (b) an oxygen split interstitial and an oxygen vacancy occur in the right and left grains respectively. Then, the oxygen interstitial in the right grain is attracted to the grain boundary in a short time in Fig. 6.10 (c). The rearrangement and recombination between vacancies and interstitials are displayed in Figs. 6.10 (c, d). At the end of the cascade in Fig. 6.10 (f), few defects remain in the lattice and only a single oxygen vacancy (the PKA site) is observed outside the GB region. The process in this figure highlights the sink property of the grain boundary that can attract the
Figure 6.10: Snapshots of a 0.4 keV cascade close to the Σ13 twist grain boundary for a \(<135>\) direction PKA. The GB region is highlighted by the light grey colour and the yellow and red lines show the boundary of the grains. The width area is 12 Å, which includes 2 layers of atoms. The red and blue circles for Mg and O interstitials respectively occur mainly in the grain boundary while the vacancies (squares) are mainly in the bulk region.
interstitial (circle) to move to the grain boundary during the collision cascade period. Moreover, squares in Fig. 6.10 (f) show that the vacancies are not attracted to the GB although they form very close to the boundary, e.g. the Mg vacancy in the figure forms in the second layer from the boundary but does not move to the grain boundary.

The attraction of interstitials to the grain boundary from the collision cascades are generally observed in all simulation results. Most interstitials which are formed within 3 layers distant will be attracted to move to the grain boundary. However, in contrast, vacancy motion to the grain boundary is not observed in the MD simulation although they may form in only the second layer from the boundary. This may be because of the grain boundary has a low attractive force for the vacancy or that interstitial atoms in the boundary have a high binding energy. This phenomena could be revealed by determination of the transition energy barriers and these will be calculated in the next section.

Table 6.5 shows the number of defects generated from the simulations and Fig. 6.11 shows some snapshots of residual defects at the end of the cascade phase for some simulations. The defects produced from whole lattice show that the number of defects generated from O and Mg PKA have similar values. When the Σ value is increased, the numbers of defects also tends to increase. The numbers of defects in the Σ 25 case are found to be around 2-3 times the values from the defects of Σ 5. However, if the numbers of defects are counted only from the region outside the GB, all of the twist grain boundaries give the similar value around 1.2 - 2 defects per simulation for the 0.4 keV PKA. This indicates that the lower Σ values have a more stable structure. Fig. 6.11 shows that the damage from simulations found in the grain boundary that come from the displaced atoms from collision cascades at high Σ value are often stuck in the space between grains rather than recombine with vacancies generated there (see Fig. 6.11 d) while for the lower Σ values the displaced atoms often recombine with the vacancies in the grain boundary. Furthermore, if only
number of defects generated outside the grain boundary are analysed, vacancies are the dominating defects. The number of interstitials from all $\Sigma$ values are found to lie between 0 and 0.5 per simulation while vacancies are observed to be from 0.3 to 1.5 per simulation. In the next section cascades initiated by a 2 keV PKA will be performed.

![Defect Snapshots](image)

**Figure 6.11:** Some snapshots of defects at the end of 0.4 keV collision cascades for the $\Sigma$ 5, 13, 15 and 25 twist grain boundaries. The small pictures show the displaced atoms at the peak damage.

**2 keV cascades**

The higher energy cascades at 2 keV were performed with 5 simulations for each Mg and O PKA. The initial PKA was chosen on both sides of the grain boundary and the simulations were performed for 4 ps. The collision cascades at 2 keV make a bigger disordered region than at 0.4 keV with small sub-cascades generated. These sub-cascades produce a variety of collisions in which some of them can move to or occur at the grain boundary while some do not move to the grain boundary but generate defects far from the grain boundary. Fig. 6.12 shows some snapshots of a collision cascade by a Mg PKA in the direction $\langle 111 \rangle$ for the $\Sigma$ 5 twist grain boundary. The cascades are started from a PKA in the middle left of Fig. 6.12(a). The small sub-
Table 6.5: The numbers of defects from 0.4 keV cascades close to twist grain boundaries.

