

- Computational simulations in materials for energy applications**
- 1. Crystal and electronic structure in Ln -U-O compounds.**
 - 2. Dynamics of point defect interaction with dislocations in bcc iron.**

**A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville**

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DEDICATION

To Me

ACKNOWLEDGEMENTS

This has been a long and unexpected journey. Certainly, as a kid I never imagined to be involved in science, in fact I disliked physics during high school, and it was not until college when I started getting involved with physics related projects. This thesis marks the end of my PhD, which could have not been possible without the help and support of the amazing many people I have been extremely lucky to meet along this journey. I would like to thank all of those that we have helped me during all these years, and I hope to make them proud.

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ABSTRACT

Nuclear energy is a viable solution to the world's energy demands. Nuclear energy applications involve rich and complex physics, with high energy events, the incorporation of fission products, and the production of point and extended defects. All these phenomena have an impact on the microstructure of the constituent materials and represent efficiency and safety concerns. A mature understanding of the microstructural evolution of the component materials in the nuclear reactor core is essential to have a safe and reliable process. Experimental investigation of materials in radiation environments is difficult and expensive, making computational simulations a suitable alternative. In this dissertation, we employ computational methods to study the microstructural evolution of both nuclear fuel and the iron based reactor structural components, and the impact on their material properties. In the nuclear fuel side, we investigate the crystallographic and electronic structure of Ln -U-O compounds that may be formed inside nuclear fuel operational life by the incorporation of lanthanide fission products using density functional theory (DFT). We used a layered atomic model to propose ordered structures and compared their stability to disordered phases. We also employed the atom-in-molecule approach to study the oxidation state of uranium atoms, and the ionicity/covalency of the U-O bonds. In the structural components side, we studied the migration mechanisms of self-interstitial dumbbells and vacancies around single edge or screw dislocations. The actual saddle point energy and configuration as a function of position with respect of the dislocation core was calculated with the self-evolving atomistic kinetic Monte Carlo (SEAKMC) method, and used this data as an input for KMC calculations. This allowed the analysis of the migration paths, the range of interaction of point defects with dislocations, and the preferential absorption of self-interstitial dumbbells over vacancies, known as dislocation bias, which is responsible for swelling in irradiated materials. The understanding of the mechanism responsible for the microstructural changes, and how these changes impact the material properties is a key aspect to be able to develop materials with enhanced radiation resistance, and achieve high performance under extreme conditions that are vital for nuclear energy generation with improved efficiency and safety.

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INTRODUCTION

Nuclear energy is a green option to fulfill the increasing energy demands of the world. It involves rich and complex physics, and requires materials that can withstand extreme environments. The microstructural evolution of the materials utilized for energy applications is of great importance for efficiency and safety concerns, since it determines the mechanical properties of the materials at a macroscopic scale.

Experimental investigation in such extreme conditions is complex, and expensive. Radioactive sample fabrication requires the proper authorization, safety protocols, and careful handling. Not all facilities are able to manage radioactive samples, and characterization of samples may be not straightforward in a logistic point of view. In the case of structural materials, the study of their microstructure evolution in radiation environments may require to expose samples in reactors for a prolonged time. In these conditions, computational simulations offer a faster, cheaper and less complicated approach to study radiation effects on materials. Besides the complimentary relationship between simulations and experiments, computational studies can be used as a guide to distinguish which experiments are needed, thus saving time and money.

In this dissertation, we use different computational methods to study both the nuclear fuel and iron based structural reactor components. The incorporation of fission products into the fuel matrix and the oxidation of the nuclear fuel have an impact in the thermodynamic properties of the fuel, and thus an impact on the efficiency. We are particularly interested in lanthanide fission products; their incorporation will lead to the formation of complex oxides in the fuel. At the same time the structural components of the reactor core are under constant bombardment of energetic particles. The mechanical properties of these materials are affected by irradiation, and it can manifest as embrittlement, swelling, radiation induced segregation, hardening and cracking. In particular, we employ density functional theory (DFT) to study the phase stability, the crystallographic and electronic structure of the complex oxides that may be formed during the fuel operational life. In the structural component side, we employ kinetic Monte Carlo (KMC) to study the interaction of the point defects created by high energy neutrons with dislocations, and their migration mechanisms.

I.1 Background

I.1.1 Nuclear energy

Nuclear energy currently provides 12% of the world's power supply [1], and it is projected to generate more energy than the all renewable energies combined in the short/medium term future [2]. It is a viable green energy alternative, especially considering the amount of energy it is able to produce against its carbon footprint, which is only related to the construction and implementation of nuclear power plants. A single UO_2 fuel pellet weighs close to 4 grams and can generate as much energy as 800 kg of coal [3]. Nuclear energy

also entails the generation of radioactive waste, but it still can be of little environmental impact with responsible handling and proper storage.

In a nuclear power plant, electricity is generated from the heat produced during nuclear fission. Nuclear fission occurs naturally by radioactive decay, in this process the nucleus of an atom splits into smaller parts, producing neutrons and a large amount of energy. In a nuclear reactor, fission is controlled and electricity is generated by converting water into steam with the heat generated from nuclear reactions, and used to generate electricity with turbines. The critical aspects of nuclear energy are the performance of the ceramic fuel and the metallic structural components of the core, which are subject to conditions of high temperature and radiation. Research on the behavior of materials under such conditions allows the prediction of performance and longevity of reactor fuel elements. Moreover, next generation reactors require a more reliable and efficient process, and less radioactive waste production. These requirements involve conditions with higher temperatures and higher levels of radiation, imposing a greater demand on the materials involved.

The nuclear fuel and the structural components of the reactor are responsible for the efficiency and safety of the nuclear energy process respectively. UO_2 is the most used nuclear fuel in light water reactors due to its chemical and thermodynamic stability [4]. The nuclear fuel is fabricated by pressing UO_2 into pellets which are sintered at high temperature and encased into metal tubes to form the fuel rods in the reactor core. The expected operational life a fuel pellet is approximately 3 years. During its life time and reactor operation conditions the UO_2 fuel pellet experiments microstructural evolution due to oxidation and the incorporation of fission products. The introduction of fission products affects the thermodynamic fuel properties, such as its thermal conductivity and melting point [5]. The change in the crystallographic structure by oxidation and the formation of complex oxides is important since it may also introduce volumetric changes. For instance, the oxidation of UO_2 into U_3O_8 produces a 36% increase of volume [6], likewise the physical state of the fission products, along with their chemical characteristics, determines the volume occupied by these compounds. If the volume of the irradiated fuel is greater than original volume of the fuel, the resulting swelling can cause the fuel pellet to exert a contact pressure on the cladding, and may severely damage the fuel rods and cladding. The high operation temperature is responsible for oxygen redistribution in the fuel, and the enhanced migration of oxygen and fission products. The chemical state of fission products and the formation of complex oxides controls the availability of oxygen within the fuel rod, thus controlling the oxygen potential of the fuel, and the reactivity of the fuel with the cladding, which may corrode and weaken the cladding [7].

Iron based alloys are currently being used as critical structural materials for various energy applications [8-11]. In addition, they are candidates for structural components for next-generation fission and fusion energy systems [12]. They constitute the pressure vessel of the reactor core, and they are also used for the canisters to store radioactive waste. These applications require alloys to work in extremely challenging conditions, demanding improved mechanical properties and radiation resistance [13, 14]. Structural components

for nuclear energy are constantly bombarded by energetic particles that displace their atoms numerous times during their lifetime. Structural reactor components suffer shape and volume changes, and their mechanical properties are affected by these displacements. It is fundamental to understand the effects of radiation to be able to design materials that can withstand these extreme conditions.

1.1.2 Radiation effects

Radiation effects in materials is a paramount area of research in materials for nuclear energy applications. Materials exposed to radiation environments are exposed to a constant bombardment of energetic causing extensive displacements of atoms from their lattice sites by collisions with energetic particles, and also the incorporation of impurity atoms by nuclear fission. These effects lead to the production of different types of crystallographic defects which have an important influence on macroscopic properties, with often detrimental consequences that hinder the materials performance and pose safety issues.

In general radiation effects can be categorized into:

Atom displacements, as particles pass through matter, its energy is dissipated by exciting local orbital electrons and by collisions with the material nuclei. These collisions can eject atoms from its lattice position, leaving vacancies and coming to rest at interstitial positions.

Impurity production, the transmutation of atoms, either by fission with the creation of fission products or by the capture of neutron, creating isotopes.

Ionization, is the process of removing or adding an electron to a neutral atom creating an ion.

Energy release, this is the local heating of a small volume due to the energy released in nuclear reactions.

Radiation effects alter a number of material properties including mechanical, chemical, magnetic, electrical properties, among others. In particular, we are concerned in the crystallographic and compositional change in the UO₂ nuclear fuel, and in the change in mechanical properties of the structural materials generated by the creation of point defects and their interaction with dislocations.

The ballistic collision between energetic particles and lattice atoms, has the capability to produce a large number of point defects and disorder in the crystalline alloys that are employed as structural reactor components. The fundamental damage process is when an energetic particle strikes a target atom, called the primary knock-on atom (PKA). This atom is displaced from its lattice site forming a vacancy, and it will eventually come to rest as an interstitial atom. If the PKA possesses sufficient energy it can produce subsequent lattice site displacements of other atoms, generating what is called a displacement cascade. After

the cascade finishes, the vacancies and interstitials produced by the displacement cascade, will recombine annihilating each other. Not all point defect will recombine leaving a small number of defects in the lattice. Figure I.1 shows the different stages of a collision cascade.

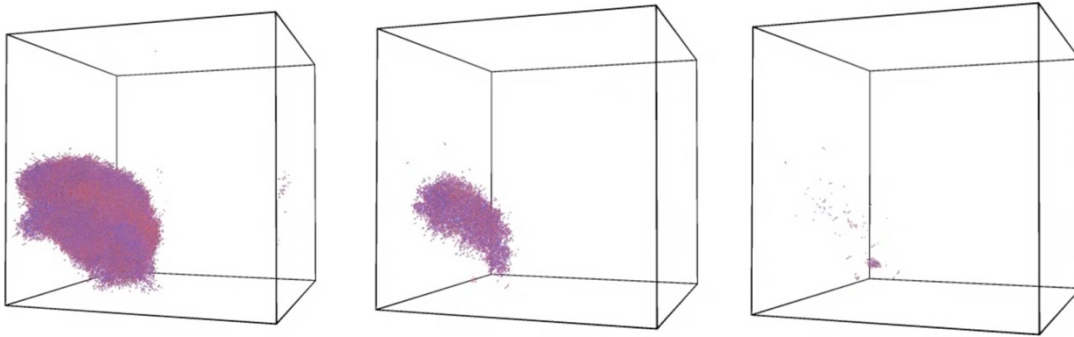


Figure I.1. Different stages of a 20keV collision cascade in iron. The dots represent point defects.

Even without the damage from radiation, real crystalline materials contain imperfections, which may be point, line, surface or volume defects. These defects alter the regular arrangement of atoms, and influence the properties of materials. The addition of point defects created during collision cascades, enhance the importance of defects on the mechanical properties. Furthermore, the high operational temperatures of nuclear reactor increase defect mobility, leading to the formation of clusters and extended defects

Atoms in a perfect crystal occupy specific atomic sites. In a pure metal, like the case of bcc iron, two types of point defects are possible, a vacant site and a self-interstitial atom. The vacancy is formed by removing one atom from an atomic site, while the self-interstitial is formed by the addition of an atom into a non-lattice site. Frenkel pairs consists of a vacancy and a self-interstitial of the same species, it is formed when an atom is displaced from its atomic position, leaving a vacancy, and goes to occupy an interstitial site. A large number of Frenkel pairs are produced by collision cascades. A schematic figure of point defects in monoatomic two-dimensional view is shown in Fig I.2.

Dislocations are line defects in the crystal structure, created by an extra plane of atoms or a shifted plane. There are two types of dislocation, edge and screw. In reality dislocations exhibit a mixed edge-screw nature. The edge dislocation is created by the insertion of an extra half plane of atoms into the crystal, distorting the nearby atoms, especially close to the dislocation line, the distortion in the atomic bonds decrease as the distance to the dislocation line increases. The screw dislocation can be thought as slicing a cube along a plane and displacing the atoms on one side relative to the other side. Resulting in a helical path resembling a spiral case or a screw, and hence the name. The dislocation structures for both edge and screw dislocations are shown in Fig I.3.

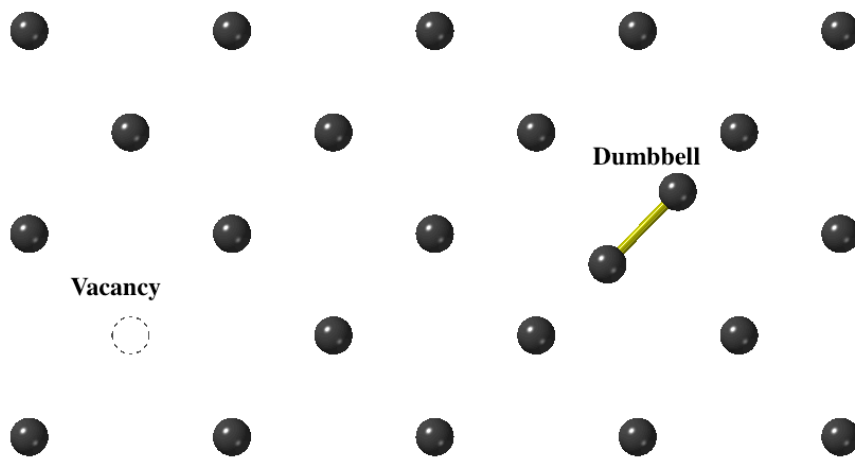


Figure I.2 Monoatomic two-dimensional lattice with vacancy and self-interstitial dumbbell point defects.

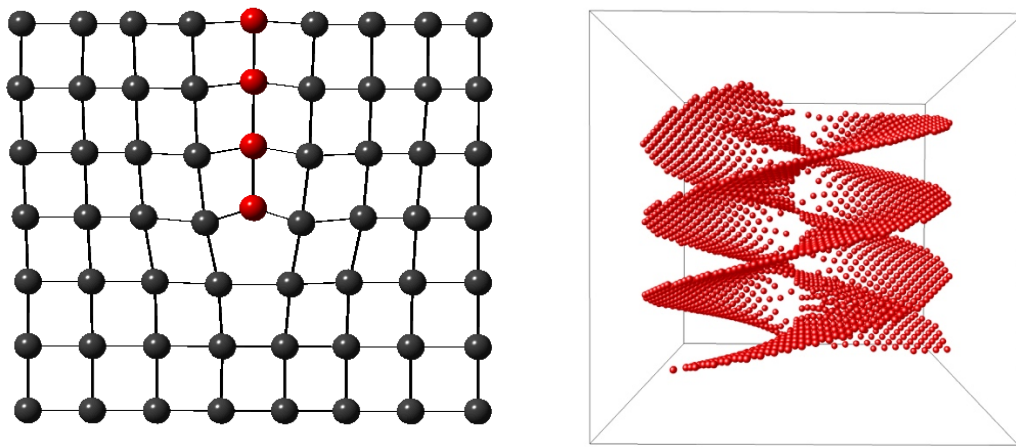


Figure I.3 (a) Edge dislocation (b) core of a screw dislocation.

1.1.4 Radiation effects on mechanical properties

In nuclear reactors, metal components are at the same time subjected to radiation fields, high temperatures and stress. The damage caused by radiation alters the crystallographic structure of materials, and is responsible for the microstructural changes suffered by structural materials, which in turn are responsible for the changes in the macroscopic mechanical behavior of materials. The high temperatures associated with the nuclear energy process enhance defect mobility. Surviving point defects in the lattice are isolated or in small clusters, but with time these defects will diffuse through the system, and can recombine, form more complex defects or migrate towards sinks such as dislocations and grain boundaries. At the same time the solutes or impurities created by irradiation have also an enhanced diffusional process, not only by the high temperature but also by the presence of vacancies. The precipitation of solute atoms alters the local chemical composition and may lead to the formation the new phases and compounds. The microstructure of materials under irradiation is in constant evolution with a continuous change in the properties of the materials.

The mechanical properties of interest for reactor performance of structural materials under irradiation are: *(i)* radiation hardening, *(ii)* embrittlement and fracture, *(iii)* irradiation creep and *(iv)* swelling. All these properties are primarily controlled by point defects, their migration and interaction with dislocations.

i) Radiation Hardening

Materials under irradiation show an increase in the yield strength, and an increase in the ultimate tensile strength. This is attributed to the pinning of dislocations by radiation produced obstacles in the vicinity of the slip plane. When irradiated bcc metals are annealed at high temperatures, the stress-strain curve of the non-irradiated material is recovered [15], indicating that the radiation produced defects are responsible for hardening.

ii) Embrittlement and fracture

Associated with the hardening there is concomitant embrittlement, measured by the decrease of total elongation during a fracture test. Radiation damage causes a loss in ductility in metals used as structural components. Fracture can occur by the propagation of cracks by the developing of intragranular voids inside metals [16]. Particularly, in bcc metals, irradiation increases the ductile to brittle transition temperature, which pose a serious problem since bcc metals are used in pressure and containment vessels in the reactor core.

iii) Radiation Creep

Creep is the time dependent deformation that a material undergoes at constant stress and temperature. Irradiation will increase the creep rate since it is controlled by dislocation climb mechanisms which is controlled by emission and absorption of point defects. [17]. Such as in the swelling case, the cause of radiation creep is rooted in the preferential absorption of dumbbells by dislocations. The excess dumbbells arriving to dislocation aid

the climb mechanism, and bring down the temperature at which creep due to dislocation climb can occur [17].

iv) Swelling

Radiation swelling is the expansion due to the formation of vacancy clusters. During the reactor operation, vacancies become mobile and form large clusters by diffusion mechanisms. The development of voids in materials signify a decrease in the density of the material, and an increase on the physical size, leading to significant implications in the structural integrity of the reactor core. Volumetric void swelling is an observed phenomenon in metals after irradiation. The origin of radiation swelling is rooted in the preferential absorption of interstitials by dislocation over vacancies. Void growth requires temperatures that allow vacancy migration, supersaturation of vacancies, and a larger number of vacancies than interstitials arriving to the voids. The preferential absorption of dumbbells by dislocations allows the last two conditions to be met, interstitial atoms will more likely migrate towards dislocations than voids because of the stronger interaction with the strain field of the dislocation, while the excess of vacancies in the lattice will migrate toward voids causing them to grow [18]. Void formation is observed between $0.3T_m$ and $0.6T_m$ (where T_m stands for the melting temperature). At low temperatures vacancies are not mobile and cannot diffuse to form clusters, the temperature needs to be high enough for vacancy mobility. At high temperatures, there is not void growth since it is prevented by vacancy emission from voids. Swelling is extremely important for all the structural components of the reactor core, and poses a concern on their structural integrity.

I.2 Methods

I.2.1 Atomic layered model

To model and analyze the structures of complex oxides, we employ an atomic layered model to assist the selection of possible ordered cation arrangements. This layer model approach was first developed by Iida [19]. Iida introduced a graphical crystal structure description in which he divided the structure into parallel triangular nets of atoms (hexanets) and subnets that contain atomic arrangements related to the hexanet. Sickafus *et al.* [20] expanded these concepts to include complex oxides with structures related to fluorite (CaF_2). Figure I.4 shows a comparison between the fluorite structure in its cubic unit cell definition (Fig. I.4a) and in the layered model representation (Figs. I.4b, c). In this approach, we consider layers of pseudo-closed-packed cations surrounded by layers of anions with the same close-packed structures. Each atomic layer consists of a perfect hexanet of atoms (Fig. I.4b). These fluorite-like structures can be considered as stacks of atomic layers, with individual blocks in the stack represented by an oxygen (O) – metal (M) – oxygen (O) motif (Fig. I.4c).

We consider first an ideal fluorite consisting of only one cation, say an M^{4+} cation, such that the compound stoichiometry is given by MO_2 . For this MO_2 fluorite compound, we define a hexagonal supercell as an alternative to the conventional cubic unit cell shown in Fig. I.4a. For an ideal MO_2 fluorite, the base of this hexagonal supercell is the prism

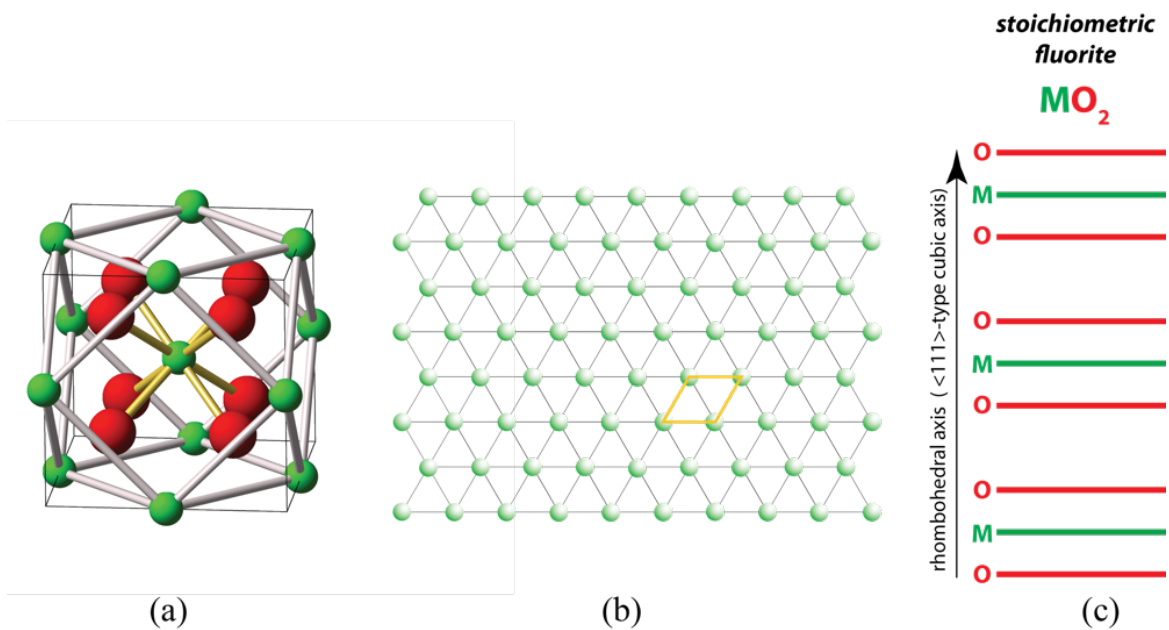


Figure I.4. Atomic Layered model (a) Schematic drawing of the cubic unit cell of a fluorite crystal structure with ideal stoichiometry, MO₂. Cations (M) are represented in green and anions (O for oxygen) in red. (b) A hexanet of M cations for an ideal MO₂ fluorite (hexanets occur in layers perpendicular to the <111> type cube axes, i.e. $\bar{3}$ axes in a fluorite). The prism highlighted in yellow is a hexcell representing the base of the hexagonal supercell used in the layered atom model description of an ideal MO₂ fluorite. (c) An edge-on schematic diagram showing the layer stacking motifs along axes the $\bar{3}$ axes in an ideal, MO₂ fluorite. M represent a pure cation layer; O a pure anion layer.

highlighted in yellow in Fig. I.4b. Heretofore, we will refer to such two-dimensional prisms within a hexanet atomic array as “hexcells.” The hexagonal supercell then consists of a 12-layer stacking of hexcells along a $\bar{3}$ crystal axis of the structure. These 12 layers consist of three metal (M) planes, six oxygen (O) planes and three empty planes. The arrangement of these layers is shown in Fig. I.4c. The resulting hexagonal supercell consists of three MO_2 formula units. There is also a registry shift between adjacent layers in the hexagonal supercell that repeats in a regular $ABCABC\dots$ pattern.

1.2.2 Atoms in Molecules (Bader analysis)

Using the framework of atoms-in-molecules (AIM) proposed by Bader [21], atoms are defined through a partitioning of real space with properties determined by the characteristics of the Hessian of electron charge distribution. The gradient of the electron density is used to define where one atom basin ends and the next begin. AIM theory provides a quantitative way to analyze the topology of the charge density ρ , by means of its first derivative $\nabla(\rho)$. At the critical points, this gradient vanishes. The characteristics of these points are determined by the Hessian of ρ . In extended solids, the Hessian is the (3x3) real and symmetric matrix of partial second derivatives. At a critical point, the eigenvalues of the Hessian are all real. The critical points are distinguished by their rank and signature. The rank is defined as the number of non-zero eigenvalues, while the signature is defined as the algebraic sum of the signs of the eigenvalues. For topologically stable critical points, the rank is always 3. The four possible critical points are: the nuclear critical point (3,-3), all curvatures negative, e.g. a local maximum that corresponds to an atom nucleus ; the bond critical point (3,-1) where two curvatures are negative and one is positive, a saddle point corresponds to interatomic bonding; the ring critical point (3,+1) and the cage critical point (3,+3), where all curvatures are positive being a local minimum of the electron charge density.

Associated with each critical point is a set of trajectories of $\nabla(\rho)$ that start at the critical point and terminate at another critical point (or at infinity in a molecule). They define a zero-flux interatomic surface, a surface that encloses each atom, resulting in a unique way of partitioning the crystal into separated atomic basins. Those surfaces are usually very far from a spherical shape that is the picture usually associated with an atom. The volume of each basin can be measured. Moreover, by integrating the electronic density within those basins where an atom nucleus is located (and eventually adding the electronic charge in nearby regions that do not include a nucleus), the total charge on an atom can be obtained. When two closed-shell atoms interact, as in the ionic picture, to fulfill the Pauli exclusion principle, the electron density is depleted from the interatomic surface and this kind of interaction is then characterized by a relatively low value of the electron density at the critical point while the charge is concentrated in each one of the atomic basins. Using the Bader-Essen rules [22] it is possible to identify the bonding nature. A negative value of the Laplacian at the bonding critical point indicates shared interactions (covalent bonding). In this case, the distribution of charge is dominated by the negative values of the curvature. The charge is concentrated along the line of interaction and shared by both nuclei. A positive value of the Laplacian indicates a closed shell interaction (ionic bonding), now

dominated by the positive curvature, contracting the charge towards the nuclei, and thus having a low value of ρ . The ratio of the principal curvatures $\frac{|\lambda_1|}{\lambda_3} \ll 1$ are characteristic of closed shell interaction [23].

1.2.3 Density Functional theory (DFT)

Ab-initio or first principle calculations only require structural and composition data, and there is no need for reference to experimental data [24]. They explicitly consider the individual interaction between atoms, via the interaction of nuclei and electrons. The motion of electrons is governed by the laws of quantum mechanics, described by the Schrödinger equation [25]. The Schrödinger equation determines the energy of a collection of atoms, and how it changes as they move. Due to the difference in mass between nuclei and electrons, the electrons respond almost instantaneously to the motion of the nuclei, and thus we can approximate it as the electrons moving in an environment of static nuclei. This is the Born-Oppenheimer approximation [26] which reduces the problem to a time independent equation, with nuclei at fixed positions. DFT is able to obtain the ground state energy and electronic structure of the material.

$$H\psi = E\psi \quad \text{Eq.I.1}$$

$$\left[-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V(r_i) + \sum_{i=1}^N \sum_{j<i} U(r_i, r_j) \right] \psi = E\psi \quad \text{Eq. I.2}$$

Where, m is the electron mass. The first term is the kinetic energy of each electron, the second the interaction between each electron and the nuclei, and the interaction between different electrons. The wave function ψ is a function of the spatial coordinates of each of the N electron, $\psi = \psi_1(r)\psi_2(r), \dots, \psi_N(r)$.

The density of electrons at a particular point in space $n(r)$ can be written as a in terms of wave functions individual electrons as,

$$n(r) = 2 \sum_i \psi_i^*(r)\psi_i(r) \quad \text{Eq. I.3}$$

The summation goes over all the individual electrons wave functions that are occupied by electrons. The term inside the summation is the probability of finding an electron at position r . The electron density $n(r)$ is a function of only 3 position coordinates.

1.2.3.1 Hohenberg-Kohn theorems

DFT is based on two fundamental theorems proved by Kohn and Hohenberg [27].

1. The ground state energy from Schrodinger's equation is a unique functional of the electron density.
2. The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrodinger equation.

This theorems state that the electron density uniquely determines the energy and wave function of the ground state. Solving the Schrödinger equation using the electron density means finding a function that only depends on 3 spatial variables, instead of $3N$ variables. The problem is that the form of the functional is not known, and approximate forms of the functional must be used. The functional in single electron wave functions can be written as,

$$E[\{\psi_i\}] = E_{known}[\{\psi_i\}] + E_{xc}[\{\psi_i\}] \quad \text{Eq. I.4}$$

where we have divided the functional in the terms which form is known, and the term whose form is unknown,

$$E_{known}[\{\psi_i\}] = -\frac{\hbar^2}{2m} \sum_i \int \psi_i^* \nabla^2 \psi_i d^3r + \int V(r) n(r) d^3r + \frac{e^2}{2} \int \int \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' + E_{ion} \quad \text{Eq. I.5}$$

The terms in the above equation are the electron kinetic energies, the Coulomb interaction between electrons and nuclei, the Coulomb interaction between electrons, and the Coulomb interaction between nuclei. The E_{xc} term is the exchange correlation functional.

1.2.3.2 Kohn-Sham equations

Kohn and Sham developed a set of equations to find the electron density [28], in which each equation involves a single electron. The solutions of these equations are single electron wave functions that only depend on three spatial variables.

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{xc}(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r) \quad \text{Eq. I.6}$$

Where the potential V defines the interaction of the electrons with the nuclei, V_H is the Hartree potential which describes the repulsion of one electron and the total electron density defined by all electrons. It includes a self-interaction contribution because the electron being described is also a part of the total electron density. Hartree-Fock methods constructs the many particle wave function from slater determinants of one electron spin orbitals. The correlation energy is the difference between the true energy and the Hartree-Fock energy.

$$V_H(r) = e^2 \int \frac{n(r')}{|r-r'|} d^3r' \quad \text{Eq. I.7}$$

The Kohn-Sham equations can be solved by a self-consistent procedure.

1. Define an initial, trial electron density, $n(r)$
2. Solve Kohn-Sham equations using the trial electron density to find the single particle wave functions $\psi_i(r)$.
3. Calculate the new electron density defined by the particle wave functions

$$n_{KS}(r) = 2 \sum_i \psi_i^*(r) \psi_i(r)$$

4. Compare the calculated electron density $n_{KS}(r)$ with the electron density used to solve the Kohn-Sham equations, $n(r)$.
5. Repeat cycle until convergence is reached.

1.2.3.3 Exchange correlation energy

The exchange correlation contains the many body effects missing from the independent-electron formulation of DFT. The many body electron interaction is the most difficult to calculate. The Coulomb interaction repels the electrons among each other. The energy of the system is reduced by having the electron apart from each other, but doing this increases the kinetic energy. Furthermore, due to the Pauli exclusion principle, there is repulsion of electrons with parallel spins, reducing the Coulomb energy of the system. This is the so-called exchange energy, and it cannot be evaluated exactly. The simplest approximation for the exchange correlation is the local density approximation (LDA) [29]. The LDA assumes that the exchange-correlation energy per electron in a system of electron with electron density is equal to the exchange correlation of a homogeneous electron gas. The LDA approximation works well with systems with slowly varying electron density. Another widely used approximation is the generalized gradient approximation (GGA). The GGA approach is an improved representation of the exchange correlation energy, it uses information about the local electron density and the local gradient of the electron density, to account for the effect of inhomogeneities. There exist several parametrizations of the GGA approach, the most commonly used are due to Perdew, Burke and Erzenhoff (PBE) [30], and Perdew and Wang (PW91) [31]. The LDA usually predicts smaller lattice constants than experiments, which results in cohesive energies that are too large, and also larger bulk moduli. GGA on the other hand, corrects this overbinding problem, but this results in an overestimation of the lattice constant [24, 32], which is accentuated in heavy elements.

1.2.3.4 Pseudopotentials

Core electrons are not fundamental in defining chemical bonding and other physical characteristics of a material. These properties are dominated by the valence electrons. A pseudopotential replaces the electron density from a chosen set of core electrons with a smoothed density chosen to match the properties established by the true ion core [32]. These are also known as frozen core calculations.

1.2.3.5 Limitations

DFT is a powerful method that allows the calculation of many physical properties of materials, but it also as with any technique has some limitations. It cannot handle large systems, the number of equations that are solved during a DFT simulation imposes a limitation on the number of atoms of the system. Currently with the most advanced computing resources DFT can handle between 600-1000 atoms. The system size limitation affects the properties can be studied, for example dynamics that depend on long range

interactions, or systems with multiple defects cannot be treated. The underestimation of the band gap is well known since this is an excited state property, and DFT is a ground state method. DFT provides the wrong band structure for elements with *d* and *f* orbitals [33].

1.2.3.6 Strongly correlated electrons.

To overcome the limitations mentioned in the previous section higher levels of theory must be used. Systems with strongly correlated electrons, such as compounds containing actinides or lanthanides are difficult to treat with conventional DFT. The unphysical repulsive interaction between the electron and itself (self-interaction energy) [24] is accentuated in systems with localized electrons. In the Hartree-Fock method the spurious self-interaction in the Hartree potential is exactly cancelled by the contribution from the energy exchange. Since DFT uses an approximate functional a systematic error arises due to the incomplete cancellation of the self-interaction energy. Self-interaction causes Kohn-Sham orbitals that are highly localized to be improperly destabilized with approximate exchange correlation functionals. Unpaired electrons tend to delocalize spatially in order to minimize self-interactions. When electronic states with many strongly localized electrons exist, these states are called strongly correlated, like actinides with partially filled *d* and *f* shells. DFT+U introduces a correction to the DFT energy that account for electron self-interaction by introducing a single numerical parameters *U-J*. This parameter is the effective Coulomb interaction, and is defined as the energy required to transfer an electron [34] same number of electrons in the *l* shell. The delocalized *s* and *p* electrons can be treated in the usual orbital independent one-electron approach. The *U* and *J* parameters can be obtained by taking a known property of some relevant material and determine which value of *U-J* gives the closest result to the chosen property.

$$E_{DFT+U} = E_{DFT} + \frac{U-J}{2} \sum_i n_{m,i} - n_{m,i}^2 \quad \text{Eq. 1.8}$$

Where $n_{m,i}$ is the occupation of the *m*-th *d* or *f* state.

1.2.4 Self-evolving kinetic Monte Carlo (SEAKMC)

Kinetic Monte Carlo (KMC) has been conventionally used to study defect evolution [35]. SEAKMC is an atomistic on-the-fly KMC method [11]. On-the fly refers that the saddle point configurations and energies are determined as the system evolves, and it presents several advantages over conventional KMC methods such as atomistic kinetic Monte Carlo (AKMC), and object oriented Monte Carlo (OKMC). Most AKMC depend on on-lattice approximations limiting their ability to describe systems where defects are not on lattice sites, such as interstitials, and more complex defect configurations. On the other hand, OKMC defects are considered as abstract objects with no atomistic details. With these approximation saddle points cannot depend on the defect configuration and the defect-defect interaction is not properly described. Both AKMC and OKMC require a defining list of possible mechanisms. SEAKMC has eliminated the requirement of predetermining the potential saddle points, the list possible processes evolve as the simulation progresses. It provides significant improvements over assumed simplified or artificial interactions used

in other models. SEAKMC focuses on defect interaction and evolution with atomistic fidelity and only requires an interatomic potential as input without assuming possible defect migration mechanisms and energies.

To perform the saddle point search SEAKMC utilizes the dimmer method [36, 37] directly without knowledge of the final state *a priori*. The dimer method is based on the harmonic approximation of transition state theory (HTST) [38, 39]. SEAKMC has been used to calculate self-diffusivity of interstitials and vacancies in bcc iron, and has showed to be in excellent agreement with MD simulations at low and intermediate temperatures, up to ~1000 K for vacancies, and ~600 K for interstitials [40]. At high temperatures result start to deviate from MD, this arises from the HTST formalism. The harmonic approximation describes the system well when it is close to ground state, as temperature increases the anharmonicity of atomic vibrations become more prominent.

A unique feature of SEAKMC is that the transition state searches are only performed within an active volume. An active volume defines a volume of interest in the system, for instance the volume around a point defect. Active volumes represent an increase in efficiency since the atoms involved in the search process are only the ones in the active volume instead of considering the whole system. Atoms that are far away from the defect will have very little effect, and thus have no impact on the accuracy of the calculations.

SEAKMC is able to study diffusion and microstructural evolution in alloys under irradiation with the kinetic Monte Carlo component of the code (KMC) [41]. KMC method employs a rigid lattice of atoms located at their crystallographic positions. The microstructural evolution is driven by the thermally activated migration of point defects by exchanging their positions with first nearest neighbor atoms. The migration direction is stochastically selected on the Monte Carlo method [35]. The probability of each event is given by,

$$\Gamma = D_0 \exp \left(-\frac{E^m}{kT} \right) \quad \text{Eq. I.9}$$

Where D_0 is the attempts frequency (set to 1×10^{12}), E^m the energy barrier, k is Boltzmann's constant, and T the absolute temperature. At each step one out of all possible events is chosen and the simulation time for a given event is evolved using time residence algorithm [42] by a quantity,

$$\Delta t = \frac{1}{\sum_i \Gamma_i} \quad \text{Eq. I.10}$$

I.3 Scope of the dissertation

In this dissertation, we have applied computational techniques to study the effects of the microstructural evolution on the crystallographic and electronic properties of the UO_2 nuclear fuel, and the radiation effects on the mechanical properties of iron based structural components. In particular, we have:

- 1) Investigated the structure of lanthanide based complex oxides that may be formed inside the nuclear fuel by the addition of fission products. We employed a layered model to propose different cation ordering arrangements in the La_2UO_6 , Ce_2UO_6 , LaUO_4 , and CeUO_4 complex oxides, and evaluated their stability using DFT.
- 2) Analyzed the electronic structure and bond nature of compounds where U atoms have a formal valence of 6+, particularly $\delta\text{-UO}_3$, $\gamma\text{-UO}_3$ and $\text{La}_6\text{UO}_{12}$ using the atom-in-molecule/Bader approach.
- 3) Studied the interaction of point defects with dislocations by calculating the real saddle point energy and configuration as a function of position with respect of the dislocation core for vacancies and $\langle 110 \rangle$ self-interstitial family of dumbbells in the presence of a single straight screw or edge dislocation, using the Self-Evolving Atomistic Kinetic Monte Carlo (SEAKMC) package. I also examined the defect anisotropy of diffusion and the range of interaction between point defects and dislocations.
- 4) Performed kinetic Monte Carlo (KMC) simulations using the real saddle point information as input data. This allowed to analyze the defect migration paths, and obtain an estimation of the dislocation bias factor.

CHAPTER I
**STRUCTURE AND CATION ORDERING IN La_2UO_6 , Ce_2UO_6 ,
 LaUO_4 , AND CeUO_4 BY FIRST PRINCIPLES CALCULATIONS**

A version of this chapter was originally published by L. Casillas-Trujillo, H. Xu, J.W. McMurray, D. Shin, G. Baldinozzi, K.E. Sickafus:

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In this chapter, I applied the atomic layered models for the studied compounds, performed all the DFT calculations, and performed the data analysis. Kurt Sickafus developed the layered model, supervised the structural models, and performed data analysis. Haixuan Xu supervised the computational simulations. J. McMurray and D. Shin contributed with the Calphad data in Figure 7. Gianguido Baldinozzi contributed with symmetry analysis, model development, data analysis and scientific discussion.

Abstract

In the present work, we have used density functional theory (DFT) and DFT+U to investigate the crystal structure and phase stability of four model compounds in the Ln_2O_3 - UO_2 - UO_3 ternary oxide system: La_2UO_6 , Ce_2UO_6 , LaUO_4 , CeUO_4 , due to the highly-correlated nature of the f -electrons in uranium. We have considered both hypothetical ordered compounds and compounds in which the cations randomly occupy atomic sites in a fluorite-like lattice. We determined that ordered compounds are stable and are energetically favored compared to disordered configurations, though the ordering tendencies are weak. To model and analyze the structures of these complex oxides, we have used supercells based on a layered atomic model. In the layer model, the supercell is composed of alternating planes of anions and cations. We have considered two different ordering motifs for the cations, namely single species (isoatomic) cation layers versus mixed species cation layers. Energy differences between various ordered cationic arrangements were found to be small. This may have implications regarding radiation stability, since cationic arrangements should be able to change under irradiation, with little cost in energy.

1.1 Introduction

During service in a light-water reactor, the chemistry of uranium dioxide (UO_2) fuel evolves to higher oxidation states of uranium with burn-up [5]. In addition, fission products, including rare earth elements, are simultaneously incorporated into the fuel matrix. At high burn-ups, this chemical evolution results in, among other things, the formation of complex (multi-component) oxides. Many of these oxides are encompassed within the ternary oxide system, Ln_2O_3 - UO_2 - UO_3 (where Ln stand for a Lanthanide species). Figure 2 shows the ternary phase space for oxide compounds consisting of mixtures Ln_2O_3 , UO_2 and UO_3 . In this diagram, we have highlighted a particular

compositional tie-line (shown in red) wherein the compositions maintain a 1:2 cation-to-anion stoichiometric ratio. Above this line, compounds are oxygen deficient and are characterized by the presence of large concentrations of oxygen vacancies. Below the red tie-line, compounds are oxygen rich, which leads to the presence of large interstitial oxygen atom concentrations. All Ln_2O_3 - UO_2 - UO_3 compounds of interest in this work possess compositions that lie on the red tie line in Fig. 1.1. Also, all of the atomic structures we consider are based on the fluorite (CaF_2) crystal structure.

Past studies of fuel composition evolution have been mainly devoted to the UO_2 - UO_3 tie line in Fig. 1.1, such that the oxidation state of U and the UO_{2+x} stoichiometry are the main considerations [43-45]. Among the complex oxides incorporating Ln species, the Ce_2O_3 - UO_2 - UO_3 system has received the most interest, since Ce is used as a surrogate for Pu in the study of mixed oxide (MOX) fuels. High temperature ternary phase stability diagrams for Ce-U-O have been developed by Lorenzelli *et al.* [46] and Markin *et al.* [47]. In addition, neutron powder diffraction characterization studies were performed on Ce-U-O for a range of compositions by Murray *et al.* [48]. Experimental studies on La_2O_3 - UO_2 - UO_3 oxides were performed in the seventies by Diehl *et al.* using high temperature x-ray diffraction [49], and Weitzel *et al.* [50] using neutron diffraction. More recently, Rojas *et al.* [51, 52] and Herrero *et al.* [53] synthesized a range of La-U-O compounds and characterized them using X-ray diffraction and transmission electron microscopy.

Computationally, density functional theory (DFT) studies of U compounds prove to be difficult due to the localized nature of the f -electrons, and the presence of local minima and metastable states [54]. In any case, there are numerous theoretical studies of uranium-bearing complex oxides published in the literature, such as calculations of the electronic structure of Uranium-Americium complex oxides using DFT by Suzuki *et al.* [55]. Another important study related to the work presented here involves molecular dynamics and DFT simulations of solid solutions of Ce_2O_3 - UO_2 - UO_3 by Hanken *et al.* [56, 57], to establish the energetics of cation mixing.

In this work we have used DFT to investigate the structure of four particular uranium lanthanide oxide compounds: La_2UO_6 , Ce_2UO_6 , $LaUO_4$, and $CeUO_4$. We have used a layered model to examine different cation ordering arrangements. Due to the highly correlated nature of the f -electrons in uranium, we have employed the DFT+U methodology for our calculations.

