

Ab-initio modelling of Zr and Be alloys
for nuclear applications

A thesis submitted in partial fulfilment for the degree of
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Abstract

Zr and Be alloys are crucially important for a number of applications in extreme environments. Here, density functional theory simulations were carried out to investigate the effect of alloying additions and second phase particles (SPPs) on the physical, mechanical and corrosion properties of the alloys.

First the partitioning of H between Zr SPPs and Zr metal is investigated. $\text{Zr}(\text{Cr,Fe})_2$ is not expected to getter hydrogen from the Zr matrix but it may act as a bridge for locally enhanced H diffusion across the oxide barrier layer. On the other hand, $\text{Zr}_2(\text{Fe,Ni})$ may getter some H from Zr solution if the Fe/Ni ratio is low. Fe always decreases the H affinity of SPPs, whilst Nb increases H affinity of Laves phases and decreases that of β -(Zr,Nb) SPPs.

Following irradiation induced SPP amorphisation, Fe and Cr dissolve and cluster in the Zr matrix. Both substitutional and interstitial accommodation are relevant to Fe and Cr additions and two new low-energy interstitial sites were identified. Local stress states affect the stability of point defects and, in turn, these cause highly anisotropic lattice strains in Zr-Fe and Zr-Cr solid solutions, which deviate from Vegard's law. The solubility of Fe and Cr, which is remarkably limited in pristine Zr, is increased dramatically by pre-existing Zr vacancies. Strong binding was predicted for the clustering of V_{Zr} and Fe_i/Cr_i defects. Furthermore, up to four Fe or three Cr atoms may be accommodated on or around a single V_{Zr} , with lower solution energies and relaxation volumes than dilute solutions.

Al and Fe are the most common impurities found in commercial Be alloys, yet the binary and ternary phases of the Be-Al-Fe system are poorly characterised. First, the Be-Fe phase

diagram is considered and a new structure and composition were identified for the Be-rich ε phase. Phonon density of states calculations indicate that ε -Fe_{2-x}Be_{17+x} phase is only stable up to ~ 1500 K, while δ -FeBe₅ is stable only above ~ 1100 K and ζ -FeBe₂ is stable at all temperatures below melting. Non-stoichiometry, elastic and magnetic properties of the intermetallics were also evaluated. Small additions of Al stabilise the δ -FeBe₅ intermetallic over ε -Fe_{2-x}Be_{17+x} and ζ -FeBe₂. Increasing amounts of Al lead to the formation of a disordered (Al,Fe)Be₂ phase.

Finally, the solubilities of selected extrinsic elements in Be metal and its SPPs were investigated. It was found that Si, Al, Li and H are preferentially dissolved in δ -FeBe₅, ζ -FeBe₂ and (Al,Fe)Be₂ over Be metal. The ability of Fe-bearing SPPs to absorb Al and Si is thought to be beneficial for the mechanical properties of Be alloys. On the other hand, if a sufficient volume fraction of SPPs is present, their high affinity for H may aggravate tritium retention in Be-based plasma facing components used in fusion reactors. SPPs were shown to not interact strongly with He. O, Mg and C preferentially form other SPPs (BeO, MgBe₁₃ and Be₂C respectively).

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List of abbreviations

AFM	Anti-ferromagnetic
APT	Atom probe Tomography
BCC	Body-centered cubic
BWR	Boiling water reactor
CANDU	Canadian deuterium uranium
DFT	Density functional theory
DOS	Density of states
EAM	Embedded atom model
EOS	Equation of state
FCC	Face-centered cubic
FFT	Fast Fourier transform
FM	Ferromagnetic
FP	Full potential
GGA	Generalised gradient approximation
HPUF	Hydrogen pick-up fraction
HCP	Hexagonal close-packed
LAPW	Linearised augmented plane waves
LDA	Linear density approximation
LO	Local orbit
NM	Non-magnetic
PBC	Periodic boundary conditions
PBE	Perdew-Burke-Ernzerhof GGA
PP	Pseudopotential

PAW Projector-augmented waves
PW Planewaves
PWR Pressurised water reactor
QM Quantum mechanics
SPP Second phase particle
SEM Scanning electron microscope
SIA Self interstitial atom
STEM Scanning transmission electron microscope
TEM Transmission electron microscope
US Ultra-soft
XRD X-ray diffraction
ZPE Zero-point energy

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1

Introduction

Beryllium (Be) and zirconium (Zr) are not commonly used materials for engineering applications — in fact, they constitute a minute fraction of the global metal production. Nevertheless, they offer unparalleled properties for specific applications in extreme environments [1, 2]. In particular, Zr is used as nuclear fuel cladding and other structural components in water cooled nuclear reactors; while Be is used as a plasma facing material in fusion tokamaks, as well as a neutron reflector and neutron multiplier in fission and fusion reactor designs respectively. These applications and the remarkable properties of Be and Zr that led to their use, are discussed in this chapter.

In the following sections, first the nuclear power generation is introduced. Then the role of Zr alloys as nuclear fuel cladding is presented in a historical context. Next, the applications of Be and its alloys are presented. Following this, an overview of the hexagonal crystal structure of Be and Zr is provided, then the mechanical and chemical properties that arise from this structure are discussed while highlighting commonalities and differences between Be and Zr. Subsequent chapters build upon this general introduction and background, and a further introductions to the specific topic of the chapters — including critical reviews of the relevant literature — are provided in sections therein.

1.1 Nuclear power: fission and fusion

1.1.1 Nuclear fission

Civil nuclear power is an attractive option for energy generation as it offers an environmentally sustainable and economically viable alternative to fossil fuel power plants and hydroelectric dams — the two main types of base-load energy production. Nuclear power plants are, in many respects, similar to conventional fossil fuel power plants. Electricity is generated by transforming water into hot dry steam, which is then used to power a turbine that is connected to a generator; see Figure 1.1. The main difference is in the process by which the water is heated: instead of burning fossil fuels (which is a chemical reaction and therefore the energy arises from breaking and forming bonds between atoms), the heat is extracted from nuclear reactions, that is from splitting the nuclei of atoms.