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<th>Defects outside width O2 PKA</th>
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| Avg. | 1 2 3 1 2 3 1 1 1 2 | 10                           | 1                | 0                            | 1 2 3             | 10                           |
| Avg. | 1 2 3 3 3 3 3 3 3 | 10                           | 1                | 0                            | 1 2 3             | 10                           |
| Avg. | 1 2 3 3 1 2 1 1 1 2 | 10                           | 1                | 0                            | 1 2 3             | 10                           |
| Avg. | 1 2 3 3 3 3 3 3 3 | 10                           | 1                | 0                            | 1 2 3             | 10                           |
cascades can be observed in the right grain while some other branches of cascades are also found on the left grain and at the grain boundary. A group of vacancy defects can be observed on the left grain during the recombination period while some Mg interstitials are attracted to move to an oxygen interstitial to form a tri-interstitial. The most intensive damage is observed in the grain boundary with a gradual recombination between vacancies and interstitials. At the end of simulation at 4 ps, the defects are well separated to be either defects in the grain boundary itself or defects far away from the grain boundary. No defects appeared at an intermediate distance from the grain boundary. This figure is typical of other common cascades near a grain boundary in MgO in which small sub-cascades branch in unpredictable directions. Some of them can go to the GB and a few may pass through into the next grain. In all cases the most concentrated damage occurs at the grain boundary itself.

Fig. 6.13 shows some snapshots of remaining defects at the end of the 2 keV cascades and their peak damage is also shown in the small boxes. Different types of collision cascade can be seen from these figures (Fig. 6.13(a) to (d)). Some collision cascades may penetrate through the grain boundary to the next grain with only small damage at the grain boundary as shown in the Fig. 6.13 (a). In Fig. 6.13 (b), some small sub-cascade branches can pass into the grain boundary leaving large damage in the grain boundary. Some cascades can produce defects inside both grains and also at the grain boundary. Fig. 6.13 (c) and (d) show cascades in which all sub-cascades reach the grain boundary but do not pass through the boundary to the next grain. From the figures, they also have some vacancy defects on their collision path with a small number of interstitials in the grains. The large number of defects observed on the Σ 25 twist grain boundary suggests that the Σ 25 boundary is less energetically favourable than some of the others. The number of interstitial and vacancy defects from 2 keV collision cascades in different PKA directions are summarised in table 6.6. The numbers of point defects from the collision cascades are found to have similar values, except for Σ 25 . However, if we consider only the number of defects inside the
Figure 6.12: Snapshot of a 2 keV collision cascade close to the $\Sigma 5$ twist grain boundary by a Mg PKA in the $<111>$ direction.
bulk, the number of defects is observed to be approximately the same. The number of defects in the bulk is lower than that from the whole lattice by around a factor of 2-3 times for Σ5, 13 and 17 and 4-7 times for Σ 25. A difference in the values between the number of vacancies and interstitials is seen in the bulk. This indicates that the interstitials are trapped at the grain boundaries and cannot move back to recombine with the vacancy as observed also with the lower energy cascades.

![Defects at the end of 2 keV collision cascades for the Σ5, 13, 15 and 25 twist grain boundaries. The small pictures show the displaced atoms at peak damage.](image)

**Figure 6.13:** Defects at the end of 2 keV collision cascades for the Σ5, 13, 15 and 25 twist grain boundaries. The small pictures show the displaced atoms at peak damage.

**Energy barrier for defect transitions near to a grain boundary**

In this section, the energy barriers for interstitial and vacancy motion near a GB will be determined by the NEB method. The study will be simplified by using the minimum energy barrier pathways which are observed in the perfect lattice rather than by a systematic check of all possible pathways. In a perfect lattice the interstitial is located at the cell centre. The minimum energy pathway for O and Mg interstitials are the replacement transition in the <111> direction. For O and Mg vacancies, the minimum energy pathway is also the transition to replace with same specie atom in
Table 6.6: The numbers of defects from the 2 keV cascades for the twist grain boundaries.