1.2 Methods

1.2.1 Geometrical models

In our calculations, we used a primitive rhombohedral supercell, related to the hexagonal supercell, but with one-third the volume of the hexagonal cell. The primitive rhombohedral supercell reduces the computational time required for the *ab initio* calculations. We consider here two model representations of ordered atomic structures: (i) the first model consists of alternating single species (“isoatomic” or “pure”) cation layers; (ii) the second

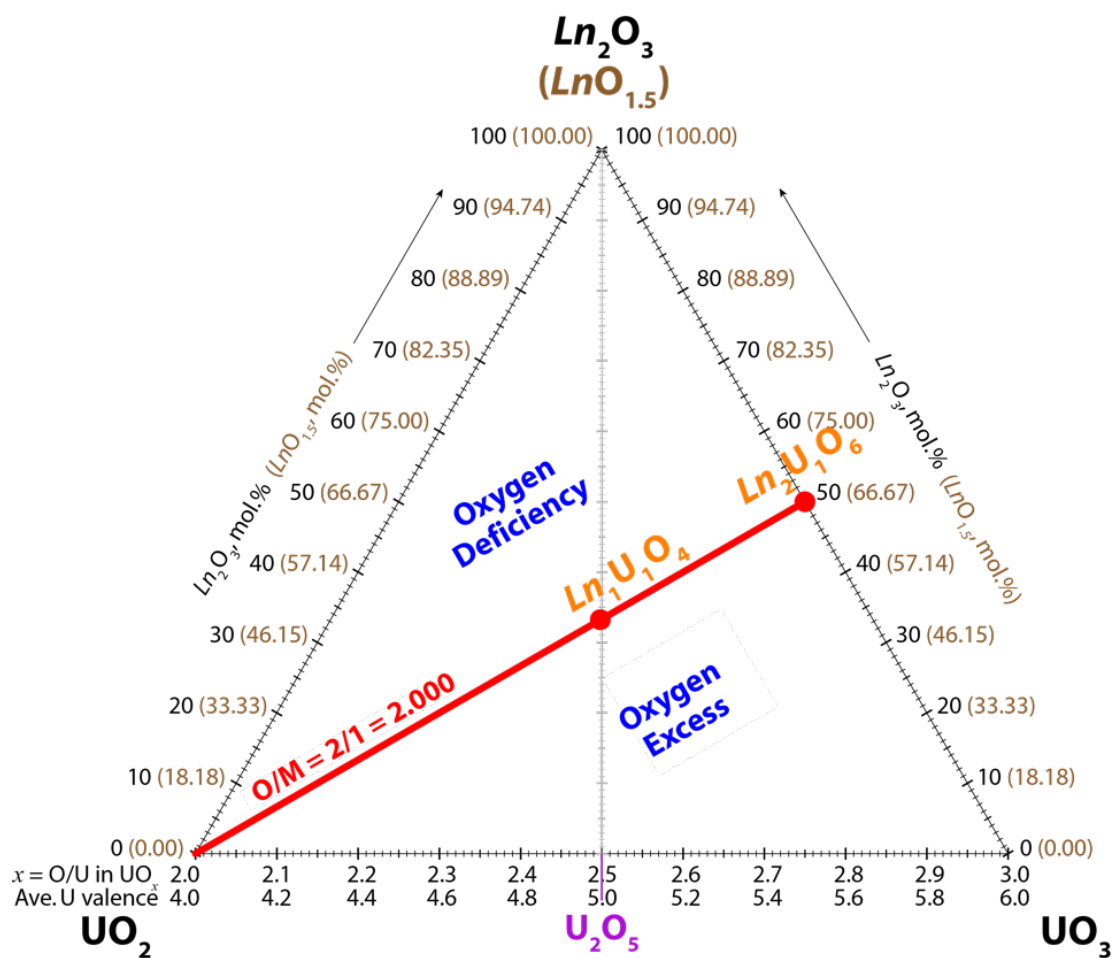


Figure 1.1. UO_2 - UO_3 - Ln_2O_3 ternary compositional space encompassing both real and hypothetical $n\text{Ln}_2\text{O}_3 \cdot (1-n)\text{UO}_x$ or $m\text{LnO}_{1.5} \cdot (1-m)\text{UO}_x$ compounds (Ln = lanthanide species). The red tie line indicates where compounds with an oxygen-to-metal ratio $\text{O/M}=2/1$ are located. Below this tie line are oxygen-rich compounds; above the line, compounds are oxygen deficient. Also shown are the compositional positions of two hypothetical compounds of interest in this study: LnUO_4 and Ln_2UO_6 .

model is characterized by two species (“mixed”) cation layers, with ordered atomic patterns within the layers. Figure 1.2 illustrates the difference between our pure and mixed layer models. Fig. 1.2a shows an inclined projection of layer stacking based on the pure layered atom model. Fig. 1.2b shows an inclined projection of layer stacking in a mixed layer atom model, where both cation species occupy sites in the same plane. Fig. 1.2c shows a single mixed cation plane from Fig. 1.2b in “plan-view”. The specific configuration shown in Fig. 1.2c corresponds to an Ln_2UO_6 -type compound. All of the cation planes in the mixed layer model for the Ln_2UO_6 structure possess the same atom pattern as shown in Fig. 1.2c. The highlighted hexcell in Fig. 1.2c indicates the fundamental repeat unit of the atom pattern. Notice that there are 3 atoms per hexcell for this compound.

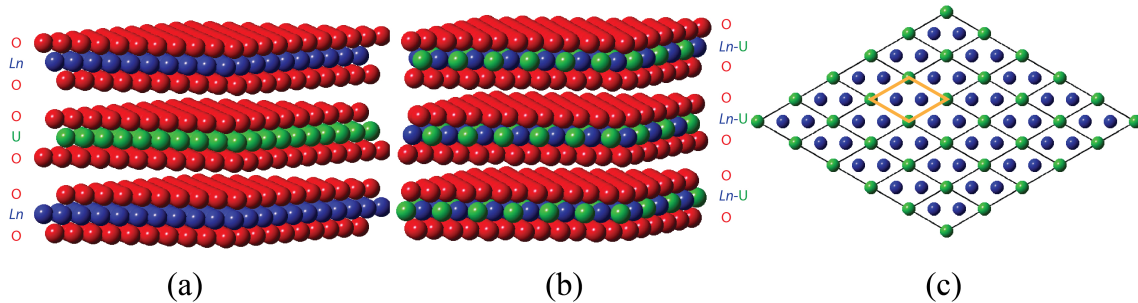


Figure 1.2. (a) Inclined view of oxygen-metal-oxygen (O-M-O) blocks in the “pure” cation layer model for Ln_2UO_6 . The Ln cations are shown in blue, U cations in green, and O anions in red. (b) Inclined view of O-M-O blocks in the “mixed” cation layer model for Ln_2UO_6 . (c) Plan-view of one cation layer in the mixed cation layer model for Ln_2UO_6 . The black lines are the traces of the hexagonal supercells through the plane of cations. The drawing shows a 6×6 hexagonal supercell array. The prism highlighted in yellow represents one hexcell, the dimensions of which represent the base of the corresponding hexagonal supercell used in the layered atom description of this compound.

It should be noted here that for any particular Ln - U - O compound of interest, the volume of the hexagonal supercell and the number of formula units per supercell (denoted Z), may not be the same as for the ideal, MO_2 fluorite. As mentioned above, the hexcell defining the area of the base of the hexagonal supercell may be larger than in MO_2 . Also, the number of layers along the c -axis may not always be 12, as described for ideal MO_2 above. For example, the ordered-pure cation layer model associated with $LnUO_4$ compounds requires a 24 layer stacking sequence along the z direction (i.e., the crystallographic c -axis), in order to obtain a complete repeat of the atomic structure (this is due to a combination of layer chemistry and $ABCABC$ registry shift between layers).

1.2.2 Computational details

For our DFT calculations, we employed the generalized gradient approximation (GGA) exchange correlation functional due to Perdew–Burke–Erzenhof (PBE) [58], and the PBE version revised for solids [59] in their standard and “soft” versions. The uranium $6s^2 6p^6$

$5f^3 6d^1 7s^2$, the lanthanum $5s^2 5p^6 5d^1 6s^2$, the cerium $5s^2 5p^6 4f^1 5d^1 6s^2$, and the oxygen $2s^2 2p^4$ electrons are treated as valence electrons. The electron-ion interaction is described by the projector augmented wave method (PAW) [60], and the plane wave basis energy cutoff was set to 500 eV. The Vienna *ab initio* package VASP [61, 62] was employed to perform the simulations. We used a $4 \times 4 \times 4$ k-point sampling grid. To account for the strongly-correlated *f*-electrons we employed the DFT+U approach on uranium atoms in the rotationally invariant Dudarev formulation [63] with parameters for U and J of 4.5 and 0.51 eV, respectively. The latter parameters were originally derived by Dudarev[34], based on experimental measurements, and have since been widely applied to uranium-based compounds [64-67]. To simulate the in-plane cation disorder (heretofore, referred to as our “disordered” model) we employed a $4 \times 4 \times 1$ supercell, wherein we distributed the cations randomly. The structures were fully relaxed with no symmetry constraints until the magnitude of the forces was below 10^{-2} eV/Å or until the internal energy was at least converged to 10^{-5} eV.

1.3 Results

Figure 1.3 shows a calculated energy comparison, based on DFT simulations, between three different models for cation arrangements in the compound, La_2UO_6 : (i) an ordered model with *mixed* cation layers; (ii) an ordered model with *pure* (isoatomic) cation layers; and (iii) a *disordered* model with random arrangements of La and U in the cation layers. We used both standard DFT (Fig. 1.3a) and DFT+U (Fig. 1.3b) to assess structural stability. In doing so, we employed four different pseudopotentials: (i) PBE; (ii) PBE for solids [59]; (iii) a “soft” version of PBE; and (iv) a “soft” version of PBE for solids. It should be noted that we chose La_2UO_6 for this pseudopotential comparison because the cations in this compound (La^{3+} and U^{6+}) contain closed shell electronic configurations.

Figs. 1.3a and 4b show that the different flavors of pseudopotentials produce the same hierarchy of energies for the various structural models, though there are significant differences in the magnitudes of the energies between the different pseudopotentials. Using standard DFT (Fig. 1.3a), the hierarchy of structures (from lowest to highest energy) is ordered-mixed layers < ordered-pure layers < disordered layers. DFT+U (Fig. 1.3b) finds a different hierarchy: ordered-pure layers < ordered-mixed layers < disordered layers. Because the hierarchy of the calculated energies is the same within a given simulation methodology (namely, DFT or DFT+U), we decided to use PBE exclusively for the remainder of the calculations performed in this study (primarily because PBE is the most widely employed of the pseudopotentials in the literature).

Figure 1.4 shows computational results obtained using DFT/PBE and DFT+U/PBE for the energies of different lanthanide uranium oxides: (a) La_2UO_6 , (b) Ce_2UO_6 , (c) LaUO_4 , and (d) CeUO_4 . In Fig. 1.4, two trends are noteworthy. First, in all compounds DFT produces substantially lower energies than DFT+U. This is to be expected from the incorporation of the correction term of the DFT+U approach. Second, our simulations indicate that in all

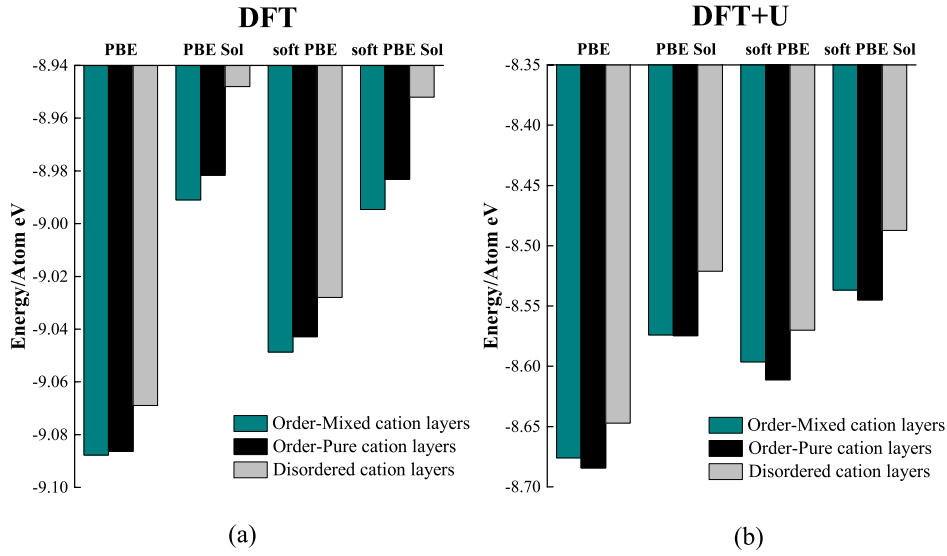


Figure 1.3. Structure stability of La_2UO_6 , based on (a) standard DFT and (b) DFT+U calculations, for four different pseudopotentials: (i) PBE; (ii) PBE for solids; (iii) a “soft” version of PBE and (iv) a “soft” version of PBE for solids.

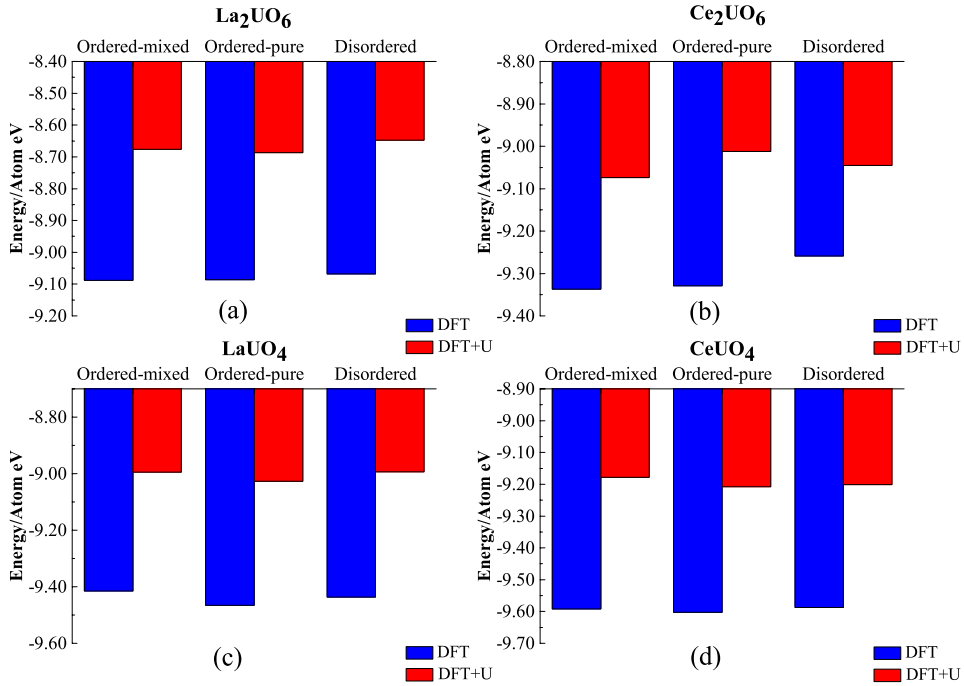


Figure 1.4. Phase stability results for (a) La_2UO_6 , (b) Ce_2UO_6 , (c) LaUO_4 , and (d) CeUO_4 using DFT and DFT+U for the different proposed ordered and disordered structures. The PBE pseudopotential was used for all calculations.

compounds, an ordered cation structure is preferred compared to a disordered arrangement of cations. For instance, for LaUO_4 (Fig. 1.4c) and CeUO_4 (Fig. 1.4d), both standard DFT and DFT+U find that an ordered-pure layer structure is preferred over either an ordered-mixed layer cation configuration or a disordered cation arrangement. In the case of La_2UO_6 (Fig. 1.4a), DFT and DFT+U results indicate that ordering, be it mixed cation layers or pure cation layers, is preferred over disordering. However, they do not agree on the specific ordered arrangement with the lowest energy. DFT predicts an ordered-mixed layer structure, while DFT+U indicates the ordered-pure layer structure is preferred. However, the energy differences between the ordered phases (in both DFT and DFT+U calculations) are too small to establish a definitive preference. Finally, for Ce_2UO_6 (Fig. 1.4d) both DFT and DFT+U predict that the ordered-mixed layer structure is the lowest energy option among the various structural models. However, DFT and DFT+U are not in agreement as to the next most favorable structure. DFT suggests that the ordered-pure layer structure is more favorable than the disordered structure, and vice versa for DFT+U.

Table 1.1 summarizes the quantitative differences in energy between the *preferred* ordered structure for each of the compounds considered in this study, versus the corresponding disordered structure. The energy difference between the ordered (*O*) and disordered (*D*) structure is a measure of the *ordering tendency* for each particular compound. The results indicate that in all cases an ordered structure is preferred, but the energy differences between the structures are small.

Table 1.1. Energy difference, ΔE , between the preferred ordered (*O*) structure versus the corresponding disordered (*D*) structure for each of the compounds investigated in this study.

	ΔE (eV/atom)	
	DFT	DFT+U
La_2UO_6	-0.0198	-0.0398
Ce_2UO_6	-0.0781	-0.0285
LaUO_4	-0.0292	-0.0325
CeUO_4	-0.0153	-0.0065

Table 1.2 shows the lattice constants for the hexagonal unit cell of the lowest energy structures for both DFT and DFT+U for each of the compounds studied in this work. The *c/a* ratio has been obtained and compared with the ideal *c/a* ratio. For the division by 3rds 12-layered unit cell used in the Ln_2UO_6 compounds, the ideal *c/a* ratio is 1.414, and for the division by 4ths 24-layered unit cell used in the LnUO_4 compounds, it is 2.449. In general, the deviation from ideality is greater for lanthanum-based compounds, since the lanthanum ion is larger than the cerium ion. The only exception to this trend occurs for the DFT+U La_2UO_6 , where La_2UO_6 possesses the pure cation layered structure, while Ce_2UO_6 the mixed cation layered structure (i.e., for lowest energy structures).

Table 1.2. Lattice parameters for the lowest energy structures for each of the Ln -U-O compounds for DFT and DFT+U.

	DFT				DFT+U			
Lattice constant	a(Å)	c(Å)	c/a	$\Delta c/a$	a(Å)	c(Å)	c/a	$\Delta c/a$
La ₂ UO ₆	6.804	9.992	1.469	0.054	6.924	9.563	1.381	-0.033
Ce ₂ UO ₆	6.650	9.514	1.431	0.016	6.722	9.525	1.417	0.003
LaUO ₄	7.854	19.454	2.477	0.027	7.945	19.583	2.465	0.015
CeUO ₄	7.724	18.878	2.444	-0.005	7.768	19.080	2.456	0.007

Table 1.3 shows the volume per atom, Ω_a , for the lowest energy ordered configuration for each compound considered in this study. Also shown in Table 1.3 are calculated results for Ω_a in the disordered structure for each compound, as well as the change in atomic volume, $\Delta\Omega_a$, upon an $O \rightarrow D$ transformation. For comparison, literature values for experimentally measured atomic volumes associated with the parent (end-member) compounds are as follows: 13.624 Å³ for UO₂ (fluorite structure) [68]; 18.0625 Å³ for δ -UO₃ (ReO₃ structure) [69]; 16.482 Å³ for La₂O₃ (A-type La₂O₃ structure) [70]; 17.216 Å³ for Ce₂O₃ (bixbyite structure) [71] and 13.204 Å³ for CeO₂ (fluorite structure) [72]. The Ω_a values shown in Table 1.3 are closest to those of fluorite-type structures listed above.

Table 1.3. Volume per atom, Ω_a , for the lowest energy ordered (*O*) structure, the disordered (*D*) structure, and the percent change in atomic volume between the *O* and *D* structures for each compound investigated in this study.

	Ω_a - ordered (Å ³ /atom)		Ω_a - disordered (Å ³ /atom)		$\Delta\Omega_a/\Omega_a \times 100$ (<i>O</i> $\rightarrow$ <i>D</i>) (%)	
	DFT	DFT+U	DFT	DFT+U	DFT	DFT+U
La ₂ UO ₆	13.768	14.710	14.095	14.362	-2.377	2.361
Ce ₂ UO ₆	13.511	13.770	13.455	13.757	0.415	0.093
LaUO ₄	14.009	14.322	15.224	15.356	-8.672	-7.223
CeUO ₄	13.459	13.882	13.461	13.882	-0.019	-0.002

1.4 Discussion

Our calculations indicate that all compounds prefer ordered (*O*) structures over disordered (*D*) structures. However, we predict that $O \rightarrow D$ transformation energies and volume changes are small. This implies that the *Ln*-U-O compounds we have investigated may be readily thermally disordered, or disordered by other energetic influences such as radiation damage. Small $O \rightarrow D$ energy and volume changes also may be indicators for high radiation tolerance (less stored energy between atomic configurations). Our calculations suggest that different atomic configurations are characterized by shallow minima in the energy landscape. If the energy barriers between these minima are also small, this implies that point defects may anneal at low temperatures.

We also find it interesting to consider in more detail the atomic dilations predicted by our first principles calculations. Atomic dilations lead to structural deviations of our *Ln*-U-O compounds compared to the *ideal* geometry of a cubic, MO₂ fluorite (Fig. 1a). Some of these dilations can be understood in the context of standard crystal chemistry concepts such as ion size, valence and coordination. To illustrate this, we consider the 1st and 2nd nearest neighbor environments of a central U cation in the four *Ln*-U-O compounds considered in this study.

Regarding 1st nearest neighbors, Fig. I.2a illustrates that in an ideal fluorite, a central M cation is surrounded by eight 1st nearest neighbor O anions in a *regular*, simple cubic geometry. The ideal $\overline{\text{MO}}$ bond distance for these 1st nearest neighbor anions in fluorite is $\sqrt{3}a/4$, where a is the cubic lattice parameter. Alternatively, the ideal $\overline{\text{MO}}$ distance in fluorite is related to the interatomic spacing, d , in the pseudo-close-packed cation (or anion) hexanets (Fig. I.2b), according to the relationship, $\overline{\text{MO}} = \sqrt{3/8} d$, where $d = a/\sqrt{2}$. However, in our $Ln\text{-U-O}$ complex oxides, the $\overline{\text{MO}}$ bond length becomes degenerate (the $\angle\text{OMO}$ bond angle also becomes degenerate). Table 1.4 shows the $\overline{\text{MO}}$ degeneracy for the lowest energy ordered structures for La_2UO_6 and Ce_2UO_6 , as presented in the previous section. In both La_2UO_6 and Ce_2UO_6 , the bond length degeneracy leads to $\overline{\text{MO}}$ bonds that are both shorter and longer than in ideal fluorite. The deviations from ideality (i.e., differences between the minimum and maximum $\overline{\text{MO}}$ bonds lengths in the two compounds) are much larger for La_2UO_6 (~12%) compared to Ce_2UO_6 (~0.5%). This discrepancy between La and Ce may be due to reduction-oxidation (*redox*) effects. Specifically, we anticipate a large valence disparity between La and U in La_2UO_6 , with La adopting its only known oxidation state, namely La^{3+} , leaving U to assume a formal valence of U^{6+} . This formal valence disparity leads to a small U^{6+} cation which, by Pauling's first rule for coordination chemistry [73], desires a "small cage" of 1st nearest neighbor O^{2-} anions surrounding the highly-charged, U^{6+} cation. In accordance with this rule, our calculations indicate that for the lowest-energy structure for La_2UO_6 , trends towards a 6-fold distorted octahedral 1st nearest neighbor anion coordination geometry, rather than the 8-fold cubic geometry found in ideal fluorite.

Table 1.4. The eight 1st nearest neighbor $\overline{\text{UO}}$ bond distances in the lowest energy ordered structures for La_2UO_6 and Ce_2UO_6 .

$\overline{\text{UO}}$ distance (Å)	
La_2UO_6	Ce_2UO_6
2.185	2.382
2.185	2.375
2.185	2.385
2.185	2.382
2.262	2.386
2.262	2.375
2.492	2.378
2.492	2.378

The story for Ce cations in Ce_2UO_6 is quite different compared to La. Ce readily assumes two distinct formal cationic valences, namely 3+ and 4+ (depending on the partial pressure

of O₂). Thermodynamic data [74] indicate that over a very wide range of temperatures and partial pressures of O₂, Ce₂O₃ serves as a reducing agent for UO₃, such that U⁶⁺ cations in UO₃ are reduced to a lower valence, while Ce itself is oxidized from the 3+ towards the 4+ oxidation state (i.e., Ce₂O₃ transitions towards CeO_{2-x}). This redox effect is illustrated in the calculated “Ellingham” type diagram shown in Figure 1.5. This redox reaction trend implies that both Ce and U in Ce₂UO₆ assume more similar valence states during compound formation (perhaps close to 4+). This, in turn, implies that the cationic radii of Ce and U in Ce₂UO₆ are more similar than are La and U in La₂UO₆, because their valences are more similar (closer to 4+/4+ compared to 3+/6+). Thus, the dilations away from the ideal fluorite 8-fold simple cubic anion coordination polyhedra in Ce₂UO₆ are less pronounced than in La₂UO₆. To summarize: U⁴⁺ in Ce₂UO₆ is content in pseudo-8-fold coordination, whereas U⁶⁺ in La₂UO₆ is not (U⁶⁺ preferring a smaller coordination polyhedron, such as a distorted octahedron). We have estimated the difference in valence states by performing bond-valence sums, proposed by Altermatt and Brown [75] and Brown and Altermatt [76]. The cation valence difference that we calculate for La and U cations is 1.64 electron charge units, compared to a much smaller calculated cation difference for Ce and U of 0.86 electron charge units. This is consistent with our anticipation of a larger valence disparity for La-U vs. Ce-U, based on our calculated bond length dilatations, which are much larger for La-U than for Ce-U.

It is also important to note that Hanken *et al.* [56] performed similar DFT simulations to ours in Ce_xU_{1-x}O₂ compounds, including both the Ce₂UO₆, and CeUO₄ stoichiometries reported here. In Ce₂UO₆, and CeUO₄, Hanken *et al.* found very similar average cation-anion bond distances compared to our results. Specifically, they reported average $\overline{\text{MO}}$ distances of 2.39 Å, compared to our average of 2.38 Å (this is the case for their “ideal charge state” (ICS) model calculations). In addition, Hanken *et al.* considered two cation ordering models equivalent to our pure layer models (namely their “CdI₂” and “CuPt” FCC prototypes described in their report).

Next, we consider the 2nd nearest neighbors in our *Ln*-U-O complex oxide structures. Fig. 1.6a shows that the 2nd nearest neighbors to the central cation in an ideal MO₂ fluorite are cations, which occur in regular, *cubeoctahedral* geometry. There are 12 of these 2nd nearest neighbor M cations surrounding the central M cation in the cubic unit cell. The lengths of these $\overline{\text{MM}}$ 2nd nearest neighbor bonds in ideal fluorite are given by $d = a/\sqrt{2}$, where a and d are defined as before. As with the previous discussion, the $\overline{\text{MM}}$ bond lengths in our *Ln*-U-O complex oxides become degenerate. However, the bond length dilations and the distortions to the cuboctahedral coordination can be partially rationalized in terms of simple crystal chemistry principles.

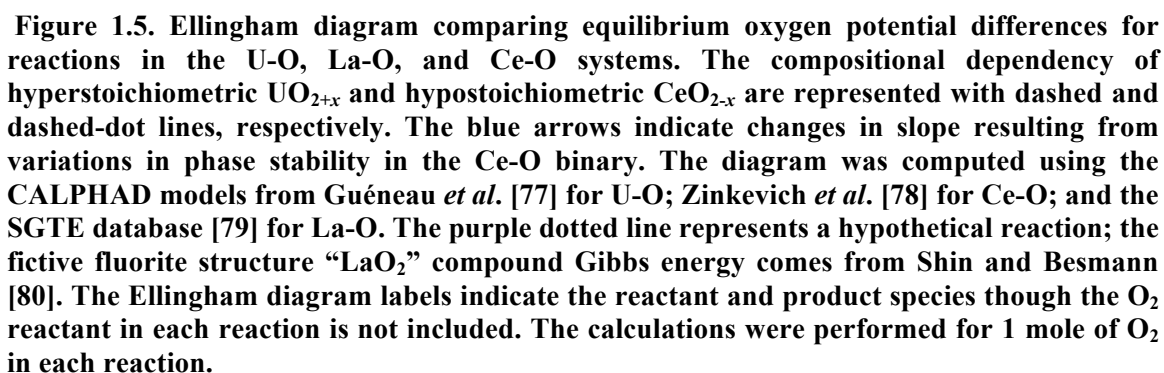


Figure 1.6 shows the 2nd nearest neighbor cubeoctahedron coordination polyhedron for a central U cation in the La_2UO_6 and Ce_2UO_6 compounds, for the pure cation layer model (Fig. 1.6a), and for the mixed cation layer model (Fig. 1.6b). In the pure layer model, there are 6 U atoms and 6 Ln atoms surrounding the central U cation. These atoms are arranged in layers within the cubeoctahedron, the 6 U atoms occupying the equatorial plane of the coordination polyhedron, while 3 Ln atoms are located above and 3 Ln below this layer of U atoms. Since the U cations are more highly charged than the Ln cations (especially for La versus U), electrostatic repulsion principles suggest that we should expect the U cations in the equatorial plane to dilate outwards, away from the central U cation, more so than the less charged Ln cations above and below this plane. The net effect should be a distorted, *ellipsoidal* 12-fold coordination polyhedron that is expanded around the equatorial plane, while the poles of the polyhedron should appear more flattened. In terms of bond lengths, our expectation is that the $\overline{\text{UU}}$ bonds will be longer than the $\overline{\text{LnU}}$ bonds. Similar arguments hold for the mixed layer model cubeoctahedron (Fig. 1.6b). In this case, there are only 2 U atoms, arranged on opposite sides of the central U atom in a linear configuration. For this configuration, the cubeoctahedron should again suffer an ellipsoidal distortion, but in this case, the distortion should be such that the 12-fold coordination polyhedron is longer along the U-U-U chain of atoms. Once again, in terms of bond lengths, we expect the $\overline{\text{UU}}$ bonds to be longer than the $\overline{\text{LnU}}$ bonds. We also performed similar analyses on the LnUO_4 compounds (results not shown here).

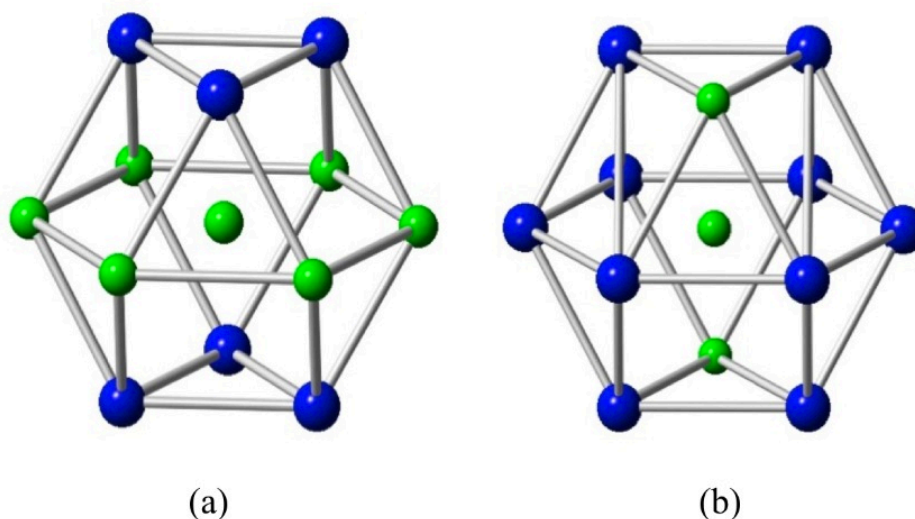


Figure 1.6 (a) 2nd nearest neighbor cation coordination polyhedron in Ln_2UO_6 , based on the ordered-*pure* layer model; (b) 2nd nearest neighbor cation coordination polyhedron in Ln_2UO_6 , based on the ordered-*mixed* layer model. In these drawings, U cations are green, while Ln cations are blue.

Table 1.5 shows the calculated bond lengths for both the pure and mixed layer models for La_2UO_6 and Ce_2UO_6 . The distortion effects are small, irrespective of the particular cation ordering model. For the La_2UO_6 compound, the $\overline{\text{UU}}$ bonds are $\sim 2\%$ larger than the $\overline{\text{LaU}}$ bonds in the pure cation layer model, and $\sim 1.3\%$ larger in the mixed cation model. For Ce_2UO_6 the $\overline{\text{UU}}$ and $\overline{\text{CeU}}$ bond distances are almost the same in magnitude, with only a $\sim 0.3\%$ difference. As it was discussed before, the similar distances may be due to the similar valence states of U and Ce. The small distortions may indicate that 2nd nearest neighbors M-M interactions are screened effectively by the intervening 1st nearest neighbor oxygen anions. Also, polarization of the O anions may play a role in decreasing the M-M distortion effects.

Table 1.5. Average 2nd nearest neighbor distances, $\overline{\text{UU}}$ and $\overline{\text{LnU}}$, in the Ln_2UO_6 compounds investigated in this study.

	Ordered-pure layers		Ordered-mixed layers	
	$\overline{\text{UU}}$ (Å)	$\overline{\text{LnU}}$ (Å)	$\overline{\text{UU}}$ (Å)	$\overline{\text{LnU}}$ (Å)
La_2UO_6	3.998	3.967	4.037	3.947
Ce_2UO_6	3.888	3.890	3.892	3.887

1.5 Conclusions

We have used a layered atom model approach to propose candidate ordered structures for the compounds La_2UO_6 , Ce_2UO_6 , LaUO_4 , and CeUO_4 . We then performed first principles calculations (DFT and DFT+U) to assess the relative structural stabilities of these model structures. Both standard DFT and DFT+U indicate a lower energy for an ordered phase in each of these model compounds. That is to say, for each compound that we investigated, an ordered structure is energetically preferred compared to a disordered structure. The energy differences between the different ordered structures that we considered are too small to reliably discern an ordered structure preference. For instance, for the La_2UO_6 compound, standard DFT indicates a preference for mixed cation layers, while the DFT+U method prefers the pure (isoatomic) cation layer model.

For the Ln-U-O compounds examined in this chapter, the distortions from ideality in the 1st and 2nd nearest neighbor polyhedra are in accord with crystal chemistry predictions. In the case of the Ce-U-O compounds, we found very small 1st nearest neighbor dilations from

ideality ($\sim 0.5\%$ variation in $\overline{\text{CeO}}$ bond lengths). This may indicate that Ce and U possess similar oxidation states in these compounds. In the La-U-O compounds, the 1st nearest neighbor dilations were more substantial ($\sim 12\%$ variation in $\overline{\text{LaO}}$ bond lengths), suggesting that the La and U oxidation states are more dissimilar in the La-U-O compounds, compared to Ce and U in the Ce-U-O compounds. Similar trends were found for the 2nd nearest neighbor coordination polyhedra. In La_2UO_6 the $\overline{\text{UU}}$ bonds are larger than the $\overline{\text{LaU}}$ bonds (by $\sim 2\%$), while in Ce_2UO_6 the $\overline{\text{UU}}$ bonds and the $\overline{\text{CeU}}$ bonds are very close in magnitude. Once again, this is likely due to the less charge disparity between Ce and U, versus La and U.

In the future, we plan to improve our simulation methodology for the disordered structure calculations, by increasing the system size and implementing the special quasirandom structures (SQS) approach [81]. The SQS method has recently been successfully employed by Wolff-Goodrich[82] to examine random solid solutions in the La-U-O system.

CHAPTER II
**A COMPARISON OF BONDING AND CHARGE DENSITY IN δ -UO₃,
 γ -UO₃, AND LA₆UO₁₂**

A version of this chapter was originally published by L. Casillas-Trujillo, G. Baldinozzi, M.K. Patel, H. Xu and K.E. Sickafus:

Casillas-Trujillo, L., Baldinozzi, G., Patel, M. K., Xu, H., & Sickafus, K. E. Comparison of bonding and charge density in δ -UO₃, γ -UO₃, and La₆UO₁₂. *Physical Review Materials*, 1(6) (2017), 065404.

In this chapter, I performed the DFT calculations to obtain the electron charge density, applied the Atom-in-molecule approach, performed the critical point search, and basin integrations. Kurt Sickafus contributed with data analysis and scientific discussion of the bond valence sums. Gianguido Baldinozzi contributed with the theory, and implementation of the AIM approach, data analysis and scientific discussions. Haixuan Xu supervised the computational simulations. Maulik Patel contributed with scientific discussions.

Abstract

This computational study examines the effect of local atomic environments on the electron charge density in δ -UO₃, γ -UO₃ and La₆UO₁₂. In particular, this study reveals differences in the uranium local atomic environments in these model oxide compounds. To examine the differences in a quantitative way, atoms-in-molecule (AIM) and Bader analysis methods were used to interrogate the electron charge density. The electron charge density distribution in each compound was obtained using density functional theory (DFT). The AIM/Bader analyses provided estimates for the so-called Bader charges on individual lattice atoms, as well as the locations of the bond critical points (BCPs) between bonding atoms and the charge densities at the BCPs. Calculation results revealed a quantitative inverse correlation between the charge density at the BCP and the U-O bond length. In addition, this inverse correlation was found to be surprisingly similar to a well-established crystal chemical relationship between bond strength and bond length.

2.1 Introduction

Complex uranium oxide atomic structures are formed during the life cycle of uranium dioxide (UO₂) nuclear fuel [83]. Fission products, especially lanthanide species are incorporated into the UO₂ matrix as the fuel ages. One suspects that the stability and durability of the fuel may be influenced by local atomic arrangements in the vicinity of individual U atoms in the fuel. First principles computational methods offer a mean to interrogate such local atomic environments in complex materials, and in particular, to determine the equilibrium electron charge density. In this context, it is possible to analyze the calculated electron charge density using so-called atoms-in-molecule (AIM) methods [21], in an effort to gain additional “chemical” insight, such as bonding ionicity or covalency. Such information may help us to better understand atomic structural stability

and even, perhaps, to predict material stability in extreme environment applications such as nuclear energy production.

AIM analyses are commonly employed in chemistry to study charge distribution in molecules, but AIM has also been used to examine electronic charge distributions in crystalline solids. Many AIM-related studies have been performed on a wide variety of materials such as cuprates [84], beryl [85], spodumene [86], lithium-based compounds [23, 87-90], silicates [91, 92], and oxides [93]. For compounds incorporating heavy elements such as lanthanides and actinides, assessment of the charge density via experiments is often difficult. Thus, computational simulation is an attractive alternative. In particular density functional theory (DFT) is capable of obtaining the electron charge densities of compounds containing heavy elements. AIM analyses (and related Bader analysis procedures) in the form of the charge basin integration have been performed on heavy element bearing oxides such as UO_2 [94, 95] and $\text{Ln}_2\text{Tc}_2\text{O}_7$ [96] (where Ln stands for a lanthanide species), but to date no study has analyzed the characteristics of the charge density at the critical points.

In this chapter, we use the AIM/Bader approach, heretofore abbreviated AIM-B, to analyze quantitatively specific features of the electron charge density in three model uranium (U) bearing oxide compounds: (i) $\delta\text{-UO}_3$; (ii) $\gamma\text{-UO}_3$; and (iii) $\text{La}_6\text{UO}_{12}$. These compounds are related in the sense that U atoms in each compound have a “formal” valence of 6+, and possess a closed-shell electronic configuration. We first obtain the electron charge density distributions using DFT. With this, we calculate the Bader charges and obtain the nature of the bonds via analyses of the principal curvatures of the charge density at the bonding critical points, as well as the Laplacian magnitude at these bonding critical points.

2.2 Structural models

$\delta\text{-UO}_3$ possesses a cubic ReO_3 -type crystal structure with one formula unit per unit cell. $\delta\text{-UO}_3$ belongs to space group $Pm\bar{3}m$ (S.G. no. 221), with a U atom at Wyckoff equipoint $1a$, and an O atom at Wyckoff equipoint $3d$ [97]. In this structure, the fundamental coordination polyhedron associated with each U atom is a regular octahedron with 2.097 Å nearest neighbor U-O bond distances, and 90° O-U-O bond angles (calculation results, this study). The crystal structure of $\delta\text{-UO}_3$ is shown in Figure 2.1. All octahedra are corner sharing in $\delta\text{-UO}_3$.

$\gamma\text{-UO}_3$ is the most thermodynamically stable polymorph of UO_3 [98], and it is the most complicated crystal structure among the compounds in this study. $\gamma\text{-UO}_3$ possesses an orthorhombic crystal structure and belongs to space group $Fddd$ (S.G. no. 70). In this chapter, we use the standardized crystal structure convention, such that the structure of $\gamma\text{-UO}_3$ is described in the 2nd setting of space group $Fddd$, such that the unit cell origin is on a center of symmetry (point symmetry $\bar{1}$) at Wyckoff special equipoint $16c$. The $\gamma\text{-UO}_3$ orthorhombic unit cell contains 32 formula units. Figure 2.2 shows the crystal structure of $\gamma\text{-UO}_3$. There are two distinct U sites: U1 at Wyckoff special equipoint $16g$ and U2 at equipoint $16c$ on the unit cell origin. There are three distinct O sites, all utilizing the general

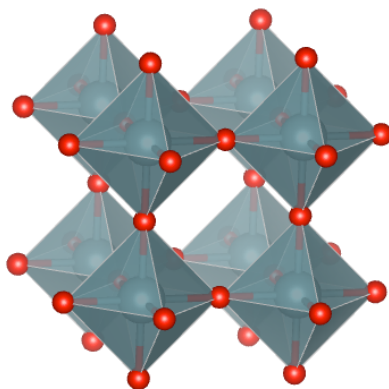


Figure 2.1. Crystal structure of $\delta\text{-UO}_3$. Oxygen atoms (shown in red) occupy the vertices of regular octahedra that constitute the nearest neighbor polyhedra of uranium atoms. Each octahedron contains a uranium (light-colored sphere) at its center. The cube formed by linking the U atoms in the diagram is the unit cell of $\delta\text{-UO}_3$.

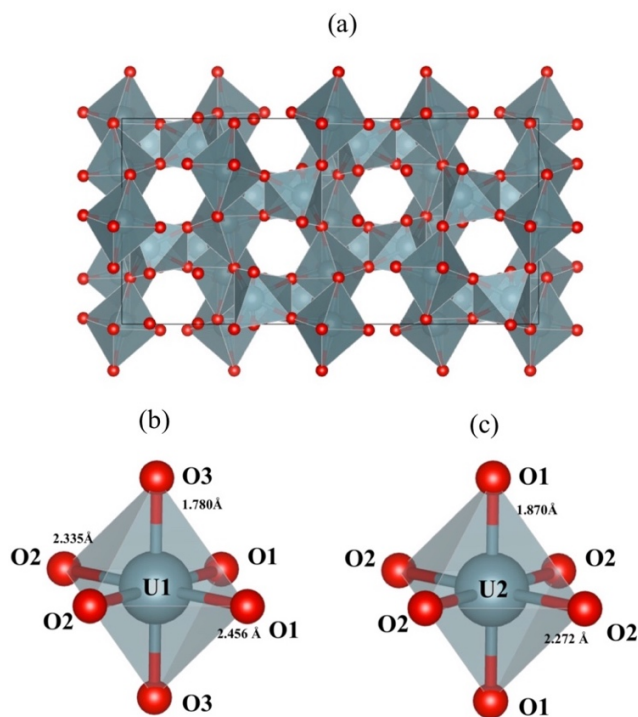


Figure 2.2. (a) Projection of the orthorhombic unit cell of $\gamma\text{-UO}_3$, viewed along the c-axis (drawing shows O coordination polyhedra around central U atoms); (b) nearest neighbor coordination polyhedron for U1 atoms; (c) nearest neighbor polyhedron for U2 atoms. The numerical bond lengths shown in (b) and (c) are based on calculation results from this study.

