THESIS FOR THE DEGREE OF LICENTIATE OF PHILOSOPHY

### Defect properties in dilute tungsten alloys from first-principles calculations

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Department of Applied Physics CHALMERS UNIVERSITY OF TECHNOLOGY Göteborg, Sweden 2015 Defect properties in dilute tungsten alloys from first-principles calculations LEILI GHARAEE

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#### Abstract

The sustainable production of energy from renewable sources represents one of the biggest challenges of modern societies, especially as the worldwide demand for energy continues to increase. Power production based on nuclear fusion is a very attractive option in this regard. A major obstacle with respect to the construction of fusion power plants concerns the development of materials that can tolerate the extreme conditions caused by the high-energy neutron flux generated by the fusion plasma.

In this context, tungsten based materials are considered for applications in fusion reactors, especially as armour materials at the divertor and the first wall. This interest is motivated by promising physical properties such as high melting point, low coefficient of thermal expansion, high thermal conductivity, and high sputtering resistance.

In this thesis, the properties of dilute tungsten alloys have been studied by means of first-principles calculations based on density functional theory. Specifically, I investigated the thermodynamic and kinetic properties of intrinsic and extrinsic defects produced during irradiation. Interstitials generally have large formation energies due to large strain fields associated with the defect core; they are, however, produced during irradiation. The calculations show that Ti, V and Re trap self-interstitials produced during irradiation. Mixed interstitial migration proceeds via a non-dissociative mechanism and is faster than the migration of vacancies. This aspect is particularly important with respect to our understanding of radiation induced segregation and radiation induced precipitation.

The results are discussed in the context of the application of tungsten alloys for structural elements in fusion environments.

**Keywords:** tungsten alloys, point defects, irradiation, structural materials, first-principles calculations.

#### LIST OF PUBLICATIONS

This thesis consists of an introductory text and the following paper:

I Defect properties in dilute tungsten alloys from first-principles calculations Leili Gharaee and Paul Erhart Submitted to Journal of Nuclear Materials

The author's contribution to the paper:

I The author carried out the calculations as well as the analysis, and wrote most of the paper.

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# 1

# Introduction

The world energy demand grows rapidly. Nuclear fusion is expected to play a key role in this regard as it is a clean and sustainable source of energy. Fusion offers important advantages such as no carbon emissions and therefore no air pollution, unlimited fuel supply and intrinsically safe technology, which would make a massive contribution to mitigating concerns about energy safety and climate change.

Currently, three main projects, JET (Joint European Torus), ITER (International Thermonuclear Experimental Reactor), and DEMO (DEMOnstration Power Plant), are hoping to pave the way for commercially viable power generation using nuclear fusion.

JET, located in Oxfordshire, UK, set the world record in 1997, for achieving (16 MW) fusion power in deuterium-tritium operation [1], the fuel proposed for the first generation of fusion power plants.

The follow-up programme, ITER will attempt to go one step further and generate more power, 500–700 MW [2], than is used to start the process. This project attempts to demonstrate the feasibility of magnetic-confinement nuclear fusion and is currently under construction in Cadarache, France.

However ITER does not represent the final step; It is the bridge toward DEMO, the first plant that will demonstrate the large-scale production of electrical power and tritium fuel self-sufficiency. The plan for DEMO is to begin its operations in the early 2030s. Conceptual designs of DEMO sketch a machine that is larger than ITER with the ability to produce fusion power up to 5000 MW [3]. The exact value varies for different designs.

The size of the machine is determined by the radius of the plasma cross-section, which is confined in a doughnut-shaped vessel. Its radius for DEMO ranges from 6 to 10 metres. In comparison, the radius in ITER measures 6.2 metres and that of the largest tokamak in operation, JET, measures about half of that [1, 2, 3].

One of the main concerns during reactor operation is the severe radiation condi-



Figure 1.1: A toroidal section through the simplified, homogeneous, DEMO model [4].

tions expected in fusion reactors, which requires the development of new materials able to withstand the harsh environment including thermal loads and radiation. The high-energy and high-intensity neutron fluxes produced by the fusion plasma have a significant lifetime-limiting impact on reactor components in both experimental and commercial fusion devices. The neutrons bombarding the materials not only produce defects but also initiate nuclear reactions, leading to transmutation of the elemental atoms. Products of many of these reactions are gases, particularly helium, which can cause swelling and embrittlement.

The fusion reaction takes place in the reactor chamber inside a vacuum vessel. The vacuum vessel is the container, which houses the fusion reaction and acts as a first safety containment barrier. At the very bottom of the vacuum vessel, the divertor is located as the next plasma-facing component, see Figure 1.1, and its function is to extract heat and helium ash –both products of the fusion reaction– and other impurities from the plasma.

The amount of plasma increases with the size of the machine, leading to even harsher radiation conditions including higher neutron energies, radiation dose and temperature. The average neutron fluence on the first wall material in ITER is 0.57-0.8 MWa/m<sup>2</sup> and the neutron flux at the first wall will reach up to  $\sim 10^{23}$  n/m<sup>2</sup>s. The average neutron fluence for DEMO is expected to be up to 15 MWa/m<sup>2</sup> with neutron fluxes of being at least a hundred times larger. Plasma current varies from 4.8 MA in JET to 15-17 MA in ITER and 30 MA in DEMO. As a result, higher heat flux and higher neutron loads in DEMO, will lead to higher displacements per atom (dpa) of up to  $\sim$  30 dpa, compared to ITER with < 3 dpa (~0.7 for tungsten tiles) in a full operational life [2, 3, 5, 6, 7, 8, 9, 10].

More energetic fusion neutrons in higher doses cause far more damage (multiple cascades) and more transmutation products due to many new nuclear reaction channels. Transmutation in turn, results in a change in material composition and will thus influences thermal, chemical, and physical properties of the wall materials, which eventually has a great influence on the resistance to thermal loads and radiation. As a result the choice of the surface material for first wall and divertor is very important and very few materials are able to withstand temperatures of up to 3000 degrees C for a reasonable lifetime of reactor operation.

In ITER beryllium has been chosen as the element to cover the first wall, and interior surfaces of the vacuum vessel will be made of high-strength copper and stainless steel. As the size of the vacuum vessel dictates the volume of the fusion plasma, DEMO will produce a greater amount of power and higher radiation load compared to ITER and therefore, other types of materials harder than steel are required. In this regard tungsten is considered for structural applications in fusion reactors. For JET, carbon tiles were used initially to cover the interior wall of the vacuum vessel, but carbon recently replaced with beryllium and tungsten tiles. In ITER as well, the plasma-facing components of divertor are being made of tungsten[2, 3, 5, 10].

Tungsten has a high energy threshold for physical sputtering ( $E_{th} \sim 200 \text{ eV}$ ) and does not form hydrides or co-deposits with tritium. In addition, it has a high melting point (3680 K), low coefficient of thermal expansion and high thermal conductivity (~150 W/mK at room temperature, which does not decrease much with temperature). This combination of promising physical and mechanical properties makes its use as a coating on the high heat flux components very attractive [11].

Yet, tungsten, as well as other body-centred-cubic (BCC) metals, generally exhibit brittle behaviour at low temperatures and ductile behaviour at high temperatures. The ductile operating window for tungsten is 700-1200 degrees C and tungsten exhibits brittle behaviour at lower temperatures ( $\leq 600$  K). Its ductile to brittle transition temperature (DBTT) lays between 150 °C and 400 degrees C [7]. The operational temperature for plasma facing components at the ITER divertor ranges from ~200 degrees C at water cooled operation temperatures to 3000 degrees C at full operation. Consequently the use of W as structural material is strictly limited to operating temperatures above the DBTT ( $\geq 600$  K) and below the high temperature creep limit (~1000 K) and this window shrinks further under neutron irradiation [7, 9, 10, 12]. In this regard, alloying has been suggested as a means to lower the BDTT. For instance, the BDTT of W–Re decreases relative to pure tungsten [13].

On the other hand, as mentioned before, alloy formation will also occur naturally due to nuclear transmutation caused by high energy neutron exposure. In this fashion pure tungsten will gradually evolve into an W-Re-Os-Ta alloy [4, 14, 15]. As an example, the variation in concentrations of He, Re and Ta, produced in pure W under neutron irradiation as a function of position(and depth) in the divertor and first wall of a DEMO design is presented in Figure 1.2.



Figure 1.2: Variation in concentrations of He, Re and Ta, produced in pure W under neutron irradiation as a function of position (and depth) in the divertor and first wall of the DEMO design. The equivalent dpa/year in pure W are also given for each position. Units of concentrations are given in atomic parts per million (appm) [4].

Alloying either intentionally or implicitly affects many properties of importance including mechanical performance, thermal conductivity, swelling resistance and oxidation behaviour under irradiation. While these properties are at least reasonably well understood for pure tungsten, the situation is quite different in the case of alloys.

With regard to applications in fusion reactors one must therefore consider the performance of the material under particle bombardment. Irradiation events lead to the localized production of lattice defects such as vacancies and interstitials. Whereas vacancies are relatively immobile, interstitials in pure tungsten, which are commonly referred to as self-interstitial atoms, can readily migrate allowing for efficient defect recombination, which is an important factor with respect to radiation tolerance. In an alloy an attractive interaction between solute atoms and interstitials can lead to trapping of intrinsic defects, increasing the defect density after bombardment and thus accelerating damage build-up compared to the pure material. Thus, while alloying might improve the mechanical properties it can potentially simultaneously cause a degradation of the irradiation tolerance.

Void induced swelling is another challenge for tungsten as a structural material. Swelling causes dimensional changes and variations in materials properties resulting in serious problems for the reactor design engineer. The swelling of tungsten is shown to be strongly reduced when alloyed with rhenium [16].

In addition, specific developments are aimed at suppressing the production of volatile tungsten oxide in case of a loss-of-coolant accident with air ingress so as to reduce the risk of releasing radioactive material. One proposed solution is to add small amounts of silicon and chromium to tungsten which leads to a glassy protection layer on the tungsten surface and can reduce the tungsten oxidation rate by up to four orders of magnitude [17].

In the present thesis, I employ computational calculations to gain insight into the response of the material to neutron irradiation, enabling the assessment of structural integrity of components in a fusion power plant. The eventual goal is to provide an assessment of tungsten-based alloys for applications in fusion environments by studying different types of point defects, interactions of intrinsic point defects and solute atoms as well as atom migration.

## Background

#### 2.1 Radiation and high energy particles

Irradiation is the process by which an object is exposed to radiation. One of the immediate effects of irradiation on a material is the displacement of some atoms from their equilibrium lattice sites [18]. Energies vary for different radiation sources and high energy particles such as photons, electrons, ions and neutrons have a stronger impact on the material.

High energy photons (~1 MeV) can be ionizing while penetrating the material. During excitation and decay processes, additional photons are generated which eventually results in electron-gamma cascades production.

Charged particles like electrons and ions interact strongly with material and lead to lots of scattering. For example 1 MeV electrons in copper (Cu) can penetrate 350  $\mu$ m, however a proton of the same energy which is heavier penetrates 380 nm. Due to its larger mass, a proton produces more damage, loses more energy while scattering and stops in lower depth compared to electrons. A gold (Au) ion of the same energy penetrates only 96 nm. Energetic ions interact with the nuclei via repulsive Coulomb potential. Since the ion mass is much higher than that of the electrons, the interaction with electrons slows down the ion, but does not change its path significantly.