Figure 1.2 shows the binding energy of nuclei (normalised by the number of nucleons in

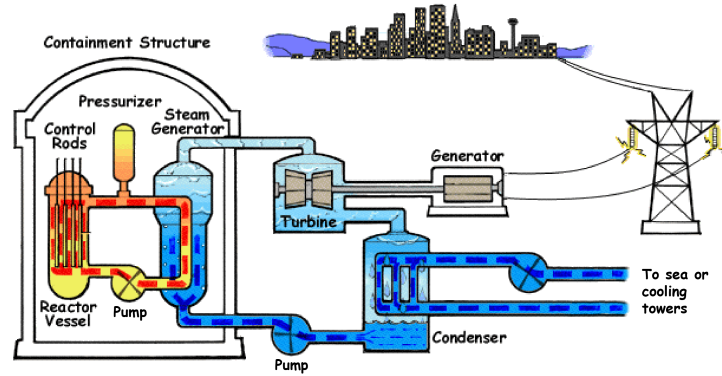
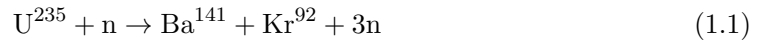


Figure 1.1: Schematic of a pressurised water nuclear power plant, modified from [3]. The Primary circuit identified in red, secondary and tertiary in blue.

the nuclei) as a function of their atomic number. It is clear that splitting a large atom into two smaller atoms would liberate some energy. For instance, a typical fission reaction



is expected to produce $\sim 0.9 \text{ MeV}$ per nucleon, equating to $\sim 180 \text{ MeV}$ per uranium atom. This energy is released mainly by the fission products, as the neutrons typically have energies around 2 MeV [1, 2].

Before the *fast* neutrons may interact with other U^{235} to continue the chain reaction, they need to be slowed down to lower kinetic energies, and become *thermal* neutrons. This is because the neutron cross-section for fission (i.e. the nuclei's probability of interaction with a neutron to produce a fission event) increases with decreasing neutron energy (as seen in Figure 1.3). This is achieved by repetitive elastic collisions of the neutron with light elements, known as the moderator. An effective moderator must also exhibit small cross-section for neutron absorption. Common moderators are water, heavy water, graphite and beryllium. Due to the simple principles of conservation of energy and momentum, lighter elements (i.e. those with a relatively smaller mass difference with respect to the neutron) are more efficient moderators. For instance a hydrogen atom (a proton) moderates neutrons faster than any other element, whilst a deuterium atom requires approximately twice as many collisions for the same level of moderation (and consequently a much larger reactor core). However, hydrogen also has a non-negligible probability of absorbing a neutron, which

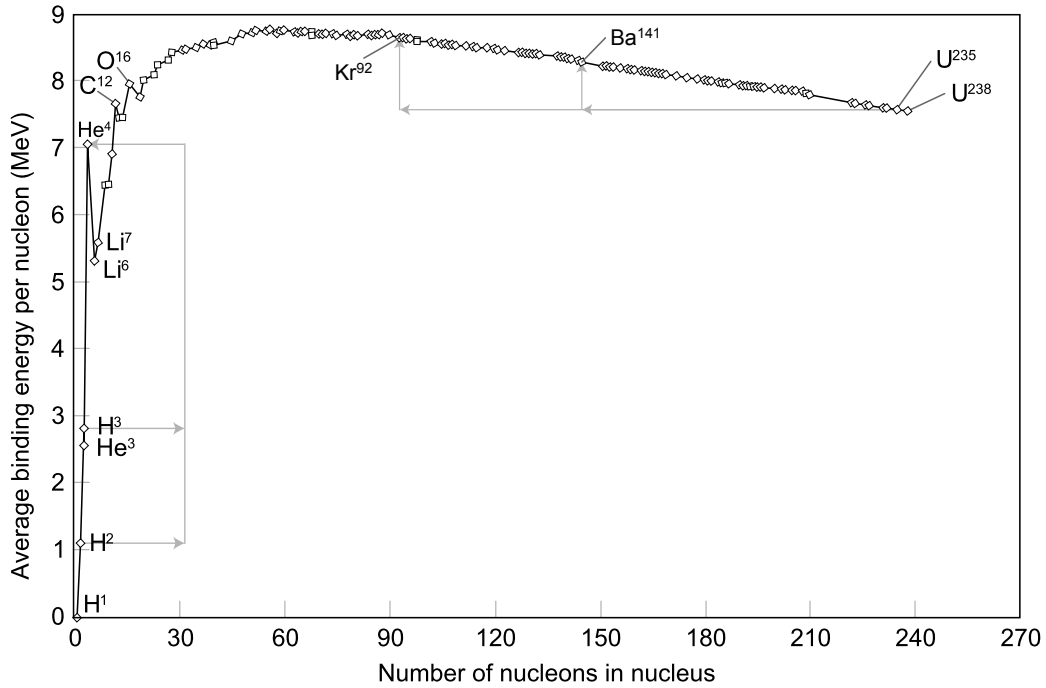


Figure 1.2: Binding energy per nucleon as a function of atomic number of isotopes. Arrows represent reactions 1.1 and 1.2. Adapted from [4].

reduces the average number of neutrons available to maintain the chain reaction. This is commonly solved by enriching the fissile material further (e.g. higher U^{235} to U^{238} ratio), or by reducing the reactor's critical volume (e.g. by using denser fuel and/or reflectors). Alternative reactor designs use graphite or heavy (deuterated) water.

Various designs of nuclear reactors exist, which may be grouped according to their choice of material for the fuel, coolant and moderator (see Table 1.1). The simplest design concept is the boiling water reactor (BWR), which is entirely equivalent to a conventional fossil fuel plant, in that the water is heated up to steam within the reactor itself. However, as depicted in Figure 1.1, which is a schematic of a pressurised water reactor (PWR), the steam that goes through the turbines does not have to be part of the same cooling loop that extracts heat from the reactor, instead a heat exchanger may be adopted. This allows for a greater flexibility in the choice of coolant (and consequently moderator) used in the reactor core. Historically, reactors have been either gas cooled (commonly CO_2 , but air and He cooled reactors have also been built) or water cooled (light water, heavy water, or water/vapour mix). Table 1.1 shows that by far the most popular reactor type in the world