Wyckoff equipoint, $32h$, but with different fractional coordinate definitions [99]. U1 atoms are bonded to six nearest neighbor O atoms, forming a distorted octahedron, having two O1, two O2 and two O3 bonds (Fig. 2.2b). There are two other O3 atoms that might be considered as nearest neighbors to U1; however, these O3 atoms are located considerably farther away than all the other neighbors at 3.23 Å (calculation results, this study).[§] U2 atoms are surrounded by 6 O nearest neighbors forming a distorted octahedron, and they are only bonded to O1 and O2 atoms (Fig. 2.2c). U2 atoms are edge sharing with other U2 nearest neighbor polyhedra and corner sharing with U1 polyhedra. It is also important to note that in γ -UO₃, the U1-O3 and U2-O1 bonds are short in a *uranyl* (O-U-O molecular unit) manner.

La₆UO₁₂, commonly referred as δ -phase in the literature, possesses a fluorite derivative structure and should not to be confused with the δ -polymorph of UO₃. This structure is typically described using a hexagonal unit cell. The La₆UO₁₂ structure belongs to space group $R\bar{3}$ (S.G. no. 148) [100] with U and La atoms at the $3a$ and $18f$ Wyckoff equipoints, respectively. There are two distinct O sites, O1 and O2, in the La₆UO₁₂ structure, both located on $18f$ Wyckoff equipoints, but with different fractional coordinate definitions. Also, the structure can be thought of as containing oxygen vacancies located at the $6c$ Wyckoff equipoint. The O vacancies are close to the U atoms in such a way that the U coordination number is 6 forming an octahedron. Octahedral coordination polyhedra are typical for U⁶⁺ ions in ionic solids. In La₆UO₁₂, U atoms only have O1 type atoms as nearest neighbors. The coordination octahedron is close to a trigonal antiprism, with U-O1 bond distance of 2.124 Å, and 83.88° O1-U-O1 angle (calculation results, this study), instead of the 90° angle associated with a regular octahedron. La has 7 nearest neighbor O atoms, being bonded to both O1 and O2 atom types. The crystal structure of La₆UO₁₂ is shown in Figure 2.3.

2.3 Computational methods

2.3.1 DFT calculations

DFT calculations were performed to obtain the electron charge densities in the model uranium oxide compounds of interest in this study. For these calculations, we used the generalized gradient approximation (GGA) exchange correlation functional due to Perdew–Burke–Ernzerhof (PBE) [58]. The uranium $6s^2 6p^6 5f^3 6d^1 7s^2$, the lanthanum $5s^2 5p^6 5d^1 6s^2$, and the oxygen $2s^2 2p^4$ electrons are treated as valence electrons. The electron–ion interaction is described by the projector augmented wave method (PAW) [60], and the plane wave basis energy cutoff was set to 500 eV. The Vienna *ab initio* package VASP [61, 62] was employed to perform the simulations. We used a $4 \times 4 \times 4$ k-point sampling grid.

[§] Some authors include 2nd nearest neighbor O3 anions in their descriptions of coordination polyhedra associated with U1 cations in γ -UO₃. When including these extra two O3 anions, the coordination polyhedron for U1 is described as a bicapped trigonal prism.

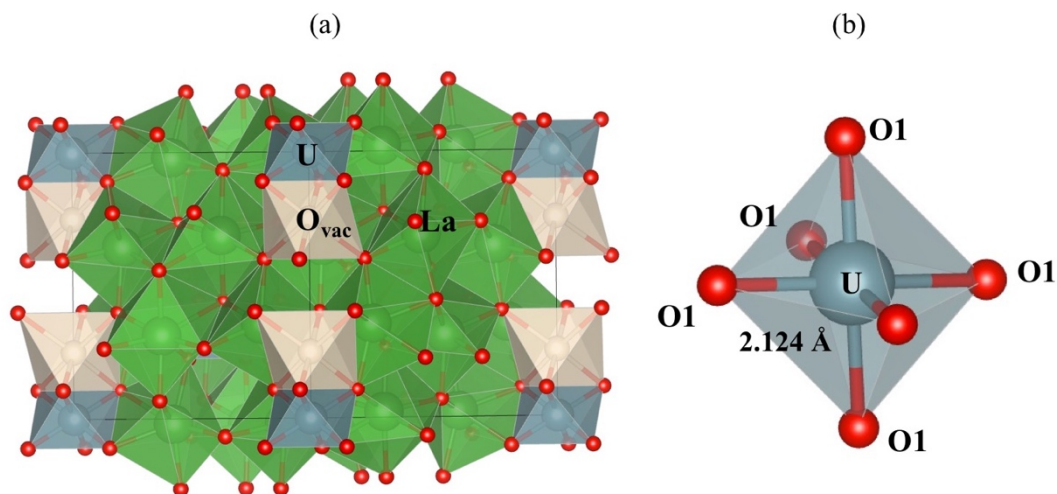


Figure 2.3. (a) Crystal structure of $\text{La}_6\text{UO}_{12}$. O atoms in red form the vertices of the coordination polyhedra. The translucent green polyhedra are the coordination polyhedra for La atoms; the translucent dark blue/grey distorted octahedra correspond to U atoms. White octahedral cages highlight the environment of the vacant sites in the oxygen sublattice. (b) Coordination polyhedron for a U atom in $\text{La}_6\text{UO}_{12}$. O atoms in red occupy the vertices of the irregular octahedron. The numerical bond length shown in (b) is based on calculation results from this study.

To account for the strongly-correlated f -electrons, we employed the $+U$ Hubbard correction in the rotationally invariant Dudarev formulation [63], with parameters for U and J of 4.5 and 0.51 eV, respectively. These parameters were originally derived by Dudarev [34], based on experimental measurements on UO_2 . We have used these values since there were no parameters available that relate specifically to our U -bearing model compounds, and they have been used previously for diverse uranium compounds including UO_3 polymorphs and provide the correct band gap of these materials [101, 102]. Nevertheless, we performed a complete assessment on the dependence of the charge density quantities on the choice of the $+U$ parameters for the $\delta\text{-UO}_3$ polymorph. In all VASP computations, the atomic positions and shape of the structures were relaxed until the magnitude of the forces was below 10^{-2} eV/Å or until the internal energy converged to at least 10^{-5} eV.

2.3.2 AIM analysis

While electron density is readily obtained from DFT simulations, the charge on a given ion is not so similarly evident, as it depends on the choice of model or theory to partition the electron density between atomic centers. There is no unambiguous means to perform the partitioning because the wave functions of electrons in the crystal are multi-centered and delocalized, as required by quantum mechanics. Using the framework of the atoms-in-molecules theory proposed by Bader [2], atoms are defined through a partitioning of real space, and the gradient of the electron density is used to define where one atom basin ends and the next begins. AIM theory provides a quantitative way to analyze the topology of the charge density, ρ , by means of its first derivative, $\nabla(\rho)$. At the critical points, this gradient vanishes. The characteristics of these points are determined by the Hessian of ρ . In extended solids, the Hessian is the (3x3) real and symmetric matrix of partial second derivatives. At a critical point, the eigenvalues of the Hessian are all real. The critical points are distinguished by their rank and signature. The rank is defined as the number of non-zero eigenvalues, while the signature is defined as the algebraic sum of the signs of the eigenvalues. For topologically stable critical points, the rank is always 3. The four possible critical points are: (1) the nuclear critical point (3,-3) with all curvatures negative, e.g. a local maximum that corresponds to an atom nucleus; (2) the bond critical point (3,-1) where two curvatures are negative and one is positive, and a saddle point corresponds to interatomic bonding; (3) the ring critical point (3,+1) where two curvatures are positive and one is negative; and (4) the cage critical point (3,+3) where all curvatures are positive, which is indicative of a local minimum in the electron charge density. Associated with each critical point is a set of trajectories of $\nabla(\rho)$ that start at the critical point and terminate at another critical point (or at infinity in a molecule). They define a zero-flux interatomic surface, a surface that encloses each atom, resulting in a unique means of partitioning the crystal into separated atomic basins. Those surfaces are usually very far from spherical in shape (the shape usually associated with an atom). The volume of each basin can be measured. Moreover, by integrating the electronic density within those basins where an atom nucleus is located, the total charge on an atom can be obtained. The lines of maximum charge density linking the nuclei of two atoms are called bond paths. The bond path crosses

the surface of the basins at the BCP. The shape of the electron density at a BCP has a saddle shape, therefore the two eigenvalues λ_1 and λ_2 of the matrix along axes normal to the bond path are positive while the eigenvalue λ_3 along the internuclear axis of the bond is negative.

The critical point searches were performed using the AIM-UC software developed by Vega and Almeida from the University of Carabobo [103], while charge basin integrations were performed using the Bader software developed by the Henkelman group at the University of Texas [104].

2.4 Results

Table 2.1 provides the crystal structure parameters obtained by DFT calculations for the compounds of interest in this study. For comparison, similar structural parameters from selected experimental studies are also shown in Table 2.1.

Table 2.1. Lattice parameters and related crystal structure data for relaxed structures of δ - UO_3 , γ - UO_3 , and $\text{La}_6\text{UO}_{12}$, obtained via DFT calculations. Selected experimental data is also shown for comparison to the DFT results.

Method	a (Å)	b (Å)	c (Å)	Volume/formula unit (Å ³ /f.u.)	Average volume/atom $\langle \Omega_a \rangle$ (Å ³ /atom)
δ - UO_3 (cubic)					
PBE+U	4.194	4.194	4.194	73.77	18.44
exp [17]	4.165	4.165	4.165	72.25	18.06
γ - UO_3 (orthorhombic) [§]					
PBE+U	9.937	9.932	20.736	63.95	15.99
exp [19]	9.711	9.813	19.930	59.35	14.84
$\text{La}_6\text{UO}_{12}$ (hexagonal)					
PBE+U	10.526	-	10.037	321.03	16.88
exp [100]	10.468	-	9.982	315.76	16.62

[§] The orthorhombic γ - UO_3 data shown here is in the *standardized* crystal structure data format, rather than the *published* crystal structure data format. In standardized form, the origin of the unit cell is at a center of symmetry ($\bar{1}$) and the orthorhombic lattice parameters are arranged such that $c > b > a$.

Next, we introduce the results of our AIM-B analyses by considering the electron charge density distribution in the compound with the highest crystallographic symmetry of those

we examined in this study, namely the δ - UO_3 phase. Figure 2.4 shows a contour map of the electron charge density for δ - UO_3 in a $\{001\}$ -type plane. In Fig. 2.4, the U atom occupies the center and it is surrounded by four O first nearest neighbors. The other two O first nearest neighbors lie above and below the U atom (out of the plane of the drawing). The electron density is higher close to the nuclear Bader critical point, and it decreases as the distance from the nuclear critical point increases. The bond critical points (BCP) are located in between the nuclear critical points.

Table 2.2 summarizes the U-O bond lengths for the different compounds examined in this study, and the position of the BCP with respect to the U and O atoms. Table 2.3 shows the partial charges along with the associated atomic volumes for U and O in δ - UO_3 , γ - UO_3 , and $\text{La}_6\text{UO}_{12}$. The partial charge values (δ) in Table 2.3 represent the numbers of electrons each atom loses or gains upon bonding. These values are obtained by the integration of charge in the atomic basins. Note that loss of electrons results in a plus sign for partial charge, while electrons gained yields a minus sign (as is the convention for describing cations and anions, respectively). Table 2.4 provides the following properties of the BCPs for the U-O bonds in the same compounds: the Hessian eigenvalues, λ_i ,^{§§} the charge density at the BCP, ρ_{BCP} , the Laplacian, the curvature ratio, $|\lambda_1|/\lambda_3$, and the ellipticity.

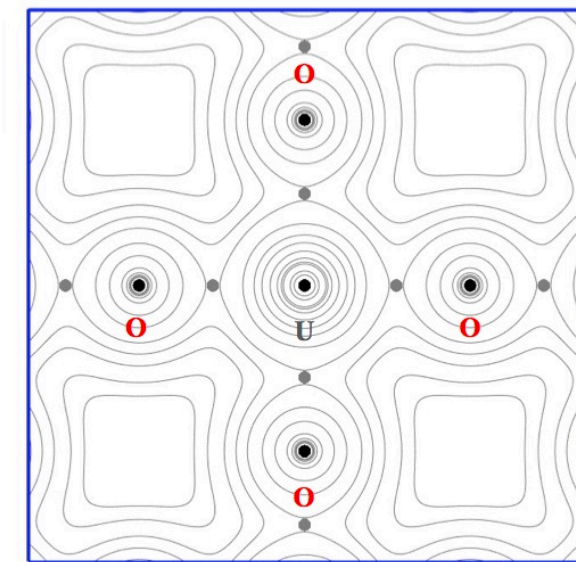


Figure 2.4. Contour map of the calculated electron charge density for δ - UO_3 in a $\{001\}$ -type plane. Nuclear U and O critical points are shown as black dots, while the bond critical points (BCP) are shown as gray dots.

^{§§} The Hessian eigenvalues, λ_i , represent the principal curvatures of the charge density at the bond critical point ρ_{BCP} .

Table 2.2. Calculated U-O bond lengths and BCP positions in δ -UO₃, γ -UO₃, and La₆UO₁₂. Also shown are the percentages of the U-O bond lengths that are assignable to the U and O ions, based on the position of the BCP.

	Bond length (Å)	BCP distance to U (Å)	BCP distance to O (Å)	U bond %	O bond %
δ -UO ₃					
U-O	2.097	1.163	0.934	55.46	44.54
γ -UO ₃					
U1-O1	2.456	1.363	1.093	55.50	44.50
U1-O2	2.335	1.282	1.054	54.88	45.12
U1-O3 [§]	1.780	0.986	0.794	55.40	44.60
U2-O1	1.870	1.033	0.837	55.24	44.76
U2-O2	2.272	1.249	1.023	54.97	45.03
La ₆ UO ₁₂					
U-O1	2.124	1.179	0.945	55.50	44.50

[§] The U1-O3 bond shown here is the “uranyl-like” 1st nearest neighbor bond. The much longer 2nd nearest neighbor U1-O3 bond is not shown in this table, but is discussed in the text (Section II) and included in the data shown in Figure 2.6.

Table 2.3. Calculated partial charge, $\tilde{\delta}$, and atomic volume, Ω_a , for U and O in δ -UO₃, γ -UO₃ and La₆UO₁₂, based on AIM-B analysis. Also shown are the partial charge and atomic volume for La in La₆UO₁₂. The γ -UO₃ compound is characterized by two distinct U atom positions and three O positions.

	Partial charge/atom $\tilde{\delta}$ (eV/atom)	Volume/atom Ω_a (Å ³ /atom)
δ -UO ₃		
U	+3.09	15.568
O	-1.03	19.403
γ -UO ₃		
U1	+2.92	15.49
U2	+2.91	16.47
O1	-0.94	15.61
O2	-1.16	14.77
O3	-0.81	17.57
La ₆ UO ₁₂		
U	+2.88	15.52
La	+2.06	19.47
O1	-1.21	15.74
O2	-1.33	15.71

Table 2.4. BCP characteristics for U-O bonds in δ -UO₃, γ -UO₃ and La₆UO₁₂, based on AIM-B analysis. Note that O2 in La₆UO₁₂ does not bond to U.

Bond	Hessian eigenvalues			Charge density ρ_{BCP} (eV/ Å ³)	Laplacian	Curvature Ratio $ \lambda_1 /\lambda_3$	Ellipticity
	λ_1	λ_2	λ_3				
δ -UO ₃							
U-O	-4.557	-4.557	17.669	0.928	+8.555	+0.258	0
γ -UO ₃							
U1-O1	-1.732	-1.546	7.933	0.395	+4.654	+0.218	0.120
U1-O2	-2.165	-2.101	9.829	0.526	+5.564	+0.220	0.030
U1-O3 [§]	-14.564	-14.268	33.040	2.141	+4.208	+0.441	0.021
U2-O1	-10.346	-10.317	28.065	1.685	+7.402	+0.369	0.003
U2-O2	-2.800	-2.608	12.273	0.644	+6.863	+0.228	0.074
La ₆ UO ₁₂							
U-O1	-4.912	-4.296	15.284	0.906	+6.076	+0.321	0.236

[§] The U1-O3 bond shown here is the “uranyl-like” 1st nearest neighbor bond length.

2.5 Discussion

2.5.1. DFT simulation results on crystal structures of model U-bearing oxides

The DFT calculated crystal structure results shown in Table 2.1 are in good agreement with the reported experimental results [97, 99, 100], differing at most by 4%. It should be noted that for all compounds investigated here, DFT finds a larger unit cell volume than experiment. Our δ and γ - UO_3 results are also in good agreement with published results from previous computational studies of UO_3 polymorphs [101, 102, 105, 106]. It should be noted that the γ - UO_3 structure has the highest atomic density of the compounds examined in this study, while the δ - UO_3 polymorph is the least dense. The higher density of γ - UO_3 compared to δ - UO_3 is largely attributable to a mixture of both edge and corner-shared octahedra in the γ -phase, versus only corner-shared octahedra in the δ -phase (edge-sharing leads to a higher packing density).

2.5.2. Coordination polyhedral unit for U1 in γ - UO_3

The U1 nearest neighbor polyhedron in γ - UO_3 is commonly presented in the literature as a complex polyhedral unit consisting of 8 nearest neighbor anions, two O1, two O2 and four O3 type atoms [101], with two of the O3 atoms located considerably more distant from the U1 central atom at 3.24 Å (number from this study), compared to the other six O anions. In Fig. 2.2 and Table 2.2, we present the nearest neighbor polyhedron for the U1 atom as a distorted octahedron, with 6 nearest neighbor atoms. In our AIM-B analysis, we did not find a BCP between U1 and the longer distance O3 atoms, indicating that bonding between these atoms is inconsequential. This is the reason we describe bonding to U1 using an octahedral first nearest neighbor anion polyhedron representation.

2.5.3. Experimental versus theoretical crystal structures of $\text{La}_6\text{UO}_{12}$

Table 2.1 indicates that for $\text{La}_6\text{UO}_{12}$, the calculated average atomic volume, $\langle \Omega_a \rangle$, is about 1.5% larger than the experimental value. But to the contrary, the calculated volume of the U octahedral coordination polyhedron in $\text{La}_6\text{UO}_{12}$ (i.e., the volume inscribed by first nearest neighbor O anions surrounding a central U cation) is about 4.3% smaller than the experimental volume (12.55 Å³ versus 13.12 Å³). This paradox is resolved when we consider the La coordination polyhedra in $\text{La}_6\text{UO}_{12}$. We find a larger La coordination polyhedron using DFT than is found in experiments (22.87 Å³ versus 21.94 Å³). Since La ions are much more numerous than U ions in $\text{La}_6\text{UO}_{12}$, this explains why we find a larger $\langle \Omega_a \rangle$ for $\text{La}_6\text{UO}_{12}$ using DFT compared to experiment.

2.5.4. AIM-B atomic radii versus classical ionic radii in δ - UO_3

Next, it is instructive to compare and contrast atomic radii obtained via AIM-B analysis (based on the locations of the BCPs) versus the Shannon [107] ionic radii. For this

comparison, we consider our *benchmark* compound, δ - UO_3 , which has the highest symmetry of the model compounds we have considered in this study. Figure 2.5 shows the gradient vector field of the electron charge density surrounding a central U atom in a $\{001\}$ -type plane of δ - UO_3 . The drawing in Fig. 2.5 includes both the nuclear critical points for the central U atom and the nearest neighbor O atoms, as well as the BCP positions between the central U and surrounding O atoms. In Fig. 2.5, we have overlaid shaded circles on the gradient vector field plot, which are intended to represent U and O ions with ionic radii corresponding to their “formal” valences of 6+ and 2-, respectively. These radii are based on Shannon [107] and correspond to VI-fold coordination of U atoms by nearest neighbor O, and II-fold coordination of O atoms by nearest neighbor U. The Shannon radius for a VI-fold coordinated U^{6+} ion is 0.73 Å, while the radius for a II-fold coordinated O^{2-} ion is 1.35 Å, giving a U-O bond length of 2.08 Å. The BCP in the AIM-B approach is located 1.163 Å from the U nucleus and 0.934 Å from the O nucleus. This leads to a U-O bond length of 2.097 Å, which is only 0.8% larger than the U-O bond length obtained using Shannon radii. The BCP position differs from the Shannon dividing point between adjacent U and O ions, being closer to O with AIM-B. The locations of the BCPs along with the gradient field of the electron charge density, serve to define the atomic basins. The shape of the atoms in the AIM-B approach differs greatly from the spherical ionic picture. One difference between the AIM-B and ionic atom descriptions arises from Shannon’s underestimation of the U ion size, which is based on its formal valence of 6+ (and corresponding overestimate of the O ion size which is based on its formal valence of 2-). A U^{6+} cation is very small due to its lack of outer valence electrons. The larger U ion from AIM-B analysis can be rationalized using Sanderson’s principle of electronegativity equalization [108]. According to Sanderson, charge transfer occurs while there are differences in electronegativity, but as the transfer progresses, the electronegativities of both elements become more similar. By consequence, charge transfer ceases long before the U and O ions achieve their formal valences of 6+ and 2- respectively.

2.5.5. BCP positions between bonding U and O ions

From Table 2.2, we find that in all cases the BCP is not located at the midpoint of the bonding distance, but rather resides closer to the O atoms. We have quantified how much of the bond length “belongs” to each atom. For all compounds, we found that ~55% of each U-O bond belongs to the U atom, versus ~45% belonging to the oxygen atom (Table 2.2). We are comparing U-O bonds in our model compounds; consequently, in Table 2.2 we did not include data for La-O bonds in $\text{La}_6\text{UO}_{12}$. The La-O bond length in $\text{La}_6\text{UO}_{12}$ is non-degenerate, with a rather short average La-O2 bond length of 2.41 Å versus a longer average La-O1 bond length of 2.65 Å. It should be noted that O2 anions are bonded only to La cations, while O1 anions are bonded to U and La cations.

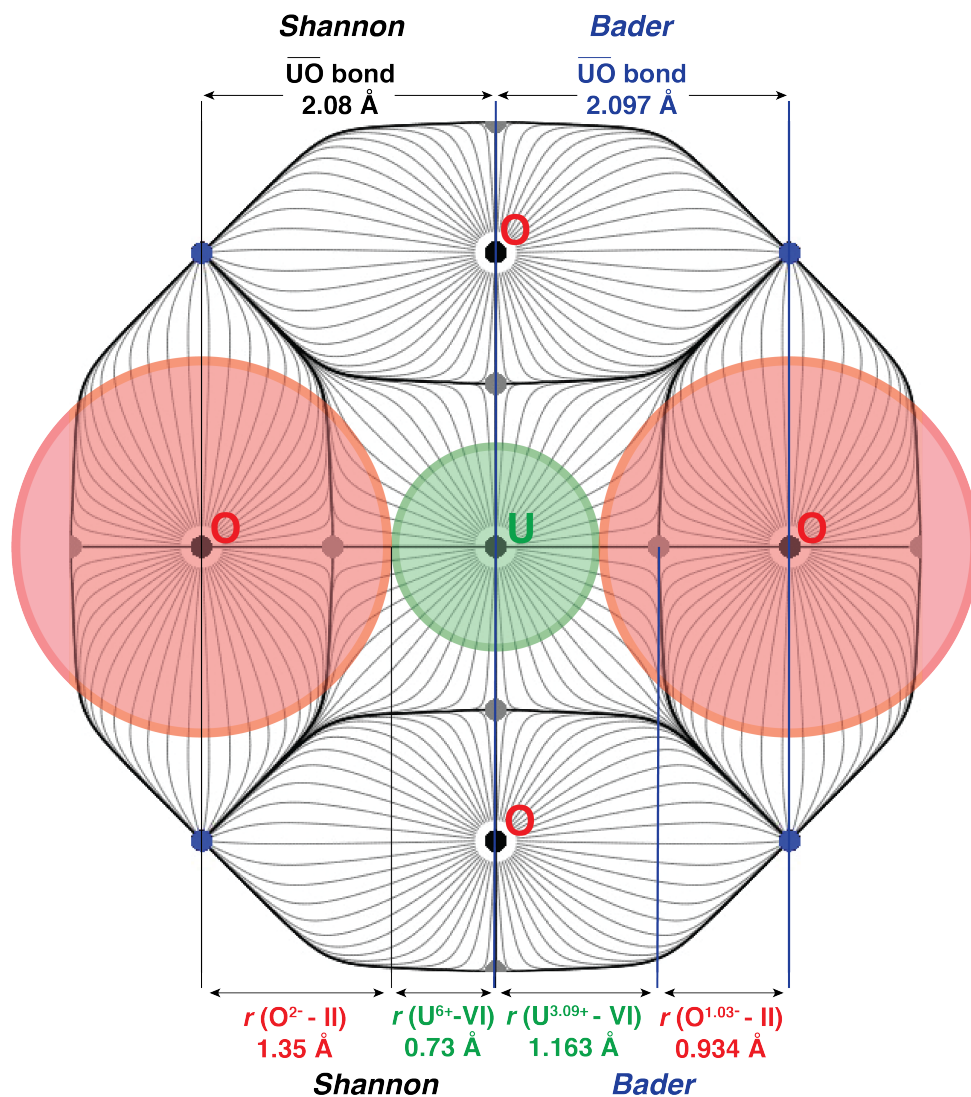


Figure 2.5. Gradient vector field associated with the calculated electron charge density for δ - UO_3 in a {001}-type plane. The shaded circles represent ion sizes in the Shannon “formal” valence approach. The position of the AIM-B BCP for the U-O bond on the right is delineated by a blue line. The Shannon bonding point for the O-U bond on the left is delineated by a thin black line.

2.5.6. Partial charges on constituent U and O ions

Next, our AIM-B analyses reveal that charge transfer from U cations to neighboring O anions (or vice versa) in the model oxides examined here is dependent on crystal structure and chemical environment. For compounds investigated in this chapter, all the charge is transferred from the cations to the anions and no charge is trapped in interstitial positions. In δ - UO_3 , each U atom loses ~ 3.1 electrons, and the charge is evenly distributed among the neighboring O atoms. For γ - UO_3 , both U1 and U2 positions have a similar net charge, each U having transferred ~ 2.9 electrons to neighboring O atoms. This transferred charge is not evenly distributed with respect to the surrounding O anions, as was the case for δ - UO_3 ; instead, each type of O atom receives a different amount of charge. In the case of $\text{La}_6\text{UO}_{12}$, the U atoms transfer ~ 2.9 electrons to neighboring O1 atoms. We also identified differences in charge transfer to O1 and O2-type atoms in $\text{La}_6\text{UO}_{12}$. The O atoms that are bonded to both U and La atoms (labeled O1 in Table 2.3) receive less charge than the O atoms that are only bonded to La atoms (labeled O2). The U atom transfers less charge to O compared to the UO_3 polymorph cases, while to the contrary, the O atoms receive more charge than for the UO_3 polymorph cases. This apparent paradox is resolved when one considers that the coordination of O is higher in $\text{La}_6\text{UO}_{12}$ than in UO_3 polymorphs (therefore more nearest neighbor cations contribute charge to a given O anion). The charge transfer values from U atoms to neighboring O atoms found in this study (ranging from +2.88 to +3.09) are slightly greater than the values obtained in previously published computational studies of oxides containing uranium. In particular, in UO_2 , the charge on U was found to be +2.6 electrons [95, 109].

2.5.7. Bond ionicity versus bond covalency

Next, we address U-O bond ionicity, or its complement, bond covalency, in our model compounds, based on application of Bader-Essen rules [22] to our AIM-B results. Certain characteristics of the BCPs are related to bond ionicity (or conversely, to covalency). For instance, positive values of the Laplacian and positive curvature ratio at the BCP are indicators of closed shell interactions, i.e., ionic bonding. Negative values of the Laplacian and the curvature ratio indicate shared interactions, i.e., covalent bonding. In our study, all of the BCPs exhibit positive values for the Laplacian and the curvature ratio. Therefore, all bonds in our model compounds are dominated by closed shell (ionic) interaction characteristics. However, we find evidence for variations in relative bond ionicity, since we observe variations in the magnitudes of the Laplacian and the curvature ratio among the U-O BCPs. The bond with the most covalent-like characteristics is the U1-O3 bond in γ - UO_3 (this is one of the *uranyl*-like bonds). This bond possesses the lowest Laplacian value and the highest value of the curvature ratio, compared to all U-O bonds evaluated in this study (note that a small magnitude for the curvature ratio, namely $|\lambda_1|/\lambda_3 \ll 1$, is indicative of closed shell interactions [23]). It is also important to note that this U1-O3 bond in γ - UO_3 exhibits the largest charge at the BCP, ρ_{BCP} , of all BCPs examined. This charge, which is representative of shared charge between atomic constituents, is also indicative of more covalency in the bond. Our AIM-B analysis revealed a strong correlation

between ρ_{BCP} and BCP curvature ratio, namely the greater the BCP curvature ratio, the greater ρ_{BCP} .

2.5.8. Charge densities at the U-O BCPs versus bond lengths and bond strengths

The most notable finding in our study is a definitive inverse (negative) correlation between the U-O bond length, r_{UO} , and the charge density at the BCP, ρ_{BCP} . We find that the shortest U-O bonds possess the largest ρ_{BCP} values, and vice versa (Tables 2.2, 2.4). We discovered that there is a quantitative trend in ρ_{BCP} versus r_{UO} , and this trend incorporates all of the compounds that we investigated. Our ρ_{BCP} versus r_{UO} data can be fit to an exponential function with rather high precision. Specifically, we find:

$$\rho_{BCP} = \rho_0 e^{\frac{r_0 - r}{B}} = e^{\frac{2.0822 - r}{0.4004}} \left[\frac{\text{eV}}{\text{\AA}^3} \right]; \quad \chi^2 = 0.00345 \quad \text{Eqn. (2.1)}$$

$$r_0 = 2.0822 \text{ [\AA]} ; B = 0.4004 \text{ [\AA]}$$

where ρ_{BCP} is the charge density at the BCP in units of $[\text{eV}/\text{\AA}^3]$; ρ_0 is the value of ρ_{BCP} at $r = r_0$ and is arbitrarily set to 1 $[\text{eV}/\text{\AA}^3]$; r is the U-O bond length (r_{UO}) in units of $[\text{\AA}]$; r_0 and B are exponential fitting parameters, both in units of $[\text{\AA}]$.^{§§§} Eqn. (1) indicates that as the U-O bond length decreases, the charge density at the BCP increases exponentially. This BCP charge is effectively the “shared” charge between the U and O ions participating in the bond. In other words, the BCP charge represents the covalent component of the mixed ionic/covalent bond, and this covalent bond component increases with decreasing bond length.

The exponential fitting function in Eqn. (1) is the same form as a function used by Zachariasen [110] to relate a parameter called *bond strength* (s) to bond length (r) in oxygen and halogen compounds containing d and f electron metal cations. In fact, if we use a set of experimentally-determined U-O bond lengths, r , in $\text{U}^{6+}/\text{O}^{2-}$ bearing compounds (using the U and O formal valences) published by Zachariasen (Table 1 in [111]), we can calculate a corresponding set of bond strengths, s , for these U-O bonds, based on the following exponential relationship between s and r due to Brown and Altermatt [76]:

$$s = s_0 e^{\frac{r_0 - r}{B}} = e^{\frac{2.075 - r}{0.370}} \text{ [esu]} \quad \text{Eqn. (2.2)}$$

$$r_0 = 2.075 \text{ [\AA]} ; B = 0.370 \text{ [\AA]}$$

where s is the bond strength in electrostatic units [esu]; s_0 is the value of s at $r = r_0$ and is arbitrarily set to 1 [esu]; r is the U-O bond length (r_{UO}) in units of $[\text{\AA}]$; r_0 and B are

^{§§§} We note that a power law functional (not shown here) provides a fit that has nearly identical precision to the exponential fit shown in Eqn. (1). We use the exponential fit in this report because it is easiest to compare to published studies relating bond strength and bond length (next discussion topic).

constants, both in units of [Å]. We note that the fitting constants r_0 and B in Eqn. (2) are very similar to the corresponding constants in Eqn. (1). In Figure 2.6, we overlay a comparison between our ρ_{BCP} versus r_{UO} computational results and the s versus r_{UO} values determined by the method summarized above. The plot in Fig. 2.6 employs reduced (dimensionless) units, namely r/r_0 for the fractional U-O bond length, ρ_{BCP}/ρ_0 for the fractional BCP charge and s/s_0 for the fractional bond strength (based on Eqns. (1) and (2)). Fig. 2.6 provides strong evidence for a direct correlation between the charge density, ρ_{BCP} , at the U-O BCP (determined via AIM-B analysis) and the U-O bond strength, s , as derived using a methodology similar to Zachariasen [110]. This relationship between ρ_{BCP} and bond strength was also identified by Gibbs et al. in DFT simulations of oxide and hydroxyacid molecules [112], and crystalline silicates and oxides [113].

To test the predictive capabilities of the ρ_{BCP}/ρ_0 versus r/r_0 curve shown in Fig. 2.6, we performed DFT calculations and an AIM-B analysis on another U-bearing complex oxide not originally selected for this study, namely BaUO₄. These results are also shown in Fig. 2.6. There are three distinct U-O bond lengths in BaUO₄ and the calculated charge densities at the BCPs for these different bonds result in data points that fall very nearly on the exponential fitting curve relating ρ_{BCP}/ρ_0 to r/r_0 . This gives us confidence that we can predict ρ_{BCP} based on knowledge of specific U-O bond lengths (either measured or calculated), at least for compounds containing U cations nominally with valence 6+.

It is useful to speculate on reasons for the surprising correlation we have found between ρ_{BCP} and s . The bond strength methodology used by Zachariasen [110, 111] was originally conceived by Pauling [114] and used to explain how oxidation of a central cation in a nominally ionic compound, can progress to the extent that the cation achieves its formal ionic valence, through bonds involving *only* 1st nearest neighbor (n.n.) ligands. For example, consider δ -UO₃ wherein each U cation is coordinated by 6 1st n.n. O anions in *regular* octahedral coordination. Pauling's *bond valence sum* (BVS) method stipulates that, in order for a U cation to achieve its formal 6+ valence, each n.n. O anion must contribute a bond strength of 1 esu. Each O anion, on the other hand, has a formal valence of 2- and these two electron charge units are donated to the O anion by two adjacent 1st n.n. U cations. This leads to a net strength of 1 valence unit that any given O anion can contribute to a bond with any particular neighboring U cation. Since there are 6 n.n. O anions to the central U cation, the net valence delivered to the U is $6 \times (1 \text{ esu}) = 6 \text{ esu}$. This satisfies the U cation formal valence requirement of U⁶⁺ in the trioxide, δ -UO₃.

However, most complex structures consist of irregular coordination polyhedra, not regular polyhedra (the latter being the case in δ -UO₃). The compounds γ -UO₃ and La₆UO₁₂, for example, are dominated by irregular coordination polyhedra. These irregular polyhedra often are accompanied by concomitant bond length non-degeneracy. We infer from this bond length non-degeneracy that all 1st n.n. bonds can no longer be equal; some bonds must

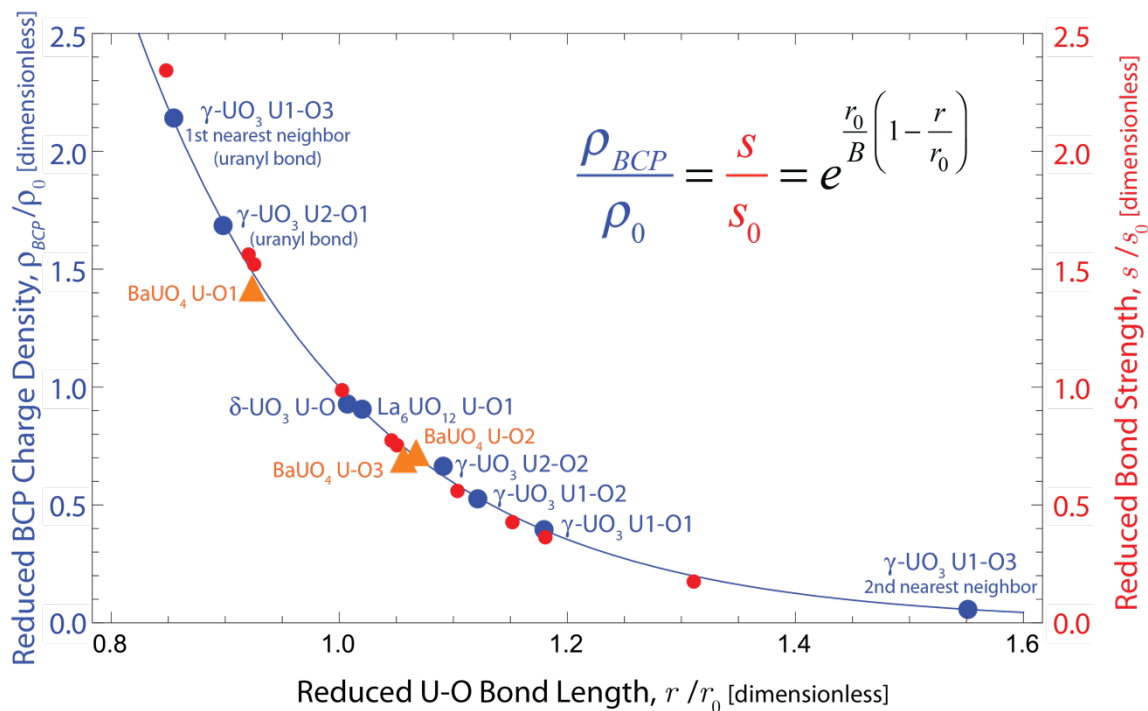


Figure 2.6. Plot showing reduced charge density at the bond critical point (ρ_{BCP}/ρ_0) and reduced bond strength (s/s_0) versus reduced U-O bond length (r/r_0). The blue data points are from this study and are labeled according to compound and particular U-O bond (these data points correspond to the left-hand ordinate in the plot). The bond lengths associated with the red data points are from Zachariassen [38] and represent a variety of U-bearing compounds containing nominally U^{6+} cations. The bond strengths associated with the red data points are calculated based on Eqn. (2) from Brown and Altermatt [39] (these data points correspond to the right-hand ordinate in the plot). The solid blue line represents a fit to the blue data points, based on the fitting equation shown as an inset in the figure and using the fitting constants, r_0 and B , provided in Eqn. (1) in the text. The fit to the red data points is not shown, but can be readily obtained from the same inset fitting equation, but using the r_0 and B fitting constants provided in Eqn. (2) in the text. The triangular data points in orange are results of DFT calculations and AIM-B analysis on the U-bearing compound, BaUO_4 (this study). These calculations were added to this study to test for possible universality of the correlation between ρ_{BCP} and s identified during the course of this work. The value of the reduced BCP charge density for the $\gamma\text{-UO}_3$ U1-O3 2nd nearest neighbor bond data point in the plot was obtained using the reduced charge density associated with the blue fitting curve. In actuality, using AIM-B, we did not identify a BCP for this long 2nd n.n. bond.

be stronger than others. Zachariasen [110] proposed that shorter bond lengths must correspond to larger bond strengths (Zachariasen also proposed a corollary to this rule, namely that bonds of equivalent length have equivalent strength). Zachariasen also proposed that a bond length / bond strength inverse correlation is applicable to bonding in compounds of any bonding type, be it ionic, covalent, or mixed.^{§§§§} In addition to having general applicability, Zachariasen's bond length / bond strength relationship has been further interpreted to suggest that shorter bonds are more covalent, while long bonds are ionic. In fact, Altermatt and Brown [75] attempted to quantify this notion, stating that "bonds with <strengths> greater than about 0.6 <esu> are those often described as covalent whereas weaker bonds correspond to those generally referred to as ionic or electrostatic." We believe that the quantitative inverse correlation between ρ_{BCP} and r_{UO} that we have identified in this study, as well as the remarkably close relationship between the $\rho_{BCP}(r_{UO})$ and $s(r_{UO})$ dependences, provide direct evidence that stronger (i.e., shorter) heteroionic bonds are a result of increased bond covalency. In particular, this increased bond covalency is manifest in the increased shared electron charge that occurs in the vicinity of the BCPs that separate bonding atoms.

2.5.9. Total BCP charge density versus partial ionic charge

In the last section, we concluded that increases in ρ_{BCP} effect corresponding increases in bond covalency. This leads us to postulate that increases in ρ_{BCP} should also be accompanied by concomitant decreases in charge transfer (i.e., decreased bond ionicity). To test this hypothesis on our model compounds, we endeavored to compare the total charge density residing at the BCPs adjacent to a central U cation, to the partial charge, $\tilde{\delta}$, on this U cation, the latter derived via charge basin integration (Table 2.3). We assume here that the total charge density at BCPs, ρ_{BCP}^{total} , can be represented by a sum of individual BCP charge densities for the U-O bonds associated with the first nearest neighbor O anions surrounding a central U cation. For instance, if we denote the BCP charge density of the i^{th} nearest neighbor O anion to the U cation as ρ_{BCP}^i , then ρ_{BCP}^{total} is given by $\rho_{BCP}^{total} = \sum_{i=1}^{i=N} \rho_{BCP}^i$, where N is the number of 1st nearest neighbor O anions to the central U cation. For all of the compounds we have investigated in this study, $N = 6$ (U cations are in regular or distorted octahedral coordination w.r.t. nearest neighbor O anions).

Table 2.5 shows a comparison between ρ_{BCP}^{total} and $\tilde{\delta}$ for U-O bonds in δ - UO_3 , γ - UO_3 , and La_6UO_{12} . This table is arranged in order of increasing ρ_{BCP}^{total} for the U atoms in the various compounds. Based on our hypothesis above, this implies that bond covalency should increase as one moves down the list of U cations in Table 2.5. Conversely, we expected

^{§§§§} This was a problem with Pauling's BVS model. Pauling assumed that atomic radii are constant, with radii dependent on the type of bonding (ionic or covalent). But in an irregular 1st n.n. coordination polyhedron, the radii of the ions that make up the polyhedron cannot all be the same.

that bond ionicity, as indicated by the magnitude of the partial charge, $\tilde{\delta}$, should *decrease* moving down the list in the table. As is apparent from the data presented in Table 2.5, this covalent/ionic inverse relationship that we postulated is not followed quantitatively. Considering only the binary oxides (δ -UO₃ and γ -UO₃) an inverse relationship between ρ_{BCP}^{total} and $\tilde{\delta}$ is nearly realized. However, inclusion of the ternary oxide, La₆UO₁₂, in the analysis does not lead to an inverse trend. There are likely several explanations for the failure of these results to support the complementarity between ionicity and covalency. For instance, in the ternary compound, La₆UO₁₂, the presence of neighboring La cations may be affecting charge transfer from the U cations to neighboring O anions. Also, in the γ -UO₃, we have not considered 2nd nearest neighbor U-O interactions. However, these interactions may influence charge transfer from central U cations.