Neutrons are not stable elementary particles and have a half-life of about 11 minutes. However free neutrons still exist in situations like natural radioactive decay, which produces neutrons with energies of a few MeV. Reactions taking place in a nuclear reactor also produce neutrons of 2 MeV in the case of nuclear fission and 14 MeV in the case of nuclear fusion. Neutrons do not interact significantly with electrons in the material, they mainly interact with the atomic nuclei via the nuclear forces. Based on their energies, neutrons can interact via several different processes. Low energy neutrons interact with atoms via elastic scattering, for neutrons with energies above 1 MeV, however, inelastic neutron scattering becomes important. During this process the kinetic energy is not preserved and the energy change goes into the excitation of the energy of the nucleus.

Nuclear reactions becomes significant for neutrons with energies above 8 MeV. During this process a nucleus absorbs the high energy neutron, generates transmutation products and releases a gamma photon [18]. This reaction is very important for damage build-up in material as the nucleus gets a recoil energy in the order of 100 eV from the emitted gamma particle. Both, fission and fusion neutrons, cause activation and irradiation damage. The more energetic fusion neutrons, however, cause far larger damage and more transmutation products due to many nuclear reaction channels and higher activation than fission neutrons [19].

#### 2.2 Applications of high energy irradiation

High energy radiation is an important area in ongoing research due to applications in different fields of technology, specifically with respect to energy generation in existing nuclear power stations and diagnostic techniques in nuclear medicine.

#### 2.2.1 Medicine

Due to its penetrating ability, high energy radiation is widely used to image the inside of objects in medical radiography and treat cancerous cells in radiotherapy. Photons used in a typical radiographical processes such as dental radiography have energies up to kilo electron volts. Radiographic images are useful in the detection of pathology of the skeletal system as well as for detecting some disease processes in soft tissue.

In the context of radiotherapy, for treatment reasons higher energy rays are used with energies up to mega electron volts and even higher [20, 21]. These high energy beams carry enough energy to ionize atoms and disrupt molecular bonds and eventually kill malignant cells or control their reproduction. Being exposed to such radiation is, therefore, harmful to living tissue. It causes radiation sickness and increases the risk of radiation-induced cancer. For medical applications this increased cancer risk is, however, greatly outweighed by the benefits.

There are two types of ionizing radiation including photon (such as x-rays and gamma rays) and particle (such as electrons, protons, neutrons, carbon ions, alpha particles, and beta particles). Ionizing radiation works by directly damaging the DNA of cancerous cell leading to cellular death. Cancerous cells are particularly vulnerable to attacks on the DNA because of their high rate of division and their reduced ability to repair DNA damage. Depending on the depth of the tumour ionizing radiation with different amounts of energy is chosen. The more energy, the more deeply the radiation can penetrate the tissues. To spare normal tissues such as skin or healthy organs, which radiation must pass through to treat the tumour, shaped radiation beams with

adjusted energies are aimed from several angles of exposure to intersect the tumour. Tissues closer to the surface of the body than the tumour, therefore, receive less radiation causing damage. It provides a much larger absorbed dose in the tumour than in the surrounding healthy tissue [20, 22].

The photon beam comes from a radioactive source such as cobalt, cesium, or a machine called a linear accelerator. Electron and proton beams are also produced by a linear accelerator. Generated beams have different energy levels to penetrate and various side-effects to surrounding tissue. For instance electrons have a low energy level and don't penetrate deeply into the body, so this type of radiation is used most often to treat the skin or tumours located close to the surface of the body. Protons and heavy ions have little lateral side scatter in the tissue, due to their relatively large mass. Carbon ion radiation which is called heavy ion radiation is usually helpful in treating cancers that don't usually respond well to radiation. Due to its heavier mass, it can do more damage to the target cell than other types of radiation. On the other hand the effects on nearby normal tissue can be more severe.

Alpha and beta particles are mainly produced by special radioactive substances that may be injected, swallowed, or put into the body. They're most often used in imaging tests, but can be helpful in treating cancer as well. In this process a medicine which is referred to as nuclear medicine, is attached to a small quantity of radioactive material. This combination is called a radiopharmaceutical and there are many different radiopharmaceuticals available to study different parts of the body depending on the condition to be diagnosed or treated.

The pharmaceutical part of the radiopharmaceutical is designed to go to a specific place in the body where there could be disease or an abnormality. The radioactive part of the radiopharmaceutical that emits radiation, known as gamma rays, is then detected using a special camera called a gamma camera. This camera which is placed a few inches over the patients body, allows the nuclear medicine physician to see what is happening inside the body. Nuclear medicine also can treat diseases. For instance patients with hyperthyroidism are treated with nuclear medicine using radioactive iodine. Although exposure to radioactivity in very large doses can be harmful, the radioactivity in radiopharmaceuticals is carefully selected by the nuclear medicine physicians to be safe[23, 24].

#### 2.2.2 Nuclear fission reactor

#### 2.2.2.1 Background

Nuclear fission is a process in which the nucleus of an atom splits. The splitting of a nucleus occurs due to radioactive decay or by bombardment by other subatomic particles. In either cases, the resulting components have less combined mass compared to the original nucleus and the missing mass is converted into kinetic energy.



Figure 2.1: Fission process in which the nucleus of an atom breaks into smaller nuclei due to bombardment by neutron, which results in the production of energy [27].

Radioactive fission happens primarily with the heavier elements. In this process, a nucleus of an unstable atom loses energy by emitting for instance alpha particles, beta particles, gamma rays and neutrons. Isotopes of U by releasing hundreds of MeV energy decay to fission products like krypton (Kr), Barium (Ba), technetium (Tc), ruthenium (Ru), palladium (Pd), etc..

In the second mechanism, when a large fissile nucleus such as uranium-235 ( $^{235}$ U) or plutonium-239 ( $^{239}$ Pu) absorbs a neutron, it may undergo nuclear fission. The heavy nucleus splits into two or more lighter nuclei -the fission products- releasing kinetic energy, gamma radiation, and free neutrons. A portion of these neutrons may later be absorbed by other fissile atoms and trigger further fission events, which release more neutrons. This is known as a nuclear chain reaction. This procedure releases a significant amount of energy compared to the energy of the neutron that started the procedure. Bombarding natural uranium with neutrons of a few eV splits the nucleus, releasing a few hundred MeV and neutrons of ~2-3 MeV [25, 26]. Controlled reactions of this sort are used to release energy within nuclear power plants. Uncontrolled reactions can fuel nuclear weapons.

#### 2.2.2.2 Fission reaction in nuclear reactor and electricity generation

Similar to the plants that burn coal, oil and natural gas, nuclear plants produce electricity by boiling water into steam. This steam afterwards drives turbines that produce electricity. Nuclear fuel includes two types of uranium, <sup>238</sup>U as well as <sup>235</sup>U and plutonium. Fuel comes in the shape of solid ceramic pellets that are packaged into long tubes. <sup>238</sup>U constitutes an important share of the fuel, <sup>235</sup>U is, however, more unstable and splits quickly. This process releases neutrons, which start the chain fission reaction. Neutrons hit other uranium atoms resulting in the release of more neutrons along with heat. When a chain reaction occurs, fission becomes self-sustaining.

In order to control the nuclear reaction, special rods are inserted among the fuel tubes in order to slow down or accelerate the reaction. They are composed of chemical elements such as boron, silver, indium and cadmium that are capable of absorbing many neutrons without undergoing fission themselves [28, 29]. Fuel tubes in the reactor are surrounded by water. The heat produced during the fission reaction turns this water into steam. The steam drives a turbine, which spins a generator to create electricity.

Nuclear power provides many big advantages. It is a clean energy and does not contributes to climate change. Almost no greenhouse gases such as carbon dioxide are emitted into the atmosphere. In addition, nuclear fission has large power-generating capacity and produces roughly a million times more energy per unit weight than fossil fuel alternatives.

There are negative sides to this way of energy production. Uranium sources are just as finite as other fuel sources and are expensive to mine, purify and transport together with the fact that they always possess a contamination risk. In addition during nuclear reactor operation, a high-level radioactive waste generated from fuel, and low-level radioactive waste in form of radiated parts and equipment are generated and disposal of radioactive waste is a complicated problem.

#### 2.2.3 Nuclear fusion reactor

With its high energy yields, low nuclear waste production, lack of air pollution and virtually limitless fuel available, fusion, the same source that powers stars, could provide an alternative to conventional energy sources.

#### 2.2.3.1 Background

Fusion is a nuclear reaction, occurs when two or more light atomic nuclei collide at very high speed and combine in such way that heavier atomic nucleus is formed. A great amount of energy is released during the process while matter is not conserved.

and the total mass of the new atom is less than that of the two, from which it was formed. As a result some of the matter of the fusing nuclei is converted to energy. Fusion is the process at the core of the Sun and other stars, in which hydrogen nuclei collide, fuse into heavier helium atoms and release enormous amounts of energy during the process [30, 31].

However creating a controlled fusion reaction has proven to be very difficult so far as the two hydrogen atoms with the same charge electrically repel each other. Very specific conditions including enormous temperature and pressure are required to make that happen. The tremendous heat of the sun, which is around ten million degrees



Figure 2.2: Fusion process: Two atoms, deuterium and tritium, fuse together, forming a helium nucleus, a neutron and lots of energy [10].

C, and its high pressure are achieved by the sun's large mass and the force of gravity compressing this mass in the core. This heat accelerates the atoms to the point where their momentum overcomes the electric repulsion [31].

Scientists are nowadays looking for ways to control the energy produced during nuclear fusion and employ it for peaceful purposes. To achieve fusion, temperature must reach approximately 100 million Kelvin which is about six times higher than the temperature of the core of the sun. These high temperatures allow the attractive forces to overcome the repulsive forces. At this temperature, the hydrogen is not a gas but a plasma, which is an extremely high-energy state of matter with free electrons [31].

There are two ways to achieve these conditions. Firstly, there is magnetic confinement, which uses magnetic and electric fields to heat and squeeze the hydrogen plasma. This method is used in the ITER project. The second approach is inertial confinement fusion, which uses laser or ion beams to squeeze and heat the hydrogen plasma [2, 32, 33].

There are different atomic combinations, which can lead to a fusion reaction. The deuterium-tritium (D-T) reaction has been identified as the most efficient combination for generating power on earth through fusion devices. ITER and the future demonstration power plant DEMO will use this combination of elements to fuel the fusion reaction [10]. In this reaction, a deuterium atom and a tritium atom combine to form an atom of Helium-4, release a neutron and an energy of 17.6 MeV per reaction. Considering that there billions of these reactions occur in each second, one can realize the potential efficiency of the fusion reaction for generating power [31].

Deuterium is a harmless isotope of hydrogen, containing a single proton and neutron. It is widely available as it can be distilled from all forms of water. Tritium is the other isotope of hydrogen and contains one proton and two neutrons. It is a fast-decaying radio-element, which is more challenging to locate in large quantities due to its 10year half-life. Rather than attempting to find it naturally, the most reliable method is to bombard lithium with neutrons to create this element. During the fusion reaction in ITER, tritium is produced, when neutrons escaping the plasma interact with lithium contained in the blanket wall of the tokamak [10].

In theory deuterium-deuterium fusion is more promising than deuterium-tritium because of the ease of obtaining the two deuterium atoms, which are not radioactive. In this reaction, two deuterium atoms combine to form a helium-3 atom and a neutron releasing 3-4 MeV energy. In practice this method is more challenging because it requires very high temperatures to occur [31].