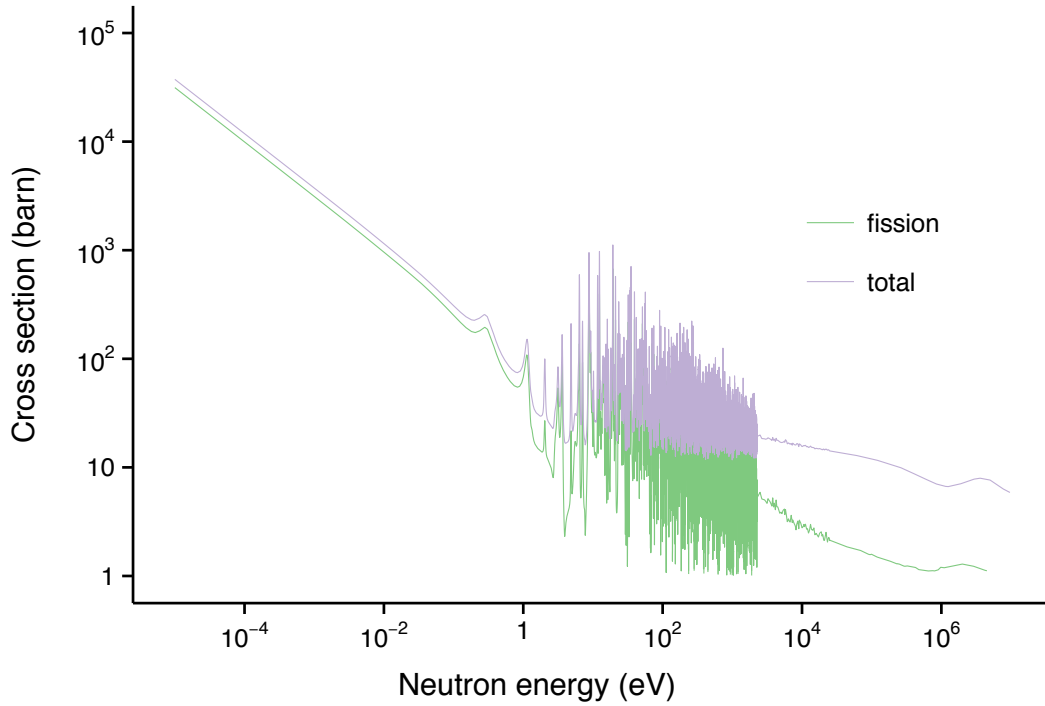


Figure 1.3: Cross-section for fission (green) and for any neutron interaction (purple) of U^{235} atoms. Lower neutron energies yield a overall cross-section as well as a higher fraction of fission events over other types of neutron-nucleus interaction. Data from NNDC [5]

is the PWR. These employ a primary loop of pressurised water, so that it retains its liquid state despite the high temperatures. The nuclear fuel is uranium dioxide (UO_2) in the form of small sintered pellets ~ 10 mm in diameter and ~ 20 mm in length (see Figure 1.4). These are encased in a Zr cladding, which protects them from a strong flow of hot, potentially corrosive water, and provides a physical barrier for diffusion of radionuclides into the coolant. These fuel pins (~ 4 m in length for PWR designs) are bundled together in assemblies for ease of handling.

Other water cooled reactors include the Canadian CANDU and Russian RBMK designs. These do not have a pressure vessel, instead the primary coolant flows through horizontal pressure tubes that cross the reactor. The moderation is then chiefly carried out by large volumes of uncompressed deuterated water (CANDU) or graphite (RBMK). The rationale behind these reactor designs is to minimise or remove the presence of hydrogen in the reactor core to improve the neutron efficiency. In fact, when the CANDU reactor was first

Table 1.1: List of common commercial reactor types.

design	fuel	coolant	moderator	cladding	no. built
PWR	UO ₂	H ₂ O	H ₂ O	Zr alloy	> 400
BWR	UO ₂	H ₂ O _(l+g)	H ₂ O	Zr alloy	> 78
CANDU	UO ₂	H ₂ O/D ₂ O	D ₂ O	Zr alloy	37
RBMK	UO ₂	H ₂ O	graphite	Zr alloy	21
AGR	UO ₂	CO ₂	graphite	stainless steel	14
GCR	U	CO ₂	graphite	Mg alloy	39

Numbers are provided to the best of my knowledge, and are likely to be slight underestimations. Refer to text for acronym meaning.

developed, Canada did not have access to U-enrichment technology, so to achieve a critical water-cooled reactor they were forced to use heavy water.

Originally, the UK and France also did not have access to enriched uranium and they overcame the limitation by developing gas-cooled reactors (GCR). The first commercial GCRs, such as the British Magnox and the French UNGG, used CO₂ cooling and, large metallic fuel rods of natural (unenriched) uranium. At the very beginning these reactors were also used to produce Pu for nuclear weapons, and consequently were not energetically very efficient. When the technology to enrich uranium became available to the UK, the Magnox reactors were superseded by advanced gas-cooled reactors (AGR), which were aimed at a higher operational temperature and consequently a higher thermal efficiency of the reactor (to date the highest thermal efficiency of any nuclear reactor type). The fuel was changed to UO₂ because of its higher melting point, and the cladding became stainless steel due to the temperature limits of operation of Mg alloys.

Other reactor types exist beside the ones listed in Table 1.1, but their use has been limited, so far, to research or prototype reactors. These include:

- organic cooled thermal reactors, which use liquid coolants with higher conductivity and heat capacity than water;
- high temperature gas reactors (HTGR), which use He or super-critical water as the coolant in combination with silicon carbide-cladded particulate fuel to obtain improved thermal efficiencies;
- gas cooled breeder reactors (GCBR), which are based on HTGR but do not moderate

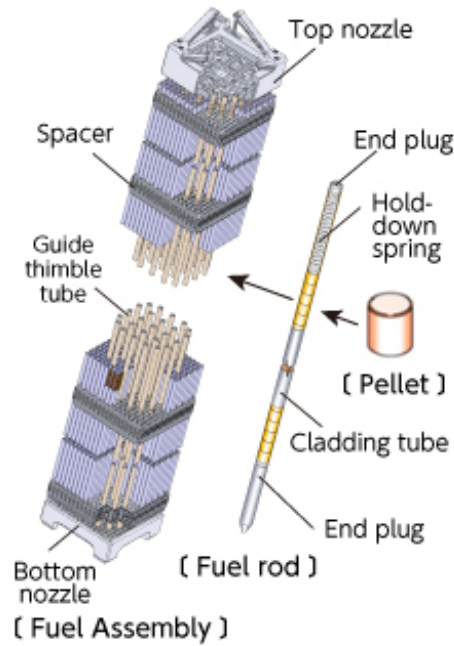


Figure 1.4: Typical PWR fuel assembly, pin and pellet design, reproduced from [6].

the neutrons which allow for breeding of fertile fuel and recycling of the Pu and minor actinides that are formed through neutron absorption by U^{238} ;

- liquid metal fast breeder reactors (LMFBR), which employ liquid sodium as primary and secondary coolant (before a final water cooling loop) to extract higher heat fluxes and reduce the maximum temperature of the core;
- molten salt breeder reactors (MSBR), in which the fuel (fissile and fertile) is dispersed in a liquid fluoride salt (typically $(Th,U)F_4 + BeF_2 + LiF$) and the fuel itself is circulated around a “core” of graphite moderators in a loop or pool type design.

Whilst only a small number of each of these have been built and are often perceived as futuristic and unlikely options for commercial deployment, it is worth noting that the very first nuclear power generation was obtained from a Na-K cooled fast breeder reactor at Argonne National Lab [2]! Development of these reactor designs — and the materials used within them — may once again become increasingly important in the next generation (Gen IV) of nuclear reactors.

Table 1.1 also highlights that the vast majority of nuclear reactors are water cooled and used Zr-based cladding. Zr is also used in many reactor designs for structural components; for instance the pressure tubes of CANDU and RBMK designs and guide plates and spacers of PWR and BWR. The combination of mechanical, corrosion and nuclear properties of Zr make it an ideal material for these applications, and it may not be easily replaced by other materials, as discussed in further detail in section 1.2.1.