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the <110> direction. The minimum energy barriers for transitions of interstitial and vacancy defects are shown in table 6.7.

Table 6.7: Minimum transition energy for MgO point defects in the perfect lattice.

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<td>O vacancy</td>
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</table>

The study will start by introducing a vacancy in the fourth layer from the boundary while an interstitial will be initialised in the intermediate site between the fourth and fifth layers. This transition direction is the same as the <011> direction in a perfect MgO lattice before twisting. Although there are other possible transitions to the grain boundary, the study will use only this pathway for a systematic comparison. This will also avoid a time consuming investigation for checking the lowest transition paths by searching methods, e.g. the dimer or TAD method. The assumed transition pathways are shown in the Fig. 6.14. The Fig. 6.14(a)-(d) shows a front view of the transitions highlighted by the yellow colour representing vacancy transitions and a light blue colour for the interstitial transitions. The top view of the transition in different twist grain boundary systems is shown in Fig. 6.14(e)-(f). The dotted squares in the Fig. 6.14 represents the unit cell of the grain boundary and the black arrow shows the twist direction used for constructing the twist grain boundary.

Fig. 6.15 and 6.16 show the energy barriers for transitions of vacancies and interstitials to the grain boundary following the directions given in Fig. 6.14. The energy barriers for the Mg and O interstitials do not show any reduction compared to the bulk values until the transition from the 3rd to 2nd layer. The energy barrier of transition from 3rd to 2nd layer is considerably reduced to around 0.02 - 0.2 eV and then, no stable site for the interstitial between the 2nd and 1st layer is observed. The interstitial there immediately moves into the grain boundary where its potential energy drops
Figure 6.14: Transition paths of the interstitial and vacancy. The \(<111>\) direction for the interstitial and the \(<110>\) direction for the vacancy. The yellow and light blue colours show the pathways for the vacancy and interstitial respectively. Figs. (a)-(d) show the transition from one perspective, the front view, while Figs. (e)-(h) give the top view.
Figure 6.15: Energy barriers of the interstitial and vacancy transitions to the grain boundary of the $\Sigma 5$ and $\Sigma 13$ twist grain boundaries.
Figure 6.16: Energy barriers of the interstitial and vacancy transitions to the grain boundary of Σ17 and Σ25 twist grain boundaries.
by around 5 eV from normal sites in the grain. This lower energy of 5 eV means that a huge barrier has to be overcome if the interstitial were to diffuse back to the grain. The total energy of the interstitial in different sites in the grain are not equivalent and there are other possible positions for the interstitial but all the site show a much lower value than the bulk value. In comparison the barriers for vacancy diffusion remain high at around the bulk values of 2.1 and 2.2 eV for Mg and O vacancies respectively although these are reduced to 1.6 eV for transition from 2nd to 1st layer. In addition the potential energy of the vacancy is barely altered for the vacancies between their bulk and GB positions.

The MD and NEB results are consistent since the energy barriers for the interstitials show that when the interstitial is present in a position closer than the 3rd layer, the interstitial should move to the grain boundary. This is consistent with the MD results where no residual interstitials were found in this region. In the case of the vacancy, the energy barrier for diffusion shows a reduction close to the grain boundary. However, the minimum energy barrier of 1.6 eV for moving from layer 2 to layer 1 is still too high to be observed on MD time scales. The implication is that mobile interstitials can diffuse and either recombine with the more stable vacancies or become trapped at grain boundaries. One therefore might expect in a real MgO material subjected to radiation, a build up of vacancies in the crystal grains.

6.3.2 Cascades in nanocrystalline MgO

In this section, the nanocrystalline structure shown in the Fig. 6.9 will be examined for radiation damage from 2 keV and 5 keV Mg and O PKAs. The structure is modelled using 15 grains with an average grain size of around 10 nm diameter. Five simulations will be performed for 2 keV cascades and 4 simulations for 5 keV cascades by O and Mg PKAs. The defect analysis will use the same method as before by dividing the nanocrystal into the bulk region and the grain boundary region. The GB
region is defined as that region 7 Å from each side of the grain boundary (or 14 Å in total).