2.5.10. Testing the effects of variations in the +U Hubbard correction on $\rho_{BCP}(r_{UO})$

The Hubbard parameters used in this study (described in Section 2.3.1) yield calculated band gaps for our model compounds similar to those found in experiments. Specifically, our Hubbard parameters, $U = 4.5$, $J = 0.51$, give band gaps of 2.19 and 2.35 eV for δ -UO₃ and γ -UO₃, respectively. These are in good agreement with reported experimental values, such as 2.17 eV for δ -UO₃ [44] and 2.38 eV for γ -UO₃ [28]. Nevertheless, we were unsure of the influence that Hubbard parameters might have on ρ_{BCP} values obtained from AIM-B analyses. To test this, we performed DFT simulations and AIM-B analyses in the model compound, δ -UO₃, wherein we varied the *Hubbard* + U difference parameter, $U-J$, from 0 to 4, with 0 corresponding to *standard* DFT (the specific values of $U-J$ we used were 0, 1, 2, 3 and 4). First, we found that DFT overestimates the cubic lattice parameter, a , for δ -UO₃, regardless of the choice of $U-J$ (see Figure A2.1 in Appendix 2). It should be noted that the equilibrium U-O bond length in δ -UO₃ scales in proportion to a ($r_{UO} = a / 2$). Second, we found that the calculated band gap for δ -UO₃ increases in accordance with increasing $U-J$ (see Fig. SM.1.1). Third, we found that, irrespective of the value of $U-J$, the BCP position between bonding U and O ions exhibited the same partitioning as discussed in Section 2.3.5, namely ~55% of the bond belongs to U and 45% belongs to O. Lastly, we found very small variations in ρ_{BCP} values as a function of $U-J$ variation. Importantly, all of our newly calculated $\rho_{BCP}(r_{UO})$ values for varying $U-J$ lie very nearly on our reduced charge density (ρ_{BCP} / ρ_0) versus reduced U-O bond length (r/r_0) fitting curve (Fig. 2.6; see also Figure A2.2 in the Appendix 2).

2.6 Conclusions

In this study, we used DFT and AIM/Bader analysis procedures to determine the electron charge density distributions in three model uranium-bearing compounds: δ -UO₃, γ -UO₃ and La₆UO₁₂. We identified the bond critical points (BCPs) between adjacent U-O atoms and we performed charge basin integrations in the AIM/Bader framework. We discovered

Table 2.5. Total BCP charge density, ρ_{BCP}^{total} , based on a BCP charge density sum over first nearest neighbor anions surrounding a central U cation, and the integrated partial charge, $\tilde{\delta}$, for U atoms in δ -UO₃, γ -UO₃ and La₆UO₁₂, based on AIM-B analysis. The total BCP charge density is given by $\rho_{BCP}^{total} = \sum_{i=1}^{i=N} \rho_{BCP}^i$, where N is the number of 1st nearest neighbor O anions to the central U cation. The partial charge values in this table are the same as those in Table 2.3. This table is arranged in order of increasing ρ_{BCP}^{total} for the U atoms in the various compounds.

	Total charge density, ρ_{BCP}^{total} (eV/Å ³)	Partial charge / U atom $\tilde{\delta}$ (eV/atom)
La ₆ UO ₁₂		
U	5.44	+2.88
δ -UO ₃		
U	5.57	+3.09
γ -UO ₃		
U2	5.95	+2.91
U1	6.12	+2.92

that there exists a close relationship between the electron charge density at the BCP, ρ_{BCP} , and the bond strength, s , where s is a bonding property originally proposed by Pauling [114] and later refined by Zachariasen [110, 111] and others. This relationship appears to be quantitative for compounds containing U-O bonds (work is in progress to test compounds containing metal constituents other than U). Our results suggest that using AIM/Bader methods, we can determine the relative covalent bonding component of each bond in an irregular coordination polyhedron, based on the bond lengths of each bond to the central atom in this polyhedron. The covalency referred to here is the magnitude of the charge density at the BCP, and this magnitude is indicative of the degree to which electron charge is shared between bonding atoms. We believe that the results of this study are directly applicable to other U-bearing compounds, in the sense that if we know U-O bond lengths for a given compound (based on crystal structure determination), we can immediately predict ρ_{BCP} for each U-O bond and assess relative covalency differences for all U-O bonds in the structure. We have already confirmed this prediction for one compound, namely BaUO₄ (DFT results shown in Fig. 2.6).

CHAPTER III
DYNAMICS OF INTERACTION BETWEEN DISLOCATIONS AND
POINT DEFECTS IN BCC IRON

A version of this chapter will be submitted to a peer reviewed journal for publication by Luis Casillas-Trujillo, Andrew S. Ervin, Liubin Xu, Alexander Barashev, H. Xu:

Luis Casillas-Trujillo, Andrew S. Ervin, Liubin Xu, Alexander Barashev, H. Xu. "Dynamics of Interaction between Dislocations and Point Defects in bcc Iron."

In this chapter, I performed all the simulations to obtain the saddle point distributions, modified the SEAKMC code to do a more efficient saddle point search, and analyzed the data. Andrew Ervin helped with the modification of the SEAKMC code, created one of the modules of the code, and with discussions on the saddle point configurations. Liubin Xu provided dislocation structures and strain calculations. Alexander Barashev provided scientific discussions for the development and implementation of the methodology, and insights about the theory and different models employed to approximate the saddle point energies. Haixuan Xu developed the SEAKMC code, designed and directed the simulations, provided data analysis and scientific discussion.

Abstract

The interaction between dislocations and point defects is crucial for many physical properties and phenomena in materials, such as strengthening mechanisms, dislocation bias and void swelling, creep, and impurity segregation around dislocations. Conventional dislocation-point defect interaction models are mostly based on elastic theory, using assumed transition states based on the binding energies of the defects. In this paper, we present the transport properties of point defects near dislocations based on the actual saddle point configuration of vacancies and self-interstitial atom as a function of position with respect of screw and edge dislocations in a model system (bcc iron) using the self-evolving atomistic kinetic Monte Carlo (SEAKMC). We found that the defect transport properties are significantly different from estimation from previous theories and models. The migration energies exhibit different trends in comparison with the results based on binding energy approaches; the interaction range between dislocations and point defects is found to be significantly larger than previously estimated values. KMC simulations reveal defect dynamics are highly anisotropic and correlated, particularly for dumbbells in the compressive field of the edge dislocation. We conclude that defect dynamics cannot be properly described using properties of local minima configuration in potential energy landscape, such as binding energies or their derivative properties, but require accurate saddle point configurations and energies. This study provides critical insights on defect dynamics to evaluate the interaction probability of defects with dislocations and the corresponding lifetime of point defects, which are essential for understanding microstructural evolution and mechanical properties of metallic materials.

3.1 Introduction

The dislocation point-defect interaction (DPDI) has a deep impact on the microstructural evolution and plasticity of materials [115-120], such as impurity segregation around dislocations and creep. This DPDI has two interrelated aspects. On one side, the presence of point defects near dislocations may influence dislocation properties. For instance, point defects could act as obstacles to dislocation glide, [121] or alter the structure of the dislocation core [122], leading to strengthening and hardening. In addition, the absorption or emission of point defects controls dislocation motion through creating kinks and jogs [121] and dislocation creep at low stresses by influencing the dislocation climb processes [123]. On the other side, the strain field exerted by dislocations affect the migration of point defects, and causes drifted and correlated diffusion of point defects around dislocations in alloys [124, 125]. This drifted diffusion leads to the formation of defect clusters and to the segregation of impurity atoms near dislocations, forming the so-called Cottrell atmospheres [124].

The effects of DPDI are enhanced in radiation environments [5, 126] and by high temperatures, where collision cascades introduce a large number of point defects and point defect mobility is enhanced, respectively. Radiation effects such as void swelling [18], radiation induced segregation [5, 127], radiation-induced creep [128], and radiation induced embrittlement/hardening [18, 119, 129-131] are controlled by the underlying atomistic interactions between point defects and dislocations. Therefore, understanding the mutual interaction between point defects and dislocations is essential to control the mechanical properties and performance of structural materials and to tailor their radiation resistance for nuclear energy applications. In addition, a fundamental understanding of DPDI may also contribute to fields where defects dominate the materials performance, such as solid oxide fuel cells and batteries.

Compared with our understanding of defect stability near dislocations based on defect formation energies and binding energies [132], relatively little is known about the transport properties and dynamics of point defects in the presence of a dislocation. One of the difficulties is to determine the saddle point energies (SPs) and corresponding migration energy barriers (MEBs) in a systematic way, which is rather complicated and computationally demanding. Bilby [133] and Cottrell [134] provided the first description of the dislocation point-defect interaction using elastic theory, by considering the elastic interaction of the strain field of the dislocation and the strain introduced by the dilatation volume of the point defect to reach approximate solutions. Another commonly used approximation is to estimate the migration energy barriers based on the binding energies of point defects. This approximation has been commonly used to study the DPDI [135-138]. It should be noted that both the Bilby-Cottrell model and the binding energy approximation are based on properties of local minimum configurations (LMC) in the potential energy landscape, and no information of the transition state considered.

In principle, a single MEB can be computed using the drag method [139], nudged elastic bands (NEB) [140, 141] or the dimer method [38], but up to now it has been computationally prohibitively to calculate the SP configuration for all the different local atomic configurations caused by the presence of dislocations. To overcome this limitation, attempts involving artificial neural networks [41, 142, 143], and genetic algorithms [144] have been made. In these methods, they use training sets to predict the SP energy of different local atomic configuration without obtaining the actual MEBS. These artificial intelligence methods are promising but they strongly depend on having a proper training set and require an *a priori* knowledge of hundreds of thousands of SP energies.

In this chapter, we have taken advantage of massive parallelization and the supercomputing resources to systematically calculate the real saddle point (SP) energy as a function of position with respect of the dislocation core for vacancies and the family of <110> self-interstitial dumbbells in the presence of a single straight screw or edge dislocation, using the Self-Evolving Atomistic Kinetic Monte Carlo (SEAKMC) [40, 145] package. We present an overview of the commonly used SP energy approximations in section 2, the computational details and system setup in section 3, and a comparison and contrast results obtained with previous methods based in local minimum configurations (LMC) with the real SP values obtained in this study. Finally, we examine the anisotropy of diffusion of the defects and the range of interaction with the dislocation.

3.2 Background

3.2.1 Saddle Point Energy

The saddle point energy of point defects will be modified by the presence of dislocations, we can separate this effect in two contributions, a change in the binding energy of the point defect, and a change in the saddle point configuration and energy, this is given by Eq. 1 [146] and schematically shown in Fig. 3.1, where E^B is the change in the binding energy of point defects, and E^m is the change in the height of the saddle point energy.

$$E^{SP}(\mathbf{r}) = E_{bulk}^{SP} + E^B(\mathbf{r}) + E^m(\mathbf{r}) \quad \text{Eq. 3.1}$$

The calculation of these contributions is complicated and different schemes have been proposed to approximate the saddle point energy. For instance, a commonly used approach is to approximate the change in the SP energy based on the calculation of the system energies before and after the migration of the point defect [147], as shown in Eq. 2. The initial $E_i^{Binding}$ and final energy $E_f^{Binding}$ can be determined by elastic theory or using interatomic potentials [132].

$$E^{SP} = E_{bulk}^{SP} + \frac{1}{2} (E_f^{Binding} - E_i^{Binding}) \quad \text{Eq. 3.2}$$

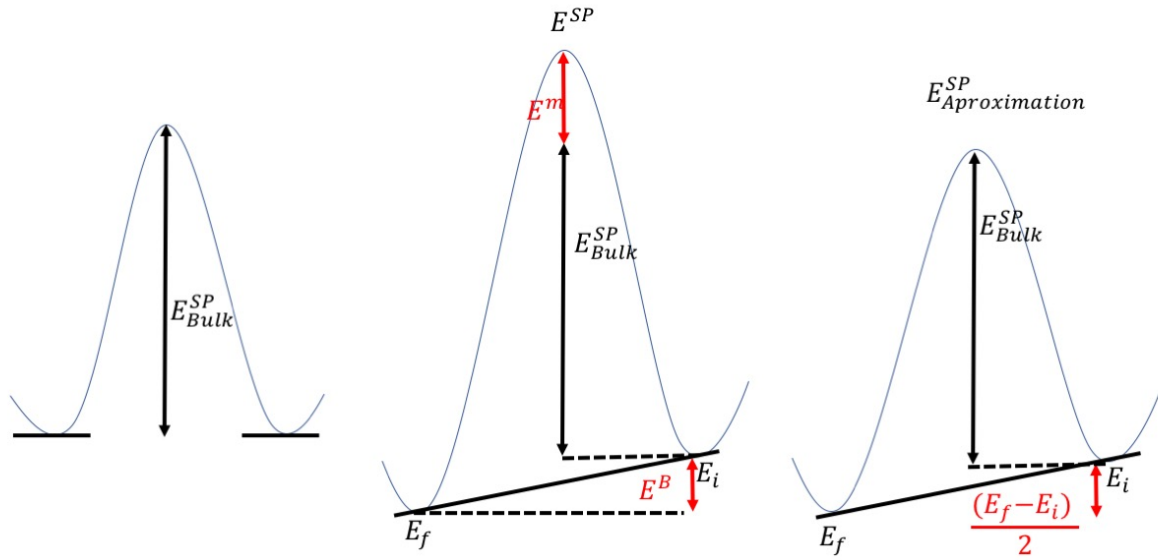


Figure 3.1. Change in the saddle point energy of point defects when a dislocation is introduced in the system.

3.2.2 Binding Energy Determination

3.2.2.1 Bilby-Cottrell Model

Conventionally, the elasticity-based Cottrell-Bilby model (CBM) is used to describe the interaction of an inclusion (e.g. point defects) with dislocations, and it has successfully explained how dislocations become pinned by the creation of “atmospheres” of inclusions that segregate around dislocations [124, 133, 134, 148]. In the Cottrell-Bilby model, the interaction energy E_β between a dislocation and a spherical inclusion in the ground state configuration is given by Eq. 3 [133, 134], where μ is the shear modulus, ν is Poisson’s ratio, and ΔV_β is the dilatation volume of the point defect. The polar angle θ is measured with respect to the slip plane and r is the distance between the point defect and the dislocation.

$$E_\beta = \frac{(1+\nu)\mu b \Delta V_\beta}{3\pi(1-\nu)} \cdot \frac{\sin \theta}{r} \quad \text{Eq. 3.3}$$

The interaction range between the dislocation and the point defect is defined in Eq. 4. A point defect will feel the presence of the dislocation at distances where the interaction energy is larger than the thermal energy [149].

$$L_\beta = \frac{(1+\nu)\mu b |\Delta V_\beta|}{3\pi(1-\nu)kT} \quad \text{Eq. 3.4}$$

3.2.2.1 Binding Energies Estimated from Elastic theory

The elastic theory estimates the binding energy by $E^{Binding} = P_{ij} \varepsilon_{ij}^d$ where P_{ij} is the elastic dipole tensor and ε_{ij}^d is the strain field of the dislocation. The strain field of the dislocation can be formulated by isotropic or anisotropic elastic theory [150]. It has been shown by Hayward [135] that isotropic elastic theory fails to properly describe the point-defect interaction, and therefore in this work we only employed the anisotropic formulation.

The strain field of the dislocation is obtained from the displacement field. The anisotropic displacement field was obtained using the equations derived by Hirth [151]. The anisotropic strain fields used in this work were obtained using the Babel software package [152].

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \quad \text{Eq. 3.5}$$

The dipole force tensor describes the influence that a point defect exerts on its neighbors, and it is measure of the distortion the defect introduces to the perfect lattice. The dipole tensor can be calculated using the Kanzaki forces.

$$P_{ij} = \sum_{k=1}^N [S_i^{(k)} + d_i^{(k)}] F_j^{(k)} \quad \text{Eq. 3.6}$$

where the summation is over the N neighbors of the defect, s is the position of a neighbor in the perfect lattice with respect to the defect, d is the displacement from the perfect position, and F is the Kanzaki force. The Kanzaki force is defined as the force required to maintain the displaced configuration when the defect is removed. In this work, we have used the dipole tensor values obtained by Hayward et. al [135] since they used the same interatomic potential in their study.

3.2.3.2 Binding Energies Estimated from Atomistic calculations

The binding energy between the point defect and the dislocation is given by:

$$E^{Binding} = [E^{Dislocation+Defect} + E^{Bulk}] - [E^{Dislocation} + E^{Defect}] \quad \text{Eq. 3.7}$$

Where E^{Bulk} is the energy of a perfect crystal system, $E^{Dislocation}$ stands for the energy of the system containing the dislocation, E^{Defect} is the energy of the perfect system containing one point defect, either a vacancy or a dumbbell interstitial, and $E^{Dislocation+Defect}$ is the energy of the system containing both the dislocation and the point defect. In this formulation, a negative binding energy indicates that the defect feels an attraction towards the dislocation. The binding energy will depend on the atomic position where the defect is introduced with respect of the dislocation.

3.3 Computational details

3.3.1 Dislocation models

The screw dislocation has a burgers vector $\frac{1}{2} \langle 111 \rangle$, and the dislocation line lies in the $[111]$ direction in bcc iron. The elastic center of the screw dislocation was made to coincide with one of the axes of the three-fold screw symmetry in the perfect lattice. The initial screw dislocation structure was created by displacing the atoms in the $[111]$ direction according to linear isotropic elasticity theory [121, 153] shown in equation 7. This initial structure is subsequent relaxed using interatomic potentials to obtain a stable configuration. Particularly, we used the Ackland potential of bcc iron [154] since it gives the correct description of the dislocation core [155]. The maximum displacement in the $[111]$ direction occurs in the $(11\bar{2})$ slip plane, making the system non-periodic in the $[1\bar{1}0]$ direction. The system size was chosen so that the displacement at the edges along the $[11\bar{2}]$ direction was close to zero, thus achieving periodicity along the $[11\bar{2}]$ direction.

$$u_y = \frac{b\theta}{2\pi} = \frac{b}{2\pi} \cdot \tan^{-1} \left(\frac{z}{x} \right) \quad \text{Eq. 3.8}$$

The Burgers vector of the edge dislocation is $\frac{1}{2}[111]$ with slip plane $(1\bar{1}0)$, and dislocation line direction is $[11\bar{2}]$. The edge dislocation was created by the procedure described by Ossetsky *et al.* [156]. The perfect crystal is divided in two halves. Initially, we have equal number of planes in the upper and lower crystals. Planes within one spacing b in the lower part of the crystal are removed. In the lower half of the crystal the length in the Burger's vector direction becomes $(N-1)*b$. To reduce the strain effects on the

simulation box, the length of the upper crystal in y direction is changed by $-b/2$ and the length of the lower crystal in y direction is changed by $+b/2$. The periodic boundary conditions in both dislocation line direction and Burger's vector direction are achieved. In Fig. 3.2 we show the coordinate system for both screw and edge dislocation, and the projection on the plane perpendicular to the dislocation line of the migration directions of the point defects.

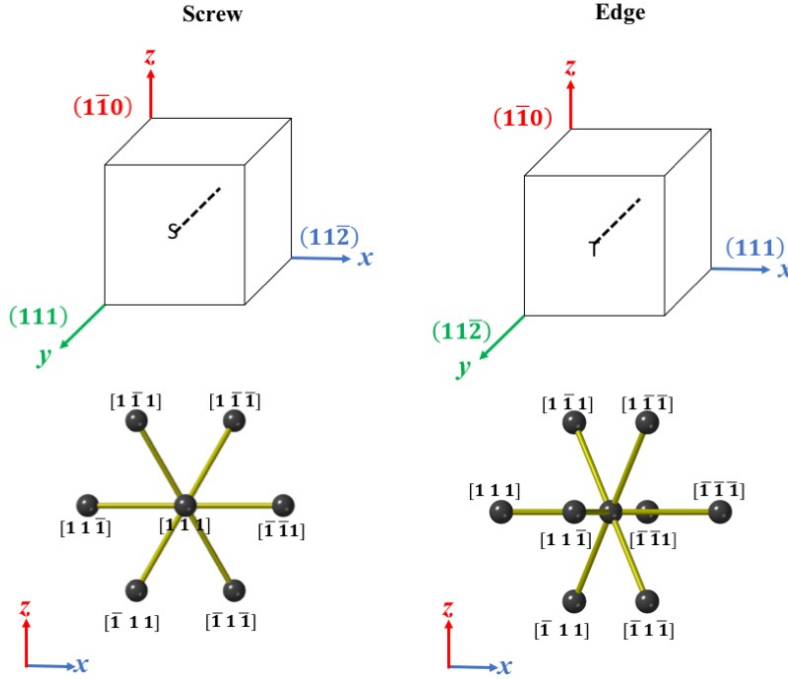


Figure 3.2. Coordinate systems for screw and edge dislocations, and the migration direction projections on the plane perpendicular to the dislocation line.

3.3.2 Simulation setup

The geometry of the simulation box is a rectangular parallelepiped with the axis of $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 112 \rangle$. These directions are chosen based on the slip system of bcc iron. In particular, we chose the (111) , $(11\bar{2})$ and $(1\bar{1}0)$ directions. The dislocation line was assigned to the y direction and the $(1\bar{1}0)$ direction was assigned to z . The block of atoms has been made infinite in the x , and y directions by applying periodic boundary conditions, thus having an infinitely long dislocation, and an infinite array of parallel dislocations. The dimension of our crystal was chosen to minimize the interaction between image dislocations such as at the boundary of the box where the strain field is negligible. The system sizes for both screw and edge dislocation are given in Table 3.1, and Fig. 3.3 show a schematic of the simulation cell for and edge dislocation.

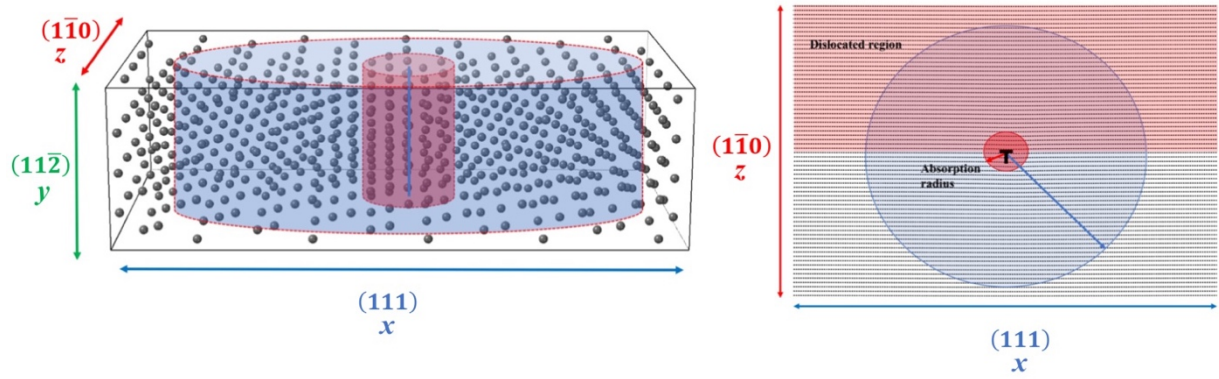


Figure 3.3. (a) Simulation cell used in this study for edge dislocation. (b) Tops view of the simulation cell.

Table 3.1. Simulation system size

	Simulation box size		
	x<112>(Å)	y<111>(Å)	z<110>(Å)
Edge	227	35	226
Screw	210	40	200

To investigate the dislocation-point defect interaction we have chosen atoms within a certain radius (R) to the dislocation line, and have denominated this region as the “effective interaction region”. Systematically we investigated one defect at a time within this effective interaction region. We have studied a vacancy and a $\langle 1\bar{1}0 \rangle$ dumbbell since it is the most stable interstitial defect in bulk iron. We have calculated the SP energies for all the $\langle 1\bar{1}0 \rangle$ dumbbell orientations: $[110]$, $[101]$, $[011]$, $[\bar{1}10]$, $[\bar{1}01]$ and $[0\bar{1}1]$. After the introduction of each defect, the system is relaxed and then the SP search is performed.

3.3.3. Saddle Point Searches using SEAKMC.

We have performed the SP search using SEAKMC. SEAKMC is an atomistic on-the-fly KMC method [40, 145]. On-the fly refers that the SP configurations and energies are determined as the system evolves. SEAKMC focuses on defect interaction and evolution with atomistic fidelity and only requires an input structure and interatomic potential as input without assuming potential defect migration mechanisms and energies. SEAKMC utilizes the Dimer method [36, 37] to search the SP directly without knowledge of the final state *a priori*. The Dimer method is based on the harmonic approximation of transition state theory (HTST) [38, 39]. To efficiently perform the SP search, we have used the SP configuration of the bulk of each defect as a starting guess of the SP configuration in the presence of a dislocation.

3.4. Results and Discussion

3.4.1 Saddle point sampling of point defects in the bulk bcc iron

First, we have calculated SP configurations in bulk bcc iron for vacancies and dumbbells. The SP searches for a vacancy predominately result in 8 SPs associated with first nearest neighbor jumps, located along the $\langle 111 \rangle$ directions (Fig. 3.4a). Comparatively, the SP distribution around a $\langle 110 \rangle$ interstitial dumbbell (Fig. 3.4b) is much more complicated than the vacancy case. Several sets of SPs that correspond to different transition states are found, including three different sets that correspond to first nearest neighbor migrations with a translation-rotation mechanism. Of these first nearest neighbor migration, two sets correspond to the nearest neighbors that lie in the direction of the dumbbell, and one set to the neighbor perpendicular to the dumbbell defect. One set corresponds to pure rotation to a $\langle 111 \rangle$ crowdion, and one set that corresponds to second nearest neighbor migration. These SP configurations are shown in Fig 3.4, as mentioned in the computational details section, these configurations obtained in the bulk system are then used as an initial guess for the SP searches near dislocations.

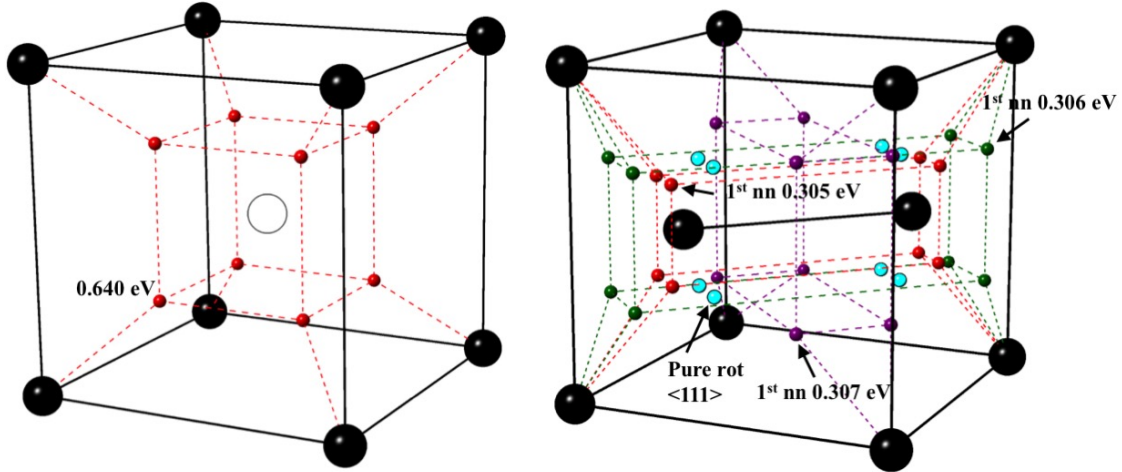


Figure 3.4 SP configuration in bulk Fe for (a) vacancy (b) $\langle 110 \rangle$ dumbbell.

3.4.2 Screw dislocation

Dislocations act as sinks for point defects [126], and thus it is generally expected that migration of point defects towards the dislocation core will be more favorable and energy barriers towards the dislocation will have a smaller value. However, from Fig. 3.5 with the SP obtained from SEAKMC, we found that the migration energy barrier towards the dislocation core is not necessarily smaller than the values of other directions, and the SP energy variation exhibit a complex and non-linear dependence as a function of distance to the dislocation core. The change of the SP energy as a function of position for the different migration directions for a vacancy in a screw dislocation environment is presented in Fig. 3.5. In this figure, we are plotting the relative energy with respect of the bulk SP energy, we have done the same for all the figures in this section. The symmetry observed in Fig. 3.5 is related to nature of the migration jumps. In the screw dislocation system, migration

in the $[111]$ and $[\bar{1}\bar{1}\bar{1}]$ correspond to migration in the dislocation line direction. According to elasticity theory the stress component in the dislocation line direction is zero, and thus we expect little change in the migration barrier in these directions as shown in Fig. 3.5. The migration to $[1\bar{1}1]$ and $[1\bar{1}\bar{1}]$ nearest neighbors are mirrored to each other, as shown in Fig. 3.2, and hence their SP maps are mirrors of each other (same applies for their negative counterparts). As expected the biggest difference in the saddle point energy is close to the dislocation core, and it decreases farther away from the core.

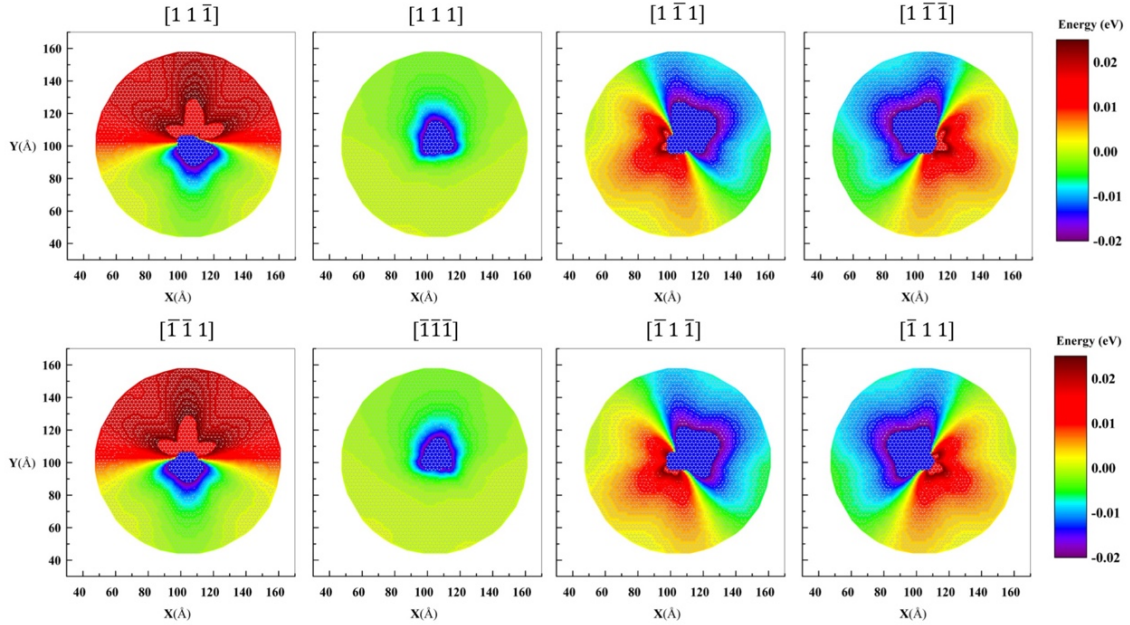


Figure 3.5 SP energy maps of nearest neighbor migration for a vacancy in the presence of a screw dislocation.

The case of a $[\bar{1}01]$ dumbbell near a screw dislocation is shown in Fig. 6. In this case, the energy maps become more complicated because of the directionality of the defect, having six different cases for each member of the $\langle 110 \rangle$ dumbbell family. The SP energy maps for the other members of the $\langle 110 \rangle$ family are given in the appendix section A3. When dumbbells migrate along the dislocation line, it interacts not only with the strain field in the migration direction but also with other components of the strain field due to the directional nature of the defect, different from the vacancy case. The SP energy maps are considerably different among each member of the $\langle 110 \rangle$ dumbbell family (appendix section A3). Just as in the vacancy case the change in the saddle point energy is more pronounced close to the dislocation core. It is possible to observe that the difference in magnitude with respect to the SP bulk value is larger for the dumbbell case, since dumbbells introduces a larger distortion in the system than vacancies.

Screw-dumbbell $[\bar{1}01]$

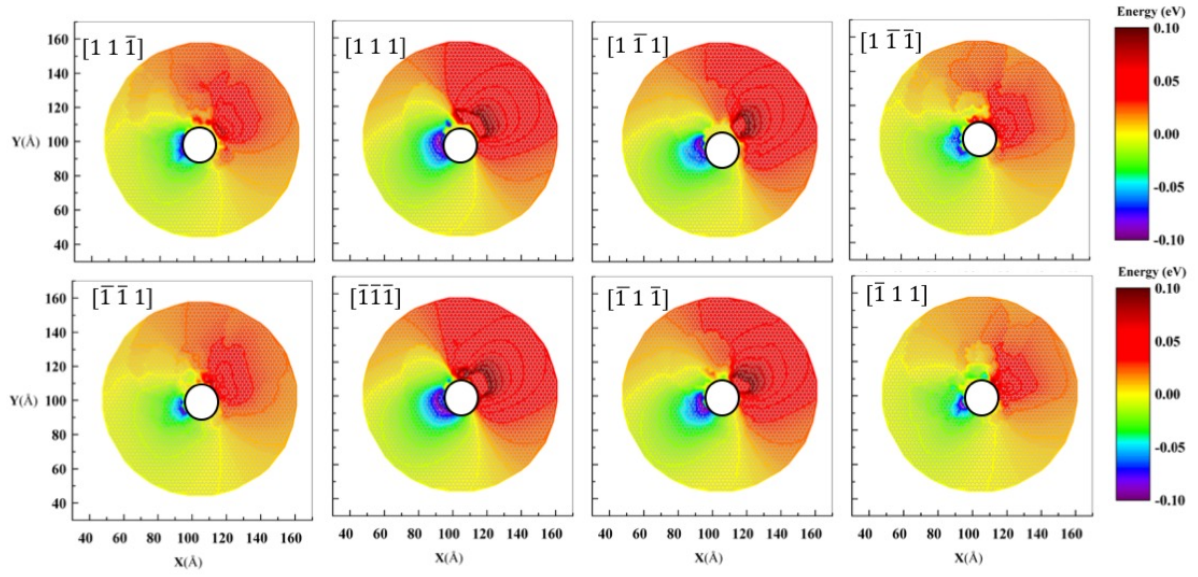


Figure 3.6. Energy barrier maps of different nearest neighbor migration directions for a $[\bar{1}01]$ dumbbell in the presence of a screw dislocation.

Fig. 3.7 shows the energy change for migration in the $[111]$ direction for all members of the $\langle 110 \rangle$ family. The symmetry relations observed in the figure are due to the direction of the dumbbells with respect to the dislocation core. This effect can be appreciated in the energy plots of the $[\bar{1}01]$ and $[0\bar{1}1]$ dumbbells, which are mirrors of each other, similar to the relationship between the $[101]$ and $[011]$ dumbbells. The directions containing a negative index have no components in the dislocation line direction, while the directions with all positive indices have components in the dislocation line direction. This results in the directions with all positive indices having a smaller change in the SP energy compared to the directions with a negative index, since the component along the dislocation line has no contribution because the stress field in that direction is zero.

3.4.3 Edge Dislocation

Fig. 3.8 shows the relative SP energies as a function of position for the different migration directions of a vacancy in an edge dislocation environment. In this case, we no longer have migration jumps in the dislocation line directions, but now the migration jumps in the $[111]$ and $[\bar{1}\bar{1}\bar{1}]$ neighbors correspond to migration in the glide direction. In these direction, the effect of the compressive and tensile stress field in the different halves of the edge dislocation is more evident, and provides the greatest changes in SP energy magnitude among all migration directions. The mirror relationship between $[1\bar{1}1]$ and $[1\bar{1}\bar{1}]$ still holds and their SP maps are again mirrors of each other.

Fig. 3.9 shows the SP energies of an $[\bar{1}01]$ dumbbell near an edge dislocation. Just as with the screw case, the SP energy maps strongly depend on the orientation of the dumbbell. The mirror symmetry relationship observed in the vacancy case for the $[1\bar{1}1]$ and $[1\bar{1}\bar{1}]$ directions are broken by the directional nature of the defect, and are only present for the $[\bar{1}10]$ and $[110]$ dumbbell directions (Appendix section A4). It can be observed that for both screw and edge dislocations, the change in SP energy for dumbbells is greater than for vacancies due to the larger distortion they introduce in the lattice. For the vacancy case, we have attempted to relate the SP energies to the strain/stress field by fitting the SP energies to analytical expressions, but none of them yield reasonable agreement with the SP data. The trends displayed in the energy maps between the screw and edge dislocations are significantly different as a result of the different nature of the strain fields generated by each type of dislocation.

3.4.4 Comparison of SP energies with previous approaches

These obtained SP energies are found to be significantly different from previous calculations that are based on binding energies, which in turn are related to the strain field of the dislocations. The SP energy maps in the $[\bar{1}\bar{1}\bar{1}]$ nearest neighbor migration direction obtained with SEAKMC searches for a vacancy (Fig. 3.10a) and a dumbbell (Fig. 3.10b) near an edge dislocation, are compared with the SP energies approximated with binding energies obtained from atomistic calculations (Fig. 3.10c and Fig. 3.10d), and with approximation based in anisotropic elastic theory (Fig. 3.10e and Fig. 3.10f). The case for the screw dislocation is given in Fig. 3.11. Heretofore we will use the SP-ABE (Atomistic Binding Energy), and SP-AET (Anisotropy Elastic Theory) acronyms to refer to the saddle

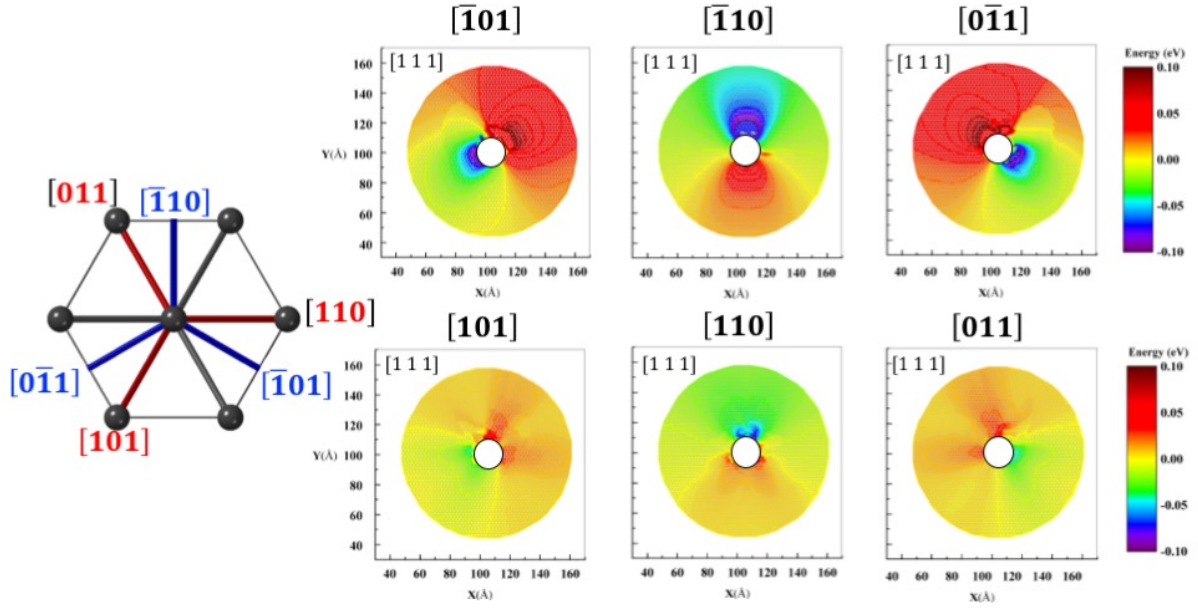


Figure 3.7. Energy barrier maps for different members of the $\langle 110 \rangle$ dumbbell family in the $[111]$ migration direction.

Edge-vacancy

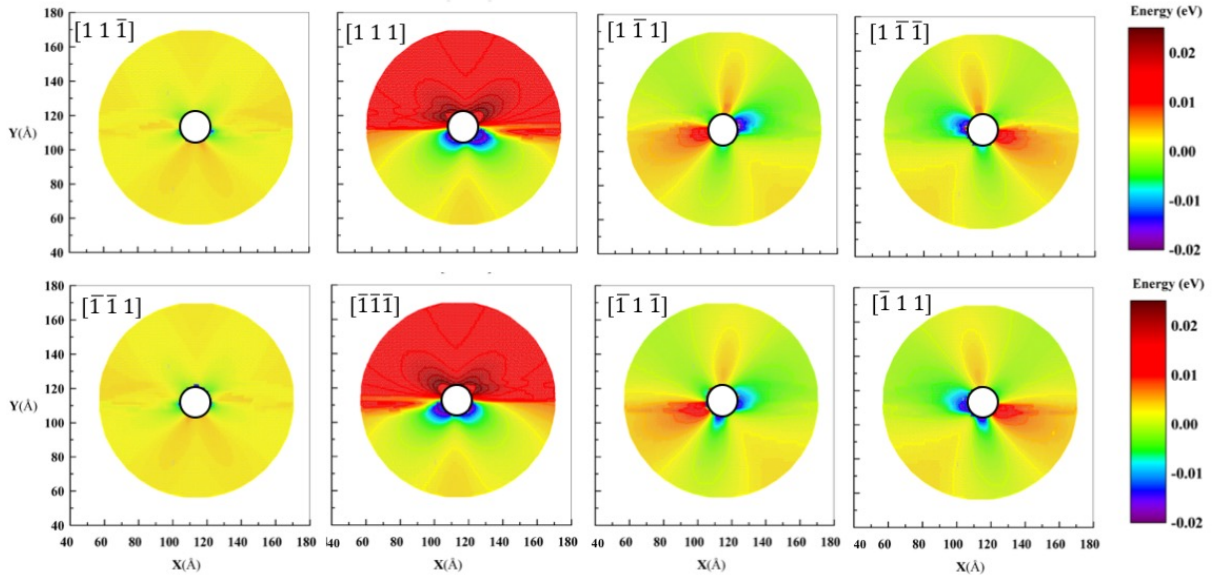


Figure 3.8 Energy barrier maps of different nearest neighbor migration directions for a vacancy in the presence of an edge dislocation.