1.1.2 Nuclear fusion

From Figure 1.2, it is clear that energy may be gained not only splitting large atoms into smaller ones, but also by fusing two low Z atoms together. In fact a much greater energy gain per nucleon is evolved, but fewer nucleons take part in a single fusion reaction, so that the total energy gain per reaction is lower. A typical fusion reaction:



is expected to yield ~ 17.6 MeV of energy, mostly in the form of kinetic energy of fast neutron (14.1 MeV is a typical neutron energy [2]).

Nuclear fusion is commonly seen as a greener and safer option than fission because all the products of the reaction are stable isotopes, therefore, in principle, no radioactive waste is produced directly by fusion. However, whilst the reactants and products of fusion reactions are not a major radiological hazard, the materials used in the surrounding structure are also subject to high energy radiation, and may transmute into radioactive isotopes. Furthermore, due to the highly energetic reactions involved in fusion, there are significant engineering challenges involved with harvesting fusion energy in a sustainable, safe and economic manner. Many of these challenges are centred around the development of novel materials that may be able to sustain the harsh environment of fusion reactors.

The most common type of fusion reactor design is the Tokamak (see Figure 1.5), a toroidal structure in which the fusion reaction occurs in a plasma that is magnetically confined to the torus. For fusion to be generated at a sustainable rate, the plasma needs to be heated up to extremely high kinetic energies (equivalent to temperatures of $\sim 2 \times 10^{10}$ K,

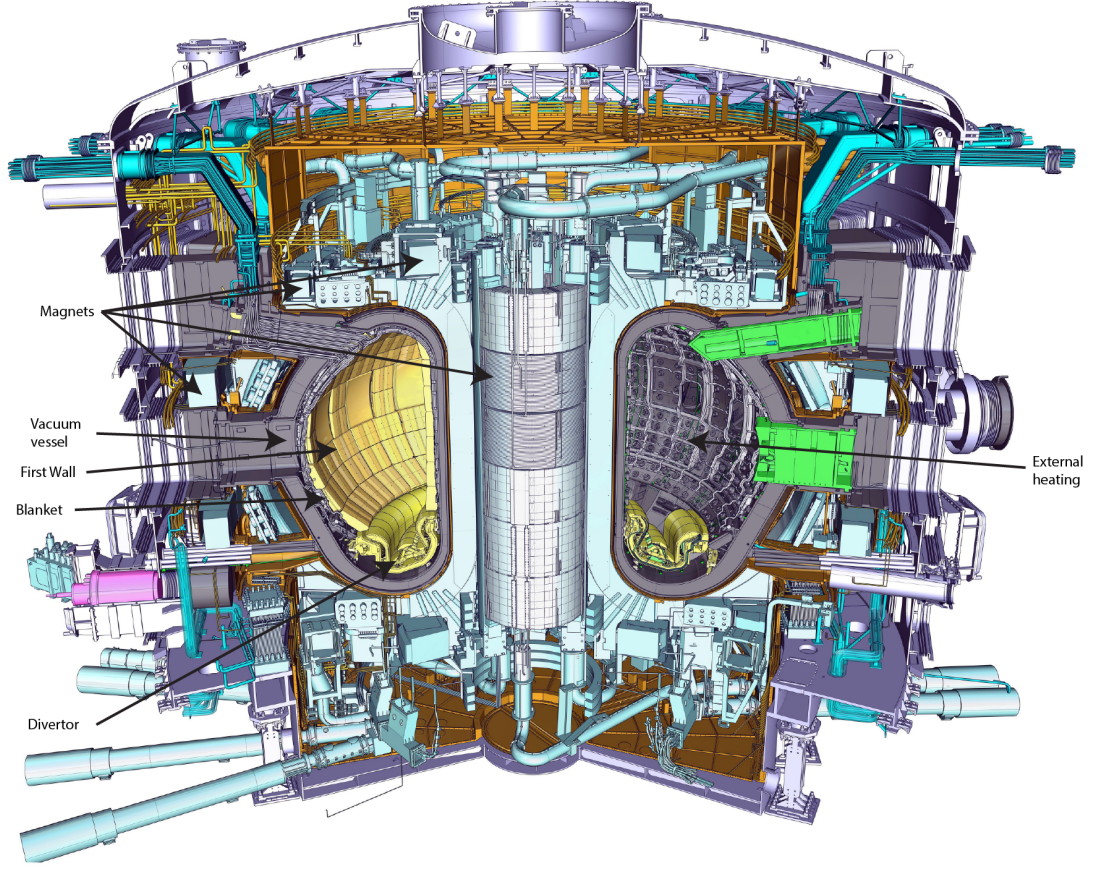


Figure 1.5: Schematic of the ITER fusion tokamak. Modified from [7].

but over a relatively small mass density). Consequently, the plasma facing material (PFM) of the first wall and the divertor are under extreme temperatures and temperature gradients, as well as high radiation fluxes. Candidate PFMs for the first wall are carbon/carbon-fibre composites, beryllium and tungsten [8–11]. For the divertor region, where the requirements are even more stringent, tungsten and molybdenum alloys are the main candidate materials [12]. Behind the first wall resides the breeder blanket and cooling system. The role of the breeder material is to produce tritium and to release it into the plasma to feed the fusion chain reaction. This is achieved by transmutation of lithium following an (n,α) reaction:



If only the neutrons from the fusion reactions are made to react with lithium (after some neutrons escape the vacuum vessel and others are absorbed by the surrounding structure) an insufficient amount of tritium would be produced. The solution is to incorporate a neutron multiplier to the breeder blanket. This is also a Be-based material, as described in section 1.3. Finally, the coolant that flows near or through the breeder blanket extracts the heat produced by the neutron collisions with the breeder material and the coolant itself and transports it to a heat-exchanger where steam is generated.

1.2 Zr in the nuclear industry

1.2.1 A brief history of Zr-based cladding

When the first reactor designs were being developed, the main candidates for cladding materials were beryllium, aluminum, steel, magnesium and zirconium [1, 13]. In general, a suitable material for the cladding and assembly must:

- be corrosion resistant in the core environment;
- withstand the high temperature and sharp temperature gradients of operation;
- maintain structural integrity when handling the fuel and during reactor operation;
- have a small neutron cross-section;
- exhibit acceptable radiation tolerance.

Each candidate material had disadvantages: Be is expensive, toxic and difficult to manufacture; Al has a low melting temperature, limited strength and corrosion resistance; steel has a relatively high neutron capture cross-section; Mg is also difficult to process, highly flammable and performs poorly in a corrosive environment; finally, Zr is relatively expensive and at the time was believed to have an unsuitably high cross-section for neutron absorption. Furthermore, of those five metals, only Al-alloys and steels had been previously manufactured and used in industrial quantities.