2 keV cascades

Fig. 6.17 show some snapshots of a collision cascade in the <111> direction by an Mg PKA. Orange lines in the figure are used to illustrate the grain boundary. The Mg PKA initialises the collision cascade near the grain boundary from the middle left of the Fig. 6.17(a). The cascade produces disorder in the bulk and on both sides of the grain boundary. After 0.45 ps, most disordered atoms have moved to the grain boundary and only vacancies are seen in the centre of the grain. In Fig. 6.17(f), the defects, i.e. vacancies in the grain are highlighted by the ellipse. Table 6.8 gives a summary of defects from collision cascade simulations in different directions. The numbers show only the defects inside the bulk excluding the GB regions and show a clear excess of vacancies.

Table 6.8: Summary of defects from 2 keV collision cascades in nanocrystalline MgO. The number of defects are determined as those that are found further than 7 Å from a grain boundary. In the case of * this distance is increased to 8 Å due to a large accumulation of defects at this grain boundary which swells the defective region.

<table>
<thead>
<tr>
<th>Direction</th>
<th>Magnesium PKA</th>
<th>Oxygen PKA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>Mg</td>
</tr>
<tr>
<td>001</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>110</td>
<td>12</td>
<td>3</td>
</tr>
<tr>
<td>111</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>123</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Avg.</td>
<td>7.4</td>
<td>0.6</td>
</tr>
</tbody>
</table>

From the table, the number of the vacancy defects are clearly higher than the number of interstitials. In comparison with 2 keV collision cascades near isolated twist grain boundaries, the numbers of vacancies observed are very similar but the
Figure 6.17: Stages in the development of a typical 2 keV collision cascade in nanocrystalline MgO. The orange colour is used to identify the boundary of the grain. The cascade induces disorder both in the grain boundary and in the bulk in (b) and the disordered interstitials in the grain are observed to move to the grain boundary in (c). At the end of the cascade in (f), the only remaining defects in the grain where the cascade initiated are vacancy defects highlighted in the ellipse.
number of interstitials in the nanocrystal are found to be fewer than in the twist grain boundary case. This could be because the small grain size of the nanocrystal has more boundaries to attract interstitials. In addition there are more orientations for the GB’s and therefore a larger possibility of some that are less stable or contain more space where interstitials can accumulate. Moreover, some cascades which pass through the boundary into the next grain have the possibility to reach another boundary in the new grain. Some pictures of collision cascades at peak damage and the end of simulations are shown in Fig. 6.18. The collision cascade in Fig. 6.18(a) illustrates that two separate boundaries in the same grain can trap defects and there are even a few that form in the next grain. In Fig. 6.18(b), the cascade penetrates into the next grain but the defects are reabsorbed by the intermediate grain boundary leaving only few defects on the collision path in the originating grain.

![Figure 6.18](image)

Figure 6.18: Two examples of 2 keV collision cascades in nanocrystalline MgO by an Mg PKA in the \(<110>\) direction (a) and an O PKA in the \(<001>\) direction (b).
5 keV cascades