The proton-proton fusion and the carbon cycle are the dominant combinations for stars like the sun with core temperatures of about 15 million degrees C. Proton-proton fusion begins with two protons and ultimately yields high energy particles such as alpha particles, positrons, neutrinos, and gamma rays. A reaction cycle yields about 25 MeV of energy. Stars with higher temperatures merge carbon rather than hydrogen atoms. Finally triple alpha process happens in stars such as red giants at the end of their phase, with temperatures exceeding 100 million degrees C. For this reaction, helium atoms are fused together rather than hydrogen and carbon [34].

#### 2.2.3.2 The working principle of a fusion reactor

In a fusion reactor, different isotopes of hydrogen come together to form helium atoms, neutrons and vast amounts of energy, see Figure 2.2. In large scale commercial designs, heat from the fusion reaction is used to operate steam turbines that drives electrical generators as in existing fossil fuel and nuclear fission power stations. It has, however, been extremely difficult for scientists to come up with a controllable, non-destructive way of performing fusion. In addition to the requirement of high pressure and temperature to make the fusion reaction happen, there are other complications such as efficiency considerations and the choice of container materials.

It is important to calculate how much energy is required to drive the reactor and how well it collects power, considering energy lost due to radiation and conduction. Choosing suitable materials for construction purposes, which will not become brittle or damaged by exposure to fast neutrons during fusion processes, is of great importance. In addition, any medium used in this process absorbs neutrons as well and eventually becomes mildly radioactive and must therefore be disposed of.

Fusion reactors are in experimental stages these days and many different fusion concepts have been developed along with several proposals for energy capture. As mentioned before, two main approaches are magnetic confinement fusion and inertial confinement fusion. The current leading design is the tokamak as a magnetic confinement fusion method. It is the most well developed and well funded approach to fusion energy. In this method a hot plasma is circulated in a magnetically confined ring. When completed, ITER will be the world's largest tokamak [2].



Figure 2.3: ITER tokamak reactor and its main parts including (1) blanket modules, (2) neutral beam injector, (3) magnetic field coils, (4) cooling equipment and (5) divertors [10].

In magnetic confinement, microwaves, electricity and neutral particle beams from accelerators are used to heat a stream of hydrogen gas to turn it into a plasma. This plasma is squeezed by super-conducting magnets, forcing the plasma nuclei closer to each other and thereby allowing a fusion reaction to occur. The most efficient shape for compressing of the plasma is a doughnut shape or toroid. A reactor of this shape is called a tokamak [2, 10].

The main parts of the ITER tokamak reactor as shown in Fig 2.3 are vacuum vessel, blanket modules, neutral beam injector, magnetic field coils, cooling equipment and divertors.

The vacuum vessel is a torus-shaped, double-wall structure with shielding and cooling water between the shells. The primary function of the vacuum vessel is to provide a high-quality vacuum for the plasma and to serve as the first confinement barrier of radioactive materials. It also provides radiation shielding, in particular, for the magnetic field coils [35]. A neutral beam injector or ion cyclotron system injects particle beams from the accelerator into the plasma to help the plasma reaching to the critical temperature. The injector is designed to provide  $\sim$ 17 MW of power, in the form of 1 MeV deuterium atoms, to the tokamak plasma during 1000 s, or even longer pulses of up to 3600 s [36].

Magnetic field coils comprises superconducting magnets. Their function is to confine, shape and control the plasma inside the vacuum vessel by using magnetic fields. The 48 elements of the ITER magnet system will generate a magnetic field of about 200,000 times higher than that of Earth. The magnet system for ITER consists of 18 superconducting toroidal field (TF) coils, a central solenoid (CS), six poloidal field (PF) coils and a set of correction coils (CCs).

The TF generate the field to confine charged particles in the plasma, the CS provide the inductive flux to ramp up plasma current and contribute to plasma shaping, the PF provide the positional equilibrium of plasma current (i.e. the fields to confine the plasma pressure) and the vertical stability of the plasma. The CCs allow correction of error field harmonics due to position errors as well as from busbars and feeders[37]. Electricity is supplied to the magnetic field coils by a central solenoid.

The cooling equipment functions as a heat transport system and the entire vacuum vessel is enclosed within this cryostat, or cold box, which provides insulation for the superconducting magnet system and other components. It is used to remove the heat in the vessel and blanket, including surface heat from plasma and nuclear heat deposited volumetrically, and also to cool down the magnets. Water and helium gas are two example coolants[2, 38].

Blanket modules are located inside vacuum vessel and provide shielding to the vessel by absorbing heat and high-energy neutrons from the fusion reaction, see Figure 2.3. The shielding blanket is divided into two parts. The back part with a radial thickness of  $\sim$ 30 cm is a pure shield made of steel. The front part, the "first wall", includes several different materials: a 1 cm thick beryllium armour protection, a 1 cm thick copper layer to diffuse the heat load as much as possible, and  $\sim$ 10 cm of steel structure. This component will become the most activated and tritium-contaminated in the entire ITER device. It could be in contact with the plasma in off-normal conditions, and thus can suffer damage from the large heat locally deposited, and may have to be repaired or exchanged [2].

Finally the divertors, situated at the bottom of the vacuum vessel, exhaust the helium products and other impurities generated during the fusion reaction, from the plasma. It comprises two main parts: a supporting structure made primarily from stainless steel, and the plasma-facing components, weighing about 700 tons. The plasma-facing components will be made of tungsten, a refractory material [2, 10].

In a fusion reactor, first a stream of deuterium and tritium fuel is heated to form a high-temperature plasma. In ITER, several heating methods will work concurrently to bring the plasma in the core of the machine to 150 million degrees C. One source of the heat within the tokamak is the changing magnetic field used to control the plasma. The

magnetic fields induce a high-intensity electrical current that when it travels through the plasma, energizes electrons and ions and causes them to collide. Collisions create resistance, which results in heat, but as the temperature of the plasma rises, this resistance –and therefore the heating effect– decreases. In order to reach higher temperatures, heating methods including neutral beam injection and high-frequency electromagnetic waves must be applied from outside the tokamak.

When the fusion reaction occurs, the high energy neutrons generated during reaction will be absorbed by lithium blankets and produce more tritium fuel. This process in turn, increases the temperature of the blanket, which cooling mechanisms are employed to decrease the blankets temperature by turning the water into steam. Eventually the steam will derive electrical turbines to generate electricity. The steam will be condensed back into water and employed again to absorb more heat from the reactor [2, 10, 38].

Despite the fact that there are many ways to produce fusion energy, nobody has put the technology into practice yet. In fact constructing an environment in which a controlled reaction occurs is one of the big challenges for the fusion research community.

#### 2.3 Radiation-induced point defects

Developing advanced nuclear energy systems depends crucially on the accurate understanding of radiation-damage processes in the respective materials. An important source of radiation damage to reactor metals is the displacement of atoms from normal lattice sites as the result of neutron-nuclear interactions. Defects produced in displacement events can include both isolated and clustered vacancies and interstitials. A starting point in the complex problem of predicting the irradiation behaviour of materials is to understand the defects physics. Research in this area tries to respond to the immense challenge of finding and designing materials that provide high radiation tolerance while fulfilling the requirements in terms of mechanical and thermal properties.

During the operation of a nuclear reactor, the immediate surrounding of the plasma is exposed to extreme radiation conditions, which leads to restructuring to submicrometresized grains and micrometre-sized spherical pores [39]. The formation, growth and dissolution of defects affects the mechanical and thermal properties of the material via diffusion of point defects and their reaction with impurities. Irradiation events lead to the localized production of lattice defects such as vacancies and interstitials [40]. Whereas vacancies are relatively immobile, interstitials in pure tungsten can readily migrate [41] allowing for efficient defect recombination, which is an important factor with respect to radiation tolerance [42].



Figure 2.4: Point defects in materials; (1) smaller substitutional impurity, (2) larger substitutional impurity, (3) interstitial atoms, (4) vacancy. Point defects usually induce a localized lattice strain.

#### 2.3.1 Point and line defects

In a perfect crystal, all the atoms are at specific atomic sites, ignoring thermal vibrations. Real crystals, however, contain imperfections, which may be point, line, surface or volume defects, and locally disturb the regular arrangement of the atoms. Under high energy irradiation, the concentration of defects increases dramatically, which affects physical properties of the material and has a decisive impact on materials performance [43].

As a result one needs to look in detail at the structure of defects. Defects can be classified according to their dimensionality. Zero dimensional defects are called point defects and are the main focus of this work.

There are two types of point defects in materials. Native defects are intrinsic to the material, such as vacancies (missing atoms) and self-interstitials (additional atoms incorporated on sites other than substitutional sites), see Figure 2.4. In addition to intrinsic point defects, crystals always contain extrinsic point defects, which are impurity atoms on substitutional or interstitial sites. Materials at finite temperatures contain a finite number of defects, the concentration of which is dictated by thermodynamics. Solute atoms play an important role in the physical and mechanical properties of all materials and their existence can be either due to alloying or transmutation [43].

In addition to point defects, there are one dimensional defects, called line defects. An example of these defects are dislocations, which mediate plasticity in most crystalline materials. As a result, they play a significant role with respect to understanding the transition between ductile and brittle fracture modes. They can be categorized into edge and screw dislocations. In Figure 2.5 (b), suppose that all the bonds across the



Figure 2.5: (a) Model of a simple cubic lattice; the atoms are represented by filled circles and bonds between atoms by strings, only a few of which are shown, (b) edge dislocation DC formed by inserting an extra half-plane on atoms in ABCD, (c) screw dislocation DC formed by displacing the faces ABCD relative to each other in direction AB [43].

surface ABCD are broken and the faces of the crystal are separated so that an extra half-plane of atoms can be inserted in the slot. The faces of the slot will have been displaced by one atomic spacing, but the only large disturbance of the atoms from their normal positions relative to their neighbours is close to line DC, which decreases with distance away from the line. This line DC is called an edge dislocation.

The arrangement of atoms around a screw dislocation can be created by displacing the crystal on one side of ABCD relative to the other side in the direction AB as shown in Figure 2.5 (c). At the end of this chapter we describe the importance of line defects with respect to the mechanical properties of tungsten.

#### 2.4 Tungsten as a first wall material

The plasma-wall interaction issues are among the most serious obstacles to the realization of fusion energy production and in this regard the choice of wall material is of pivotal importance. This interaction is a key factor, which determines the lifetime of the wall components and thus the overall cost-effectiveness of the facility.

The structural material has to meet a vast numbers of criteria to be safe, suitable and efficient for fusion environment. For example it has to show low erosion, which favours for heavy elements such as Mo or W. In addition it is required for the material to have a high melting point and a high thermal conductivity, for which the candidate materials are C and W. For low radiation loss and low nuclear activation lighter elements such as Be and C are good candidates. Low propensity to absorb tritium is also very important; tungsten and -to a lesser extent- steel and beryllium meet this criterion. Tungsten and tungsten alloys are therefore considered for structural applications in fusion reactors, especially for armor materials at the divertor and first wall [9, 44, 45, 46].

For ITER these considerations have led to the choice of tungsten as the wall material for the regions of highest heat load (divertor, see Figure 2.3) and beryllium for the larger main wall surface area that is exposed to less severe heat load. For DEMO the same considerations point to tungsten for most of the regions, but there are major unresolved issues that we describe in following sections. As a result properties such as the resistance to fracture and the behaviour under radiation have to be investigated carefully.

#### 2.4.1 Behaviour under irradiation

With regard to applications in fusion reactors one must consider the performance of the material under particle bombardment. During fusion reactor operation, as a result of high energy neutron exposure, defect formation, displacement damage as well as transmutation elements are produced, which will cause changes in evolving material properties such as thermal conductivity and swelling. Nuclear transmutation results in compositional changes as well as hydrogen and helium production and is a sever problem for first wall materials. Compositional changes influence thermal, chemical, and physical properties of the wall materials, which has a great impact on resistance to thermal loads and erosion.