Magnesium alloys were later used in the British gas-cooled Magnox reactors, but were deemed unsuitable for water-cooled reactors. Steel was also used with some success in

AGRs, most fast breeder reactors and other experimental or military water-cooled reactors, and is still considered a potential alternative to Zr as an accident tolerant fuel cladding [14–16]. However, its inferior neutron absorption properties require a higher enrichment of the nuclear fuel, thereby increasing the cost of energy production. The main designs for water-cooled reactors included steel cladding until the discovery by Kaufman and Pomerance that naturally occurring zirconium contains $\sim 2\%$ hafnium, an element with an extremely high cross-section for neutron absorption. This suddenly made zirconium metal the most attractive cladding material for water reactors [13, 17]. The extremely small neutron cross-section of pure Zr, meant that a thicker cladding could be made without affecting the neutronics of the core. The issue of the high cost of production was later solved by the development of the Kroll process [18].

The first Zr-base alloy developed was named Zircaloy-1, and contains 2.5 wt % Sn to increase the strength and creep resistance of the metal with marginal consequences to the neutronic properties. It was soon discovered that Zircaloy-1 had unsatisfactory corrosion resistance, and significant effort was made to find new alloy compositions. An ingot of test alloy that had been accidentally contaminated with stainless steel, thereby containing small amounts of Fe, Cr and Ni, exhibited remarkable corrosion properties [13]. The new alloy was named Zircaloy-2, and has been used, with only small compositional variations, in hundreds of water cooled-reactor up to the current time. Later alloy development led to the formulation of Zircaloy-4, in which most of the Ni is replaced with Fe to reduce the H pick-up fraction [13, 19, 20]. This has been in most common use for the last decade.

Concurrently to the development of Zircalloys, Nb-containing Zr alloys were developed and used in other reactor designs [21], such as CANDU, VVER and RBMK. Unlike Sn, which is an α -Zr stabiliser, Nb is a strong β -Zr stabiliser (see section 1.4), and therefore the alloys exhibit a markedly different microstructure. Nb-containing alloys commonly contain some Fe additions, partly because Fe is an impurity in the Zr sponge that is difficult to remove, and partly because it is thought to improve the corrosion properties of the alloy. Recently developed alloys, such as Westinghouse’s ZirloTM, often include both Nb and Sn and nearly always contain some Fe and minor quantities of other transition metals such as Cr and Ni [19, 22].

Due to their limited solubility [23–30], most alloying elements precipitate into second phase particles (SPPs) [31]. In particular, intermetallic $\text{Zr}(\text{Cr,Fe})_2$ are the main SPPs observed in Zircaloy 4 [32, 33], but are also observed in Zircaloy 2 in conjunction with $\text{Zr}_2(\text{Fe,Ni})$ [34]. In Zr-Nb alloys, the prevalent SPPs are β -(Nb,Zr) [35, 36]. In alloys containing Nb and Fe, ternary Fe-Nb-Zr intermetallics are observed, with the same Laves structure as ZrFe_2 but where Nb substitute for either Zr or Fe [35, 37]. Zr alloys are commonly alloyed to very low levels, seldom above 2.5 wt %, consequently SPPs occupy a only minute volume fraction of the alloys, yet they are known to severely affect the mechanical and corrosion properties of the alloys.

1.2.2 Corrosion of Zr alloys

During reactor operation, the Zr cladding is exposed to a hot stream of water solution or water/steam mix. The solution commonly contains boric acid (as a neutron poison), lithium hydroxide (to partially balance the pH of the boric acid), free hydrogen (to getter free oxygen and reduce corrosion of steel and nickel components), organic contaminants and many free radicals formed as a result of radiolysis of water and impurities. Two limiting factors for the increase in fuel lifetime are the oxidation rate of the cladding and its H pick-up. Both are related to the general corrosion reaction with water:



which may be broken down into anode (eq. 1.6) and cathode (eq. 1.7) half-cell reactions, as depicted in Figure 1.6.



Considering first the anodic reaction, an initial nano-crystalline oxide layer of tetragonal ZrO_2 forms at the Zr-water interface. Under equilibrium conditions and at the temperatures of operation, the expected stable phase of ZrO_2 is the monoclinic form, not the observed

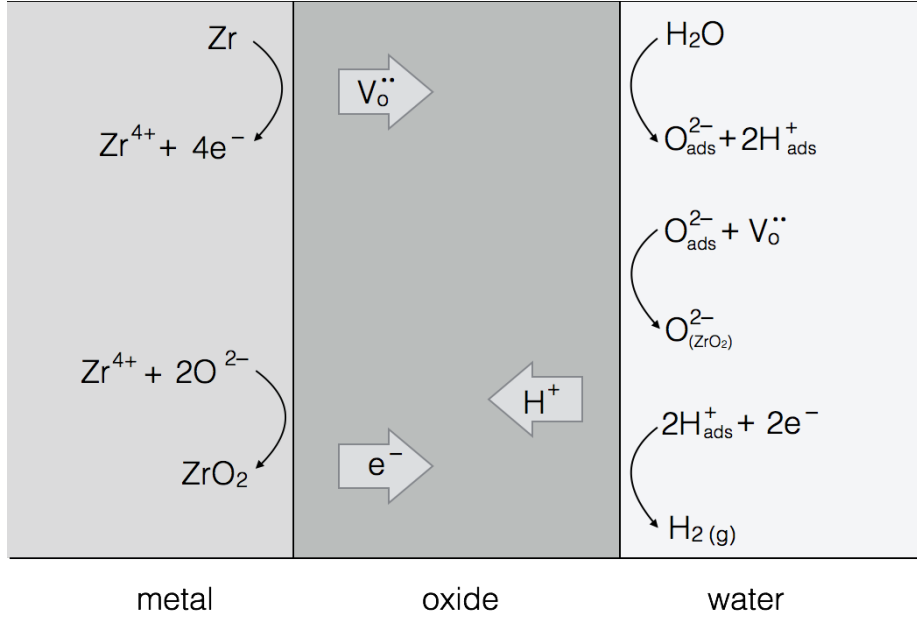


Figure 1.6: Schematic of the Zr oxidation process. Modified from [38].

tetragonal polymorph. However, tetragonal- ZrO_2 is stabilised partly by the large stresses caused by the metal/oxide interface, partly by the nano-size grain microstructure and partly by the presence of aliovalent alloying additions such as Sn [39–43]. As the oxide grows, all but the inner-most layers transform into monoclinic ZrO_2 , which exhibits a porous non-protective morphology, whilst the region in proximity of the metal-oxide interface retains the tetragonal structure [41–44].