The simulations at 5 keV are performed using the same method as for the 2 keV cascades with the same lattice size. The higher energy produces more complicated cascades by the cascade penetrating into more grains than observed for the 2 keV case. Generally, the sub-cascades produce the most residual defects in the first two grains along the PKA path. The penetration distance of the cascades is found to be shorter than for collisions in a single crystal or across an isolated grain boundary. However, in some channelling directions, the cascades can move over a very long distance by utilising the space between grains. For these cases the lattice is too small and cannot contain the full extent of the cascade for both O and Mg PKAs. Only cascades that are fully contained within the system are considered here. Some snapshots of a collision cascade initiated by an Mg PKA in the $<1\bar{1}1>$ direction are shown in Fig. 6.20. The collision is started from the top left of Fig. 6.20(a) and the cascade spreads into small sub-cascades into the 4 grains on Fig. 6.20(b). In Fig. 6.20(c) - (e), the cascade curtailed by the grain boundary and one can see accumulation of defects in the areas that are highlighted by orange lines. At the end of the cascade in Fig. 6.20(e), the disordered atoms are widespread on the 4 grains. The analysis of remaining defects in the grains themselves, defined by defects living further than 7 Å from a grain boundary, is employed for identifying damage. These defects are shown in Fig. 6.20(f). In this case the colour scheme is changed from our previous coding and the red and blue spheres represent oxygen and magnesium interstitials respectively with orange and light blue spheres being oxygen and magnesium vacancies respectively. The remaining defects in the bulk can be seen only in 3 grains in the Fig. 6.20(f). In the middle grain, the remaining defects are found to be only a group of vacancies without interstitials. This group defect is similar to ones observed for 2 keV cascades. On the top grain in the image, a large defect accumulation is observed near where three grains intersect. These defects, are categorised as being in the GB only when the GB width is increased to 8 Å. The increase of width was necessary only in these regions and for only 2 PKA directions which are marked by the * in table 6.9. Some
samples of collision cascades by an Mg PKA in the \textlangle111\rangle direction and an O PKA in the \textlangle1\bar{1}1\rangle direction are shown on Fig. 6.21. The figure show similar results to Fig. 6.20 where most displaced atoms are absorbed into the grain boundary at the end of cascade. The summary of numbers of defects from collision cascades in different directions is shown in table 6.9. The results show the similar values with 2 keV cascades in which the most defects observed in the grains are vacancies. The damage can be compared to that in a single crystal and Fig. 6.19 compares the number of defects from collision cascades in single crystal, across an isolated grain boundary and for a nanocrystalline material as a function of the PKA kinetic energy. Excluding the GB region, the number defects tends to be lower than that observed in the single crystal, except for vacancy defects for the isolated grain boundary case at 0.4 keV, while the nanocrystalline material also shows the lower defect numbers than the isolated grain boundary case for both vacancies and interstitials. This illustrates that the grain boundary will affect the number of defects over short time scale and as the number of available grain boundaries increases the number of bulk defects decreases.

![Figure 6.19: Group of number of defect from collision cascades on grain boundary (GB) and nanocrystalline (NC) in the function of PKA kinetic energy. The number of Frenkel pair defects use the data from ref [116]. Error bars show the standard deviations.](image-url)
Figure 6.20: Some snapshots of a 5 keV collision cascade in nanocrystalline MgO form an Mg PKA in the $<1\bar{1}1>$ direction. (f) show shows only the bulk defects from (e) which lie further than 7 Å from grain boundaries. The red and blue spheres represent O and Mg interstitial respectively whereas light blue and orange spheres show the Mg and O vacancies respectively.
Figure 6.21: Other examples of defects from 5 keV collision cascades in nanocrystalline MgO from an Mg PKA in the $<111>$ direction (a) and an O PKA in the $<\overline{111}>$ direction (b).

Table 6.9: Summary of defects from 5 keV collision cascades in nanocrystalline MgO. The defects are counted when they lie further than 7 Å from the boundary. * indicates the directions when this distance is increased to 8 Å due to accumulation of defects close to where three grains intersect.
6.4 Discussion and Conclusion

In this chapter, MD simulations of collision cascades were examined for isolated twist grain boundaries and also for nanocrystalline MgO. The twist grain boundary results show a resistance of small cascades to pass through the grain boundary into the next grain. In the low energy cascades, only a few PKA directions can penetrate through the grain boundary. In most cases, the displaced atoms which penetrated to the next grain were observed only during the peak damage period and at the end of the cascade most of them moved back to the grain boundary. This property is also observed for the higher energy cascades when the cascades branch into smaller sub-cascades.

Another phenomena from collision cascades is the sink property of grain boundaries to nearby interstitial defects. From simulation results, the interstitial defects always disappeared from the grains up to 3 layers from the boundary while the vacancies can be observed near the grain boundary. The remaining defects in the bulk also show that there is always a lower number of bulk interstitials than vacancies for the isolated grain boundaries.