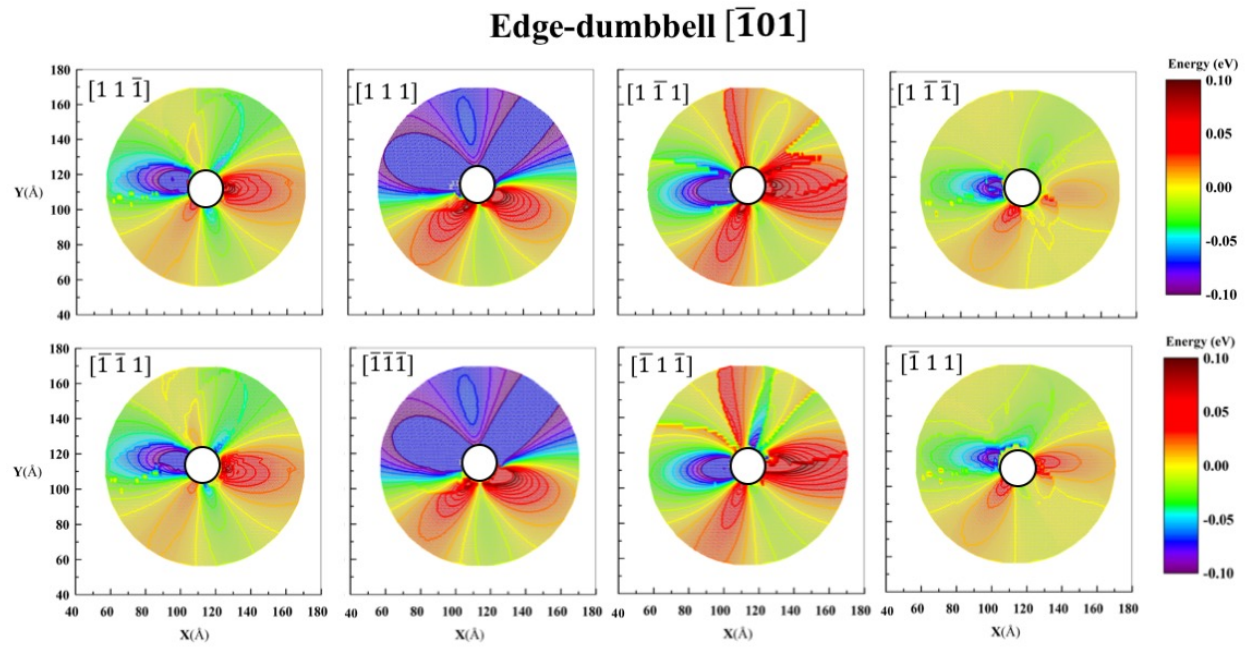


Figure 3.9. Energy barrier maps of different nearest neighbor migration directions for a $[\bar{1}01]$ dumbbell in the presence of an edge dislocation.

point approximation from binding energies obtained by atomistic calculations, and anisotropic elastic theory respectively. In these plots, we again have subtracted the actual migration energy barriers from the corresponding bulk values. It should be noted, there is an order of magnitude difference between the color bars of SP values between SEAKMC and the SP-ABE and SP-AET approaches in Fig. 3.10. We used this scheme in order to be able to appreciate the fine details of the SP-ABE and SP-AET approaches. In contrast, we used the same range for the color bar in Fig. 3.11 where the energy changes in the SP-ABE and SP-AET are barely appreciated. This indicates that DPDI is significantly stronger when the real SP values are used, and that previous approximations severely underestimate the DPDI. The SP-ABE and SP-AET approaches qualitatively show a similar behavior as expected, which is best appreciated in Fig. 3.10. In general, the SP magnitude of the SP-AET approach is smaller than the SP-ABE approach, in agreement with the results obtained by Hayward [135].

In Fig. 3.12 we have plotted the binding energy as a function of position calculated from atomistic calculations for vacancies and dumbbells interacting with screw and edge dislocations. We note that there is an order of magnitude difference in the color bar between vacancies and dumbbells, since dumbbells introduce a bigger distortion in the lattice and thus having a stronger interaction with dislocations than vacancies. We show the strain field of a single edge (Fig. 3.12c) and screw dislocation (Fig. 3.12f). In the screw case the threefold symmetry details are appreciated in both strain and binding energy plots. Likewise, for the edge case the effect of the compressive and tensile fields below and above the dislocation are appreciated in both images. Based on Fig. 3.10c and 3.10d and Fig. 3.11c, and 3.11d, we consider the values using SP-ABE approach are related to the strain field, likewise for the SP-AET approach. The discrepancy in the patterns between the SP search and the SP-ABE, SP-AET approaches is a strong indication that the SP energy does not depend on properties of LMC in the potential energy landscape. Instead, the SPs need to be determined based on transition state configurations. Therefore, the unjustified linearity imposed in the saddle point approximations (Eq. 3.3) has been proved unfulfilled [132, 157] and imposes a limit the range of values the SP energy [142]. In addition, the dilatation volumes that enter the Cottrell-Bilby model, or the elastic dipole tensor are based on the stable configuration, and do not provide information on the saddle point configuration, this is a significant source of errors since the ground states (or LMC configurations) are different from those for the SP configurations. Furthermore, the dilatation volumes used in the Bilby-Cottrell model use an approximate description of point defects, based on the assumption of spherical objects. In this context, the description of an anisotropic defect, such as dumbbell in bcc iron, may be incorrect, and even a vacancy in the SP configuration is an anisotropic defect (produced anisotropic strains) and, strictly speaking, cannot be described correctly in this approach. It has been suggested [158-160] that the anisotropy of point defect at the saddle point has an effect on the sink strength of dislocations. Recently, Carpenier [161] calculated the elastic dipole tensors at the saddle point configurations to estimate the DPDI, and concluded that the influence of the saddle point anisotropy leads to more complex trajectories than in the LMC case.

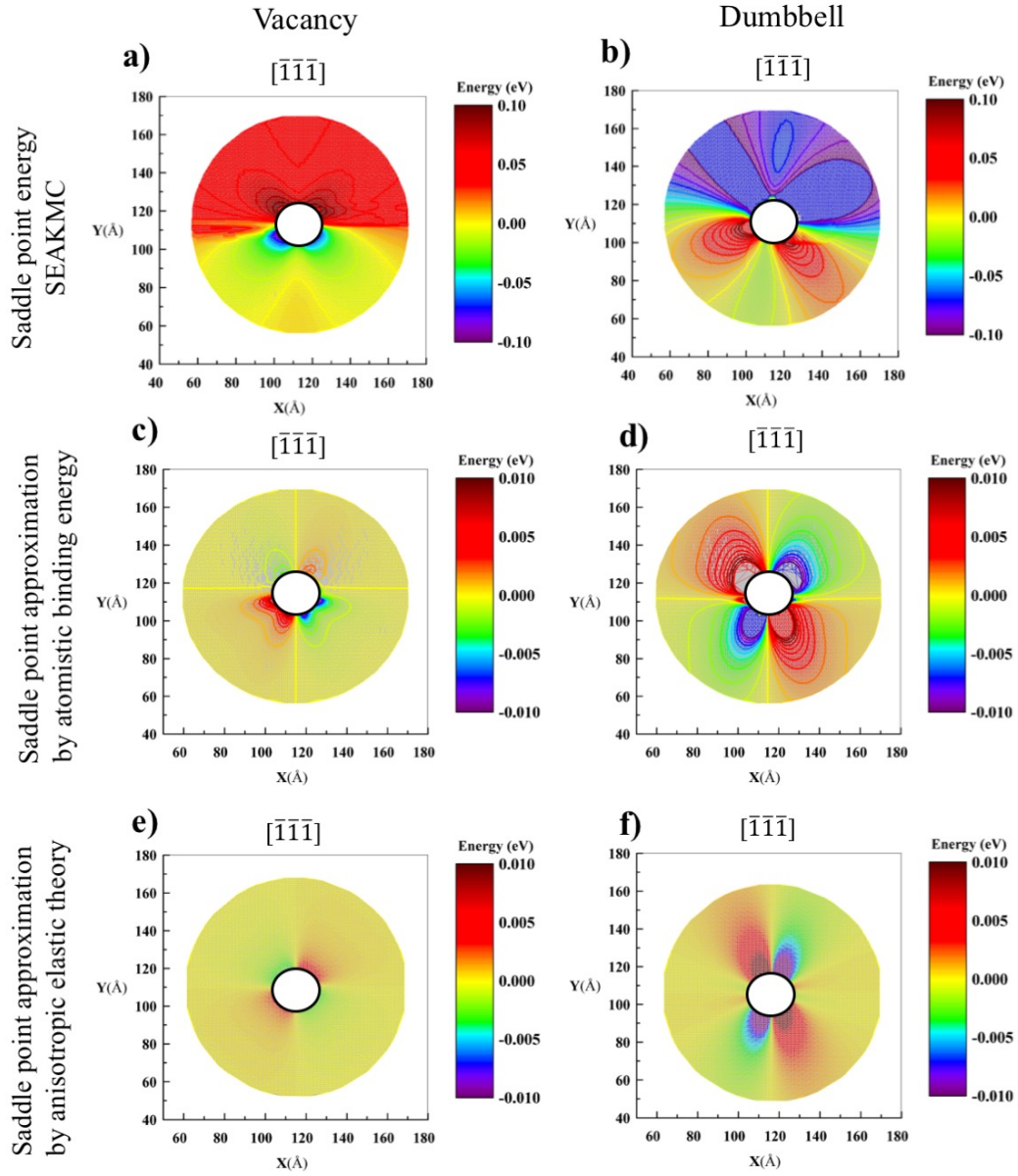


Figure 3.10 SP energy maps comparison of selected $[\bar{1}\bar{1}\bar{1}]$ nearest neighbor migration directions for a vacancies and dumbbells in the presence of an edge dislocation between (a,b) SP search (c,d) SP-ABE approach and (e,f) SP-AET approach.

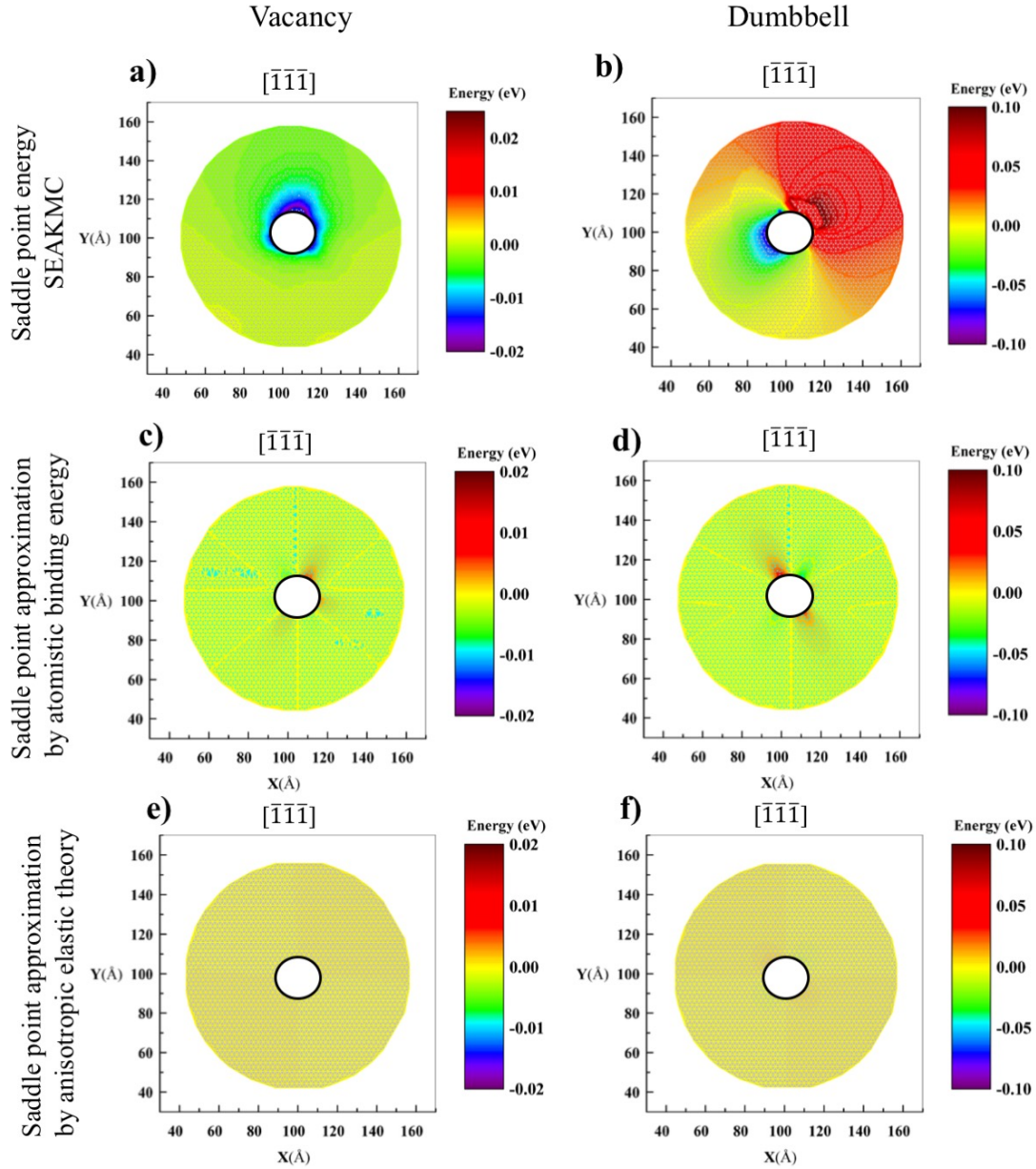


Figure 3.11 SP energy maps comparison of selected $[111]$ nearest neighbor migration directions for a vacancies and dumbbells in the presence of a screw dislocation between (a,b) SP search (c,d) SP-ABE approach and (e,f) SP-AET approach.

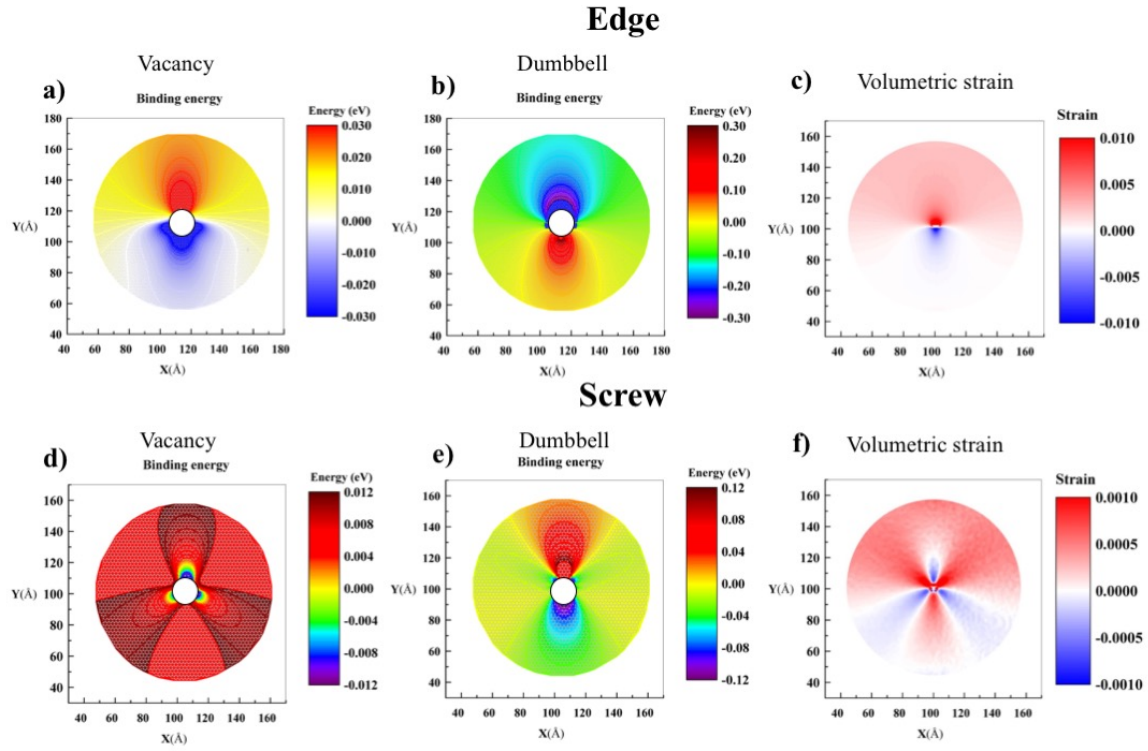


Figure 3.12 Binding energy maps for vacancies and dumbbells in the presence of screw, and edge dislocations, and volumetric strain for screw and edge dislocations.

3.4.5 Diffusion anisotropy

In the bulk point defect migration will exhibit a random walk motion; the presence of the dislocation changes the SP configurations and energies, resulting in a certain migration direction having a higher probability than the other directions. If there is a large difference in SP energy, a particular migration direction will be chosen more often, resulting in anisotropic diffusion. To analyze the diffusion anisotropy, we have taken the difference between the smallest and largest SP energy values as function of position with respect of the dislocation core, as shown in Fig. 3.13 for both screw and edge dislocations. In general, dumbbell defects will have a higher anisotropy of diffusion due to the directionality nature of the defect and the larger strain it introduces. The anisotropy of diffusion will lead to more complex diffusion paths. Particularly, the higher anisotropy of diffusion for dumbbells near both edge and screw dislocations indicates they will have more defined migration paths, and may suggest the preferential absorption of dumbbells over vacancies.

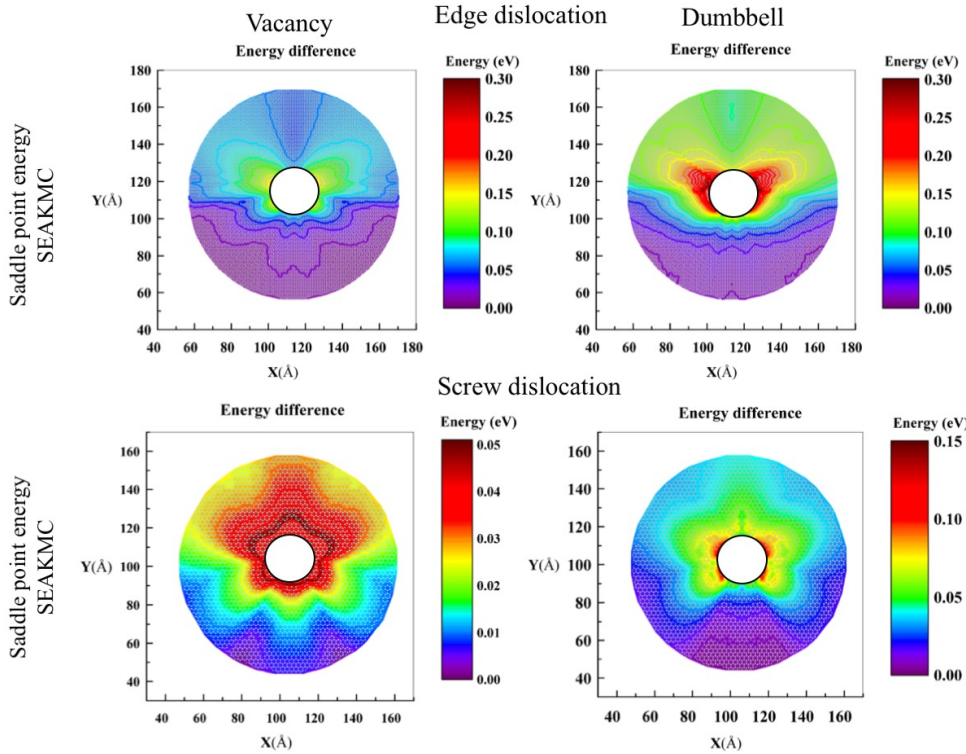


Figure 3.13. Anisotropy of diffusion for vacancies and dumbbells in an edge and screw dislocation.

From the SP searches we can also obtain the direction of the SP with the lowest energy barrier at each position, and construct the “most probable migration path maps”. This type of plots permits to visualize what would be the most probable migration path of a point defect as a function of position with respect to the dislocation line. This path will be more often followed at low temperatures, where effect of the difference between energy barriers is more prominent, and as the temperature rises the migration of point defects approaches random walk. The most probable migration path for vacancy and dumbbell defects in a

screw dislocation environment is given in Fig. 3.14. The most probable path maps presented in Fig. 3.14 are in good agreement with the results of Sivak *et al.* [137, 138] for the vacancy cases where the strain field is small, but our results differ in the dumbbell cases. Fig 3.14.b is the most probable path for the $[\bar{1}10]$ dumbbell, for each different member of the $\langle 110 \rangle$ dumbbell family there will be a different most probable migration path.

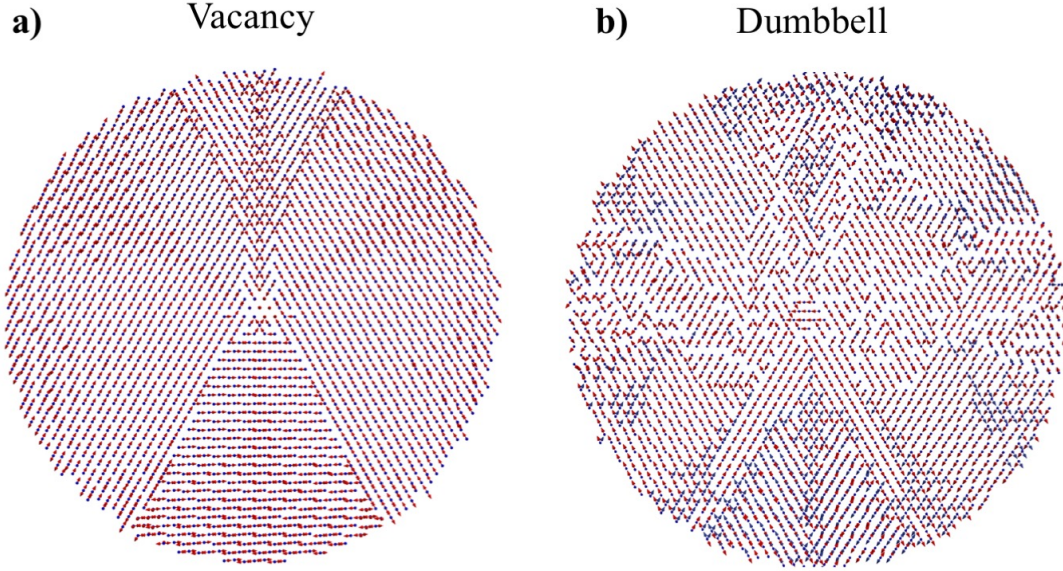


Figure 3.14. (a) Most probable migration path map for a vacancy (b) most probable migration path map for a dumbbell, in a screw dislocation environment.

3.4.6 Interaction range

We have also investigated the interaction radii between dislocations and point defects. It is commonly believed that the point defects are able to “feel” the presence of the dislocation up to a few lattice constants [121]. We examined the change in SP energy for selected directions (shown in the appendix section A8, Fig. 3.15), and compared the results of the SP search and the values obtained using the SP-ABE and SP-AET. In Fig. 3.15, we show the results for the direction given by line 3 in the appendix section A.7. Again, in these plots we have subtracted the bulk value of the SP energy. It can be observed that in all plots the interaction range obtained with the SP search is significantly greater than those obtained with the SP approximations, both SP-ABE and SP-AET. In general, the DPDI from SEAKMC has a range of ~ 40 Å for dumbbells in both screw and edge, ~ 20 Å for vacancies around a screw dislocation, and ~ 25 Å for vacancies around an edge dislocation, where diffusion anisotropy starts to become negligible, in contrast with the binding energy approaches which have a considerably shorter interaction range [135, 138]. This increased interaction range may lead to different estimations of preferential absorption of self-interstitial atoms by dislocations over vacancies that was used to model the long-term microstructural evolution of materials [162].

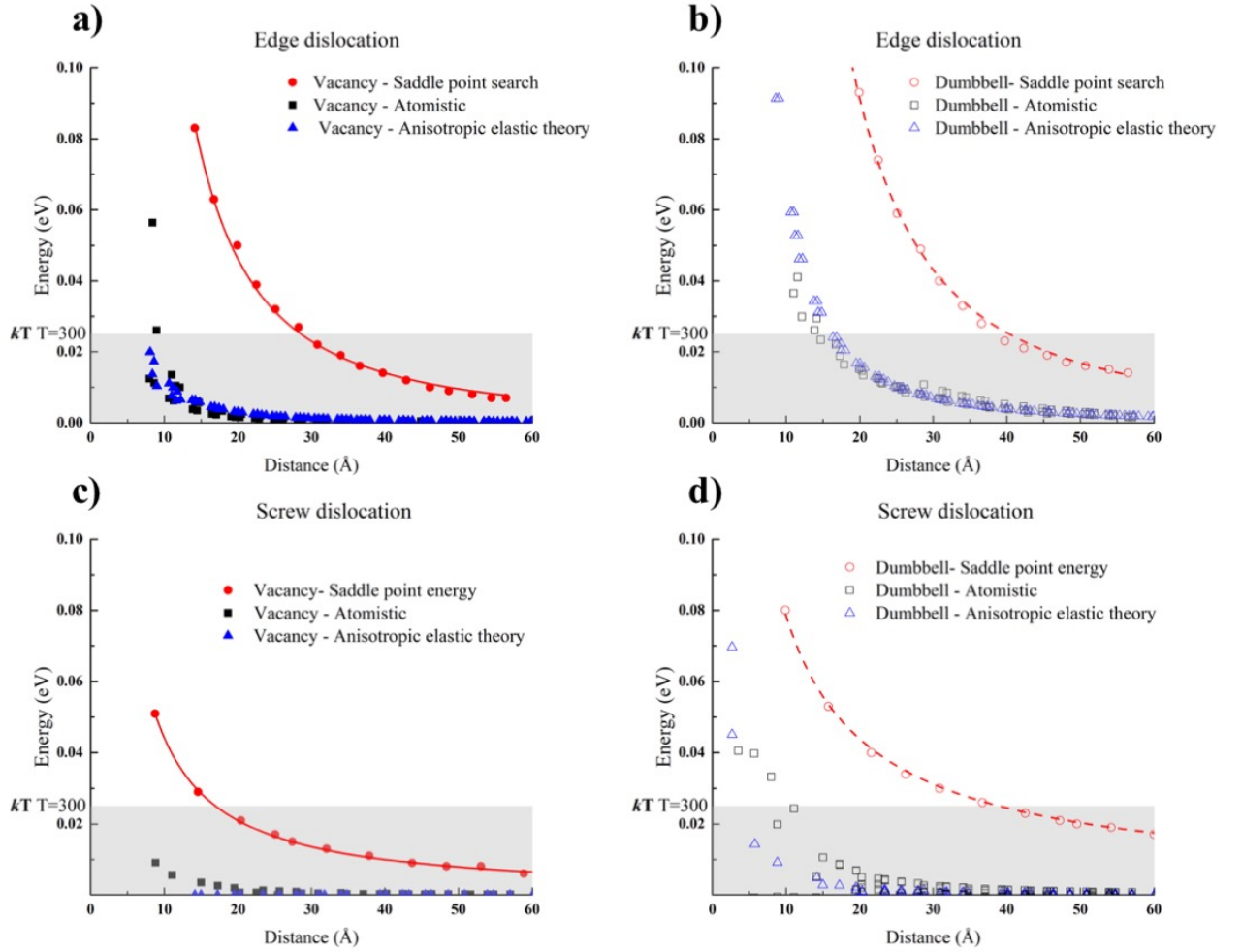


Figure 3.15. Comparison of the Interaction range between SP energy, and SP approximation using the binding energy obtained from atomistic calculations (SP-ABE) and from anisotropic elasticity (SP-AET). (a) edge dislocation and vacancies, (b) edge and dumbbells, (c) screw dislocation and vacancies, (d) screw dislocation and dumbbells.

3.5. Conclusions

In this chapter, for the first time we have presented the actual SP configuration and energies for vacancies and dumbbells as a function of position in the presence of a dislocation. The SP approach captures the complexity of the migration mechanisms of point defects, and effect of different local atomic environments introduced by dislocations. We have compared the current results of SPs with previous models that are commonly used in the literature. We found that previous methods significantly underestimate the effect of dislocations on point defects, and their range of interaction. Based on the maps of SP configuration and energies, we find that the atomistic processes of DPDI (for both vacancy and interstitial) is highly anisotropic and correlated. We found a discrepancy in the migration SP energies found in the studies and the energies calculated with LMC approximations. This provides evidence that the assumption to use LMC approach is incorrect and does not properly capture the dynamics of point defects. The anisotropy of diffusion is appreciated with the “most probable migration” maps constructed, and by the trajectories of dumbbells around dislocations that must escape the compressive region of the dislocations to be absorbed. The effect of the saddle point configuration on migration energies must be taken into account to be able to capture the real dynamics point defect migration, and transport phenomena. As it was showed, the data obtained in this study can be used as an input for upper scale models, such as mean field rate theory, to provide a realistic description of point defect dynamics, and it allows to study material properties that depend on diffusion mechanisms, such as swelling and creep, that are of interest for various applications.

CHAPTER IV

DISLOCATION BIAS IN BCC FE

A version of this chapter will be submitted to a peer reviewed journal for publication by Luis Casillas-Trujillo, Andrew S. Ervin, Alexander Barashev, H. Xu:

Luis Casillas-Trujillo, Andrew S. Ervin, Alexander Barashev, Haixuan Xu. "Dislocation bias in bcc iron."

In this chapter, I developed the KMC code, ran all the simulations, and analyzed the data. Andrew Ervin helped with the debugging the KMC code and discussion on the dislocation bias definition. Alexander Barashev provided discussion on the dislocation bias models, and established the theory and models to assess bias. Haixuan Xu, developed the SEAKMC code, established the definitions for dislocation bias, supervised the code development, designed and directed the simulations, and provided scientific discussion and data analysis.

Abstract

The preferential absorption of self-interstitials atoms by dislocation over vacancies is responsible for is the fundamental cause of void formation, radiation-induced climb, and microstructural evolution of materials exposed to irradiation. The bias factor has been included in rate theory models as an empirical parameter to quantify this preferential absorption. In this work, we employ kinetic Monte Carlo to study the absorption of point defects by straight edge and screw dislocations in bcc iron using the real migration energy barrier for the dislocation point defect interactions. We assess the bias factor using the life time of the defect based on capture efficiency. We find that the bias factor is a function of temperature and dislocation density rather than a parameter.

4.1 Introduction

Structural components for nuclear energy applications such as iron alloys are exposed to radiation damage during its operational life. The result of radiation damage is the production of a large number of point defects. After recombination, the remaining defects are either absorbed by sinks, such as dislocations. While investigating gas bubble nucleation and growth in irradiated materials Greenwood *et al.* [118] suggested that dislocations in a crystalline material would show a preference for self-interstitial absorption rather than vacancies because self-interstitial atoms would have a stronger elastic interaction with the stress field of the dislocation. They suggested that radiation dimensional changes were due to the excess vacancies migrating towards voids, causing them to grow. This behavior was confirmed by Cawthorne and Fulton [18] when they reported a 7% void volume increase in irradiated stainless steel. With the discovery of void swelling, the preferential absorption of self-interstitials was incorporated into models in the form of an empirical parameter denominated the dislocation bias factor.

Over the years several attempts to determine the dislocation bias factor have been made. The first attempt was done by Foreman [163], by solving the diffusion equation with drift using perturbation theory. Foreman, treated the dislocation point-defect interaction with elastic theory considerations. Foreman concluded that the bias value was larger than the empirical estimates. An analytical solution was obtained by Heald [164] who used the solution of Ham [149], and modeled defects as centers of dilatation. Heald and Miller [165] proposed that the bias factor should be a function of the dislocation density. The bias factor should increase with increasing dislocation density. Heald and Miller also made a distinction in the bias factor between an isolated dislocation and an array of dislocations (dislocations with overlapping stress fields). The bias factor for an isolated dislocation is higher than for an array of dislocations, the effect of neighboring dislocations becomes progressively more important as the dislocation density is increased. Miller concluded that the variation in assumptions and approximations lead to different values of the dislocation bias [166], such as the approach of Bullough and Newman [167] of not considering angular dependence, allowing dislocations to attract defects from all directions and leading to an overestimation of the dislocation sink strength. Wolfer and Ashkin [17] also used perturbation theory to solve the diffusion equation, and also included the effects of externally applied stresses. More recently, Chang *et al.* [168] applied the finite element method to assess the bias factor in both screw and edge dislocations, and compared the effect of using interaction energies based on elasticity theory and interatomic potentials.

Theoretical studies systematically overestimate the magnitude of the bias factor by at least an order of magnitude higher than experimental estimations. Several attempts have been made to account for this discrepancy. The production bias concept [169] argued that the excess of vacancies is released from collision cascades since self-interstitials cluster together. Molecular dynamic simulations [170, 171] showed that these clusters are mobile and are attracted to dislocations, and they actually contribute to the bias factor. Bullough and Quigley [172] suggested that the density of jogs along the dislocation line could decrease sink strength. More recently Wolfer [146] suggested that the high estimations of the bias are correct since the observed low swelling in irradiated materials is due to intra-cascade recombination, but low swelling rates have also been observed in electron-irradiation where no intra-cascade recombination is present [173].

The discrepancy between theory and experiments still persists, and the magnitude of the preference for interstitials remains uncertain. Radiation swelling is a direct consequence of dislocation bias. An accurate description of dislocation bias is key to successfully perform simulations to assess void swelling in new radiation resistant materials. Besides swelling the absorption of interstitial of excess interstitials assists dislocation climb, leading to radiation induced creep [128] and can also impact plastic properties by altering the microstructure of dislocations [122].

In this chapter, we investigate the dislocation bias factor in perfect straight edge and screw dislocations in bcc iron. We employ kinetic Monte Carlo (KMC) to study the absorption of defects by dislocations, and employ the real migration energy barrier for the dislocation

point defect interactions. We assess the bias factor using the life time of a defect, which is an efficiency based bias definition, similar to the definition used in rate theory. Finally, we examined the migration paths of defects and assessed the anisotropy of diffusion of point defects.

4.2. Background

4.2.1 Dislocation bias in rate theory

In rate theory, the dislocation point defect interaction superimposes a drift flow on the random motion of point defects. Dislocation bias arises from this drift, represented in the second term of Fick's law,

$$J = \nabla(DC) + \frac{DC}{kT} \nabla E_\beta \quad \text{Eq. 4.1}$$

In this equation, D is the diffusion coefficient of the point defect, C the point defect concentration, k the Boltzmann constant, T the temperature and E_β the interaction energy.

The largest contribution to the dislocation point defect long-range interaction is due to the Cottrell size effect. In this context, point defects are regarded as centers of dilatation in a continuum medium. Defects produce a local volume change, and the stress field generated by this volume change will interact with the hydrostatic stress of the dislocation. To calculate the volume change, which is usually referred to as the relaxation volume, it is necessary to employ discrete lattice models. The interaction energy between an isolated dislocation and a point defect h given by Cottrell [134] and Bilby [133],

$$E_\beta = \frac{(1+\nu)\mu b \Delta V_\beta}{3\pi(1-\nu)} \cdot \frac{\sin \theta}{r} \quad \text{Eq. 4.2}$$

where μ is the shear modulus, ν is Poisson's ratio, and ΔV_β is the relaxation volume around the point defect. The polar angle θ is measured with respect to the slip plane and r is the distance between the point defect and the dislocation. The interaction range between dislocations and point defects is given by,

$$L_\beta = \frac{(1+\nu)\mu b |\Delta V_\beta|}{3\pi(1-\nu)kT} \quad \text{Eq. 4.3}$$

The sink strength is a measure of the capture efficiency of a point defect of a given type by the dislocation due to their interaction. The sink strength of a defect type α , is given by,

$$Z_\alpha = \frac{J_\alpha}{D\bar{C}} \quad \text{Eq. 4.4}$$

Where, J is the flux of the defect, D is the diffusion coefficient, and $\bar{C}$ is the mean concentration of defects in the cell centered at the dislocation. The bias factor in rate theory

is a measure of the relative defect capture efficiency by the dislocation. The swelling rate of a material is linearly proportional to the dislocation bias.

$$B = \frac{(Z_I - Z_V)}{Z_I} \quad \text{Eq. 4.5}$$

4.2.2 Dislocation bias

We employ an efficiency based definition of dislocation bias, based on the absorption time of a point defect, similar to the efficiency based definition of bias employed by rate theory. We call life time of a defect the time needed for a point defect to be absorbed by the dislocation starting in a given position in a system that only contains a single dislocation, e.g. no other sinks are present in the system. We take the ratio of the time of the defect interacting with the dislocation and the time the defect would reach the dislocation core by a random walk. Then the bias is given by,

$$B = \frac{t_v - t_i}{t_i} \quad \text{with } t = \frac{t_\alpha}{t_\alpha^r} \quad \text{Eq. 4.6}$$

where, t_v is the life time of a vacancy, t_i is the lifetime of an interstitial, and t_α^r is the random walk time of a defect of type α . Fig 4.1. Shows the comparison life time of a vacancy in a screw dislocation and a random walk as a function of distance to the dislocation core.

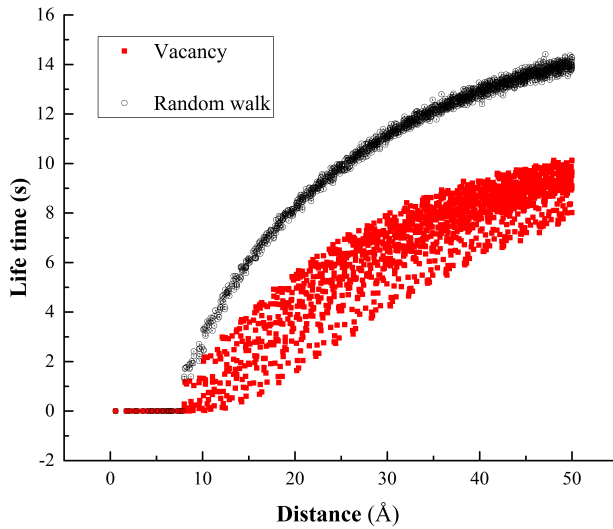


Figure 4.1. Comparison between the life time of a vacancy in the presence of a screw dislocation, and with a random walk.

4.3. Computational Methods

4.3.1 Migration energy barriers

The bias factor depends on the energy of interaction between dislocation and point defects. The migration energy barrier strongly depends on the local atomic configuration. In the previous chapter, we calculated the real migration barrier distribution around vacancies and self-interstitial dumbbells as a function of position with respect of screw and edge dislocations with the self-evolving atomistic kinetic Monte Carlo software (SEAKMC) [145]. In such work, we discussed that the migration energy barrier depends on the transition state. Previous investigations of the bias factor are mostly based on the elastic theory, calculating the interaction energy with Equation 4.2, with the relaxation volume dictating the value of the interaction energy. This relaxation volume corresponds to the volume in the local minimum configuration (LMC), and it is not representative on the dilatation of the defect in the saddle point configuration.

In bulk bcc Fe, the saddle point searches for a vacancy obtained 8 migration energy barriers, corresponding to a migration to each of the first nearest neighbors. We have chosen the $\langle 110 \rangle$ type self-interstitial dumbbell since it is the most stable interstitial defect in bulk iron, and found 24 migration barriers corresponding to first nearest neighbor migrations. The migration mechanism for a $\langle 110 \rangle$ self-interstitial dumbbell is a translation-rotation mechanism as illustrated in Fig. 4.2. The migration barrier search was done for all the of the $\langle 110 \rangle$ family of directions, and the KMC code implements the translation-rotation.

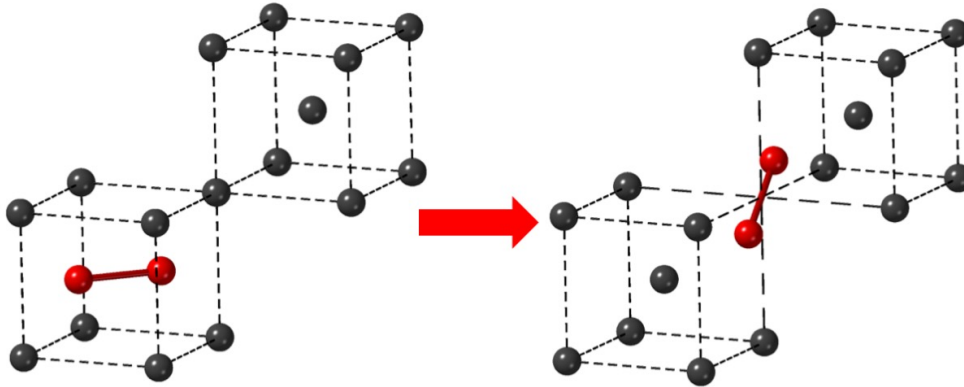


Figure 4.2. Migration mechanism for self-interstitial dumbbells.

4.3.2 Simulation system.

We have introduced a single straight dislocation in the middle of a block of atoms. We have chosen to use the directions of the slip system for convenience. The block of atoms has been made infinite in all directions by applying periodic boundary conditions, thus

having an infinitely long dislocation and an infinite array of dislocations. Varying the dimension of the system allows us to vary the dislocation density. The Burgers vector of the edge dislocation is $\frac{1}{2}[111]$ with slip plane $(1\bar{1}0)$, and dislocation line direction is $[11\bar{2}]$. The edge dislocation was created by the procedure described by Ossetsky *et al.* [156]. A plane is removed from one of the halves of the crystal, and the structure is relaxed. The resulting dislocation will be in the center of the crystal. The screw dislocation has a Burgers vector $\frac{1}{2}\langle 111 \rangle$, and the dislocation line lies in the $[111]$ direction. The elastic center of the screw dislocation was made to coincide with one of the axes of the three-fold screw symmetry in the perfect lattice. The screw dislocation was introduced in the middle of the block by displacing the atoms in the $[111]$ direction according to linear elasticity theory [121, 153]. We have systematically introduced a point defect for each atomic position located less than a distance R from the dislocation core, and performed KMC simulation until it was absorbed by the dislocation. Fig. 4.3 show a schematic of the simulation cell for and edge dislocation.

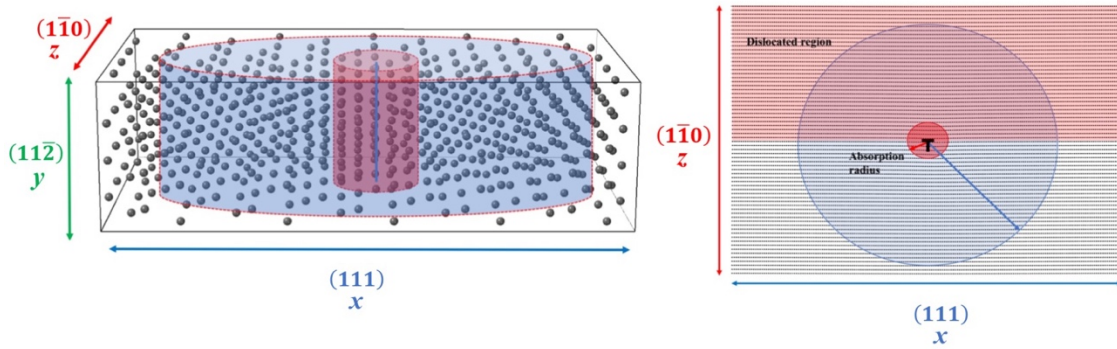


Figure 4.3. (a) Simulation cell used in this study for screw dislocation. (b) Tops view of the simulation cell.