Growth of the oxide requires transport of O^{2-} (mediated by $\text{V}_\text{O}^{\bullet\bullet}$) from the oxide/water interface, through the protective oxide layer, to the metal/oxide interface as well as the transport of electrons in the opposite direction. Since the electronic conductivity is lower than the ionic conductivity in ZrO_2 , it has been proposed that the transport of e^- is the rate limiting step [45]. Other models, which are discussed in greater detail in section 3.1, suggest that part of the charge compensation of $\text{V}_\text{O}^{\bullet\bullet}$ is provided by hydrogen (either in the form of H^+ or OH^-), and the combined conductivity of electrons in one direction and protons or hydride ions in the other direction determines the maximum oxidation rate of uniform corrosion. Experimentally it is observed that the protective layer of tetragonal ZrO_2 , typically tens of nm to $1\text{ }\mu\text{m}$ thick, slows down further oxide growth in a parabolic fashion, until the build-up

of internal stress of the growing oxide causes a break-away process, known as transition [46]. This is schematically represented in Figure 1.7. Following transition, the corrosion rate of the now bare metal reverts to the initial fast rate of oxidation until a new protective film is formed and the process repeats. Towards the end of fuel life, the individual transition events become less distinguishable (potentially occurring at different regions of the cladding at different rates) and the overall corrosion rate assumes a more linear behaviour. For this reason it is beneficial to design alloys with a delayed first transition.

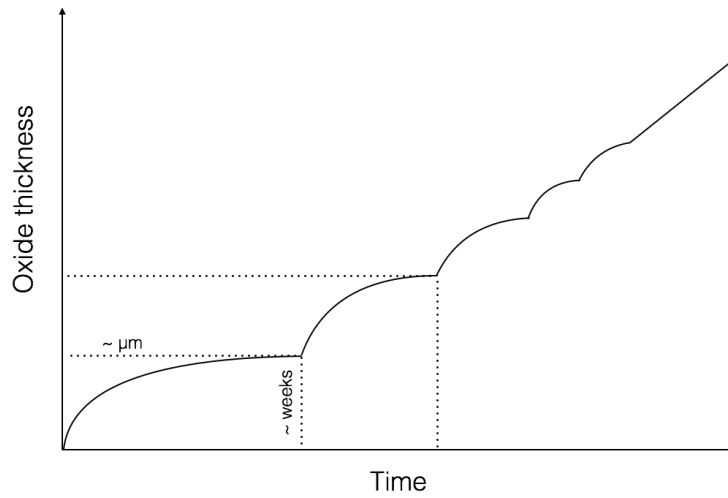


Figure 1.7: Typical corrosion kinetics of Zr cladding in PWR environment. First and second transition are highlighted by dotted lines.

A correlation between the SPP dissolution (caused by irradiation) and a sudden increase in corrosion rate has been observed [47, 48]. To date, this is not fully explained. Understanding the underlying mechanism behind the sudden increase in oxidation may lead to the development of improved cladding with longer operational lifetime (for high burn-up fuel) or larger safety margins. This is investigated at an atomic scale in chapter 4.

Over the past decades, much effort has been expended in improving the oxidation resistance of Zr alloys, by changing the chemical composition of the processing route [43, 49–51]. As a result, the limiting factor for operational longevity of Zr cladding is often no longer the oxidation resistance, but instead is the amount of H that is picked up as a byproduct of oxidation. The presence of H in the cladding is a concern because it may lead to embrittlement, dimensional changes, and delayed hydride cracking [52–54]. The relevant

measure is the H pick-up fraction (HPUF), which is defined as the ratio of H that enters the material over the total H liberated due to the corrosion reaction. Considering the cathodic reaction of eq. 1.7, the resulting H may incur one of two fates: either two H atoms recombine and undergo H_2 gas evolution, in which case it is released in the coolant, or the H adsorbs onto the Zr metal and is retained in the cladding.

A correlation between H pick-up and alloy composition was already established in the early days of alloy development [13, 19, 55]. In fact, it was the main reason behind the formulation of Zircaloy 4, an alloy similar to Zircaloy 2 but with reduced Ni content [13]. Since then, many theories have been proposed to explain the role of intermetallic particles on the corrosion and H pickup, but all are subject to challenge [56–64]. Hatano *et al.* [56] suggested that as the oxide layer thickens, the larger SPPs residing at the oxide-metal interface will oxidise more slowly than the surrounding Zr. These partially metallic particles could then act as a H migration pathway (bridge) through the oxide layer, see Figure 1.8. Various studies [40, 65–68] have shown that SPPs may exhibit either delayed or simultaneous oxidation behaviour compared to Zr, and it is not clear when one or the other occurs. It has been noted by Shaltiel *et al.* [69], who were investigating potential hydrogen storage materials, that intermetallic $Zr(Fe,Cr)_2$ compounds have a tendency to absorb H with no activation process at ambient temperature and pressure. Lelièvre *et al.* [57] conducted experiments with deuterated steam, and found that in the early stages of oxidation, deuterium-rich hydrides were precipitating in the vicinity of SPPs that were still in contact with the metal and therefore still metallic. This correlation vanished in the samples that were oxidised for longer. This led to the conclusion that SPPs may act as bridges through the oxide layer only if still in contact with the metal, and if they are relatively large. With a similar argument, Tägstrom *et al.* [60] found that the number density of the SPPs was more important than the size, as they may act as favourable sites for ingress of hydrogen only when the oxide barrier layer is thin, while size distribution and number density of SPPs appear to have little effect in the later stages of oxidation. Whilst the theories outlined above discuss the importance of SPP size, morphology and distribution, it is important to note that SPPs only comprise a very small volume fraction of commercial Zr alloys (typically $< 2\%$ [22, 70]). Some authors have therefore proposed

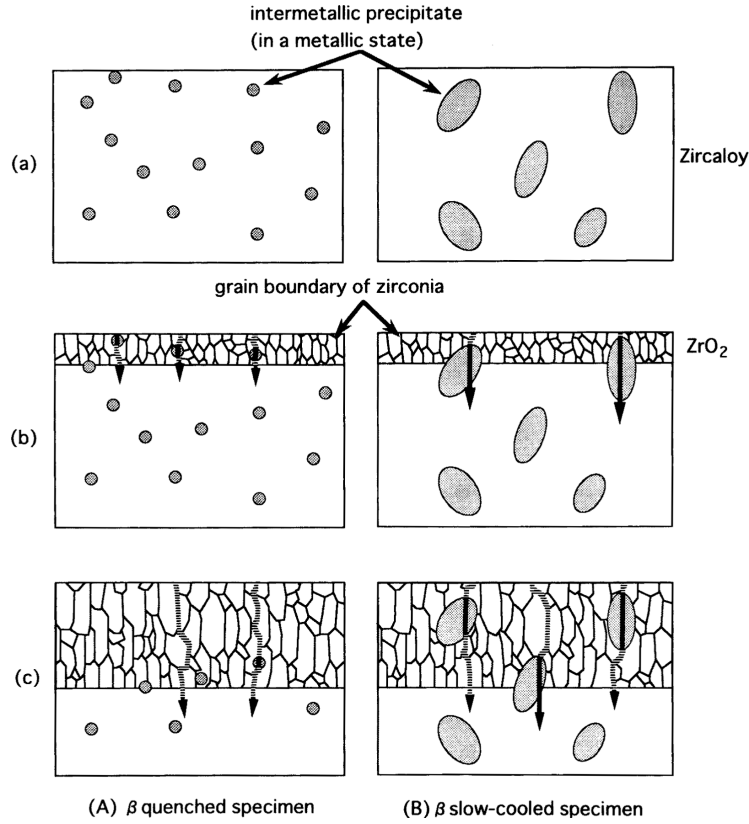


Figure 1.8: Schematic of the H bridge model of Hatano *et al.* [56], from where the figure was reproduced.

that the role of SPPs in H uptake is related to catalytic activity on the Zr surface rather than H diffusion through the oxide layer [57, 71, 72].