The NEB method is used to examine the transitions of interstitials and vacancies to a grain boundary. The energy barrier of interstitial shows only a small reduction until at the 2nd layer from grain boundary where the energy barrier drops to 0.02 - 0.2 eV, depending on the GB orientation. The position of the interstitial at the grain boundary also drops the total system energy by around 5 eV, indicating a very stable site in the GB compared to the bulk. There is therefore a large energy barrier for the interstitial to move back into the grain and it will therefore remain trapped there at room temperature. In the vacancy case, the NEB shows some reduction in the energy barrier from 2.1 and 2.2 eV to a lower value of around 1.6 eV. However, the barrier of 1.6 eV is still be very high for the vacancy to move at room temperature. In addition
the energy difference between the vacancy in the bulk and at the GB is very small. Thus in heating to moderate temperatures, enough to allow vacancies to move, would be insufficient to move interstitials away from the grain boundaries but the GB’s would have no effect on vacancy mobility.

Nanocrystalline MgO with an average grain size of around 10 Å diameter were examined with collision cascades generated by 2 keV and 5 keV PKAs. It was found that the number of vacancy defects in the grains themselves was considerably higher than that of interstitials by a factor of around 2-3 times. This is because many interstitials are attracted to move to grain boundary and many sub-cascades do not penetrate through the boundary regions. The vacancies are often be observed as group of vacancy at the centre of some grains.

Previous work in crystalline MgO has shown that the largest number of defects that are formed at PKA energies of 2 and 5 keV are isolated interstitials and vacancies with a smaller number of di-interstitials and di-vacancies and even few tri-interstitials and tri-vacancies. The energy barriers for interstitials to move in the bulk are quite small. For nanocrystalline MgO there are fewer interstitial defects in the grains but these interstitials can either move to recombine with nearby vacancies or can diffuse to GB’s where they remain trapped. The smaller the grain size, the more chance that the interstitials will move to the boundaries leaving a larger excess of vacancies in the bulk than if the grain size is larger. This implies that nanocrystalline MgO with small grain size would be less radiation tolerant than MgO with a large grain size due to the build up of vacancies in the grains. As the vacancy density increases there would be more of a tendency to group with other vacancies since the energy barriers for unlike vacancies to group is lower than a single defect move, (for two close vacancies to form a di-vacancy an energy barrier of only 0.99 eV has to be overcome [116]). An investigation in copper examined by modelling [118] found a similar result that vacancies are found to be higher in number than interstitials in the bulk. However, in
that case over the longer times, the interstitials at a grain boundary could recombine
with vacancies nearby. These mechanism found in the metal should not occurred in
MgO. Since the interstitial at the grain boundary has a much lower energy than that
in bulk (5 eV), which is much lower than that observed in the copper (around 1.6
eV). Moreover, the vacancy transitions in MgO have very high energy barriers so it
is impossible for them to move to a grain boundary at room temperature. Therefore,
the vacancies that could not induce a self-healing mechanism to get rid of damage as
suggested in copper and from these data, irradiation tolerance should be not enhanced
with nanocrystalline MgO.
Chapter 7

Conclusions and future work

7.1 Conclusions

In this thesis, MD simulations were used to examine some aspects of radiation damage in materials with the bixbyite and NaCl structures. After a description of the various computational techniques used (chapter 2), in chapter 3 two physical quantities that can be used as a measure of radiation tolerance, namely the displacement threshold energy and the Frenkel pair formation energy for a number of different materials with these structures was investigated in detail.

In chapter 4 MD cascade simulations in Er$_2$O$_3$ were undertaken to investigate radiation effects in this material. This investigation followed previous work at Loughborough and Los Alamos with spinel and MgO so that a more complete picture of what constitutes a radiation tolerant material has now begun to form. Some results from the point defects found in the MD simulations were then incorporated into long time scale techniques for the evaluation of radiation damage over longer time scales in chapter 5. Various long time scale methods were compared and some issues highlighted and resolved. Finally in chapter 6, MD simulations were performed for collision cascades near grain boundaries and in nanocrystalline MgO, the first time that this
has been achieved in oxide materials.