4.4. Results and discussion

4.4.1 Point defect Migration anisotropy

KMC simulations are able to provide the migration path of point defects around dislocations. At low temperatures, the effect of the difference between energy barriers is enhanced, and the most favorable path is more often followed. We find that the diffusion of point defects near dislocations is highly anisotropic and strongly correlated. This correlated behavior is shown in Fig. 4.4. In fact, in some regions around the dislocations dumbbells need more migration steps to reach the dislocation core due to the repulsion they experiment from the strain field. In Fig. 4.4 we have identified these less favorable dumbbell zones in blue. This is in line with the observations of Heald and Miller [165], who noted that in edge dislocation some interstitials will find themselves in the compressive side of a dislocation and must move around to the tension side before being

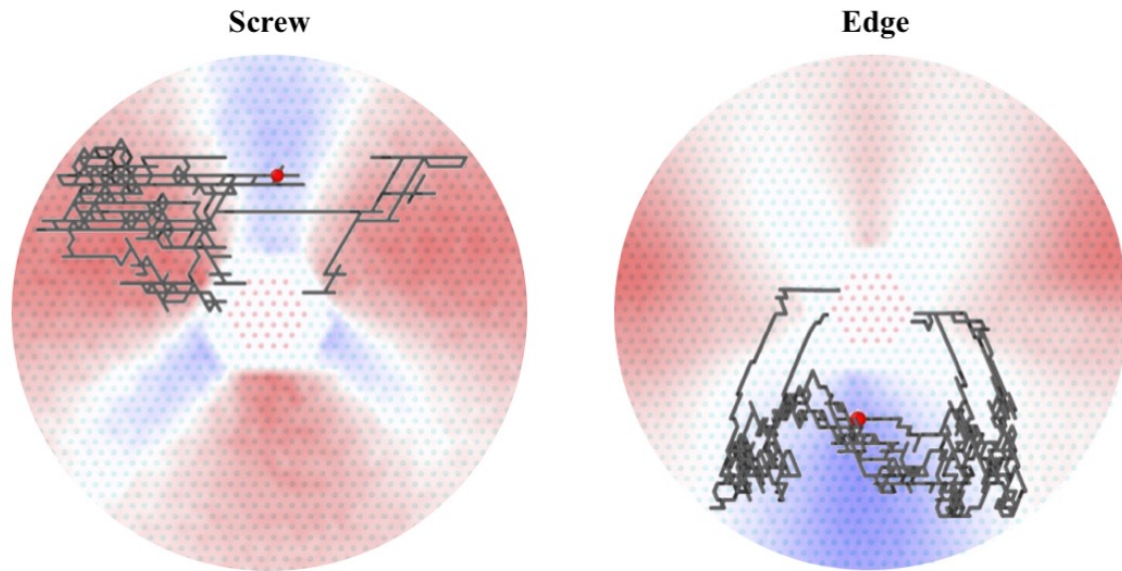


Figure 4.4. Dumbbell migration path around a (a) screw (b) edge dislocation. The larger red circle represents the dumbbell starting position. The dislocation core is represented by the red colored atoms.

absorbed, having longer diffusion paths for some defects. We also have plotted several dumbbell migration trajectories for both screw and edge dislocations. Fig 4.4. graphically shows how dumbbells must move around to find preferential absorption zones.

4.4.2 Dislocation bias

The absorption time for point defects at 300K as a function of position with respect to the dislocation core is shown in Fig. 4.5 for the screw case, and Fig. 4.6 for the edge case. As expected the required time of absorption increases with distance but it is also a function position with respect of the core. At these temperature, there is a big difference in the time scale between dumbbells and vacancies, we chose this low temperature to be able the show the features of the surface. As the temperature increases this difference becomes smaller, and comparable in magnitude for the reactor operation temperatures.

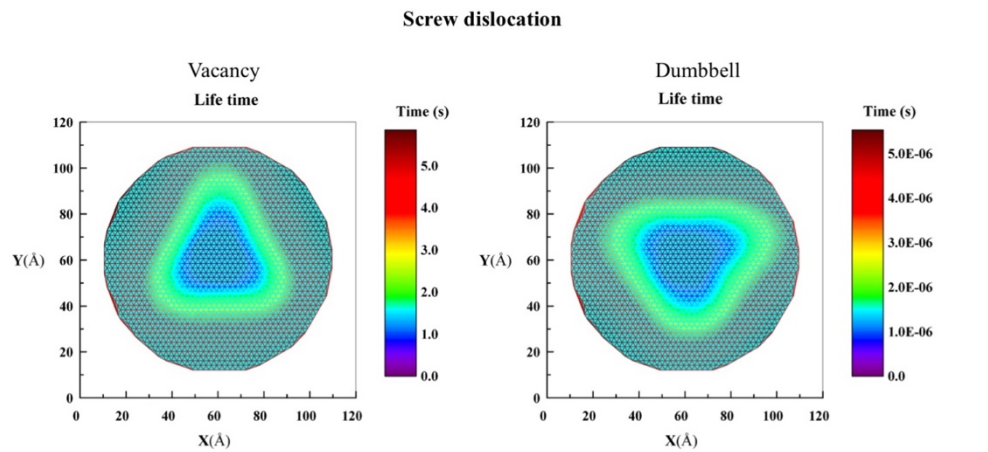


Figure 4.5. Time of absorption by a screw dislocation at 300 K for (a) vacancy (b) self-interstitial dumbbell.

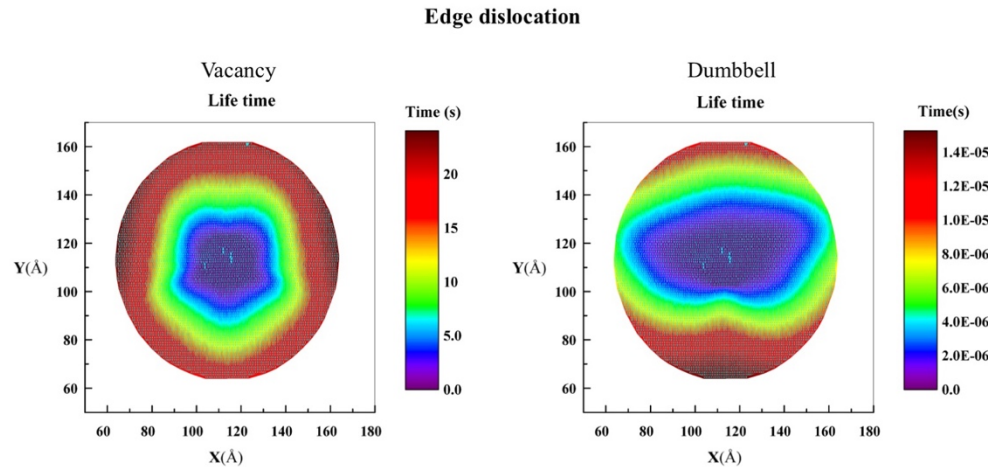


Figure 4.6. Time of absorption by an edge dislocation at 300 K for (a) vacancy (b) self-interstitial dumbbell.

Dislocation bias arises because vacancies and interstitials do not randomly diffuse to a dislocation but are subjected to a force field arising from the dislocation-point defect interaction. Physically the dislocation bias has been attributed to difference in dilatation and the related stress-field topology between SIA and vacancy. Fig. 4.7 shows the dislocation bias calculated with the life time of a defect for different temperatures. The bias factor decreases with increasing temperature as both vacancies and dumbbell behavior approach random diffusion. In the screw case the preference is accentuated at lower temperatures where anisotropic diffusion is stronger. In the edge dislocation case at low temperatures lead to a low dislocation bias value, as discussed before, this is the result of dumbbells having to move from the compression side of the edge dislocation to the tensile side.

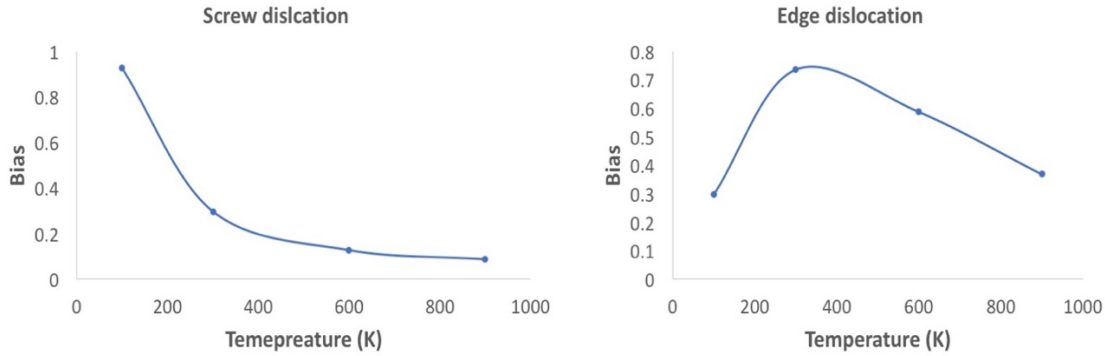


Figure 4.7. the dislocation bias calculated with the life time of a defect approach for (a) Screw (b) edge dislocation.

4.5. Conclusions

In this chapter, we have used the real saddle point distribution of point defects around straight edge and screw dislocations obtained from dimer searches as an input for KMC simulations. In these simulations, we have included the translation-rotation mechanism of dumbbells having obtained the saddle point distributions for all $\langle 110 \rangle$ dumbbell orientations. We conclude that this mechanism is fundamental to the description of dumbbell migration, and the effect different $\langle 110 \rangle$ orientations must be included in models. The KMC simulations reveal the real dynamics of point defects around dislocations, revealing that the migration of point defects is highly anisotropic and correlated. We have obtained estimation of the dislocation bias factor. We find that the bias is a function of temperature and dislocation density. With an increase of temperature point defects migration will approach random walk behavior decreasing the value of the dislocation bias. The bias factor used in rate theory or diffusion models should be a function of temperature and dislocation density rather than an empirical parameter.

SUMMARY, FUTURE WORK AND OUTLOOK

C.1 Summary

In this dissertation, we have employed computational methods to assess different properties of materials used for nuclear energy applications. DFT was employed to obtain the crystallographic structure of Ln -U-O compounds that are formed during the lifetime UO_2 nuclear fuels, and their electronic structure and bond nature examined with AIM approach. The real distribution of saddle point energies was obtained by SEAKMC saddle point searches, and this data was used as an input for KMC simulation to obtain the real diffusion mechanism and migration paths of point defects around dislocations.

We employed a layered atom model approach to propose ordered structures for the La_2UO_6 , Ce_2UO_6 , $LaUO_4$, and $CeUO_4$ compounds, and DFT calculations to assess the relative structural stabilities of these model structures. We found ordered phases in each of these compounds are preferred. To assess the electronic structure, we used the AIM/Bader approach to analyze the electron density procedures obtained from the DFT calculations in three model uranium-bearing compounds: δ - UO_3 , γ - UO_3 and La_6UO_{12} . We identified the bond critical points between adjacent U-O atoms and we performed charge basin integrations in the AIM/Bader framework. We discovered that there exists an inverse relationship between the U-O bond distance and the electron charge density at the BCP, shorter bonds accumulate more charge density at the BCP. We determined the relative covalent bonding component of each bond in an irregular coordination polyhedron, based on the bond lengths of each bond to the central atom in this polyhedron. The covalency referred to here is the magnitude of the charge density at the BCP, and this magnitude is indicative of the degree to which electron charge is shared between bonding atoms. The AIM approach used to analyze the electronic structure of uranium bearing compounds, has been commonly used in chemistry to study molecules, but this is the first time it has been fully used to assess radioactive compounds.

We studied the point defect interaction with dislocations by calculating SP configuration and energies for vacancies and dumbbells as a function of position in the presence of a dislocation. We found that the interaction range and the anisotropy of migration of point defects is greater than previously reported. We compared the results of the real saddle point energy with results from methods that approximate the saddle points from local minimum configurations. The maps of SP configuration and energies indicate that the properties do not correlate with LMC and that the SP strongly depends in the transition states. With the real saddle point distribution of point defects, we performed for KMC simulations. In these simulations. We studied the migration mechanism and trajectories of point defects around dislocations. Finally, we used the time of absorption of point defects to obtain an estimate of the dislocation bias factor, and found that the bias is a function of temperature and dislocation density. This is the first time that a massive and accurate estimation of saddle points has been made, and showed that the approximations used up to this point are not

good enough to properly describe the defect dynamics, and the showed the strong dependence of the transition states on the point defect migration.

Computational simulations are a powerful and convenient tool to study materials in extreme conditions where experiments may be difficult or impossible to perform such as with materials under irradiation. The understanding of the impact of microstructural evolution of materials under irradiation on the material properties allows to tailor materials with better radiation resistance, and with better performance under irradiation conditions. The study of crystallographic structure of the compounds that may be formed inside the fuel pellet provides information on the change in volume and thermodynamic properties which are of safety and efficiency interest respectively. Besides the technological application, it provides fundamental knowledge in how the electronic structure changes with the local atomic environment and its effect on bonding. The information that can be extracted from the AIM approach can be used to shed light in the oxidation state of uranium that has been continuously under debate, and to be able to tailor materials with better radiation resistance properties. The relationship between charge density at the BCP and bond length present predictive capabilities, and can be used as a guiding tool to the difficult x-ray diffraction measurements of uranium complex oxides. The understanding of migration mechanisms and interaction of point defects with dislocations will eventually contribute to the development of structural materials that can better withstand the extreme reactor conditions. The actual saddle point configuration and energies enable the simulation of the real dynamics of point defects, up to now only approximations were available. Real migration mechanism results not only have an impact on dislocation bias and mechanical properties but in all the material properties that depend on diffusion processes.

C.2 Future work

The evolution of the nuclear and structural components is a complex process and there are many aspects that are still open for research. The next step in this research is to compare the predicted structures and properties obtained by computational simulations against experimental data. We intend to fabricate and characterize samples of the U-La-O compounds studied in this dissertation. In the simulation side, there are a myriad of compounds to be examined by moving to compounds above and below the tie line from Fig. 1.1, which represent oxygen deficiency, and oxygen excess respectively, where we suspect we will find ordered patterns of oxygen vacancies and interstitials. Finally, we can improve the accuracy of the simulations with higher levels of theory, such as hybrid functionals, and the implement the SQS approach to model disorder.

In the structural materials side, we only studied the interaction of isolated point defects with single straight dislocations, in reality there are networks of dislocations, and the presence of other sinks. The methodology used to study the interaction of point defects with dislocations can be employed to study the interaction of point defect with other sinks and extended defects, such as defect clusters, dislocation loops, and grain boundaries. To

be able to consider a more complex picture, improvements in the efficiency of the saddle point search must be done, to allow a faster calculation in bigger sampling areas. This may be achieved by implementing adaptive scheme for the initial guess of the saddle point search, and the use of local relaxation volumes.

C.3 Outlook

The microstructural evolution of the reactor core components due to radiation effects is extremely complex because of the many different factors and processes occurring at the same time inside the nuclear fuel and structural materials. The insights gained on the behavior of materials under irradiation and data obtained from this dissertation lay a foundation to simulate the complex environment that affect the evolution of the reactor core components. In the nuclear fuel side, mesoscale simulations are needed to estimate the change in the thermal conductivity, that also consider the addition of not only lanthanide fission products but also noble fission gases like helium and xenon. The presence of different compounds and oxygen compositions in the fuel matrix should be considered to have a more realistic approximation of the fuel evolution. A realistic picture of the evolution of the structural materials require the presence of multiple point defects, and different kind of sinks, including the overlapping effects of these different sinks, and point defects interacting with each other. Microstructural evolution is a dynamic environment, the growth of grain boundaries, cavities and dislocation mobility by the absorption of point defects. In addition, the effects of alloying can be studied with the incorporation of impurities such as chromium and nickel. It can easily be seen that a complete picture of the microstructural evolution has many complex ingredients, and there is a significant amount of research to be done, particularly, to achieve the ultimate goal of simulating the complete nuclear energy process, which require a complete understanding of the individual phenomena occurring in the fuel, cladding, and structural components.

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APPENDIX

APPENDIX 1

This Appendix provides the *unrelaxed*, initial structures used in the *ab initio* calculations for each of the *Ln*-U-O compounds and each of the ordered cation models investigated in this study. Note that the crystal structure models shown are all hexagonal supercells. The rhombohedral cells actually used in the *ab initio* calculations are the primitive unit cells associated with each of the hexagonal supercells shown in this Appendix. The volume of each primitive rhombohedral unit cell is 1/3 the volume of the corresponding hexagonal supercell. Details regarding conversion from the conventional hexagonal cell to the primitive rhombohedral unit cell can be found in numerous textbooks on crystallography.

The hexagonal supercells described in this Appendix include structures consisting of 12-layer atom stacking sequences and 24-layer atom stacking sequences along the *z*-direction of the hexagonal supercell coordinate system. The *z*-direction is parallel to the *c*-axis (or equivalently, the *c_{hex}*-axis) associated with the hexagonal supercell. In the 12-layer stacking model, the supercell length *c* spans the layer stacking diagram from height *z* = 0/12 to *z* = 12/12 (the latter is O/12 repeated). In the 24-layer stacking model, the supercell length *c* spans the layer stacking diagram from height *z* = 0/24 to *z* = 24/24 (the latter is O/24 repeated). The cubic fluorite lattice constant, *a_{cube}*, used to determine the basal hexagonal

axis, *a_{hex}*, was obtained using the expression
$$a_{cube} = \frac{4\sqrt{3}}{3} (r_O^{IV} + \langle r_M^{VIII} \rangle)$$
, where *r_O^{IV}* is the ionic Shannon radius of a four-fold coordinated oxygen atom and $\langle r_M^{VIII} \rangle$ is the weighted average of the Shannon radii of the eight-fold coordinated cations in any given compound.

The *disordered* cation layer stacking models discussed in this report are not shown in this Appendix. For the disordered cation models, the starting structures are the same as the 12-layer atom stacking models shown in this Appendix, except that the *Ln* and U cations are randomly mixed on the cation sites shown in the 12-layer structure diagrams. For these disordered structures, the occupancies of the cation sites are based on the *Ln*:U stoichiometry of each compound of interest (2:1 or 1:1 for the compounds considered in this report).

A1.1. 12-layer hexagonal supercell description of La_2UO_6 (all cation layer models)

Lattice Parameters:

$$a_{\text{cube}} = 5.6127 \text{ \AA}$$

$$a = b = a_{\text{hex}} = \sqrt{3} \frac{a_{\text{cube}}}{\sqrt{2}} = 6.87412 \text{ \AA}$$

$$c = c_{\text{hex}} = a_{\text{hex}} \sqrt{2} = 9.7215 \text{ \AA}$$

$$\alpha = \beta = 90^\circ \quad ; \quad \gamma = 120^\circ$$

Based on these lattice parameters and given the number of formula units per supercell ($Z=3$), the atomic volume of this unrelaxed structure is given by:

$$\Omega_{\text{a}} = 14.7345 \text{ \AA}^3/\text{atom}$$

A1.2. 12-layer hexagonal supercell description of Ce_2UO_6 (all cation layer models)

Lattice Parameters:

$$a_{\text{cube}} = 5.5885 \text{ \AA}$$

$$a = b = a_{\text{hex}} = \sqrt{3} \frac{a_{\text{cube}}}{\sqrt{2}} = 6.8445 \text{ \AA}$$

$$c = c_{\text{hex}} = a_{\text{hex}} \sqrt{2} = 9.6796 \text{ \AA}$$

$$\alpha = \beta = 90^\circ \quad ; \quad \gamma = 120^\circ$$

Based on these lattice parameters and given the number of formula units per supercell ($Z=3$), the atomic volume of this unrelaxed structure is given by:

$$\Omega_{\text{a}} = 14.5448 \text{ \AA}^3/\text{atom}$$

The models in A1.1 and A1.2 above consist of 3 Ln_2UO_6 ($\text{Ln} = \text{La}, \text{Ce}$) formula units per hexagonal supercell ($Z = 3$). The unrelaxed positions of all the atoms in the supercell are shown in the layer stacking diagram in Figures A1.1 (ordered-pure layer model) and A1.2 (ordered-mixed layer model). The rhombohedral cells actually used in the *ab initio* calculations consist of 1 Ln_2UO_6 formula unit per hexagonal supercell ($Z = 1$).

Ln_2UO_6 ($\text{Ln} = \text{La}, \text{Ce}$)
12-layer ordered-pure model

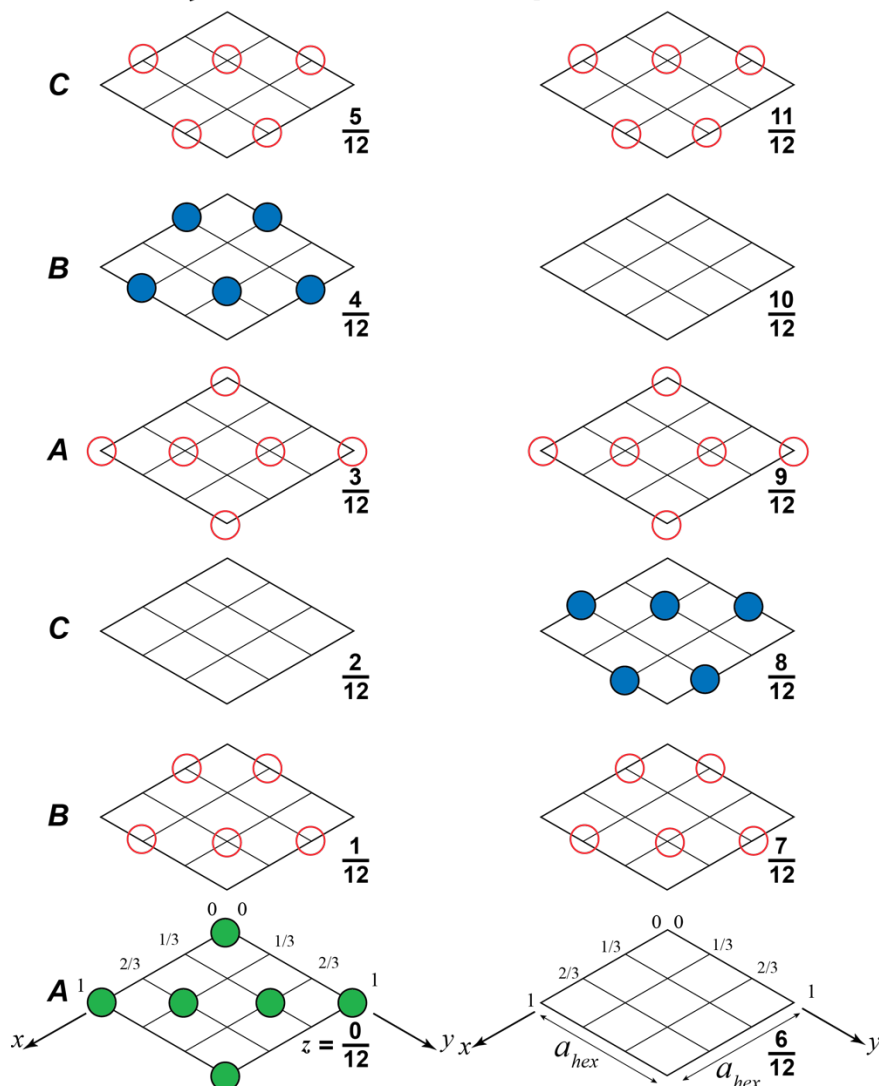
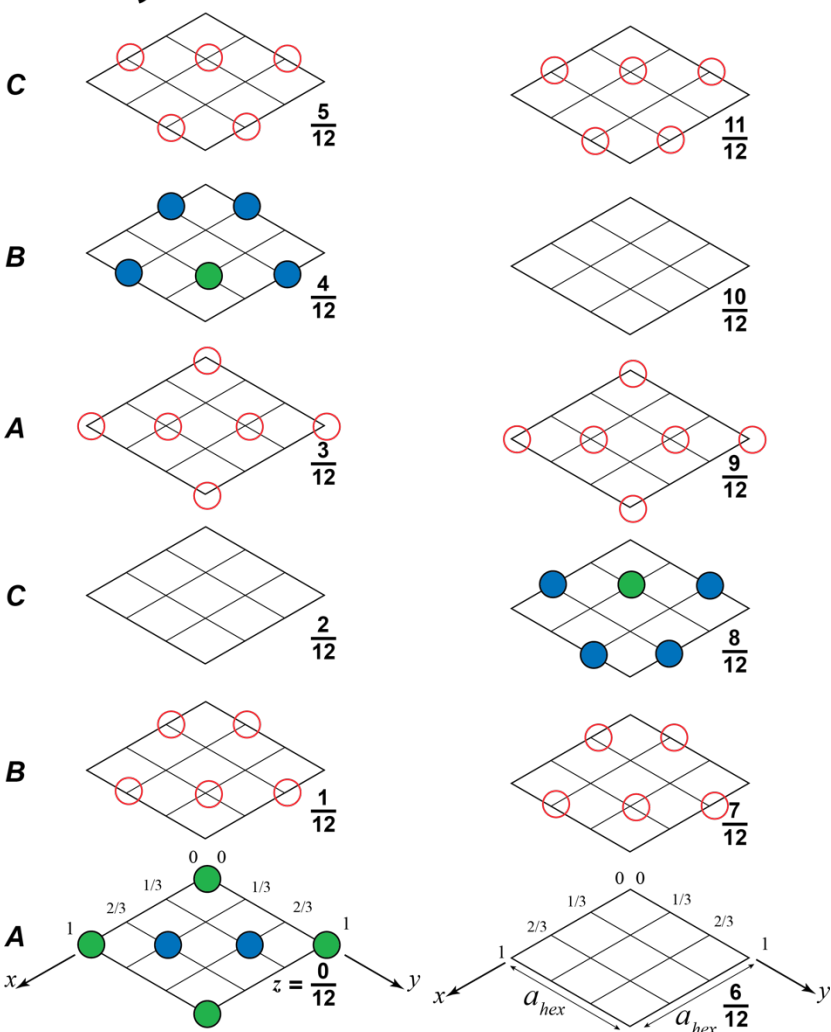


Figure A1.1. 12-layer ideal *unrelaxed* Ln_2UO_6 ordered-pure layer stacking model along the z -direction (c_{hex} crystallographic axis) of the hexagonal supercell. U cations are green. Ln ($\text{Ln} = \text{La}, \text{Ce}$) cations are blue. O anions are outlined in red. The hexcells at each z -height are subdivided and labeled so that the (unrelaxed) fractional coordinates of the atoms in the supercell can be readily evaluated by inspection of the diagram.



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A1.3. 12-layer hexagonal supercell description of LaUO₄ (ordered-mixed and disordered cation layer models)

Lattice Parameters:

$$\begin{aligned}a_{cube} &= 5.5370 \text{ \AA} \\a = b = a_{hex} &= \sqrt{2}a_{cube} = 7.8306 \text{ \AA} \\c = c_{hex} &= a_{hex}\sqrt{\frac{3}{2}} = 9.5905 \text{ \AA} \\ \alpha = \beta &= 90^\circ \quad ; \quad \gamma = 120^\circ\end{aligned}$$

Based on these lattice parameters and given the number of formula units per supercell ($Z=3$), the atomic volume of this unrelaxed structure is given by:

$$\Omega_a = 14.1468 \text{ \AA}^3/\text{atom}$$

A1.4. 12-layer hexagonal supercell description of CeUO₄ (ordered-mixed and disordered cation layer models)

Lattice Parameters:

$$\begin{aligned}a_{cube} &= 5.5185 \text{ \AA} \\a = b = a_{hex} &= \sqrt{2}a_{cube} = 7.8043 \text{ \AA} \\c = c_{hex} &= a_{hex}\sqrt{\frac{3}{2}} = 9.5584 \text{ \AA} \\ \alpha = \beta &= 90^\circ \quad ; \quad \gamma = 120^\circ\end{aligned}$$

Based on these lattice parameters and given the number of formula units per supercell ($Z=3$), the atomic volume of this unrelaxed structure is given by:

$$\Omega_a = 14.0050 \text{ \AA}^3/\text{atom}$$

The models in A1.3 and A1.4 above consist of 6 $Ln\text{UO}_4$ ($Ln = \text{La, Ce}$) formula units per hexagonal supercell ($Z = 6$). The unrelaxed positions of all the atoms in the supercell are shown in the layer stacking diagram in Figure A.2. The rhombohedral cell actually used in the *ab initio* calculations consists of 2 $Ln\text{UO}_4$ formula units per hexagonal supercell ($Z = 2$).

We wish to note here that many other ordered-mixed layer models are possible for the $Ln\text{UO}_4$ structure, including both 12-layer and 24-layer periodicities. Due to space limitations, we present in this report only results obtained on the 12-layer ordered-mixed model shown in Fig. A1.3.

A1.5. 24-layer hexagonal supercell description of LaUO₄ (ordered-pure cation layer model)

Lattice Parameters:

$$a_{cube} = 5.5370 \text{ \AA}$$

$$a = b = a_{hex} = \sqrt{2}a_{cube} = 7.8306 \text{ \AA}$$

$$c = c_{hex} = a_{hex} 4\sqrt{6} = 19.183 \text{ \AA}$$

$$\alpha = \beta = 90^\circ \quad ; \quad \gamma = 120^\circ$$

Based on these lattice parameters and given the number of formula units per supercell ($Z=3$), the atomic volume of this unrelaxed structure is given by:

$$\Omega_a = 14.1468 \text{ \AA}^3/\text{atom}$$

A1.6. 24-layer hexagonal supercell description of CeUO₄ (ordered-pure cation layer model)

Lattice Parameters:

$$a_{cube} = 5.5185 \text{ \AA}$$

$$a = b = a_{hex} = \sqrt{2}a_{cube} = 7.8043 \text{ \AA}$$

$$c = c_{hex} = a_{hex} 4\sqrt{6} = 19.1168 \text{ \AA}$$

$$\alpha = \beta = 90^\circ \quad ; \quad \gamma = 120^\circ$$

Based on these lattice parameters and given the number of formula units per supercell ($Z=3$), the atomic volume of this unrelaxed structure is given by:

$$\Omega_a = 14.0050 \text{ \AA}^3/\text{atom}$$

The models in A1.5 and A1.6 above consist of 12 $Ln\text{UO}_4$ ($Ln = \text{La, Ce}$) formula units per hexagonal supercell ($Z = 12$). The unrelaxed positions of all the atoms in the supercell are shown in the layer stacking diagram in Figure A1.4. The rhombohedral cell actually used in the *ab initio* calculations consists of 4 $Ln\text{UO}_4$ formula unit per hexagonal supercell ($Z = 4$).

LnUO_4 ($\text{Ln} = \text{La}, \text{Ce}$)
24-layer ordered-pure model

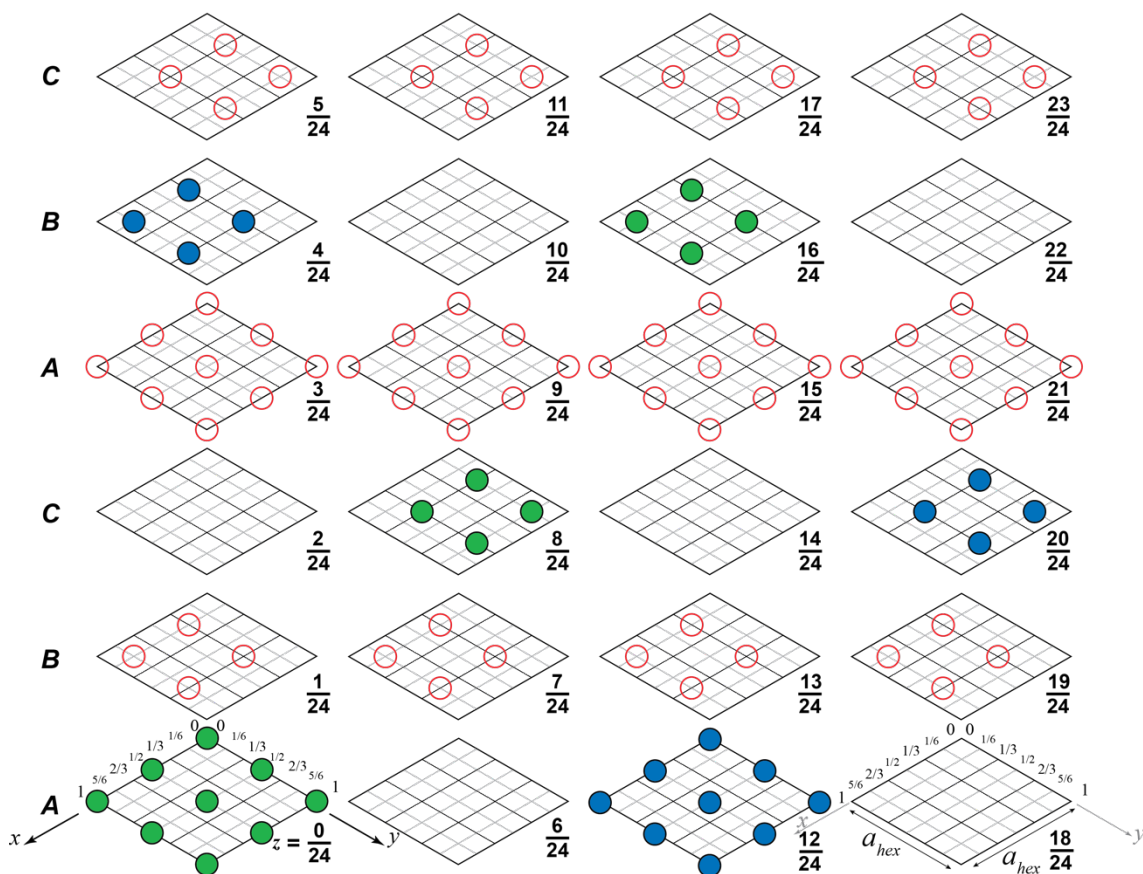


Figure A1.4. 24-layer ideal *unrelaxed* LnUO_4 ordered-mixed layer stacking model along the z -direction (c_{hex} crystallographic axis) of the hexagonal supercell. U cations are green. Ln ($\text{Ln} = \text{La}, \text{Ce}$) cations are blue. O anions are outlined in red. The hexcells at each z -height are subdivided and labeled so that the (unrelaxed) fractional coordinates of the atoms in the supercell can be readily evaluated by inspection of the diagram.

APPENDIX 2

A2.1. Computational Methods – Additional Information

The analysis of the charge density distribution may provide quantitative aspects of the interatomic interactions responsible for crystal packing, polymorphism, phase transitions and many other phenomena. Modeling charge densities in extended solids is an active field of materials science, and we only want to focus our attention onto a limited number of points that are relevant for the systems under investigation. In many systems, the thermally averaged electron charge density of a system in its ground state can be experimentally measured via a diffraction experiment. In a calculation using DFT software, the modeling of the electron charge density is usually performed for the equilibrium geometry. Depending on the characteristic elements that constitute the crystal, it may be possible to compare results obtained by experiments to numerical results obtained by *ab initio* simulations. Unfortunately, this direct comparison for the systems in this study cannot be done with high accuracy. The main concern when confronted to heavy atoms is the appropriate modeling of thermal motions, and it is then necessary either to deconvolute the experimental charge density from the thermal smearing or to convolute the theoretical density obtained by *ab initio* techniques. Anharmonic thermal motions that are expected even in the ground state can be significant for the cores of heavy scatterers like actinide and lanthanide atoms: one of the key features of thermal motion of those atom cores with a large number of electrons is that the averaged thermal motion also respects the local symmetry at the atom site, and therefore it can strongly interfere with the deformation densities related to chemical bonds that are expected to affect mostly the valence electrons. The other approximation that we need to admit at this point is that core density polarization in chemical bonding is neglected. That approximation is generally performed in DFT calculations performed using VASP where pseudopotentials are used, and core and valence electrons are not handled in the same way. The direct consequence of those approximations is that the values of the so-called deformation density (difference between the actual density and the density of an equivalent crystal with spherical core and valence electronic charge distributions) might not be accurate close to the position of the nuclei (typically in a sphere of radius 0.3Å centered at the nuclear position). On the other hand, those approximations have a more limited effect on the accuracy of other quantities like the integrated charge in a basin and the positions of the bonding critical points (BCP) that will be the main focus of our analysis. When two closed-shell atoms interact, as in the ionic picture, to fulfill the Pauli exclusion principle, the electron density is depleted from the interatomic surface and this kind of interaction is then characterized by a relatively low value of the electron density at the critical point while the charge is concentrated in each one of the atomic basins.

Correlations effects of the 5*f* electrons play an important role in determining the properties of U oxides. These properties cannot be predicted correctly by a conventional band-structure approach. Strong electron-electron correlations between *f* electrons enhance the effective electron mass and favour the appearance of a Mott insulator. For the U oxides, most of the 5*f* electrons are expected to concentrate in narrow bands with narrow overlap,

located about 1 eV below the Fermi level, while the wider band of O $2p$ states having the same energy as the valence electrons of the actinide is located between -3 and -8 eV below the Fermi level [SM.1, SM.2]. The bonds with the O ligand atoms can produce a charge transfer from the metal to the ligand. Indeed, in UO_2 , $6d$ and $7s$ electrons are likely mixed with the O $2p$ valence electrons with possibly a small yet significant contribution of U $5f$ states. The number of U $5f$ electrons engaged in the bonding is of the order of 0.4e while two $5f$ electrons are still localized on each uranium site in a triplet state, thus making the effective charge of the uranium ions in UO_2 less than +4 and providing a partially covalent character to the bond. The levels immediately above the Fermi level in the conduction band are predicted to be unoccupied $5f$ levels. In the other uranium oxides, U_3O_8 and UO_3 , the uranium oxidation state progressively increases and the number of the localized $5f$ electrons is expected to decrease. When a localized electron becomes a delocalized state, this delocalization increases the valence as well as the cohesive energy. Therefore, increase of the cohesive energy following the contribution of a $5f$ electron into a bonding orbital is supplied by the delocalization process. The occurrence of metastable configurations that are a significant feature in UO_2 [SM.3] are not expected in this work because the U atoms in our model compounds ideally transfer most of their f electrons to the ligands and aim at acquiring a closed shell configuration. For similar reasons, we did not include spin polarization in our calculations. The choice of GGA approximation is expected to underbind the systems and produce a systematic increase of the calculated lattice parameters. It should be noted that the use of this correction will further increase the GGA tendency to overestimate the equilibrium lattice parameters of these phases.

We analyzed the dependence of the Hubbard parameters on the charge density at the bond critical point in $\delta\text{-UO}_3$. We employed (U - J) values of 0, 1, 2, 3, and 4. The increase of the U - J parameters produce a systematic overestimation of the lattice constant shown in Fig. A1.1. In $\delta\text{-UO}_3$ the only change of the position of the BCP is related to the lattice expansion that scales as the U-O distance. The variation of the charge density at the BCP is extremely small and it is represented in Fig. A1.2 along with the predicted U-O line.

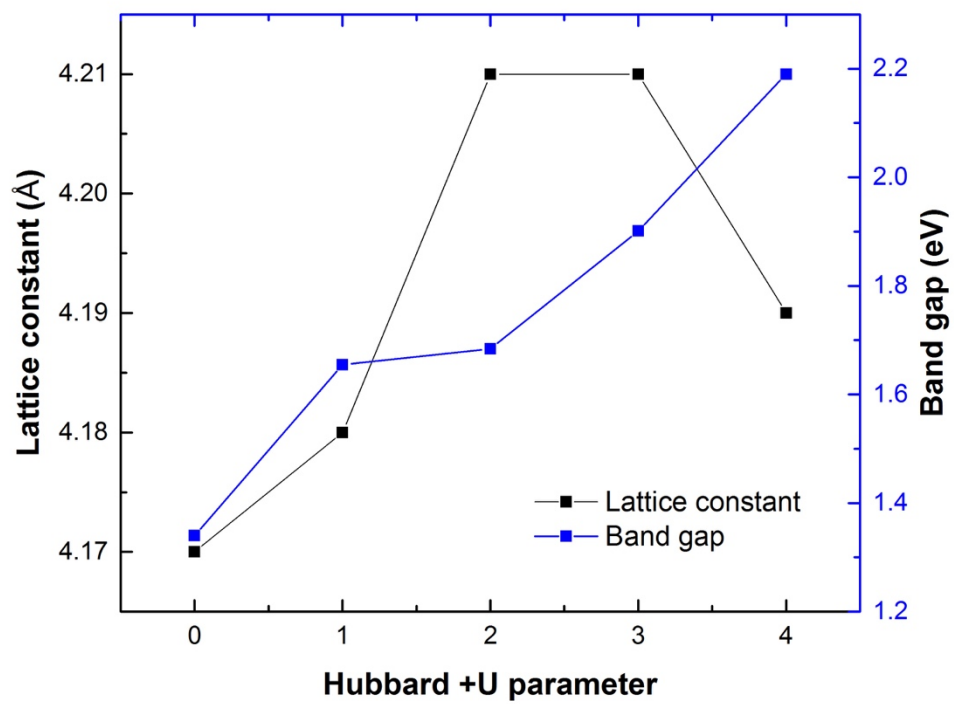


Figure A2.5 Lattice parameter vs Hubbard U - J correction.

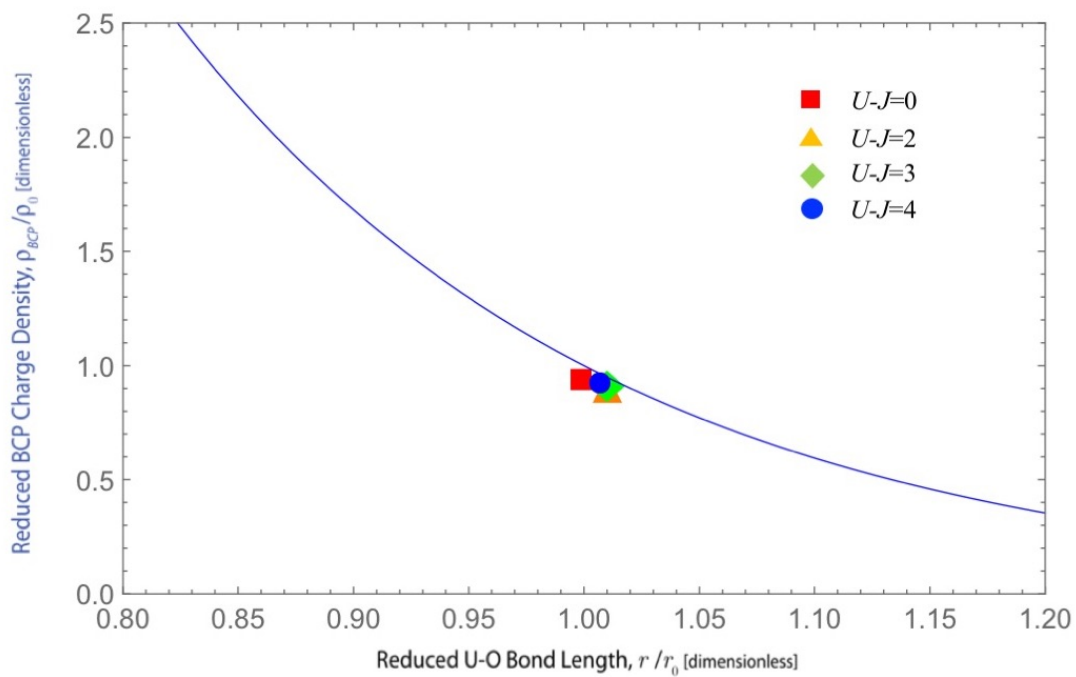


Figure A2.6. Plot showing reduced charge density at the bond critical point (ρ_{BCP}/ρ_0) versus reduced U-O bond length (r/r_0) for δ - UO_3 using different $+U$ values.