An important property of tungsten is its high rate of transmutation to rhenium, osmium and also iridium in a fusion neutron environment [14, 47, 48, 49, 14].

It has been estimated that after five years of operation pure tungsten will have been transmuted into a W-Re-Os alloy with 3% Re,2% Os, and 0.6% Ta [14, 4], see Figure 1.2.

In ITER a displacement damage of up to ~0.7 dpa and transmutation to 0.15% Re would be produced in the W divertor after a fluence of 0.15 MWa/ $m^2$  at 200-1000 degrees C. The displacement damage for the tungsten first wall in ITER reaches 1 dpa while for a DEMO-like reactor the displacement damage is reported to be up to 30 dpa for full operation and Re concentrations of up to 6% are produced [50, 7, 6].

The radiation hardening in BCC alloys at low temperatures (< 0.3  $T_M$ ), where  $T_M$  is the melting temperature (3422 degree C for tungsten), is generally pronounced even for doses as low as 1 dpa. The amount of radiation hardening typically decreases rapidly with irradiation temperature above 0.3  $T_M$ , and radiation-induced increases in the BDTT may be anticipated to be acceptable at temperatures above 0.3  $T_M$ .

In addition to neutrons, it is known that bombardment by helium, which is one of the products of the D-T fusion, leads to micro-structural evolution, including the formation of dislocation loops and helium holes and bubbles [51, 52, 53, 54]. Helium irradiation on tungsten changes the surface morphology dramatically by forming a fuzz-like nano-morphology, which is a highly undesired phenomenon. Such surface features could change materials properties such as heat transfer, fuel (deuterium/tritium) retention as well as embrittlement of the divertor [55, 56].

From the experimental results in divertor simulators, the key factors for the forma-

tion of nanostructures on tungsten surfaces by helium plasma irradiation are found to be the surface temperature and the incident ion energy. Nanostructures are formed when the temperature is in the range of 1000-2000 K, and the incident ion energy is higher than 20 eV. Typically, the necessary helium fluence to form the nanostructure is on the order of  $10^{25}$  m<sup>-2</sup>. On the basis of the helium irradiation experiments performed in the divertor simulators, it is shown that nanostructure formation can also occur in other metals such as molybdenum. It is related to pinholes appearing on the bulk part of the material, and the rough structure subsequently develops into a much finer nanostructure [51].

In general, irradiation events lead to the production of lattice defects such as vacancies and interstitials [40]. Whereas vacancies are relatively immobile, interstitials in pure tungsten can readily migrate [41], allowing for efficient defect recombination, which is an important factor with respect to radiation tolerance [42]. In an alloy an attractive interaction between solute atoms and interstitials can lead to trapping of intrinsic defects, increasing the effective defect density compared to the pure material. Thus alloying can potentially cause a degradation of the irradiation tolerance.

Previous studies show that irradiated tungsten shows swelling around 800 degrees C. The addition of 25% rhenium, however, to tungsten almost completely suppresses the swelling in the irradiation temperature range, and no voids have been observed [57].

#### 2.4.2 Mechanical properties

Some materials are brittle and shatter like glass, whereas others are ductile and deformable. Several materials, such as BCC metals, exhibit both types of behaviour with a brittle-to-ductile transition (BDT) at a characteristic temperature. Tungsten, specifically exhibits brittle behaviour at low temperatures and ductile behaviour at high temperatures. The BDT temperature (BDTT) of pure tungsten is high which poses a challenge with respect to its applications in fusion environment [9, 13, 58].

A crack can be introduced into a material by mechanical loading. If the material near the crack tip does not show sufficient plasticity to slow down or arrest the crack, it propagates leading to brittle fracture. The BDTT is strongly dependent on the strain rate, which allows an activation energy for the BDT to be determined. This activation energy has been shown to be equal to that for dislocation motion, which suggests a mobility-controlled BDT.

Gumbsch *et al.* [59] by performing mechanical tests on tungsten single crystals have shown that the preexisting dislocation density and the availability of dislocation sources can be increased by plastic deformation. The materials response to externally-applied load is, however, complicated and depends on factors such as temperature, applied strain rate and the preexisting microstructure of the material [43].

At higher temperatures up to the BDTT, a higher loading rate always lowers the fracture toughness and the BDTT increases significantly with loading rate. When the



Figure 2.6: Schematic illustration of the potential energy surface of a dislocation line gliding via kink mechanism [43].

temperature is sufficiently high, a large number of dislocations are activated. In addition, the density of dislocation increases with temperature due to the activation of additional dislocation sources. These two factors produce higher shielding of the crack tip which can improve the size of the plastic zone.

At intermediate temperatures, the beneficial effect of the predeformation vanishes and the fracture toughness decreases. This can be attributed to the increased yield strength and lower dislocation mobility produced by work hardening. The reduced dislocation mobility will not only decrease the fracture toughness but must also be expected to shift the BDTT to higher temperatures.

The low-temperature fracture toughness shows a dependence on the state of predeformation and the crystallographic orientation of the crack, and varies not only with the cleavage plane but also with the propagation direction within a given cleavage plane. At low temperatures, dislocation nucleation is the limiting process because of the scarcity of active sources.

The increase of the fracture toughness with temperature in the semibrittle fracture regime below the BDTT is more difficult to interpret. The significant increase in fracture toughness with temperature has to be interpreted as the beginning of plastic deformation in the vicinity of the crack tip. The increased dislocation activity causes a blunting of the crack tip. Furthermore, dislocations cause a severe stress relaxation at the crack tip by shielding it from the applied load [12, 59].

In BCC metals, there are certain crystallographic slip planes placed along  $\langle 111 \rangle$  directions. However, the apparent slip plane varies with composition, crystal orientation, temperature and strain rate. When the crystal is deformed, screw dislocations dictate the slip characteristics since edge dislocations are about 10 times more mobile and do not affect this process [59].

The slip behaviour in BCC metals is determined by the atomic structure of the core region of the screw dislocation. There are two main core structures non-degenerate and degenerate (or compact). The screw core has a distinctive non-planar character. This leads to high lattice resistance to glide of the screw dislocation and consequently to strong temperature and strain rate dependencies of the yield stress [43]. Ab initio methods indicate that the screw dislocation for tungsten has the non-degenerate (compact) core, which means dislocation segments cannot move on different planes. This, in principle, decreases the possibility for gliding with lower barriers [43].

In order to glide, the dislocation tends to lie as close as possible in the position of minimum energy. If the dislocation is unable to lie entirely in one energy minimum, it can develop kinks when moving from one minimum to the next, as shown in Figure 2.6. In this mechanism, dislocation glide proceeds via a two-stage process involving the nucleation of kinks and the lateral propagation or growth of kinks along the dislocation line, both of which are thermally activated processes [60].

It has been found that the ductility of tungsten can be improved by alloying with rhenium [61, 62], which also is a transmutational element in tungsten [14]. In fact density functional theory calculations (DFT) show that Re switches the core structures of screw dislocations to degenerate core, while significantly reducing the Peierls stress (the driving force needed to move a dislocation within a plane of atoms in the unit cell) [63]. In this study the virtual crystal approximation was employed, in which compositional inhomogeneity is treated in an average way. Therefore no information about local structure and differences in chemical bonding are included, which motivates for a more accurate study on the interaction of solute atoms with screw dislocations in the future (see Chapter 5).

# Computational details and methodology

#### 3.1 Density functional theory

#### 3.1.1 The quantum-mechanical many-body problem

In principle, all properties of a system can be derived from the quantum mechanical wave function of the system. This wave function can be obtained by solving the time independent Schrödinger equation

$$H\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{R}_1, \mathbf{R}_2, ...) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{R}_1, \mathbf{R}_2, ...).$$
(3.1)

Here  $\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{R}_1, \mathbf{R}_2, ...)$  is the quantum mechanical wave function of the system and  $\mathbf{r}_i$  and  $\mathbf{R}_I$  denote the position of *i*th electron and *I*th nucleus. *E* corresponds to the ground state energy of the system.

A complete description of the Hamiltonian of the system is

$$H = -\frac{1}{2} \sum_{i} \nabla_{i}^{2} - \frac{1}{M_{I}} \nabla_{I}^{2} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} - \sum_{i,I} \frac{Z_{I}}{|\mathbf{r}_{i} - \mathbf{R}_{I}|} + \frac{1}{2} \sum_{I \neq j} \frac{Z_{I} Z_{j}}{|\mathbf{R}_{I} - \mathbf{R}_{j}|}$$
(3.2)

where atomic units,  $\hbar = m_e = e = 4\pi\epsilon_0 = 1$  have been used and  $Z_i$  and  $M_I$  denote charge and mass of the nuclei.

This equation can be written as

$$H = T_e(\mathbf{r}) + T_N(\mathbf{R}) + V_{ee}(\mathbf{r}) + V_{eN}(\mathbf{r}, \mathbf{R}) + V_{NN}(\mathbf{R})$$
(3.3)

where  $T_e$  and  $T_N$  are the kinetic energy operators for the electrons and nuclei respectively and  $V_{ee}$ ,  $V_{eN}$  and  $V_{NN}$  represent the potentials due to Coulomb interactions between electrons and nuclei.

Obtaining a direct numerical solution of the Schrödinger equation is, however, a difficult task as any finite-size piece of material contains a number of electrons and nuclei on the order of Avogadro's constant ( $N_A \sim 10^{23}$ ). As the exact solution is only possible for very small systems, simplifications and approximations are required.

#### 3.1.2 The Born-Oppenheimer approximation

A key observation in applying quantum mechanics to atoms is that atomic nuclei are much heavier than individual electrons, which means that electrons respond much more rapidly to changes in their surrounding than nuclei.

The Born-Oppenheimer approximation takes advantage of this phenomenon and makes the assumption that the ions are stationary and their motion can be treated classically while solving the electronic Schrödinger equation.

As a result the physical problem is split into two parts; the electronic structure problem and the ionic problem and the wavefunction of the system becomes the product of electronic and ionic wavefunctions. Thus, the electronic Hamiltonian reduces to

$$H_e = T_e(\mathbf{r}) + V_{ee}(\mathbf{r}) + V_{ext}(\mathbf{r}, \mathbf{R})$$
(3.4)

where  $T_e$  and  $V_{ee}$  have been introduced above while  $V_{ext}$  is the external potential from the nuclei including the electrostatic interaction between nuclei. In this approximation, wavefunction and ground state energy depend on the positions of the nuclei in a parametric way,

$$H\Psi(\{\mathbf{r}\};\{\mathbf{R}\}) = E(\{\mathbf{R}\})\Psi(\{\mathbf{r}\};\{\mathbf{R}\}).$$
(3.5)

The function  $E({\mathbf{R}})$  represents the so-called Born-Oppenheimer potential energy surface, which in many cases is an excellent approximation [64].

The nuclei are considered as classical point particles, which move in the Born-Oppenheimer potential energy,  $E({\mathbf{R}})$ . The force exerted on a nucleus can be derived from

$$F_{i} = -\partial E(\{\mathbf{R}\}) / \partial \mathbf{R}_{i}.$$
(3.6)

The forces can be used in minimization schemes to find ground state configurations or to study dynamical properties via molecular dynamics.