For the displacement threshold energy ($E_d$) in materials with the NaCl and bixbyite structures, the $E_d$ values were investigated using a statistically representative set of trajectories projected onto an irreducible symmetry zone. The $E_d$ values were found to be strongly dependence on the direction of the PKA. Some slight correlation between $E_d$ values can be observed especially peak and low $E_d$ values for materials with the same structure in similar directions. The average $E_d$ values were found to be ordered so that $E_d$ (MgO) > $E_d$ (SrO) > $E_d$ (NaCl) for both cation and anion PKAs whereas $E_d$ (Er$_2$O$_3$) and $E_d$ (Dy$_2$O$_3$) had the similar values. For the Frenkel pair formation ($E_{Fp}$) energy, the results were similarly ordered so that $E_{Fp}$ (MgO) > $E_{Fp}$ (SrO) > $E_{Fp}$ (NaCl) for both cation and anion Frenkel pairs whereas Er$_2$O$_3$ and Dy$_2$O$_3$ had similar $E_{Fp}$ values. The comparison between $E_{Fp}$ and $E_d$ showed that the $E_d$ was greater $E_{Fp}$ by a factor of between 4 and 10. No simple relation between $E_{Fp}$ and $E_d$ for materials with the same structures was discovered but a higher $E_d$ value was found to correspond to a higher $E_{Fp}$.

The study of MD cascade simulations in Er$_2$O$_3$ showed that number of displaced atoms in the collisional phase of a cascade, varied linearly with the PKA kinetic energy. The damage occurred more frequently on the oxygen sub-lattice rather than displacing Er atoms and the average number of O defects was found to be higher than the Er defects by around 2 times. The heavier mass of the Er PKA caused a denser cascade than an O PKA which produced cascades that spread over much larger distances. Groups of disordered of oxygen atoms were observed at the centre of a high energy recoiling path of a PKA and this increased in size when the PKA energy was increased. After irradiation there was some evidence of a disordered fluorite structure appearing, with oxygen atoms randomly arranged on structural vacancies. The phase transformation from cubic to monoclinic phase was not directly observed from simulations but some
hint of phase change occurred through an increasing of cation coordination from 6 to be 7 atoms in the damage region.

The disordered fluorite structure observed experimentally could occur by an interchange of sites on the O sub-lattice such as in the case of the O-square defect observed in the simulations. The high formation energy of the O-square defect (~4.5 eV) might suggest that the disordered fluorite structure could help absorb energy from collision cascades but release energy back to perfect lattice over a longer time since there is a fairly low energy barrier (~0.5 eV) for the reverse process. The substantial barrier reductions for recombination of an Er Frenkel pair when the interstitial and vacancy are near to each other, could mean that these recombine faster than the O Frenkel pairs since the O atoms are more widely separated.

Long time scale techniques were implemented to examine the kinetics of point defects. These showed that the most mobile isolated defect was the oxygen vacancy with a high minimum energy barrier for diffusion of 1 eV. This was in contrast to previous work in MgO and spinel where the interstitials were far more mobile. The second most mobile point defect was found to be the O interstitial. Other isolated defects had high energy barriers for diffusion but these were found to be considerably reduced when lying close to other defects of opposite charge. KMC simulations were performed to determine the diffusion coefficients and pathways of isolated O interstitials and vacancies. There was found to be no observable directional dependence but in determining the transitions and rate constants, some rank 2 saddles were discovered. It was found that such saddle points are relatively common in ionic systems, especially where the potential energy surface is ridge-like in a direction orthogonal to the minimum energy path. A method which determined the prefactors for use in the Vineyard method for rank 2 saddles was implemented. Comparison between TAD and the Vineyard method showed good agreement at low temperatures but less so at high temperatures when
anharmonic effects play a role.