APPENDIX 3

A1. Screw dislocation vacancy

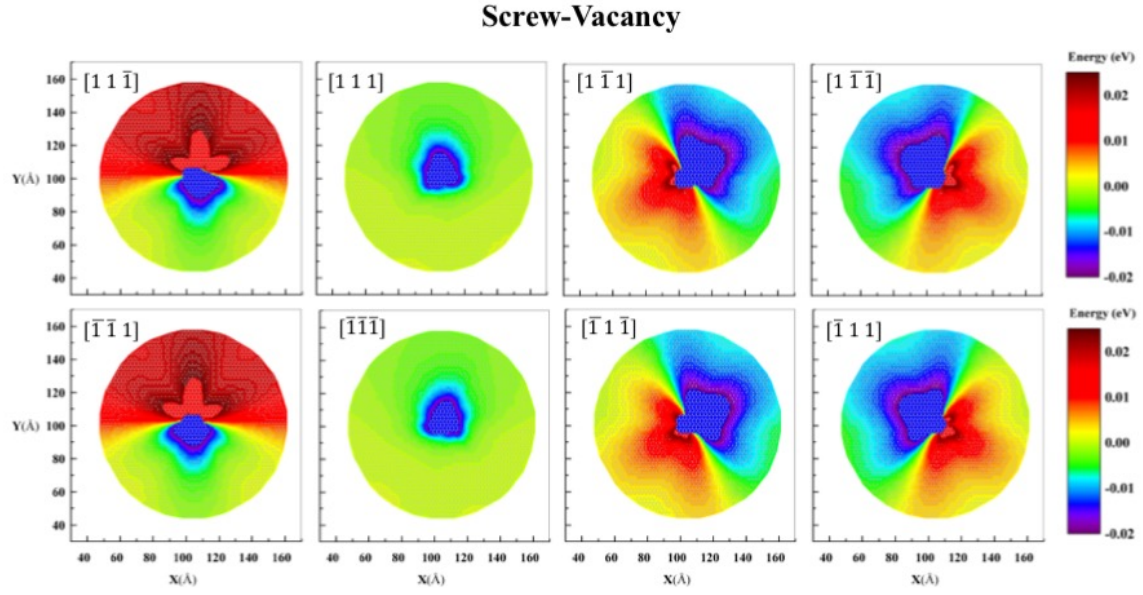


Figure A3.7. Energy barrier maps of different nearest neighbor migration directions for a vacancy in the presence of a screw dislocation.

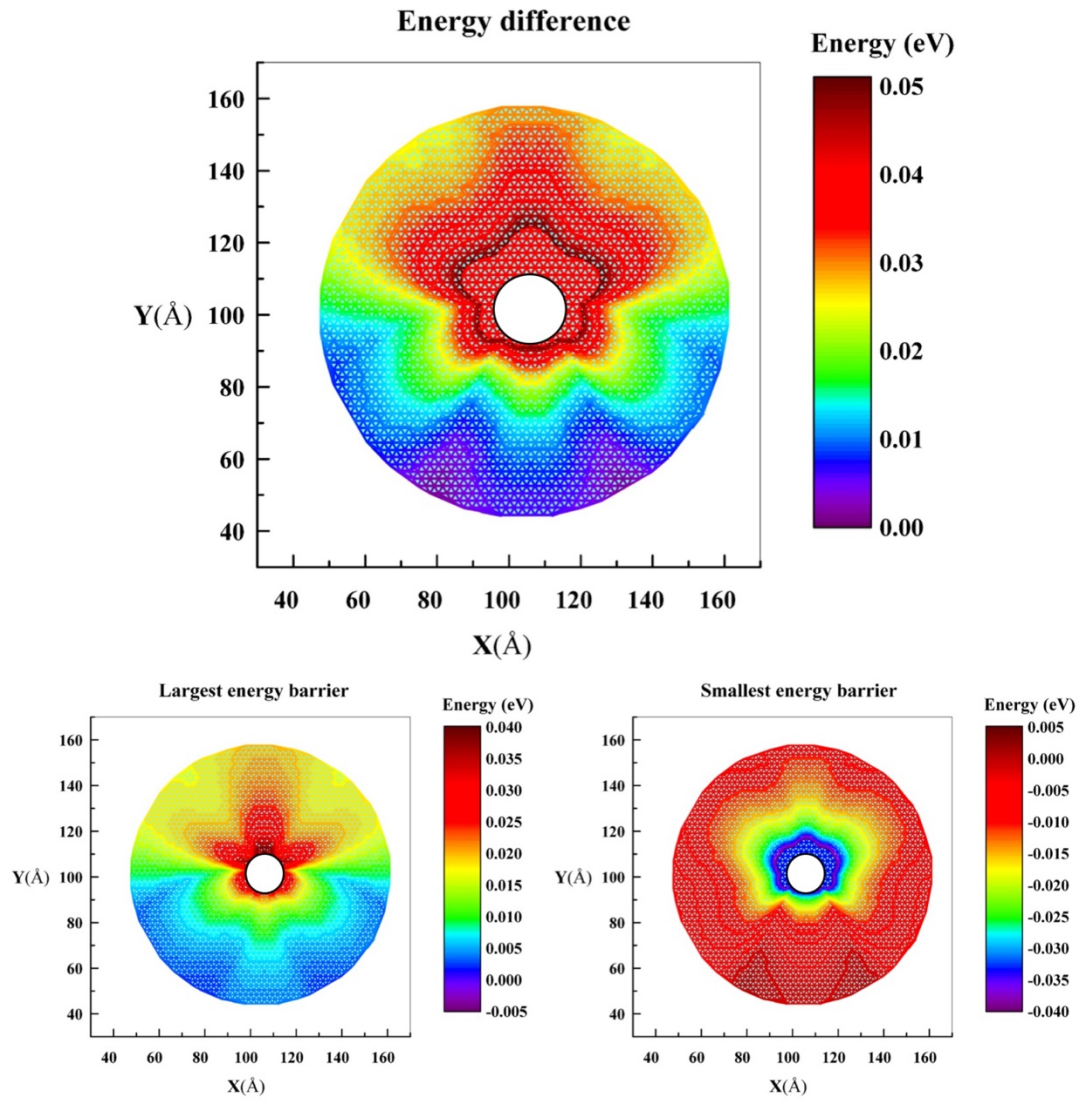


Figure A3.8. Energy barrier maps for the largest, smallest, and the difference between the largest and smallest energy barriers for a vacancy in the presence of a screw dislocation.

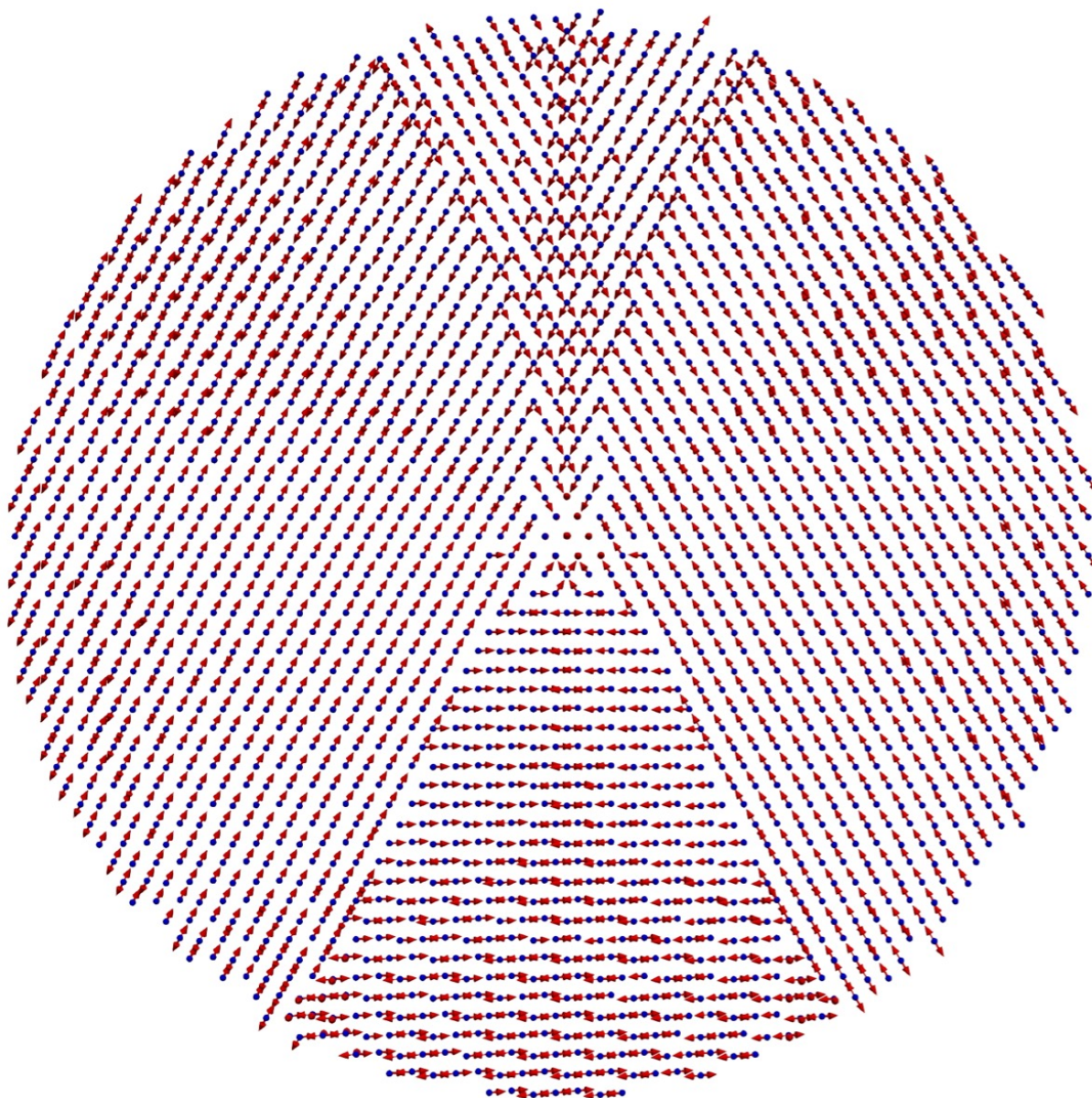


Figure A3.9. Most probable path map for vacancy in the presence of a screw dislocation.

A2. Edge dislocation vacancy

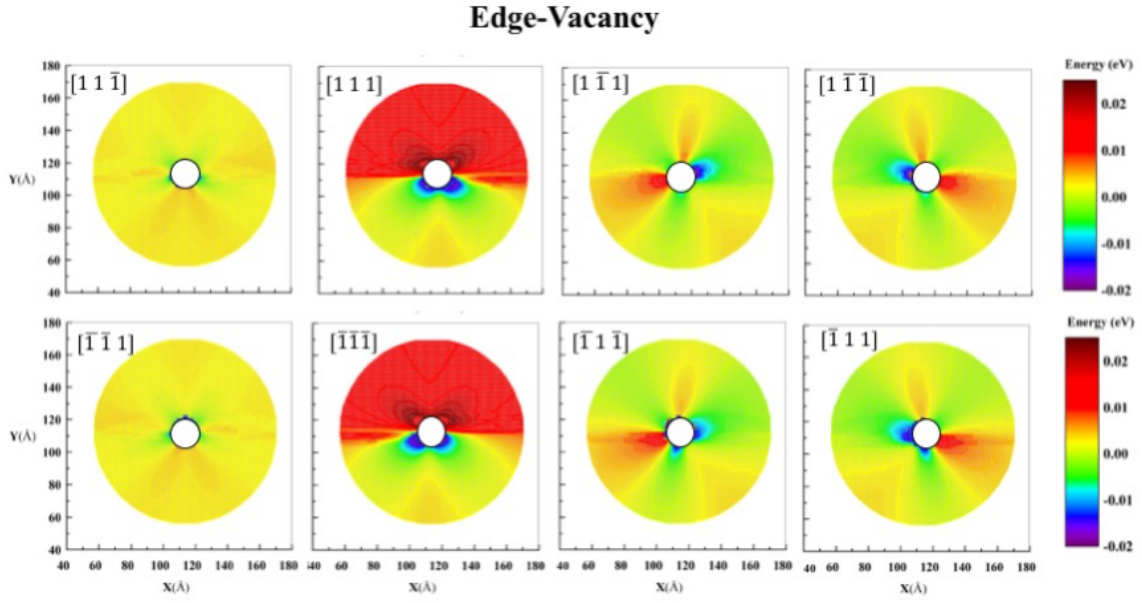


Figure A3.10. Energy barrier maps of different nearest neighbor migration directions for a vacancy in the presence of an edge dislocation.

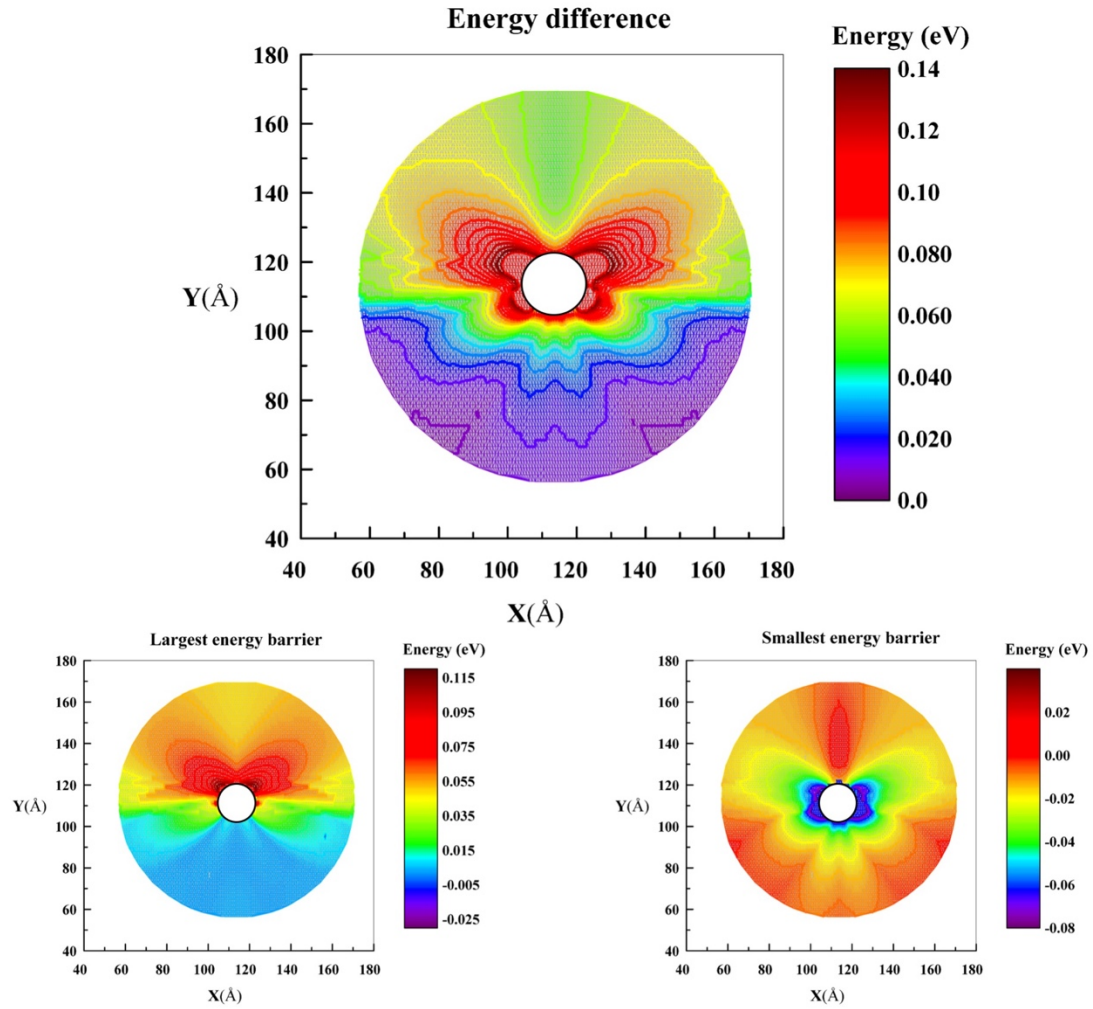


Figure A3.11. Energy barrier maps for the largest, smallest, and the difference between the largest and smallest energy barriers for a vacancy in the presence of an edge dislocation.

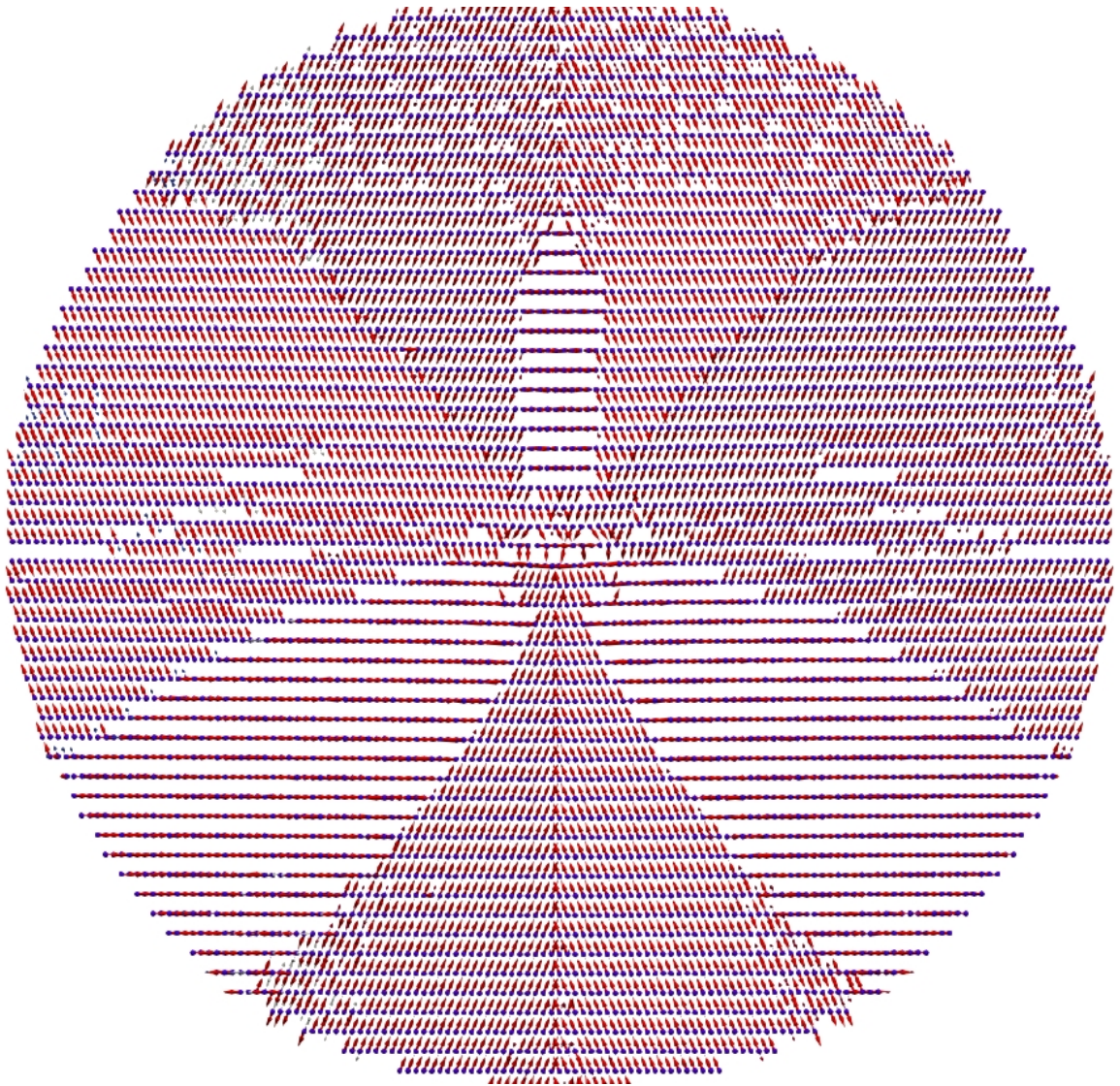


Figure A3.12. Most probable path map for vacancy in the presence of an edge dislocation.

A3. Screw dislocation dumbbell

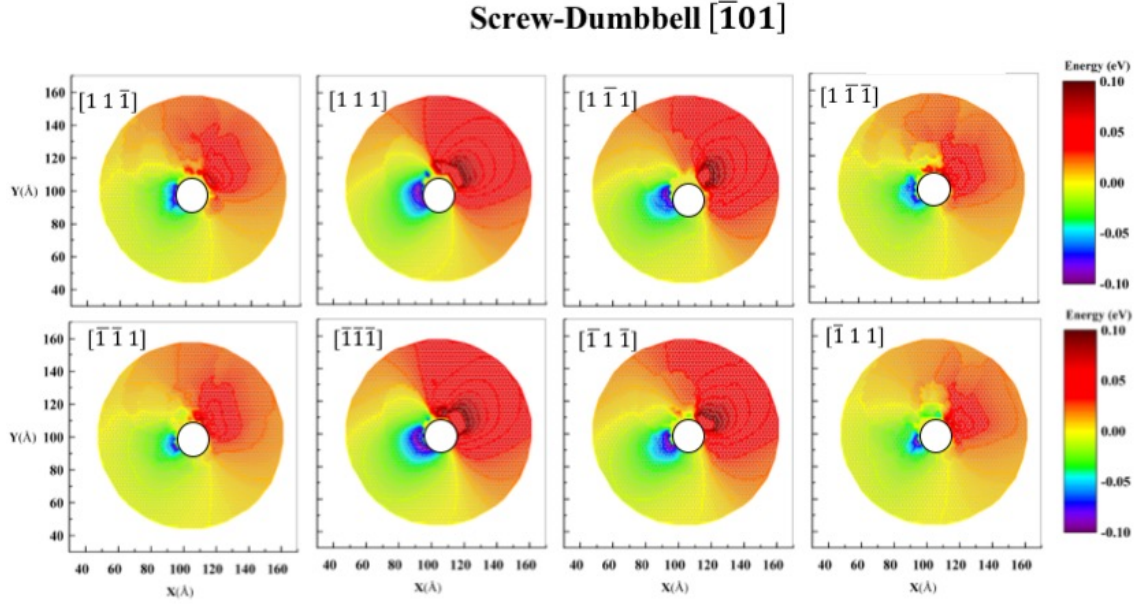


Figure A3.13. Energy barrier maps of different nearest neighbor migration directions for a $[\bar{1}01]$ dumbbell in the presence of a screw dislocation.

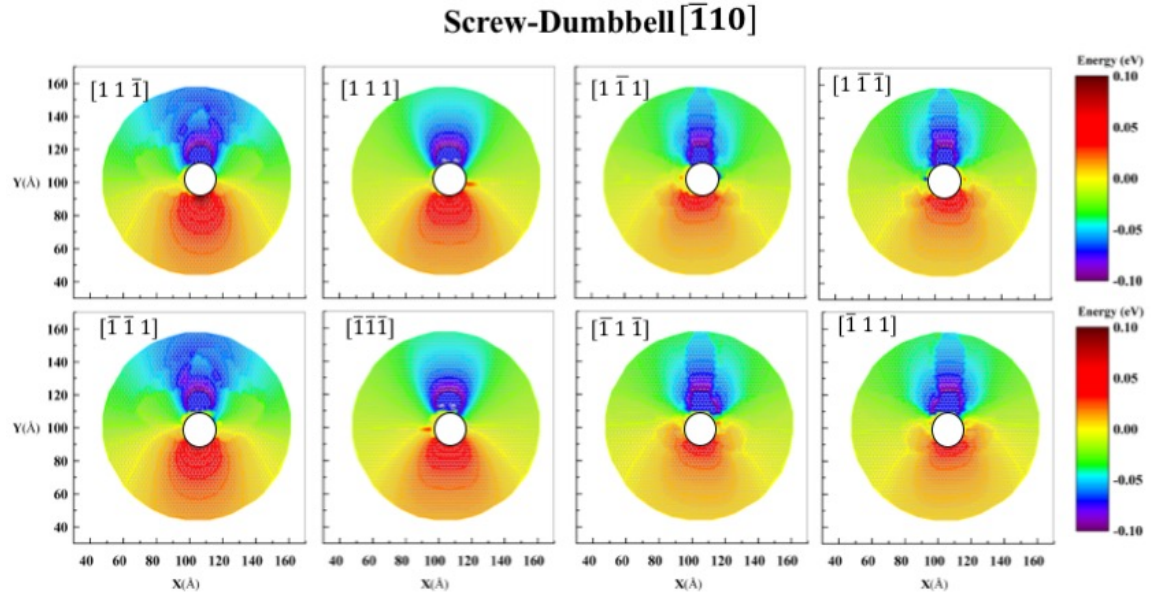


Figure A3.14. Energy barrier maps of different nearest neighbor migration directions for a $[\bar{1}10]$ dumbbell in the presence of a screw dislocation.

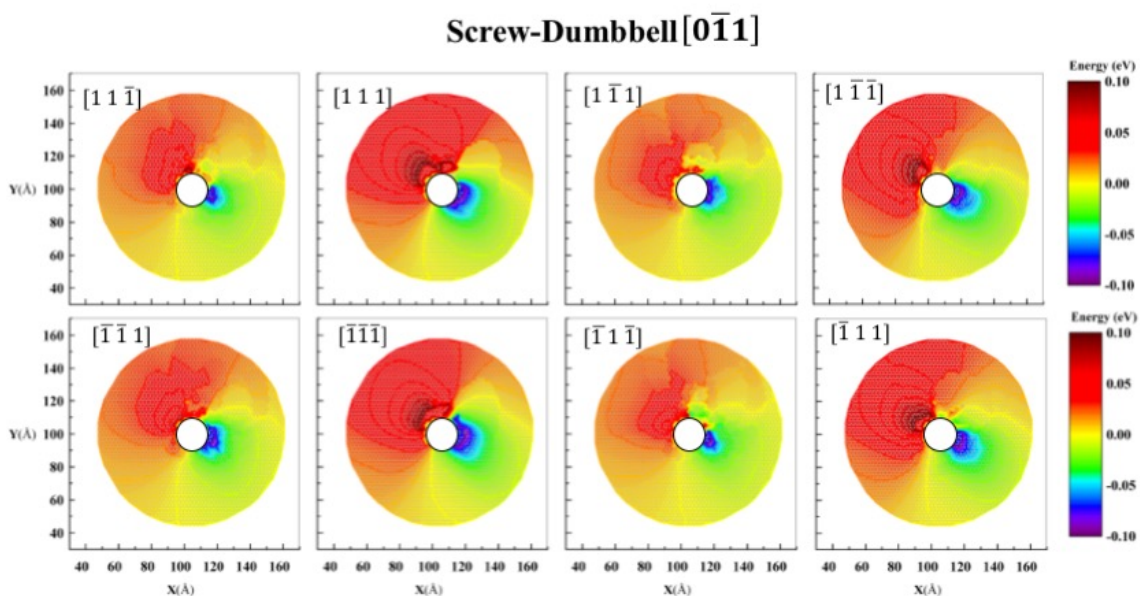


Figure A3.15. Energy barrier maps of different nearest neighbor migration directions for a $[0\bar{1}1]$ dumbbell in the presence of a screw dislocation.

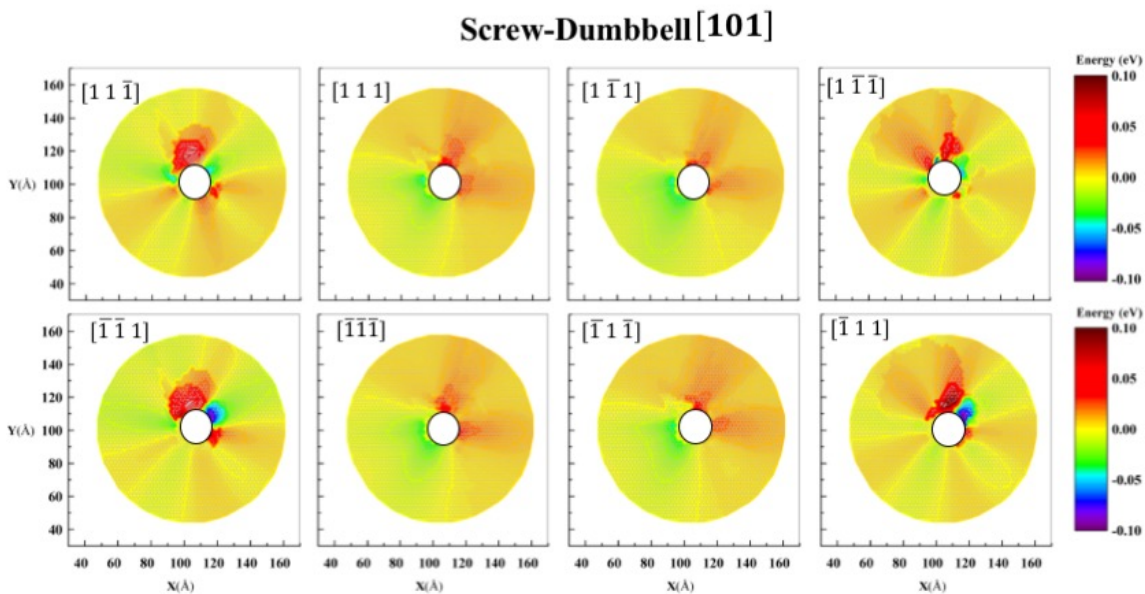


Figure A3.16. Energy barrier maps of different nearest neighbor migration directions for a $[101]$ dumbbell in the presence of a screw dislocation.

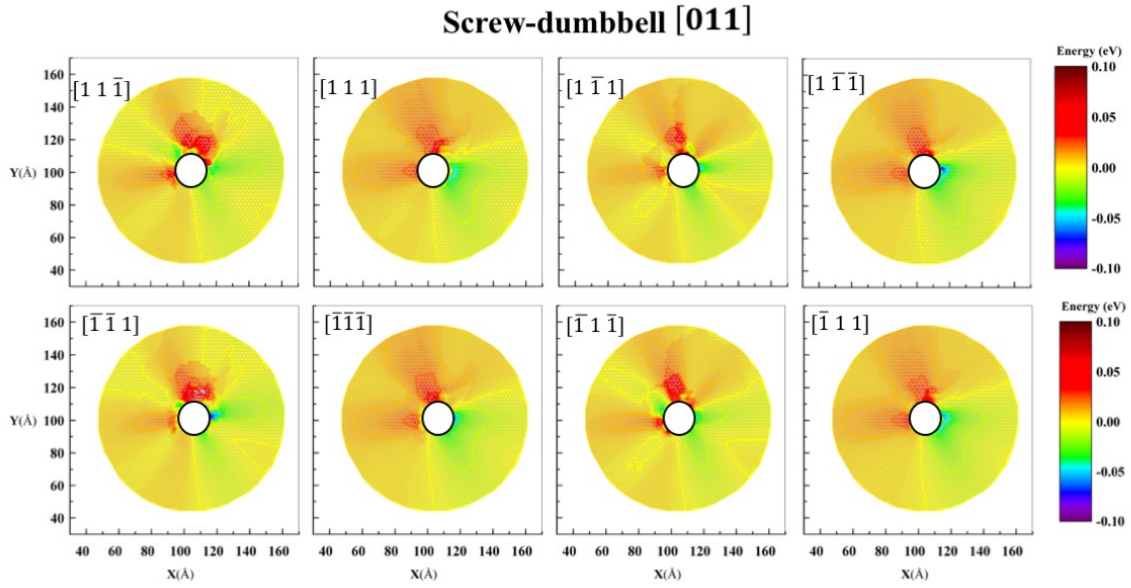


Figure A3.17. Energy barrier maps of different nearest neighbor migration directions for a [011] dumbbell in the presence of a screw dislocation.

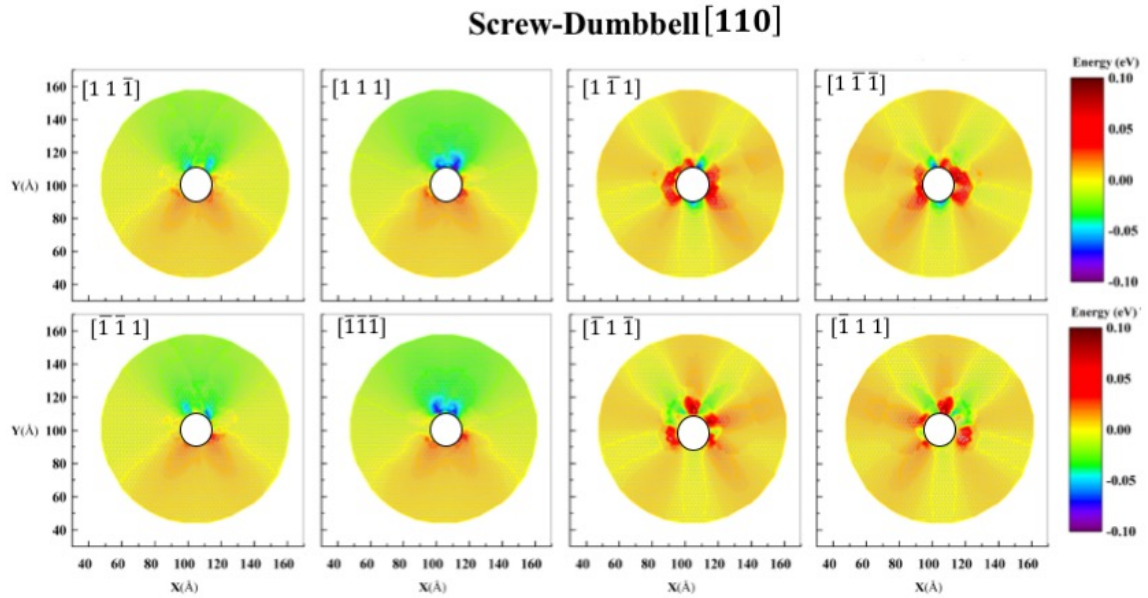


Figure A3.18. Energy barrier maps of different nearest neighbor migration directions for a [110] dumbbell in the presence of a screw dislocation.

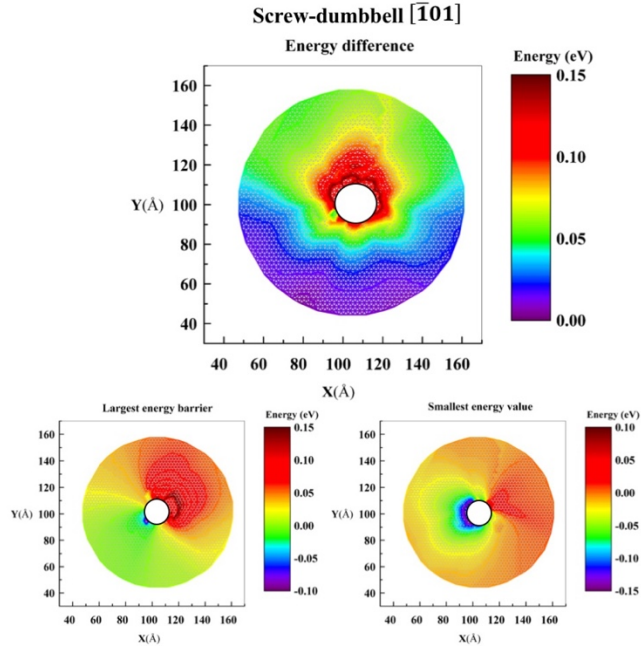


Figure A3.19 Energy barrier maps for the largest, smallest, and the difference between the largest and smallest energy barriers for a $[\bar{1}01]$ dumbbell in the presence of a screw dislocation.

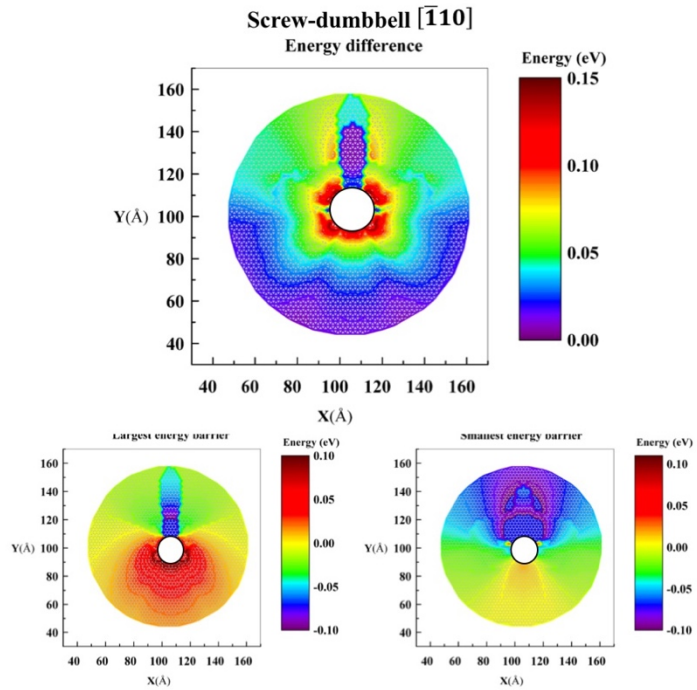


Figure A3.20. Energy barrier maps for the largest, smallest, and the difference between the largest and smallest energy barriers for a $[\bar{1}10]$ dumbbell in the presence of a screw dislocation.

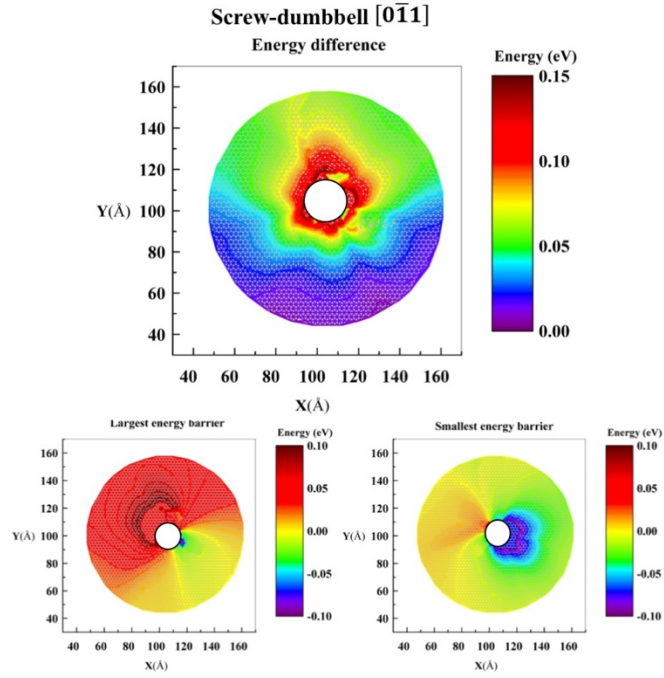


Figure A3.21. Energy barrier maps for the largest, smallest, and the difference between the largest and smallest energy barriers for a $[0\bar{1}1]$ dumbbell in the presence of a screw dislocation.

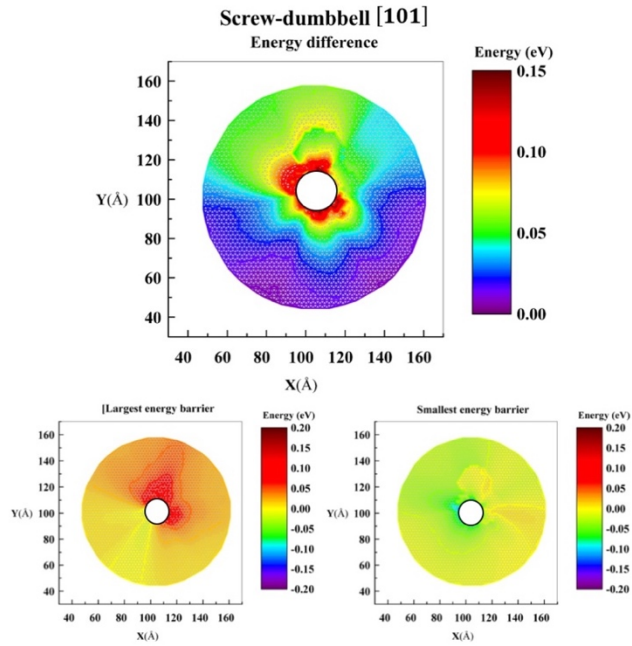


Figure A3.22. Energy barrier maps for the largest, smallest, and the difference between the largest and smallest energy barriers for a $[101]$ dumbbell in the presence of a screw dislocation.

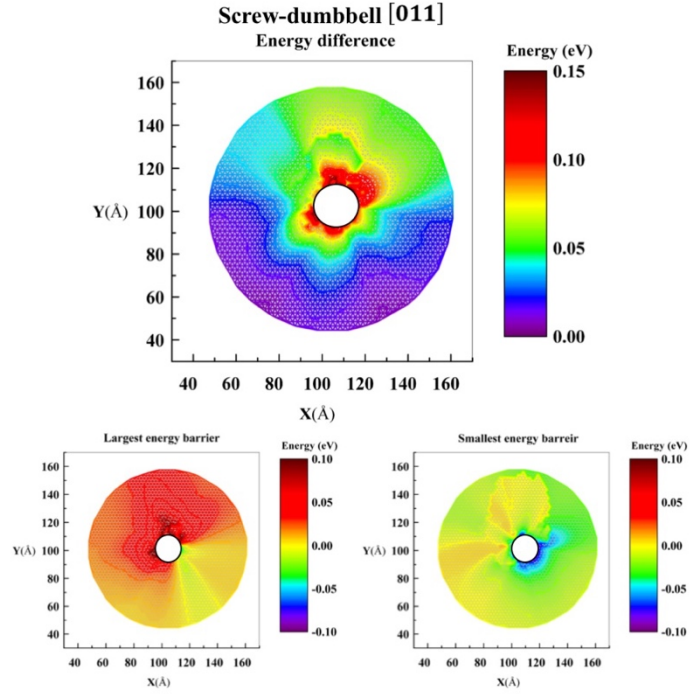


Figure A3.23. Energy barrier maps for the largest, smallest, and the difference between the largest and smallest energy barriers for a $[011]$ dumbbell in the presence of a screw dislocation.

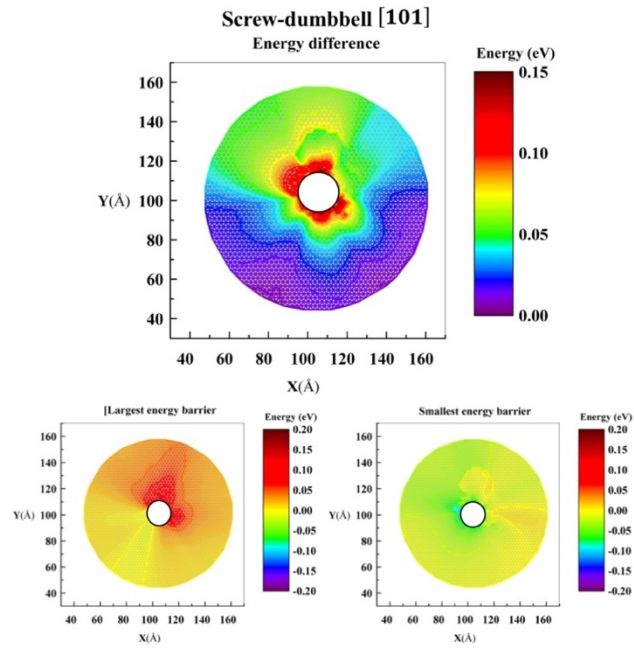


Figure A3.24. Energy barrier maps for the largest, smallest, and the difference between the largest and smallest energy barriers for a $[110]$ dumbbell in the presence of a screw dislocation.