#### 3.1.3 The Hohenberg-Kohn theorems

Density functional theory (DFT) is a first-principles method that benefits from the fact that the ground-state energy of the system is a function of electron density. It means the basic variable for solving the Schrödinger equation is the electron density, which as described below can be determined by considering a system of independent particles. The electron density is a function of three spatial variables, rather than the wave function of a system of interacting electrons with *3N* variables.

The entire field of density functional theory rests on two fundamental theorems proved by Kohn and Hohenberg and the derivation of a set of equations by Kohn and Sham in the mid-1960s [65, 66].

The first theorem proved by Hohenberg and Kohn states: *The ground state energy from Schrödinger's equation is a unique functional of the electron density* [65]. This implies that the ground state energy derived from the electron density is sufficient for determining all the properties of the system.

The second theorem defines an important property of electron density functionals: The electron density that minimizes the energy of the overal functional is the true electron density corresponding to the full solution of the Schrödinger equation. In other words, regarding the relationship between the ground state energy and the electron density, there exists an energy functional

$$E[n(r)] = F[n(r)] + \int n(r) V_{ext}[n(r)] dr,$$
(3.7)

whose minimum is given by the ground state density  $n_0(\mathbf{r})$  and corresponds to the ground state energy  $E_0$  of the system

$$E_0 = E[n_0(\mathbf{r})] = \min_{n(\mathbf{r})} E[n(\mathbf{r})].$$
(3.8)

It is, in principle, possible to find the ground state energy and electron density by minimizing the energy functional which is a 3-dimensional problem now. However, even if the problem has been simplified, an explicit representation of  $F[n(\mathbf{r})]$ , which contains all effects of electron-electron interaction, is not known.

#### 3.1.4 The Kohn-Sham equations

In 1965 Kohn and Sham [66] presented a scheme for computing the ground state density and the corresponding energy. They replaced the problem of *interacting electrons in an external potential* with the problem of *noninteracting electrons in an effective potential*. Using this approach, they isolated the many-body effects of the real system into an unknown term, which makes the problem much easier to solve.

Kohn and Sham wrote the energy functional in the form

$$E_{KS}[n(\mathbf{r})] = T_s[n(r)] + E_H[n(r)] + E_{xc}[n(r)] + \int n(r)V_{ext}[n(r)]dr$$
(3.9)

where  $T_s[n(r)]$  is the kinetic energy functional of the non-interacting electrons and  $E_H[n(r)]$  is the Hartree energy. <sup>1</sup>. Finally  $E_{xc}[n(r)]$  is the energy due to exchange (Pauli principle) and correlation effects.

<sup>&</sup>lt;sup>1</sup>Hartree energy is the electrostatic energy stored in the charge density  $n(\mathbf{r})$  and given by:  $E_{H}[n(r)] = \frac{1}{2} \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$ 

The exchange correlation functional,  $V_{xc}$  can be defined as a functional derivative of the exchange-correlation energy

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{cx}(\mathbf{r})}{\delta n(\mathbf{r})}.$$
(3.10)

The Kohn-Sham potential now, can be written as

$$V_{KS}(\mathbf{r}) = V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) + V_{ext}(\mathbf{r})$$
(3.11)

which enters the Kohn-Sham equations, a set of Schrödinger equations for non-interacting electrons that are coupled through the electron density

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}).$$
(3.12)

Here the density is  $n(\mathbf{r}) = \sum_{i} f_{i} |\psi_{i}(\mathbf{r})|^{2}$  while  $f_{i}$  is the occupation number of electronic state corresponding to  $\psi_{i}(\mathbf{r})$ .

To solve the Kohn-Sham equations, we need to define the Hartree potential, and to define the Hartree potential we need to know the electron density. However to find the electron density we must know the single-electron wave functions, and to know these wave functions we must solve the Kohn-Sham equations. To break this circle the problem is usually treated in an iterative self-consistent way.

The solution is the ground state electronic density  $n_0(\mathbf{r})$ , from which the ground-state energy is determined as

$$E_0 = \sum_{i} f_i E_i - E_H[n_0(\mathbf{r})] + E_{xc}[n_0(\mathbf{r})] - \int n_0(\mathbf{r}) V_{xc}(\mathbf{r}) d\mathbf{r}.$$
 (3.13)

#### 3.1.5 Exchange-correlation functionals

So far, no approximation has been mentioned and Kohn-Sham theory is, in principle, exact. The exact (not true) form of the exchange-correlation functional is, however, not generally known.

The local density approximation (LDA) uses only the local density to define the approximate exchange-correlation functional, so it is called the local density approximation.

To this end the exchange correlation (XC) energy is given by

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int n(\mathbf{r}) \epsilon_{xc}^{LDA}[n(\mathbf{r})] d\mathbf{r}.$$
 (3.14)

In spite of the simplicity of this approximation, it is remarkably successful for describing a wide range of materials and properties. Another common class of functionals besides LDA are called generalized gradient approximation. As the electron density is in general inhomogeneous, this approach uses information about the local electron density as well as gradient of the electron density. The XC energy in this case is represented by

$$E_{xc}^{GGA}[n(\mathbf{r})] = \int n(\mathbf{r}) \epsilon_{xc}^{GGA}[n(\mathbf{r}), \nabla n(\mathbf{r})] d\mathbf{r}.$$
(3.15)

There is, however, no unique GGA, because there are many ways in which information from the gradient of the electron density can be included. The two most widely used GGA functionals in calculations involving solids are Perdew-Wang functional (PW91) and the Perdew-Bruke functional (PBE).

The GGA functional PBE has been employed in calculations in this thesis due the fact that it predicts the cohesive energy and lattice constant of the system better than LDA.

#### 3.1.6 Plane wave basis sets and pseudopotentials

So far by introducing the Kohn-Sham equations, we have simplified the original electronic problem. To find a solution, however, to the Kohn-Sham equation further considerations are required. A common computational approach is to expand the wave function in a basis set. Different basis sets are possible but for crystalline systems it is natural to use plane wave basis sets and to employ periodic boundary conditions, due to the periodic nature of the crystal.

As a result of Bloch's theorem [67], a complete basis set is given by plane waves with wave vectors  $\mathbf{k}$  within the first Brilluin zone, according to

$$\Psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}).\mathbf{r})}$$
(3.16)

where the sum is over all reciprocal lattice vectors **G** and *n* is the index of the eigensolutions and correspond to different bands. Since there is an infinite set of **G** vectors the sum is truncated in practice by choosing a cut-off energy  $E_{cut}$  which limits the number of **G** vectors according to  $\frac{1}{2}|k+G|^2 < E_{cut}$ . For perfect crystalline systems this approach is ideal since for representing properties of an infinite piece of material, calculations made for primitive unit cells suffice.

While using plane wave basis simplifies the problem, the downside of this approach is that the sum converges very slowly for rapidly varying wave functions close to nuclei. Core electrons do not actively contribute to chemical bonding unlike valence electrons and as a result they can be treated differently.

It is therefore common to only include the valence electrons in DFT calculations. The potential of a nucleus is then replaced with an effective potential referred to as a pseudopotential which includes the combined potential of nucleus and core electrons. The pseudopotential is constructed in a way that it produces a smooth function within the core region, which requires a lower cut off energy, while it produces the all-electron wave function outside the core region.

Employing pseudopotentials allows for density functional theory calculations to be performed with greater computational efficiency as only the valence electrons are treated explicitly.

There is no form for pseudopotentials as long as certain conditions are required. This has allowed for different implementations such as norm-conserving pseudopotentials [68], ultrasoft pseudopotentials [69], and the projected augmented wave method (PAW) [70]. The latter has been employed for all DFT calculations in this work.

The PAW method is based on a transformation between smooth pseudo-wave-functions and the true all-electron Kohn-Sham wave functions. Near the nucleus, valence wavefunctions show rapid oscillations. Many Fourier components or a very fine mesh are, therefore, required for accurately describing these wavefunction. The PAW approach addresses this issue by considering the core states of the atoms to be frozen. Core electrons are pre-calculated in an atomic environment and kept frozen in the remaining calculations. Transforming to the smooth wavefunction makes the calculation of all-electron properties computationally more efficient [71].

#### 3.2 Supercell calculations for point defects

As seen in the previous section, the use of plane wave basis sets imposes periodic boundary conditions (PBC) on the system. As long as the system has translational symmetry, this is unproblematic. Introducing a defect to the system, however, breaks the symmetry and therefore modelling the system with the commonly employed PBC, results in periodic repetition of defects. If the size of the supercell is large enough, this point defects do not interact with each other and there is no problem of using PBC, since the properties of a single point defect are not affected by the presence of its neighbours.

The common approach when modelling non-periodic structures is to separate the non-periodic features by making the supercell large enough such that they do not interact with each other. The effect of increasing the size of the supercell can be checked by studying the convergence of properties with respect to supercell size. When the property no longer changes with increasing size, one therefore obtains the result for real isolated defect and the errors due to interactions are negligible.

In this thesis, in which the focus is on uncharged point defects, the dominant defectdefect interactions are elastic in nature. Elastic interactions arise from the fact that ions surrounding the defect will relax to different stable configurations, when the defect is introduced. To avoid the error caused by elastic interaction, supercells need to be chosen large enough, such that the strain field caused by the defect is contained within the supercell. Hence, the ions at the edges of each supercell do not feel any strain


Figure 3.1: Formation of a vacancy in a bulk material.

caused by the defect.

A linear elasticity model of point defects in isotropic elastic media made by Mishin *et al* [72] has shown that the energy caused by spurious elastic interaction falls off as  $1/R^3$ , where *R* is the distance from the defect. In supercell calculations, one has a choice in boundary conditions, to keep the volume of the supercell constant, or to keep the pressure in the system constant equal to zero. According to the model by Mishin et al., the obtained elastic energy is either underestimated or overestimated based on the choice of relaxation. If during relaxation, the volume is kept constant, the resulting elastic energy is overestimated and for zero-pressure calculations the energy is instead underestimated. Extrapolation of both relaxation modes should converge in the infinite-size limit and the difference is an estimation of error bars.

## 3.3 Point defects thermodynamics

## 3.3.1 Defect formation energies

Defect formation in materials is associated with a change in the Gibbs free energy. Consider a perfect crystal with N atoms in the system. As a simple example, a single vacancy is formed by moving a host atom from its equilibrium site in the bulk, to the surface of the crystal, see Figure 3.1.

The quasi-chemical reaction for the creation of a vacancy can be expressed as

$$\underbrace{\underbrace{NA}}_{\text{bulk}} \to \underbrace{(N-1)A}_{\text{bulk}} + \underbrace{A}_{\text{far away}}.$$
(3.17)

The change in free energy of the total system due to creation of this defect is

$$\Delta G_f = G[(N-1)A] + G[A] - G[NA]$$
  
=  $G_{defect} - G_{ideal}$   
=  $n\Delta G_f - k_B T l n \omega$  (3.18)

where  $\Delta G_f$  is the free energy of formation and  $\omega$  is the number ways in which *n* defects can be distributed over *N* sites. At equilibrium, the free energy of the system must be

minimum

$$\frac{\partial \Delta G_{defect}}{\partial n} = 0 \tag{3.19}$$

and in the dilute limit ( $n \ll N$ )

$$\frac{\partial \Delta G_{defect}}{\partial n} = \Delta G_f - k_B T \ln(\frac{N!}{n! (N-n)!}) = 0$$
(3.20)

from which the defect concentration can be obtained as

$$c = \frac{n}{N} = \exp\left(-\frac{\Delta G_f}{k_B T}\right). \tag{3.21}$$

This relation reflects thermodynamic equilibrium in the dilute limit with negligible defect-defect interactions.