The study of collision cascades near twist grain boundaries in MgO showed that the boundaries exhibit a property of penetration resistance to a cascade. They can therefore absorb energy from a collision cascade. When the cascades are generated from a low energy PKA, the grain boundary can prevent the cascades to pass into the next grain while displaced atoms (interstitials) from these cascades are absorbed into the grain boundary. The grain boundaries thus possess a sink property for interstitials. Interstitials therefore have a lower number in the grains than vacancies. The NEB method show that the energy barrier of interstitial lying closer to a grain boundary than layer 3 is reduced so interstitials are also attracted to a grain boundary. If the interstitial is trapped at a grain boundary it was shown that its energy is less than in the bulk by around 5 eV. The vacancies also show a reduced energy barrier in this region down from 2.1 or 2.2 eV to 1.6 eV. The barrier of 1.6 is too high for a vacancy to diffuse at room temperature and this will not be seen over MD time scales. In addition the energy of a vacancy in the grain boundary compared to the bulk is approximately the same.

Cascades in nanocrystalline MgO also showed a reduction of interstitial defects in the bulk but the number of vacancy defects in the grains themselves was considerably higher than that of interstitials by around 2-3 times. This again provided confirmation that grain boundaries act as a sink for interstitials. Vacancies were often observed as a group at the centre of a grain. The excess of vacancy defects in nanocrystalline MgO gives the possibility that the nanocrystalline material is less radiation tolerant than single crystal MgO.
7.2 Future work

Although many ionic systems have now been investigated there are many other oxide systems that have not been and investigation of these tied to experiment, could provide further information as to what constitutes a radiation tolerant material. In addition long time scale methods are now becoming more feasible. A combination of MD with long time scale methods could provide much more detailed information about radiation effects in these complex systems. The LBOMD code is an MD simulation code which is limited to examine radiation over the time scale of at most nanoseconds. However, the evolution of damage in materials takes place over longer time scales than a nanosecond. The on-the-fly kinetic Monte Carlo using the modified Vineyard method to determine prefactors would be a useful way to study radiation damage over longer time scales. It would be my intention to develop such a code concentrating on speeding up a simulation by developing new parallel computer algorithms, which will enable the study not only of point defect diffusion but also of more complex defect structures. The code could be used to continue my current work by studying on defect evolution from irradiation in bixbyite but also be used for many other materials.

The on-the-fly kinetic Monte Carlo technique could also be used to examine the accumulation of vacancies with or without the presence of grain boundaries. Void formation in irradiated materials is a serious problem which is not yet fully understood. Such an investigation in nanocrystalline MgO could change my prediction of less radiation tolerance for the Mg grain boundary. If some phenomenon can be observed from a longer time simulation such as self healing, observed for example, from simulation of Cu grain boundaries with vacancy migration to the grain boundary then this would be very beneficial. Furthermore, study of irradiation damage at a grain boundary in other ionic systems such as bixbyite or in nanocrystalline Er₂O₃ is also an interesting topic.
Understanding the precise details of phase transformations in ionic systems and in bixbyite in particular is also an interesting topic to continue investigating. Higher energy cascades and dose effects are possible ways to investigate phase transformation. Multi-PKA cascades by performing a first collision cascade for a nanosecond before starting a later cascade into the same region can help understand dose effects, essential for phase transformations. This could be combined with the KMC methods described above to model diffusion between overlap cascade events. Dy$_2$O$_2$ and Lu$_2$O$_3$ which also possess the bixbyite structure are also possible materials to study and compare with Er$_2$O$_3$.

The development of new and improved potentials is also a new challenge for my future career. The pair potential functions with fixed charges could give different results from other techniques, especially for the grain boundary work where ab-initio or variable charge models might be more accurate. A study with a new potential model may give different results which can help us to understand new phenomena concerning radiation damage which may be missing from a fixed charge model with a pair potential function. Furthermore, the extension of the models to new materials such as metals, semi conductors, polymers or biological materials can give me to new research topics which help my future career at a university in Thailand.
Bibliography


Bibliography