More recently — after part of the work that is presented here was published in peer reviewed journals [73, 74] — Yao *et al.* [63] have proposed that H may not diffuse through the oxide in its elemental form, but more likely in the form of hydroxide ions (OH^-). They also note that the microstructure characteristics of the metal/oxide interface (size distribution, volume fraction, composition and morphology of SPPs) affects the cathodic reaction. Indeed, they observed increased HPUF with samples with a higher volume fraction of SPPs or larger SPPs. But this trend was reported to be compositionally dependent. Yao *et al.* [63] also report that the relevant SPPs ($\text{Zr}(\text{Fe},\text{Cr})_2$, $\text{Zr}_2(\text{Fe},\text{Ni})$ and $\text{Zr}(\text{Fe},\text{Nb})_2$) all have stronger reversible ability for hydrogen absorption than α or β Zr. They proceed, thereby, to suggest a mechanism by which more H is absorbed in the SPPs than in the Zr matrix during the initial stages of reactor operations (small oxide thickness, high temperatures,

low neutron irradiation conditions), which is then released into bulk Zr when the conditions change (SPP oxidises or dissolves due to irradiation or the temperature is lowered after an operating cycle). In chapter 3, the interaction of H with intermetallic SPPs is calculated and compared against its behaviour in Zr metal. The results are then discussed in the context of the literature presented here.

Lindgren and Panas [64, 75] have considered the corrosion reaction from an electrochemical point of view and they define the cathodic half-cell reaction (Eqn. 1.7) in terms of hydride ion (H^-) production:



The latter form emphasises that the proton may be retained as a hydroxyl group (OH^-) at hydroxylated grain boundaries of ZrO_2 . In either case, the reaction may lead to the formation of H^- , which then reacts with the Zr metal to form Zr hydrides, or may recombine with a proton, leading to H evolution:



If the electron-proton recombination (eqn. 1.8 and 1.9) occurs far from metallic Zr, then H_2 gas evolution is the most likely outcome. If, on the other hand, the electron-proton recombination occurs near a high work function medium (such as the Zr metal, the sub-oxide ZrO layer), then H may be retained in a metallic form, leading to hydrogen pick-up. Within this interpretation of the corrosion reaction, it is evident that more electronically conductive oxide layer will lead to more electron-proton recombination occurring further away from the metal/oxide interface, thereby reducing HPUF. Related *ab-initio* work was carried out by colleagues to investigate the effect of alloying addition to the electronic conductivity of ZrO_2 [76].

1.3 Beryllium in the nuclear industry

Beryllium is element number 4 and as a consequence it is outstandingly light. Because of its HCP structure, it is also stiffer than most metals, and more importantly it exhibits exceptional strength-to-weight ratio. For this reason it has been used (sometimes alloyed with aluminium) in structural and engine components of cutting edge motor vehicle and aircrafts, where weight saving is crucial. Furthermore, it exhibits a relatively constant coefficient of thermal expansion at low temperatures [77] and favourable interaction properties with many types of irradiation. These properties, combined with its high stiffness and low density, make Be the ideal material for optical and structural components of satellites [78]. Another consequence of its low atomic number is that Be is relatively transparent to x-rays and γ -rays, thereby facilitating use as a radiation window material for x-ray diffraction.

Beryllium also exhibits remarkable nuclear properties. Figure 1.9 shows that Elastic scattering dominates over all other interaction types for all neutron energies. This makes Be

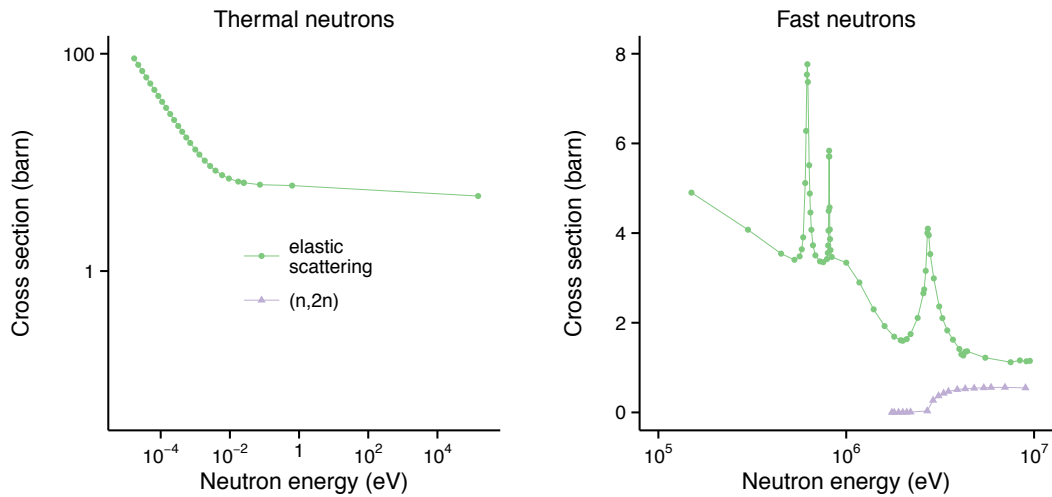


Figure 1.9: Neutron cross-section of Be for the main interaction types: elastic scattering (green circles) and neutron multiplication ($n, 2n$) (purple triangles). Cross-sections of thermal neutrons are represented on a log scale, whilst cross-sections of fast neutrons on a linear scale. The common point at 2×10^5 eV is made to match on the two scales. Data from NNDC [5].

an excellent reflector and/or moderator. In fact, Be reflectors are used in nuclear submarines to reduce the critical size of the reactor. At neutron energies above 2.7 MeV, the ($n, 2n$)

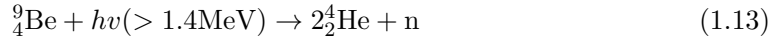
reaction is also observed, with a rate of approximately one in three interactions. The $(n, 2n)$ reaction proceeds with the absorption of a neutron and the decay of the nucleus into two α particles and two more neutrons:



Consequently, Be may be used as a neutron multiplier. This is a crucial process in tokamak reactor designs to sustain the fusion chain reaction. Finally, Be may also produce neutrons as a consequence of α irradiation:



and photon irradiation:



Be may therefore be used as a neutron source when combined with an α -emitter such as natural Ra or Po, or a suitable γ -emitter such as Co-60.