The change in free energy of formation can be expressed in terms of the enthalpy of formation,  $\Delta H$ , and the entropy associated with the formation of the defects,  $\Delta S$ ,

$$\Delta G_f = \Delta E_f + p \Delta V_f - T_f \tag{3.22}$$

 $\Delta E_f$  is the defect formation energy,  $\Delta V_f$  is the formation volume and  $\Delta S_f$  is the formation entropy, which contains local terms associated with changes, (vibrational, electronic, etc.) due to the introduction of the defect. Defect formation energy and formation volume will be described in more details in this section and as the last term is only important in high temperatures, it has been neglected in our calculations.

The formation energy is the difference in the total energy of the structure before and after the defect is created. In this process because some of the atomic bonds are stretched or broken leading to a change in energy.

The formation energy of a defect is calculated as

$$E^{f} = E^{defect} - E^{ideal} - \sum \Delta n_{i} \cdot \mu_{i}$$
(3.23)

where  $E^{defect}$  is the energy of the defective system and  $E^{ideal}$  is the total energy of the perfect reference cell. The variation of the formation energy with the chemical potential of the constituents is given by the last term in equation (3.23) [73].

#### 3.3.2 Formation volume tensors

In order to investigate the elastic distortion caused by the defect, we calculated formation volume tensors for different configurations. They indicate how the shape as well as the size of the supercell change when a defect is formed. Formation volume tensors quantify the effect of stress on diffusion of crystal defects and the trace of volume tensor indicates the defect formation volume. For a simple cubic cell changing isotropically from edge length  $L_0$  to L, the relaxation volume is defined as

$$\nu^{rel} = L_0^3 \ln\left(\frac{L}{L_0}\right)^3 \tag{3.24}$$

$$\simeq L_0^3 \left(\frac{L - L_0}{L_0}\right)^3.$$
 (3.25)

Instead, we have three non-orthogonal vectors, forming a transformation matrix  $L = L_{ij}$ , which are changing in arbitrary directions. We may generalize equation (3.25) as [74],

$$\nu^{rel} = \det(L_0) \ln \left( L_0^{-1} L \right)$$
  
\$\approx \delta \epsilon(L\_0)(L - L\_0) L\_0^{-1}.\$ (3.26)

When the structure is not allowed to fully relax, within the continuum linear elasticity assumptions, the average stress can be used to estimate the relaxation volume tensor from constant volume calculations. When the size and the shape of the supercell are fixed, the elastic dipole causes a strain field  $\epsilon_{ij}$ , and for any boundary conditions, the observed tensorial volume change from the original defect-free state,  $\Delta V_{ij}$ , is

$$\Delta V_{ij} = V_0 \cdot \epsilon_{ij}$$
  
=  $V_0 \cdot C_{ijkl}^{-1} \cdot \sigma_{lk}$  (3.27)

where  $C_{ijkl}^{-1} = S_{ijkl}$  is the compliance tensor and  $V_0$  is the undeformed volume.

#### 3.3.3 Defect kinetics

Finally we determine migration energies to complete the parametrization of a model for kinetic Monte Carlo simulations of screw dislocation migration in tungsten. The migration processes of atoms in solids can be described as a sequence of jumps between neighbouring stable sites. In this description the migrating particle spends the majority of the time residing in a potential well, corresponding to a stable position. Collective vibrations of the system can be interpreted as attempts of the particle to break out of the well. If the temperature of the material is sufficiently high, the particle will occasionally succeed crossing a potential barrier and end up in the well corresponding to a neighboring site, see Figure 3.2.

Transition state theory (TST) can be used to calculate the jump rate [75]. In essence TST treats the jump from one site to the next like a chemical reaction and the jump rate is found by comparing the initial state of the system with the transition state. In the initial state the system is in the configuration corresponding to the particle in the



Reaction coordinate

Figure 3.2: Example of potential energy along a certain migration path. In moving from point A to point E the particles has to overcome transition barriers AB and CD, with corresponding barrier heights  $\Delta E_{AB}^m$  and  $\Delta E_{CD}^m$ .

initial potential well, while the transition state corresponds to a particle being at the top of the barrier. Assuming equilibrium, the jump rate is then given by

$$v^{TST} = \frac{k_B T}{h} \exp\left(-\Delta G_m / k_B T\right)$$
(3.28)

where *h* is Planck's constant and  $\Delta G_m$  is the change in free energy associated with bringing the system from the initial state to the transition state. Within the harmonic approximation the jump rate simplifies to

$$v = v_0 exp(-\Delta E^m/k_{\rm B}T) \tag{3.29}$$

where the activation energy  $\Delta E^m$  is equal to the migration barrier as indicated in Figure 3.2.

The binding energy between solute and point defect is a key factor in understanding defect and solute migration. It represents the dependence of defect formation on the chemical environment.

In the present work, the convention is adopted that binding energies between impurity and interstitial are defined as the difference between the formation energy of interstitial and the sum of the formation energies of self-interstitial and substitutional defects

$$E_X^b = E^f([X - W])_W - E^f([W - W])_W - E^f(X)_W.$$
(3.30)

Note that by this definition, negative (positive) binding energies imply attractive (repulsive) interactions between defects.

## 3.3.4 Nudged elastic band method

The nudged elastic band (NEB) is a method to calculate the migration energy. It is an efficient method for finding the minimum energy path (MEP), and saddle point of the potential energy surface between initial and final stable configurations of a transition such as chemical reactions and diffusion processes in solids [76].

The method works by minimizing the energy of a number of intermediate images along the MEP. The energy of each image is optimized in such way that all the neighbouring images in this string of atoms maintain approximately equal spacing. To achieve this constrained optimization, only the the perpendicular component of the true force and the parallel component of spring forces are included. The saddle point correspond to the highest energy along the path represents the activation energy barrier. This barrier enables estimating transition rates within the harmonic transition state theory [77].

It is important to make sure that the highest saddle point is found, therefore one of the images is made to climb up along the elastic band to converge on the saddle point. This modification is considered in the climbing image NEB (CI-NEB) method [78], which is employed in this thesis.

# 4

# **Results and discussion**

The aim of this work is to find suitable elements for alloying tungsten, with the eventual goal of improving the properties of tungsten for applications in fusion reactors. For this purpose, the solubility of the different alloying elements is one of the conditions to be met, which is relevant with respect to radiation-induced segregation and precipitation. In addition, such materials have to have high radiation tolerance. This can be achieved via defect recombination through defect diffusion.

To this end, in this section results of calculations concerning structural, thermodynamics, elastic and kinetic properties of point defects in tungsten are presented.

## 4.1 Convergence considerations

## 4.1.1 Finite size effects

In order to assess finite size effects intrinsic to the supercell approximation, calculations were performed using both ionic and full relaxation methods for supercell sizes of  $2 \times 2 \times 2$  to  $5 \times 5 \times 5$ , which enables us to obtain quantities in the dilute limit. In constant volume relaxation, only the ionic position of the atoms are allowed to relax. In fully relaxed calculations, which is also referred to as the fully relaxation or constant stress mode as well, the system is allowed to change its cell shape and size, which equilibrate the stress to zero.

Formation energies between constant volume and constant pressure calculations are carefully compared, and it is confirmed that the two methods yield matching results when extrapolated to the dilute limit ( $V \rightarrow \infty$ ), see Figure 4.1.

Results of constant volume calculations appear to be larger than the fully relaxed data. Due to the presence of point defects, the system experiences a nonzero pressure on its borders, which induces a change in the system volume together with atomic



Figure 4.1: Extrapolation of  $\langle 110 \rangle$  mixed interstitials formation energies with respect to number of atoms in the supercell for the elastic error. Constant volume calculations overestimate the elastic energy while zero-pressure calculation underestimate it.

displacements to reach a zero stress state. In Figure 4.1 the extrapolation of formation energies for Ti, V, Zr, Nb, Hf, Ta, W and Re are plotted for  $\langle 110 \rangle$  dumbbell interstitials, with respect to the inverse number of atoms in the supercell. Plotting versus the inverse number of atoms is important as it is a measure of the length of the supercell  $(\frac{1}{N} \sim \frac{1}{V} \sim \frac{1}{L^3})$ , which N is the number of atoms in supercell, V is the volume and L is the length of the supercell). Based on this assessment we estimate the error bar on calculated formation energies due to the supercell approximation to be 0.05 eV. All data reported below have been extrapolated to the dilute limit, unless otherwise noted.

#### 4.1.2 *k*-point sampling and basis set

For a periodic system, integrals in a real space are extended infinitely. In order to perform calculations, one needs to replace these infinite integrals by summations over a finite number of k-points in the first Brillouin zone, which is called a k-point grid. The choice of a sufficiently dense k-point grid is crucial for obtaining accurate results. It necessitates performing convergence tests to obtain converged parameters for calculations.

For the following calculations, ideal supercells were formed with 16, 54, 128 and 250



Figure 4.2: Convergence of vacancy formation energy with supercell size and k-point mesh.



Figure 4.3: Convergence tests for a tungsten primitive cell. Convergence of (a) the total energy and (b) the pressure with respect to the cut off energy. All the data are plotted with respect to the cut off energy of 500 (eV) as the target calculation.

atoms. Occupation of electronic states was performed using the first order Methfessel-Paxton scheme, with a smearing width of 0.2 eV. For the structural optimization, internal coordinates were relaxed until the atomic forces converged to within 10 meV/Å, for both constant volume and constant pressure modes. Using a  $15 \times 15 \times 15 k$ -point mesh for the primitive cell, we obtain a lattice constant of 3.167 Åfor bcc W, which agrees well with experiment as well as previous DFT calculations [67, 79, 80, 81, 82].

The convergence of the results was carefully checked with respect to the *k*-point grid, and based on that, a Monkhorst-Pack *k*-point grid of  $6 \times 6 \times 6$  was used for all supercell sizes, see Figure 4.2. As a result, for a  $5 \times 5 \times 5$  supercell this choice of *k*-point grid results in a  $30 \times 30 \times 30$  mesh. This very fine sampling of the Fermi surface can be due to the presence of Friedel oscillations. In addition, the convergence of the results was checked also for plane wave cut-off energy and supercell pressure, see Figure 4.3 and based on that the plane wave energy cut-off of 230 eV was chosen.

## 4.2 Formation Energies

The formation energies for substitutional solute atoms are compiled in Table 4.1. The results show that Ti, V, Nb, Hf, and Ta substitutionals have negative formation energies. As a result these defects have a tendency to form solid solutions with BCC–W which is likely to prevent precipitation. It makes them potentially good candidates for alloying tungsten in order to improve its mechanical properties for applications in fusion reactors. These trends are in accord with available experimental phase diagrams. In Fig. 4.4 results for substitutional point defects as a function of atomic number are presented.

During the systematic investigation of interstitial configurations associated with solute atoms in BCC tungsten, three distinct configurations were identified corresponding to different local minima on the potential energy surface, see Fig. 4.5. In addition to the well known (111) and (110) dumbbell configurations [41, 45, 83] a third configuration [see Fig. 4.5(a)] was identified, which in the following is referred to as bridge interstitial. This configuration can be understood as a lower symmetry derivative of the (111) dumbbell configuration, in which the solute atom has moved away from the (111) direction along of the three perpendicular  $\langle 2\bar{1}1 \rangle$  directions. This results in a bond angle with the nearest neighbours of approximately 150° compared to 180° in the case of a straight dumbbell interstitial.