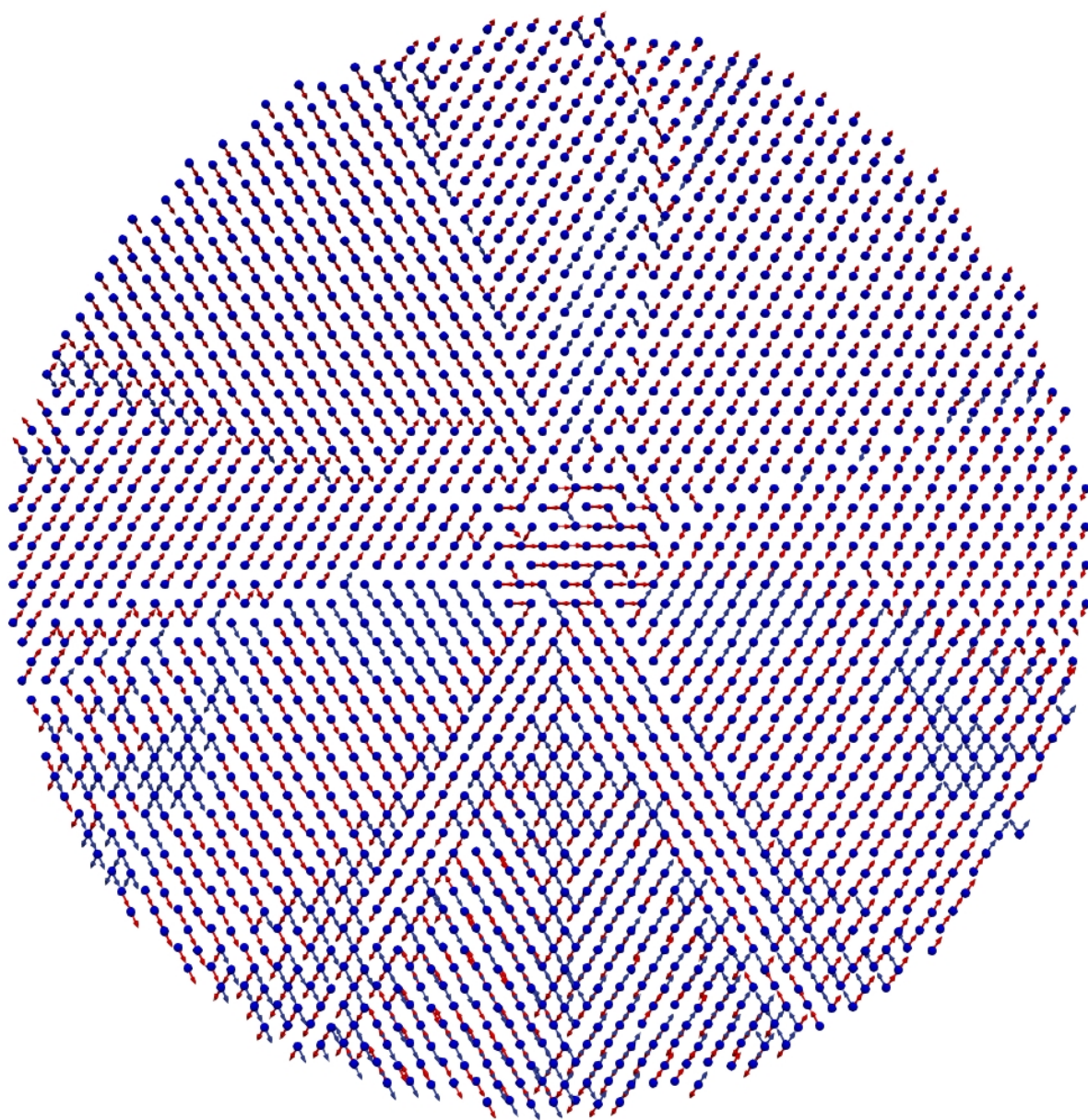


Figure A3.25. Most probable path map for a dumbbell in the presence of a screw dislocation.

A4. Edge dislocation dumbbell

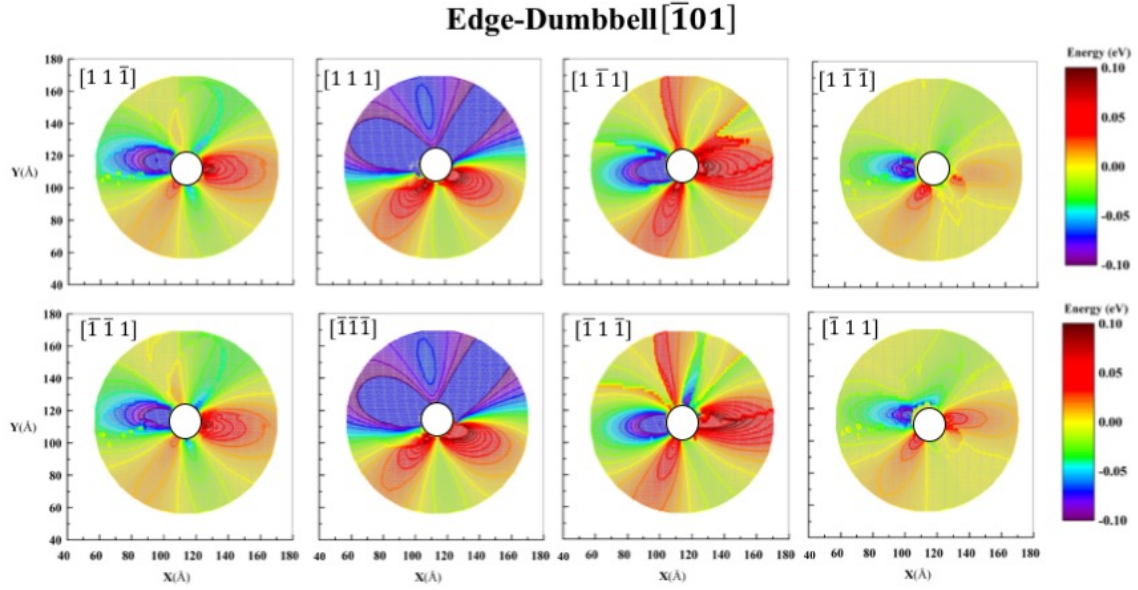


Figure A3.26. Energy barrier maps of different nearest neighbor migration directions for a $[\bar{1}01]$ dumbbell in the presence of an edge dislocation.

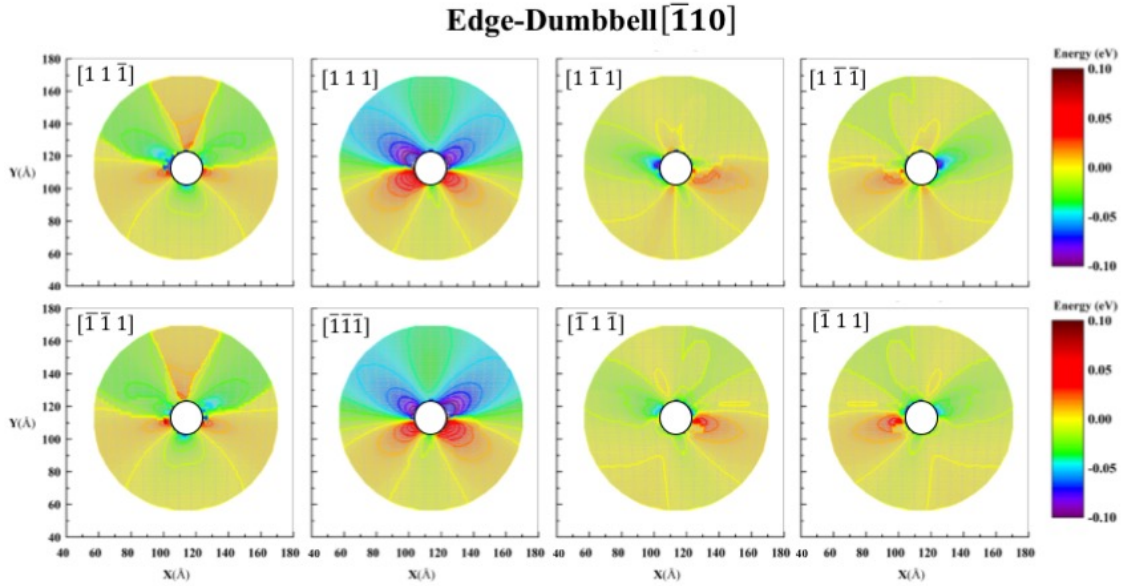


Figure A3.27. Energy barrier maps of different nearest neighbor migration directions for a $[\bar{1}10]$ dumbbell in the presence of an edge dislocation.

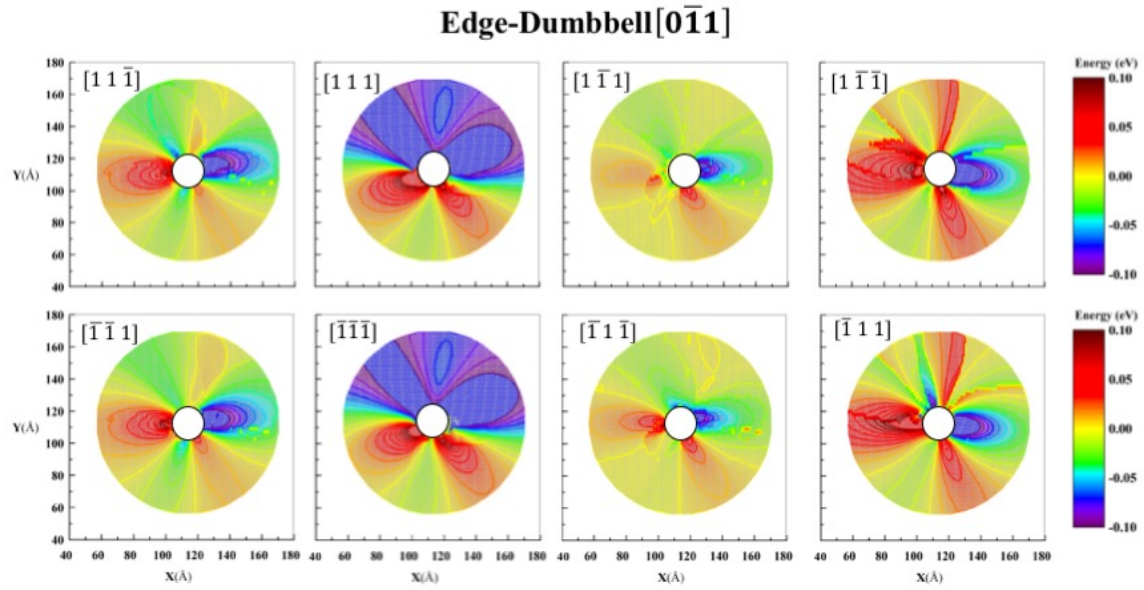


Figure A3.28. Energy barrier maps of different nearest neighbor migration directions for a $[0\bar{1}1]$ dumbbell in the presence of an edge dislocation.

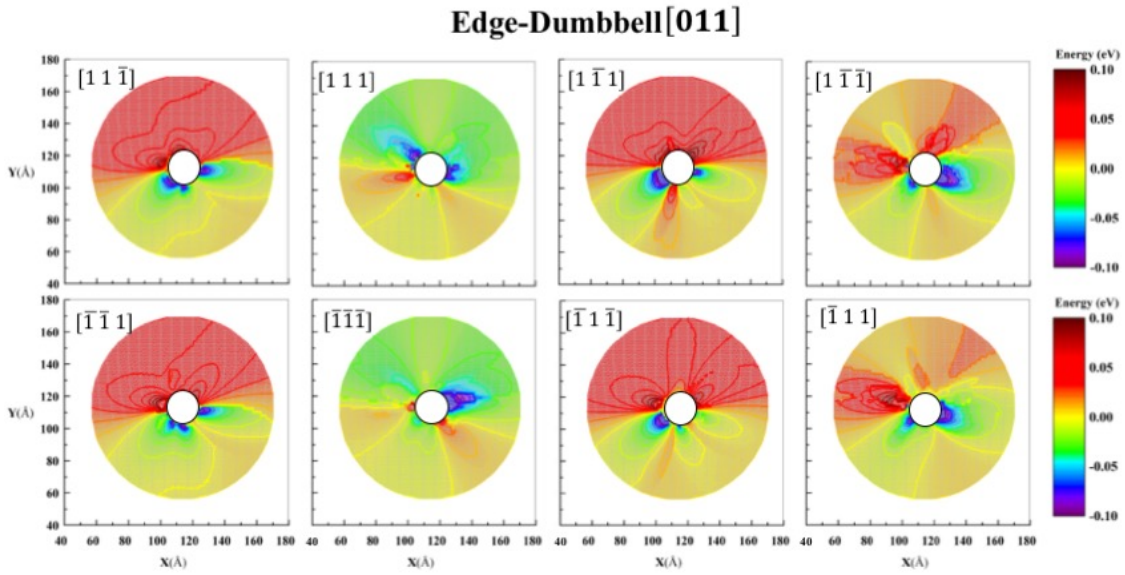


Figure A3.29. Energy barrier maps of different nearest neighbor migration directions for a $[011]$ dumbbell in the presence of an edge dislocation.

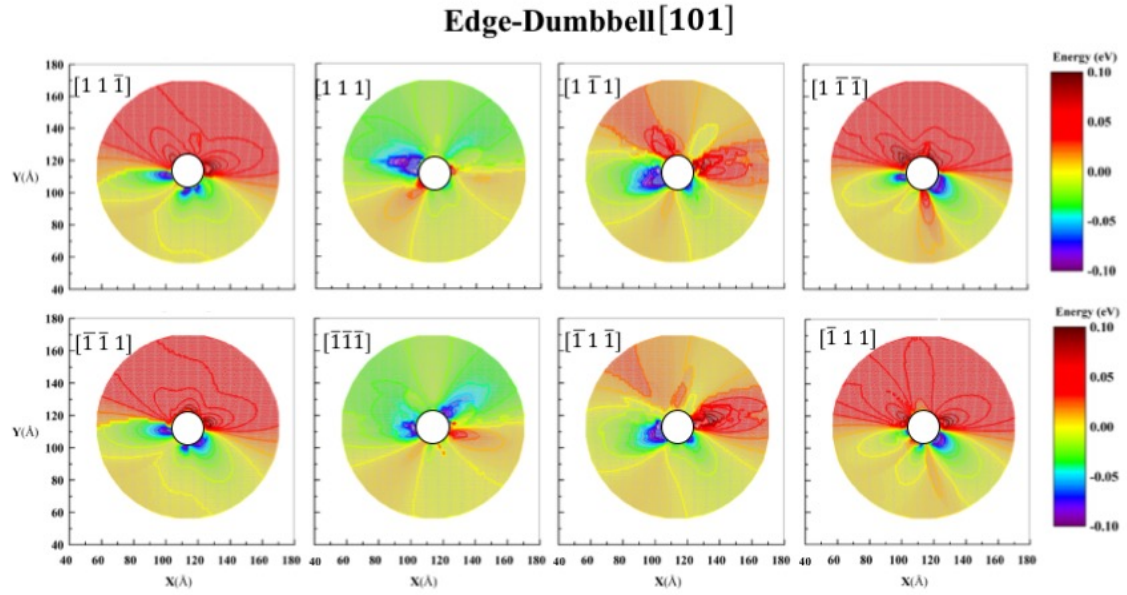


Figure A3.30. Energy barrier maps of different nearest neighbor migration directions for a $[101]$ dumbbell in the presence of an edge dislocation.

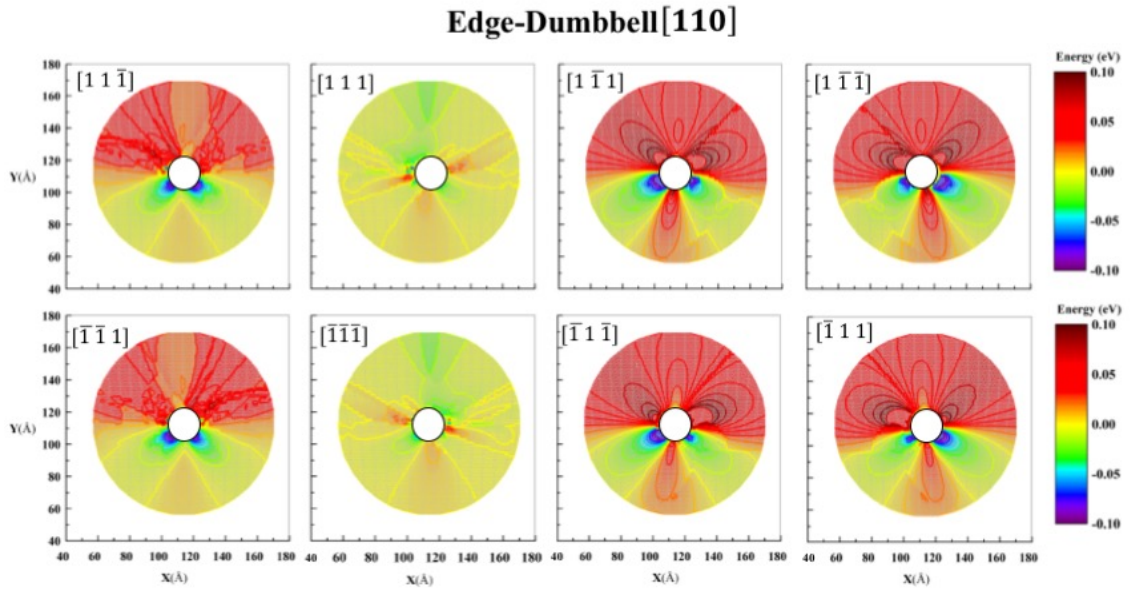


Figure A3.31. Energy barrier maps of different nearest neighbor migration directions for a $[110]$ dumbbell in the presence of an edge dislocation.

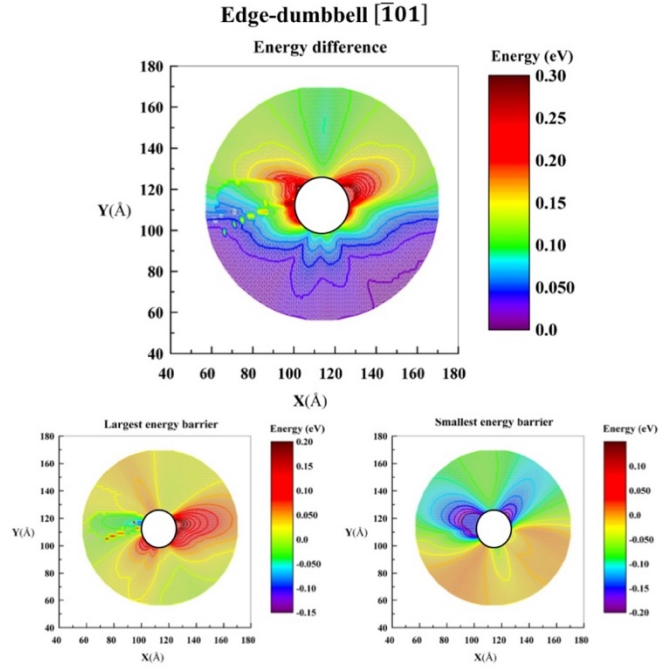


Figure A3.32. Energy barrier maps for the largest, smallest, and the difference between the largest and smallest energy barriers for a $\bar{1}01$ dumbbell in the presence of an edge dislocation.

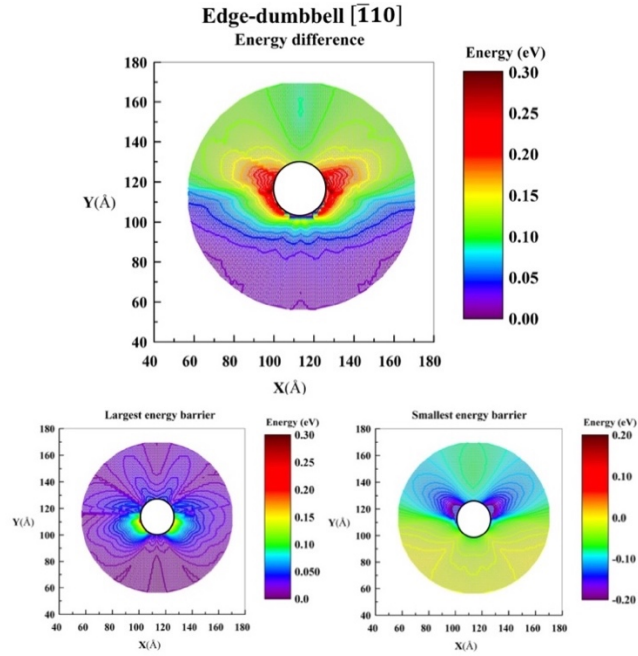


Figure A3.33. Energy barrier maps for the largest, smallest, and the difference between the largest and smallest energy barriers for a $\bar{1}10$ dumbbell in the presence of an edge dislocation.

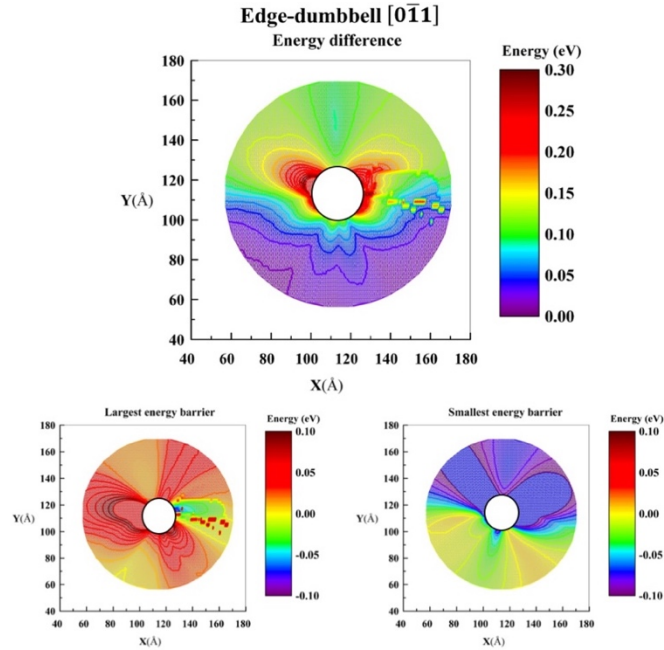


Figure A3.34. Energy barrier maps for the largest, smallest, and the difference between the largest and smallest energy barriers for a $[0\bar{1}1]$ dumbbell in the presence of an edge dislocation.

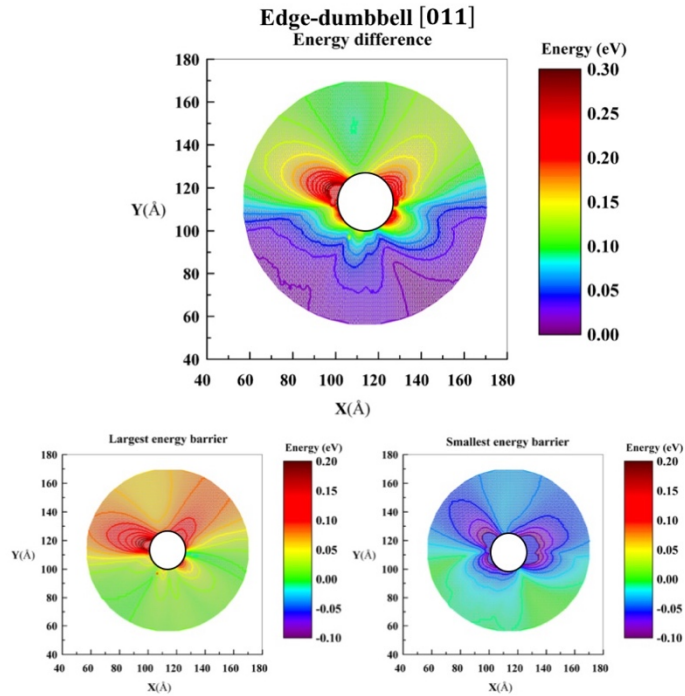


Figure A3.35. Energy barrier maps for the largest, smallest, and the difference between the largest and smallest energy barriers for a $[011]$ dumbbell in the presence of an edge dislocation.

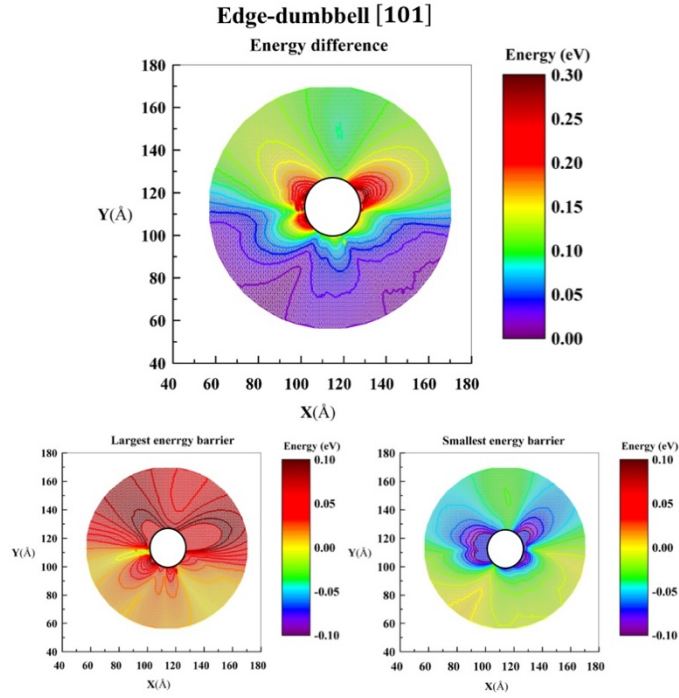


Figure A3.36. Energy barrier maps for the largest, smallest, and the difference between the largest and smallest energy barriers for a [101] dumbbell in the presence of an edge dislocation.

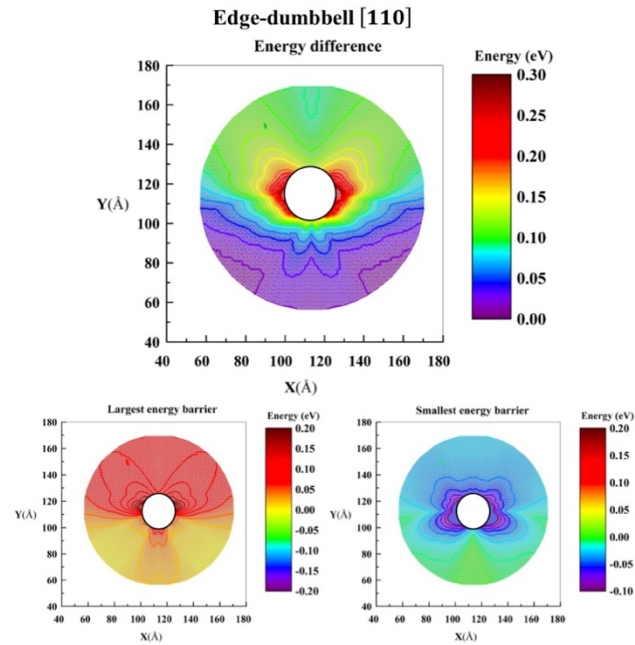


Figure A3.37. Energy barrier maps for the largest, smallest, and the difference between the largest and smallest energy barriers for a [110] dumbbell in the presence of an edge dislocation.

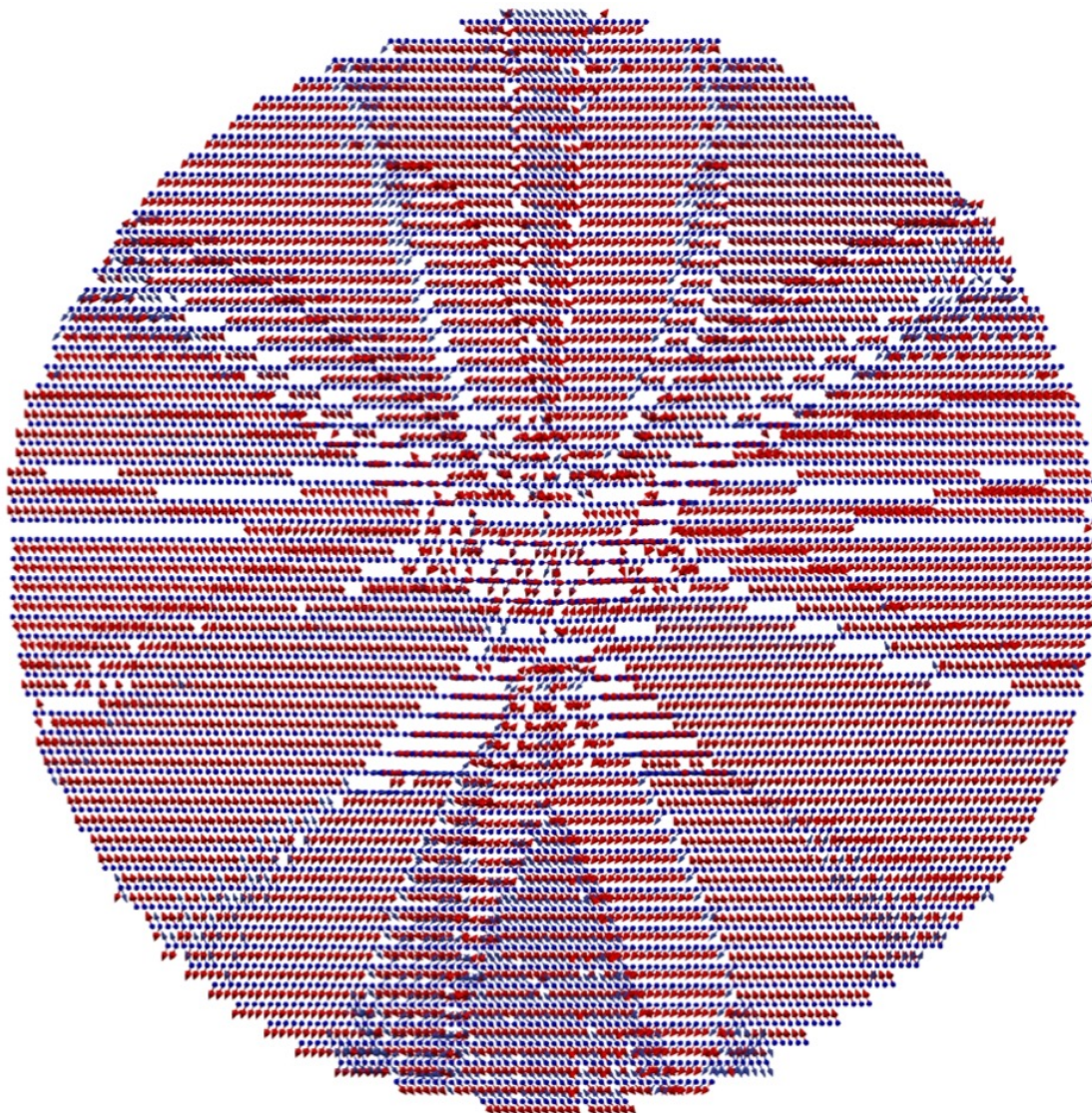


Figure A3.38. Most probable path map for a dumbbell in the presence of an edge dislocation.

A5. Anisotropy of diffusion

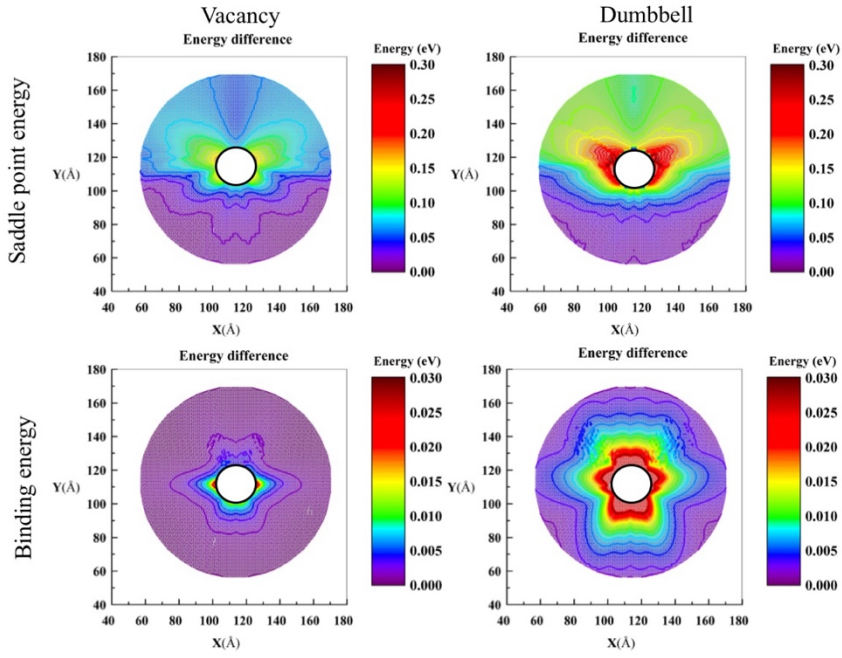


Figure A3.39. Comparison of the anisotropy of diffusion between the saddle point search and atomistic binding energy approximation in an edge dislocation.

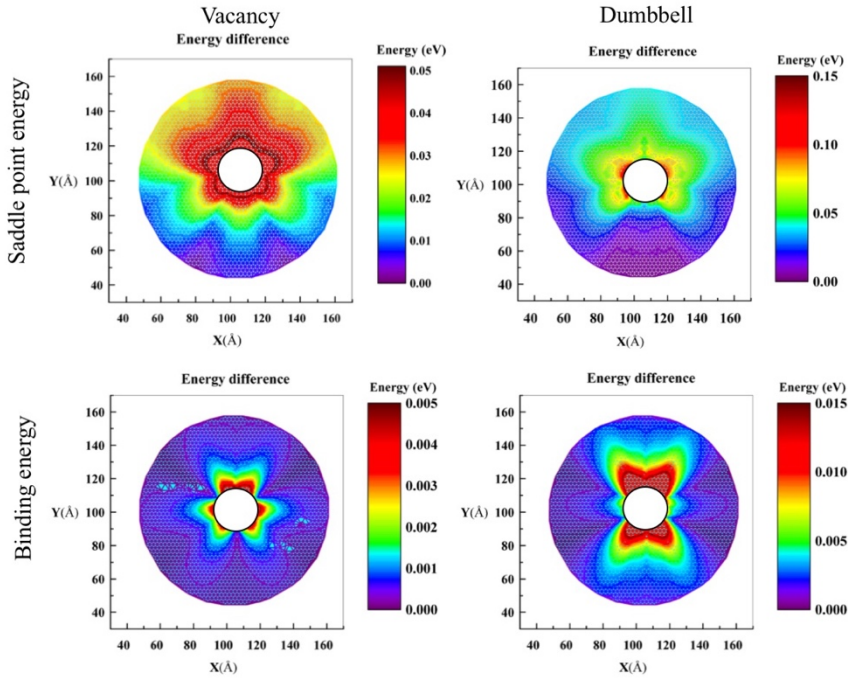


Figure A3.40. Comparison of the anisotropy of diffusion between saddle point search and atomistic binding energy approximation in a screw dislocation.

A6. Interaction range comparison between saddle point approaches

We have investigated the interaction radius between dislocations and point defects. To examine the range of this interaction we performed the saddle point search along selected directions up to 250 Å from the dislocation core. We compared with the saddle point approximation using binding energy from atomistic calculations and the binding energy calculated with anisotropic elastic theory. Figures A3.36 and A3.37 show the results for screw and edge dislocations. The saddle point energy has a greater magnitude than the one obtained with binding energy approaches. It is also possible to observe that the difference in energy is pronounced up to 50 Å and it becomes almost negligible at 100 Å. The binding energy methods underestimate the interaction range. We have combined the results of line 3 and 4 since they are symmetrically equivalent.

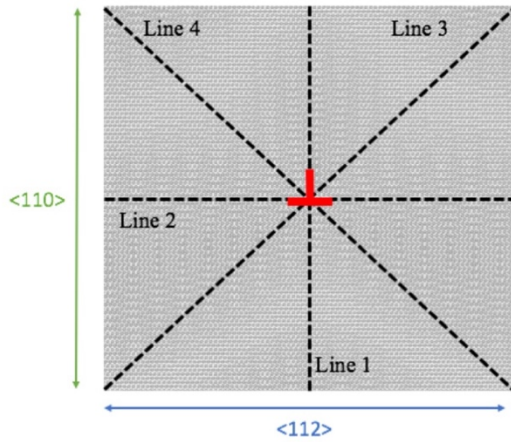


Figure A3.41. Selected lines for SP energy comparison between different approaches.

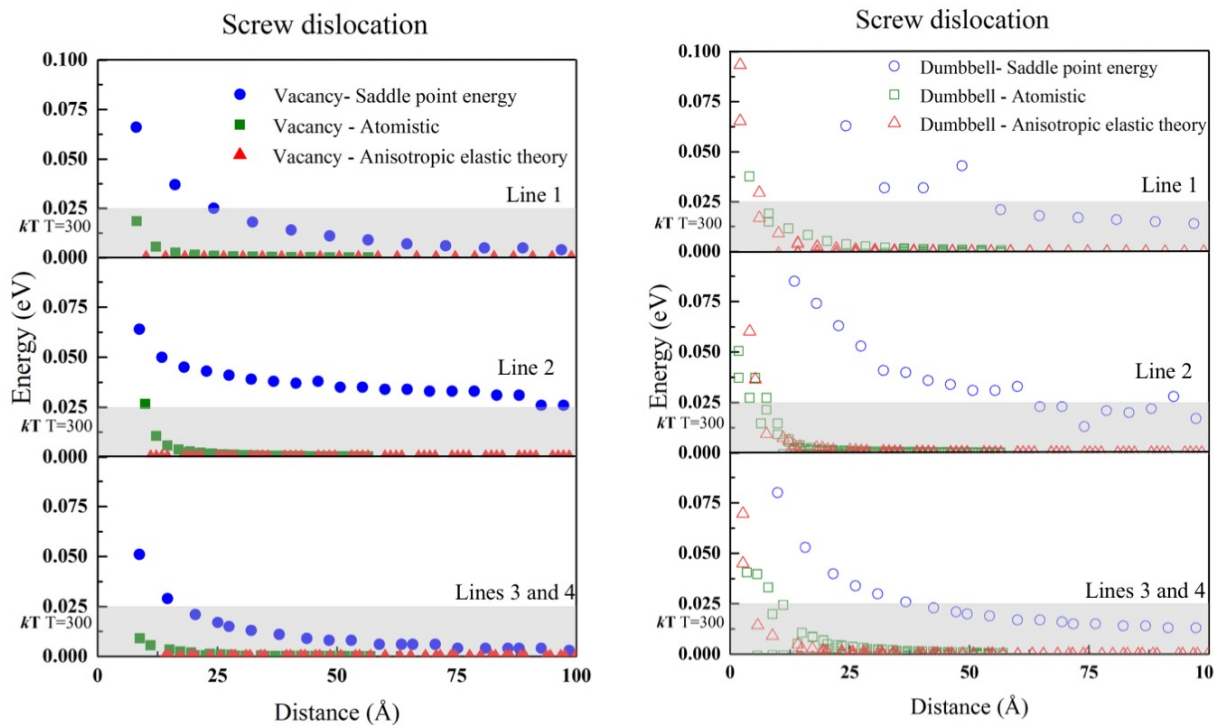


Figure A3.42. Comparison of saddle point energies obtained by saddle point searches with SEAKMC, and saddle point approximations using the binding energy obtained by atomistic calculations and anisotropic elastic theory for vacancies and dumbbells in the presence of a screw dislocation.

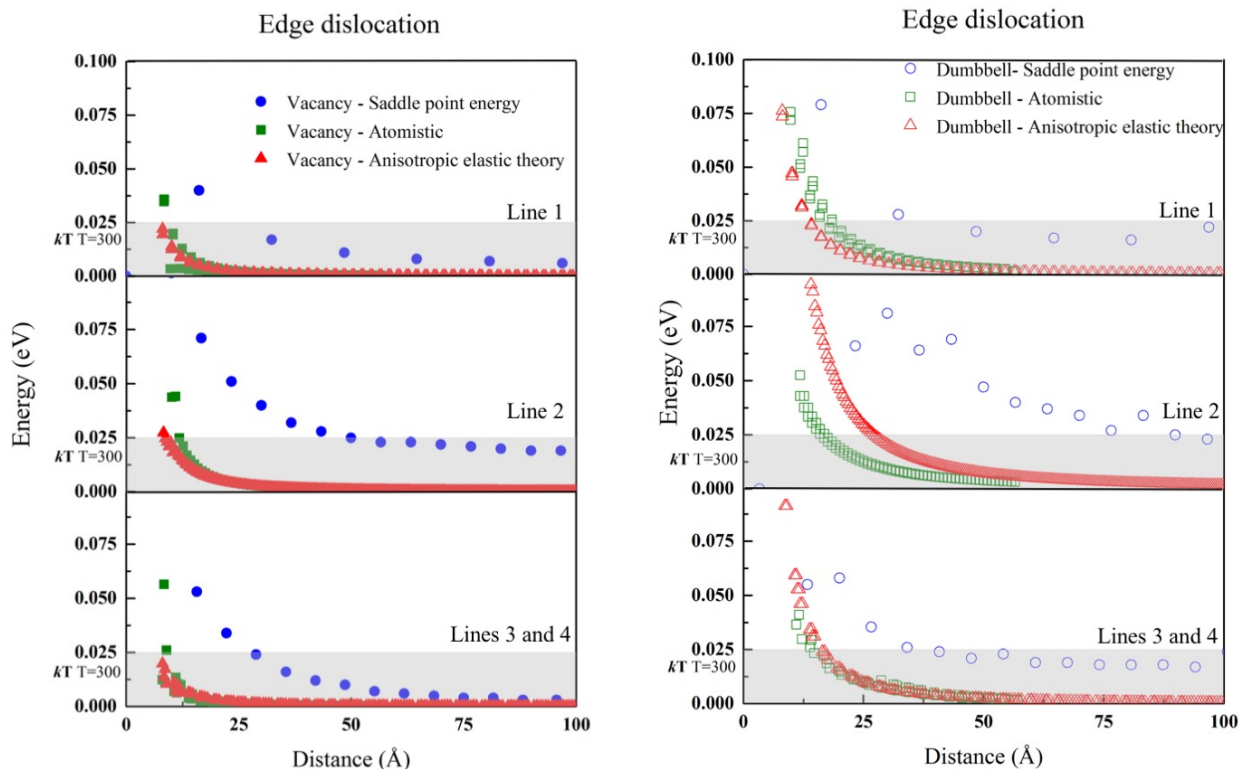


Figure A3.43. Comparison of saddle point energies obtained by saddle point searches with SEAKMC, and saddle point approximations using the binding energy obtained by atomistic calculations and anisotropic elastic theory for vacancies and dumbbells in the presence of an edge dislocation.

VITA

Luis Alberto Casillas Trujillo was born in Merida, Yucatan, Mexico. He received a bachelor's degree in Industrial engineering from the Universidad Marista de Merida. Since then he felt an inclination towards programming and solid state physics and did internships at CINVESTAV Merida with Dr. Manuel Rodriguez and Dr. Javier Espinosa. He spent one year as a post baccalaureate research assistant at Los Alamos National Laboratory working with Dr. Steven Conradson. He obtained an Erasmus Mundus scholarship in the Mathmods Master's program, where he enjoyed the Abruzzo region in Italy, walks along the Cote d'Azur, and learnt about the Polish Winter. After obtaining his Master's degree he did a one year internship at Los Alamos National laboratory, working with Dr. David Andersson. He joined the Materials Science PhD program at the University of Tennessee where he was advised by Prof. Kurt Sickafus and Prof. Haixuan Xu, and defended his doctoral dissertation in December 2017. During his PhD, he spent three months working with Prof. Gianguido Baldinozzi at Centrale Supélec in Paris. Luis enjoys modern art and classical cinema, and pretends he understands it, he always strokes his chin while at museums, and cites Mondrian, Deschamps and Jodorowski more often than needed.