The formation energies of extrinsic as well as intrinsic interstitial configurations are compiled in Table 4.1 and shown in Fig. 4.6. The bridge interstitial is found to be the most stable configuration for Ti, V, Nb, Hf, and Re interstitials. The bridge configuration can be up to 0.2 eV in energy lower than any of the dumbbell configurations. In the case of Zr and Ta the  $\langle 111 \rangle$  dumbbell shows the lowest formation energy.

In the case of the W self-interstitial the bridge and  $\langle 111 \rangle$  dumbbell/crowdion configurations are energetically very close. In crowdion configuration, four atoms are shar-



Figure 4.4: Formation energy of substitutional point defects.

ing three lattice sites in a string oriented along a close-packed direction in the lattice. A dumbbell interstitial is obtained if two atoms share the space of one. For smaller supercell sizes the bridge interstitial is slightly lower in energy than the  $\langle 111 \rangle$  dumbbell/crowdion, the energy difference quickly drops with supercell size and in the dilute limit the crowdion is energetically favourable. In absolute numbers our results are very close to previous calculations [83, 84]. The  $\langle 100 \rangle$  dumbbell interstitial for tungsten, exhibits the formation energy of 11.7 eV, which agrees with the previous first principle calculations [83, 84] for possessing the highest formation energy among interstitial configurations. Generally interstitials show very large formation energies because of the large local strain field associated with the core of the defect.

The vacancy shows a fairly low formation energy,  $E^f = 3.1$  eV, which is in a good agreement with previous DFT studies and experimental results[84, 85, 86]. By removing an atom from a perfect lattice, the neighbouring atoms partly tend to re-bond in ways that make the defect less symmetric, particularly in a covalently bonded crystal like tungsten. In the case of the vacancy, this re-bonding leads to a low formation energy which is still remarkably higher than substitutional defects studied here. This suggests that the cost of removing an atom from the system is significantly higher than substituting one of the host atoms by an impurity.

The complete set of data for energy of formation is summarized in Table 4.1. For tungsten interstitial formation energies, two sets of previous DFT calculations together with experimental results are provided for comparison.



Figure 4.5: Representative configurations of (a) bridge, (b)  $\langle 110 \rangle$  dumbbell, and (c)  $\langle 111 \rangle$  dumbbell interstitial defects in tungsten. The  $\langle 111 \rangle$  crowdion configuration closely resembles the  $\langle 111 \rangle$  dumbbell configuration with a slightly larger spacing of the defect atoms along  $\langle 111 \rangle$  axis. The figure shows a slice parallel to a {110} plane of the structure. Small (blue) spheres indicate tungsten atoms wherese large (gray) spheres indicate aloying elements in the case of extrinsic and tungsten atoms in the case of intrinsic defects. Thicker (yellow) cylinders indicate bond lengths shorter than 2.3 Åwharese thinner (gray) cylinders indicate bond lengths shorter than 2.5 Å.



Figure 4.6: Formation energy of bridge,  $\langle 111 \rangle$  and  $\langle 110 \rangle$  interstitials(left axis). The energy difference between  $\langle 111 \rangle$  and  $\langle 110 \rangle$  with bridge interstitial (right axis).

		Formation energies				
Element	Sub	$\langle 111 \rangle$ –int	$\langle 110 \rangle$ -int	bridge-int		
W		9 89	10 1	9 83		
DFT[83]		9.55	9.84	7100		
DFT[84]		9.82	10.10			
Expt.[86]		9.06 ± 0.63				
Ti	-0.68	8.60	8.40	8.37		
V	-0.45	7.80	7.65	7.47		
Zr	0.20	11.4	11.7	11.52		
Nb	-0.16	10.44	10.84	10.36		
Hf	-0.17	10.24	10.9	10.08		
Та	-0.95	10.1	10.5	10.41		
Re	0.16	9.20	9.20	9.17		

Table 4.1: Formation energies of intrinsic and extrinsic point defects in tungsten. Values for energy of formation are reported in units of electron volts (eV).

## 4.3 Binding energies

Interactions of impurities and alloying elements with point defects are of great importance as they can significantly affect the mobility of defects and are crucial in the context of radiation-induced segregation and eventually radiation-induced precipitation [46].

We have therefore calculated binding energies between impurities and interstitials. As shown in Fig. 4.7 and Table 4.2 negative values are obtained for Ti, V and Re interstitial configurations, while for the remaining elements binding energies are positive. Here we adopt the convention that negative values imply a thermodynamic driving force for binding.

A previous study [46] has also reported an attractive interaction between Re and selfinterstitial atoms of  $E^b = -0.8$  eV, the orientation of the mixed intersitial was, however, not specified. In our calculations for Re the binding energies are  $E^b_{\text{bridge}} = -0.82$  eV,  $E^b_{\langle 111 \rangle int} = -0.85$  eV and  $E^b_{\langle 110 \rangle int} = -1.2$  eV. The negative binding energies for Ti, V and Re imply attractive interactions with

The negative binding energies for Ti, V and Re imply attractive interactions with self-interstitial atoms. These elements therefore can trap self-interstitials and radiation induced precipitation is probable. The binding is very strong ( $\sim 1 - 2 \text{ eV}$ ) in all three cases, indicating that thermal detrapping is unlikely. Trapping is furthermore a precursor to segration and thus associated with radiation induced segregation and precipitation. Previous experimental studies have confirmed radiation–induced Re pre-



Figure 4.7: Binding energies of interstitial defects according to Eq. (3.30) (left axis) as well as the differences in binding energy between  $\langle 111 \rangle$  and  $\langle 110 \rangle$  configurations with bridge interstitial (right axis). Units are electron volts.

Solute atom	Binding Energy (eV)		
Ti	-1.00		
V	-2.10		
Zr	+1.30		
Nb	+0.72		
Hf	+0.53		
Та	+1.14		
Re	-1.20		

Table 4.2: Binding energies calculated via Eq. (3.30) for interstitial defects.

cipitation in tungsten [15, 87], yet no equivalent experimental data has been reported for Ti and V.

## 4.4 Formation volumes and volume tensors

A solute atom can affect point defect migration either by a direct "chemical" interaction or via the strain field associated with the defect core. The strain field can modify e.g., the saddle points during point defect migration [88]. Similarly, it can affect the barriers for dislocation motion and thus change the plastic response [89]. Formation volumes quantify the induced strain in terms of linear elasticity theory and provide information concerning the orientation and anisotropy of the strain field.



Figure 4.8: Formation volumes of intrinsic and extrinsic defects in tungsten (left axis). For comparison the atomic radii are shown on the right axis.



Figure 4.9: Anisotropy of (111) dumbbell, (110) dumbbell and bridge interstitials with respect to atomic radius.

	Formation volumes						
Element	$v^f_{Sub}$	$v^f_{\langle 111 \rangle}$	$A_{\langle 111 \rangle}$	$v^{f}_{\langle 110 \rangle}$	$A_{\langle 110 \rangle}$	$v^f_{\mathrm{bridge}}$	$A_{\mathrm{bridge}}$
W	-	1.63	9.05	1.66	6.16	1.64	12.10
Ti	0.01	1.38	8.99	1.30	8.34	1.33	9.45
V	-0.18	1.21	16.37	1.19	14.93	1.20	24.37
Zr	0.28	1.85	5.18	1.83	3.35	1.85	5.62
Nb	0.12	1.73	7.42	1.74	4.44	1.73	7.49
Hf	0.25	1.86	8.25	1.64	4.96	1.85	7.04
Ta	0.06	1.70	7.58	1.67	5.48	1.69	8.03
Re	-0.02	1.56	15.25	1.63	8.72	1.60	18.68

Table 4.3: Formation volumes of intrinsic and extrinsic point defects in tungsten. Values for volume of formation are reported in units of atomic volume( $\Omega_0$ ).

From calculations, in which both ionic positions and cell shapes were allowed to fully relax, the change in cell shape due to defect formation  $L - L_0$ , can be obtained. Using that, one readily obtains the formation volume tensor  $v^f$ , using Eq. (3.26). All solute atoms are associated with a symmetric lattice relaxation whence the formation volume tensor can be written as  $v^f = v^f I$ , where  $v^f = \text{tr} v^f$  is the formation volume.

The complete set of data for volume of formation is summarized in Table 4.3. In addition we have plotted the formation volumes as a function of ions radius in Figure 4.8. Results show that the formation volumes are closely correlated with the atomic radius.

For vacancy and substitutional defects, the volume tensor is isotropic due to the fact that the site symmetry is not disturbed. In the case of the vacancy, it is remarkable that the formation volume is close to zero, which can be attributed to partially covalent bonding. In all supercell sizes the vacancy formation volume is smaller than the atomic volume with a negative value which implys the supercell compression.

For interstitials the formation volume tensor reflects the orientation of the defect. In this case, the volume tensor has off-diagonal components. Interstitials thus possess an anisotropic strain field that correlates with the directional nature of these defects.

Figure 4.10 shows the geometries of defects in relation to a cubic unit cell of tungsten together with volume ellipsoids of the ideal structure and two interstitial defects, including a  $\langle 111 \rangle$  dumbbell interstitial and a  $\langle 110 \rangle$  dumbbell interstitial. The strongly elongated shape of the ellipsoids indicates a large degree of anisotropy. The latter can be measured by the ratio *A* of the largest and smallest eigenvalues of the formation volume tensor, see Table 4.3. Large values of *A* are obtained with typical values in the range from 6–10. For V and Re the anisotropy is even larger with *A* values up to 24. Anisotropy of the elements are plotted in Figure 4.9 with respect to atomic radius.



Figure 4.10: Geometries of defects in relation to a cubic unit cell of Tungsten: configurations of pure Tungsten supercell with 54 atoms(left), Ti-interstitial in  $\langle 111 \rangle$  direction(center), and Ti-interstitial in  $\langle 110 \rangle$  direction(right). Atomic volume of ideal system (left), volume ellipsoid of Ti-interstitial placed in  $\langle 111 \rangle$  direction (center) and volume ellipsoid of Ti-interstitial in  $\langle 110 \rangle$  direction (right). Local coordinates are indicated in RGB.

## 4.5 Migration energies

Diffusion of vacancy and interstitials in tungsten-based alloys are studied by means of climbing image nudged elastic band (CI-NEB) method as described in Section 3.3.4. Migration pathways were constructed with three intermediate images for vacancy and self-interstitial as well as Ti, V and Re mixed interstitials. Fully relaxed  $4 \times 4 \times 4$  supercells were employed for calculations.

## 4.5.1 Vacancy

In the mono-vacancy diffusion mechanism, the migration direction of atoms is opposite to the vacancy flow direction. The necessary energy to break bonds between neighbours during the jump from one lattice site to the other, comes from the thermal energy of atomic vibration.

It can be seen that the migration barrier, to the first nearest neighbour along  $\langle 111 \rangle$  direction, is lower with the value of 1.71 eV which is in a good agreement with previous experimental results [90], finite electron-temperature LDA calculations [91], as well as previous ab initio calculations [92]. Migration to the second nearest neighbour site,



Figure 4.11: vacancy migration along crowdion direction in tungsten. From left to right, configurations are corresponding to initial, saddle point and final configurations during migration. The number with apostrophe is showing the saddle point.



Figure 4.12: Vacancy migration path along crowdion direction to its first nearest neighbour in tungsten. The barriers are obtained in constant pressure relaxation mode. Numbers are associated with the configurations in Figure 4.11.

along [100] direction , has the barrier of 5.44 eV.

We also increased the number of images and found that the height of the barrier does not change, however the shape of the path does. A chain with five images with small perturbations from the MEP, appears to be stable and converged, however it takes much longer to converge.

## 4.5.2 Self-interstitial

It is well known that in tungsten, self-interstitials can travel with very high mobility along  $\langle 111 \rangle$  direction. The migration barrier corresponding to this path is very small in the range ( $\leq 0.046$  eV). This value was obtained from experimental results of radiation-induced point-defects in tungsten [93]. High diffusivity of crowdion is due to the fact that their migration involves small displacements of each constituent atom along the the string containing the defect [45].

In addition, as the energy differences between bridge, crowdion and  $\langle 111 \rangle$  dumbbell are on orders of meV from our calculations, it suggests that during migration, transformation between these three states happens frequently due to very small barrier.

Considering the fact that the energy difference between  $\langle 111 \rangle$  and bridge self-interstitial is between 10-20 meV and our calculated  $\langle 111 \rangle$  migration barrier is 27 meV, this could be a possible explanation for deviation from experiment as the measured migration barrier is 45 meV [41].

The rotation path from SIA's  $\langle 111 \rangle$  configuration to  $\langle 110 \rangle$  state, is a relatively low barrier mechanism of migration in W-based alloys. The calculated barriers are 0.36 eV for fully relaxed structure. During this process,  $\langle 111 \rangle$  interstitial first relaxes to bridge interstitial with lower energy and then rotates to  $\langle 110 \rangle$  dumbbell interstitial.

#### 4.5.3 Mixed interstitials

In this section, the result for migration of mixed interstitials (extrinsic defects) in tungsten are reported. Among the elements studied in this thesis, Ti, V and Re have negative binding energies and tend to trap interstitials. Studying the possible migration pathways and migration barriers of these elements gives an understanding of materials behaviour exposed to irradiation and the probability of radiation-induced segregation and possibly precipitation.

Plots for Ti migration pathways with corresponding barriers and configurations are presented in figures 4.13-4.17. The complete set of migration barriers is reported in Table 4.4. For the three elements considered here, the bridge configuration is the most stable state. Thus the bridge interstitial configuration has been chosen as the starting state and non-dissociative and dissociative migration pathways have been considered.

In non-dissociative migration the impurity migrates through the path. In the dissociative mechanism, however, the impurity stays in a substitutional site and the selfinterstitial migrates. Here we have studied three different non-dissociative diffusion pathways, see Figures 4.13-4.15.

In figure 4.13(a), transition of a bridge mixed interstitial along  $\langle 111 \rangle$  direction is shown. The initial state, which is marked with a circled 1, is a bridge interstitial and the saddle point, marked with a circled 1', is very close to a  $\langle 111 \rangle$  dumbbell interstitial configuration. By placing an impurity along the crowdion direction the structure is subjected to a substantial strain field and tends to push the impurity away from the  $\langle 111 \rangle$  direction. As a result the final state, marked with a circled 2, relaxes to the bridge mixed interstitial again. This transition for Ti occurs with a barrier of 0.20 eV.

In figure 4.13(b) the rotation of a bridge mixed interstitial into a  $\langle 110 \rangle$  mixed dumbbell is presented. This rotation is ~15° and has a barrier of 0.04 eV for Ti.

The next non-dissociative migration mechanism is represented in 4.14(a and b). Here  $\langle 110 \rangle$  mixed interstitial migrates along  $\langle 100 \rangle$  via two different mechanisms, which involve both rotation and translation. Barriers for these pathways are reported in Table



Figure 4.13: Non-dissociative migration of mixed interstitials in tungsten. Configurations are corresponding to (a) bridge interstitial migration along  $\langle 111 \rangle$  and (b) bridge interstitial rotation to  $\langle 110 \rangle$  dumbbell. Numbers with apostrophes indicate saddle points.

4.4.

In the dissociative migration mechanism, the interstitial leaves the impurity behind and travels as a tungsten self-interstitial atom. In figure 4.16(a) the  $\langle 110 \rangle$  mixed interstitial travels to the second nearest neighbour, along the  $\langle 100 \rangle$  direction with a barrier of 1.84 eV. The starting configuration is a mixed dumbbell in a pure tungsten lattice, which changes to a self-interstitial atom with an impurity in its neighbourhood at the end of the path.

Figure 4.16(b) represents the continuation of the previous path and shows that the  $\langle 110 \rangle$  self-interstitial now has to overcome a lower barrier of 1.17 eV, as the attractive binding with the impurity decreases with distance.

Comparing the barriers of dissociative and non-dissociative pathways indicate that the probability of a non-dissociative mechanism to happen is higher. As a result alloying with Ti, V and Re is likely to increase the radiation tolerance via defect recombination process.

The strong tendency of impurities to bind with interstitials causes the interstitial to localize and reduces its mobility dramatically. In this context it is important to quantify the range of the SIA–solute interaction as it provides a measure for the effective capture



Figure 4.14: Non-dissociative migration of mixed interstitials in tungsten. Configurations are corresponding to  $\langle 110 \rangle$  dumbbell transition along  $\langle 100 \rangle$  direction via two different mechanisms. Numbers with apostrophes indicate saddle points.



#### Reaction coordinate

Figure 4.15: Non-dissociative migration path of Ti mixed interstitials in tungsten. The barriers are obtained in constant pressure relaxation mode. Numbers are associated with the configurations in Figures 4.13 and 4.14. Numbers with apostrophes indicate saddle points.





Figure 4.16: Dissociative migration of mixed interstitials in tungsten. Configurations are corresponding to (a)  $\langle 110 \rangle$  dumbbell migration along  $\langle 100 \rangle$  direction to the 1<sup>st</sup> nearest neighbour and (b)  $\langle 110 \rangle$  dumbbell migration along  $\langle 100 \rangle$  direction to the 2<sup>nd</sup> nearest neighbour. Numbers with apostrophes indicate saddle points.



Reaction coordinate

Figure 4.17: Dissociative migration path of Ti mixed interstitials in tungsten. The barriers are obtained in constant pressure relaxation mode. Numbers are associated with the configurations in Figure 4.16. Numbers with apostrophes indicate saddle points.

	Migration barrier (eV)		
Migration path	V	Re	Ti
_			
Dissociative path:	-		
bridge to bridge transition	0.004	0.023	0.170
$\langle 110 \rangle$ along $[100](1^{st}n.n)$	1.80	1.63	1.84
$\langle 110 \rangle$ along[100](2 <sup>nd</sup> n.n)	1.10	1.30	1.17
Non-dissociative path:	-		
bridge to bridge transition	0.25	0.14	0.20
bridge to $\langle 110 \rangle$ rotation(~ 15°)	0.024	0.01	0.04
$\langle 110 \rangle$ 120° rotation	0.05	0.08	0.24
$\langle 110 \rangle$ along [100](1 <sup>st</sup> n.n)	1.04	1.30	1.10
$\langle 110 \rangle$ along [100] (with rotation)	1.42	2.08	1.70

Table 4.4: Migration paths and corresponding migration barriers for Ti, V and Re interstitials in tungsten.



Figure 4.18: Distance dependence of W self-interstitial formation energy with a Ti impurity.

radius associated with a substitutional solute atom.

Figure 4.18 shows the formation energy of solute-interstitial configurations as a function of the distance between interstitial center and solute atom for the case of Ti. The data indicate a short interaction range as binding is practically absent outside a radius of approximately 2.5 Å. Thus, SIAs and substitutional Ti atoms have to be second nearest neighbours of each in order to bind. This knowledge will be used to parametrize for example kinetic Monte Carlo simulations in the future (see Chapter 5).

## **Conclusion and outlook**

The aim of this project is to understand the behaviour of tungsten based alloys under irradiation, which is critical for applications in fusion reactors. For this purpose, I studied formation, interaction and mobility of solute atoms in tungsten at the dilute limit by means of first-principles atomistic methods based on density functional theory. Formation, binding and migration energies as well as formation volume tensors have been determined for vacancy, substitutional, and interstitial defects.

Although interstitials are relatively rare in metals compared with vacancies under normal conditions, they are both plentiful and of prime importance in high-energy radiation environments. Thus, knowledge of the structure and dynamics of interstitials is essential for understanding properties of materials under irradiation.

Calculations have been done in both constant stress and constant volume modes. As predicted by continuum linear elasticity, the calculated quantities, for both modes of relaxation, converge to the same value in the large-size limit.

As an outcome of the calculations, it is concluded that Ti, V, Nb, Hf and Ta substitutional atoms tend to form solid solutions with tungsten, which is important in terms of preventing precipitation.

Another interesting finding was that in addition to the high symmetry dumbbell configurations known so far  $-\langle 111 \rangle$ ,  $\langle 110 \rangle$ ,  $\langle 100 \rangle$  dumbbell interstitials and the crowdion configuration—, another interstitial configuration was found, which is referred to as a bridge interstitial in this thesis. For mixed interstitials, Ti, V, Nb, Hf and Re tend to choose bridge configuration rather than  $\langle 111 \rangle$  or  $\langle 110 \rangle$ . For Zr and Ta, the  $\langle 111 \rangle$ dumbbell state is more stable. The present DFT calculations of point defects formation energies in tungsten, reveal that bridge mixed interstitial configurations are up to 0.2 eV more stable than any of the other configurations.

Results show that for vacancy and interstitial configurations, the formation energy is higher than for substitutional defects, due to the fact that these defects induce larger

#### strain fields.

The binding energies of solute atoms and self-interstitials have been calculated. Results show that Ti, V and Re impurities bind to self-interstitial atoms and thereby trap interstitials. As a result the mobility of interstitials is highly affected by the presence of impurity.

With regard to diffusion mechanisms, the present study shows that migration of interstitials is typically faster than of vacancies due to the fact that bonding of interstitials to the neighbouring atoms is generally weaker and there are more interstitial sites than vacancy sites to jump to. More importantly, calculated migration barriers for Ti, V and Re indicate that non-dissociative migration mechanisms are more probable to occur.

Looking to the future, there are areas of particular interest that I want to pursue in this project. The next logical step following the current study is to investigate the effect of increasing the concentration of mixed interstitials in tungsten. For high defect concentrations, defect-defect interactions become important, which may lead to the creation of separated phases in the material that will influence in particular the mechanical properties. Secondly, the effect of solute atoms on the structure of the screw dislocation core is of great importance with respect to reducing the DBTT and improving the mechanical properties. Finally, quantities determined in this thesis are of interest with respect to the construction of e.g., kinetic Monte Carlo models of defect migration and dislocation mobility as well as as reference data for the construction of empirical potentials [94].

# Acknowledgments

Almost three years ago, when I started my study at Chalmers university, besides the fascinating project I started to work on, what motivated me the most were the many bright people that I got the chance to meet and work with.

I wouldn't be able to come so far without the patient guidance and excellent support from my main supervisor, Paul Erhart. Thank you Paul for giving me the chance to work on this interesting project and all the insightful discussions! From all the red inks in my manuscripts, I learned to pay more attention to the details and I cannot skip mentioning that I enjoyed spending hours and hours on tiny changes in defects migration paths!

I also want to thank my examiner Göran Wahnström for his help and useful comments to my work. Thanks Göran for your pieces of advice and contribution to my research!

And my amazing friends and colleagues! Thanks a lot for always cheering me up and all the fikas, parties and fun!

Last but not least, I want to thank my family; my dear parents Mohammad and Farzaneh and my beloved sister Shaili. Thank you for your truly unconditional love and support! I love you!

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## Paper I

**Defect properties in dilute tungsten alloys from first-principles calculations** Leili Gharaee and Paul Erhart Submitted to Journal of Nuclear Materials