Because of its exceptional neutron properties and its transparency to x-rays, Be is used as a plasma facing material in current fusion reactors. Here, it is subject to extreme temperatures and irradiation from high energy neutrons (14.1 MeV), protons and α particles. Other requirements of plasma facing material are a low sputtering yield, high melting temperature, tolerance to radiation damage and low tritium retention [79]. Unfortunately, Be has a relatively high erosion rate due to sputtering and lower melting temperature than other candidate materials (e.g. carbon — as graphite or carbon fibre composites — and tungsten) [8–11]. Be is also hard to manufacture due to its inherent brittleness [79–81]. Despite these drawbacks, which may limit its use in future commercial fusion reactors, it will be used in the ITER tokamak design [82].

The other crucial role that Be will play in fusion energy production is as a neutron multiplier in the breeder blanket. In the current design of ITER, the breeder blanket is located behind the first wall and the coolant and is still subject to significant amounts of irradiation. Nevertheless, the neutrons from the plasma do not produce a sufficient amount

of tritium in Be-free breeder blankets to sustain the fusion reaction, therefore Be multipliers are employed. Because Li and Be are used exclusively for their neutron interaction properties — and are sacrificial materials — they do not need to be employed in their metallic form. In fact, lithium metatitanate (Li_2TiO_3) and lithium orthosilicate (Li_4SiO_4) have proved to be suitable and stable materials [12, 83]. Similarly, many design proposals employ Be-rich intermetallics such as Be_{12}Ti , Be_{12}V , Be_{12}Mo , Be_{12}W , Be_{22}W and Be_{13}Zr instead of pure Be [83–85]. This is because these beryllides exhibit high melting temperatures and have good oxidation resistance [86].

Alternative designs of fusion reactors employ liquid breeder material, with the obvious advantage that the tritium diffusion in liquid material is higher than in solid materials. In such reactor designs, the breeder material is often a Li-Pb eutectic, where Pb acts as the neutron multiplier [83]. However, liquid metal cooled fusion reactors have obvious drawbacks linked with the flow of a hot, corrosive and explosive liquid. Furthermore, as the fluid is metallic it may severely affect the magnetic confinement field and, vice-versa, the heat transfer properties of the liquid metal are also influenced by the magnetic field [87, 88].

Whilst many options are being considered for alternative fusion reactor designs, Be has a clear role as plasma facing material and neutron multiplier in the fusion tokamaks that are currently being build and designed.

1.4 Crystal structure and metallurgy of Be and Zr

Subsequent chapters of the thesis will deal with atomic scale issues associated with specific materials technological challenges of nuclear energy production. Thus it is appropriate to begin with a review of the atomic structure (i.e. crystallography) of Be and Zr and how this fundamental aspect influences their properties. The more complex structures of specific SPPs that form within the alloys are review in the relevant chapters.

At low temperatures, Be and Zr exhibit an hexagonal closed packed (HCP) crystal structure, the α phase. At high-temperatures, a body centred cubic (BCC) structure, the β phase, is formed. The α – β transition occurs at 1270 °C for Be, only ~ 20 °C below its melting temperature, while it occurs at 863 °C for Zr, more than 1000 °C below its melting

point. Consequently, for most applications, the hexagonal α phase is the predominant one, although careful alloying may lead to the presence of large quantities of β phase, as discussed in section 1.2.1.

Figure 1.10 shows that the HCP structure is based on the A-B-A-B stacking of close-packed planes, where A and B are two of the three equivalent sites potentially occupied by atoms in such planes. Using a hard sphere model, the ideal c/a ratio is calculated to be 1.633, that is the ratio for which the bond distance across planes is that same as the in-plane bond distance. However, all real HCP metals exhibit some deviation from the ideal c/a ratio (see Table 1.2). The layered HCP crystal structure causes the strongly anisotropic properties exhibited by HCP materials, which include thermal and electrical conductance, elastic stiffness and plastic flow [89].

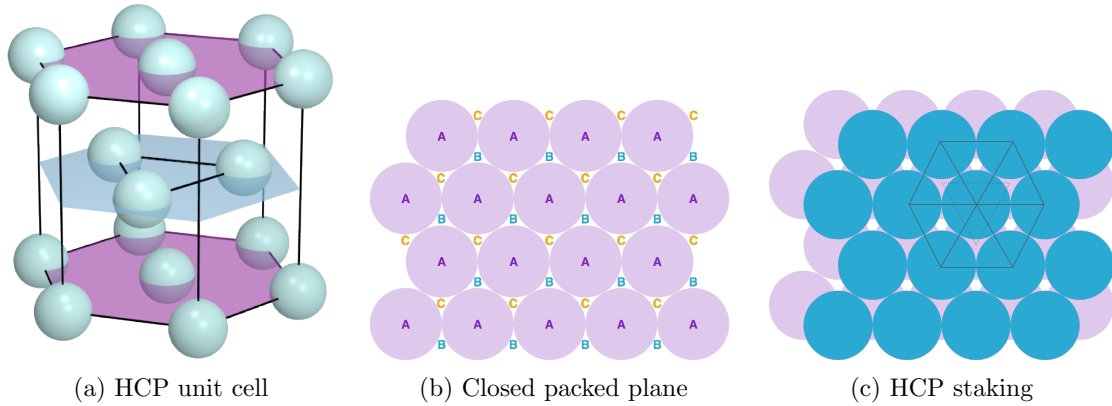


Figure 1.10: (a) Full unit cell of the HCP crystal structure with (0001) basal planes, (b) an A close packed layer with positions where the B or C layers may be staked and (c) the B layer now on top of an A layer.

Table 1.2: c/a ratios of selected HCP metals. The vertical break at $c/a = 1.633$ (ideal packing).

Be	Er	Y	Os	Ru	Ti	Sc	Zr	Mg	Na	Li	Zn	Cd
1.568	1.571	1.572	1.578	1.583	1.587	1.591	1.593	1.624	1.634	1.637	1.857	1.886

HCP metals exhibit three common families of slip systems (for the definition of the planes see Figure 1.11), which share a common slip direction: on basal planes $\{0002\} \langle 11\bar{2}0 \rangle$, on prismatic type-I planes $\{10\bar{1}0\} \langle 11\bar{2}0 \rangle$ and on pyramidal type-I planes $\{10\bar{1}1\} \langle 11\bar{2}0 \rangle$. Basal and prismatic planes provide two independent slip modes each, whilst pyramidal planes provide further four independent slip modes [90].

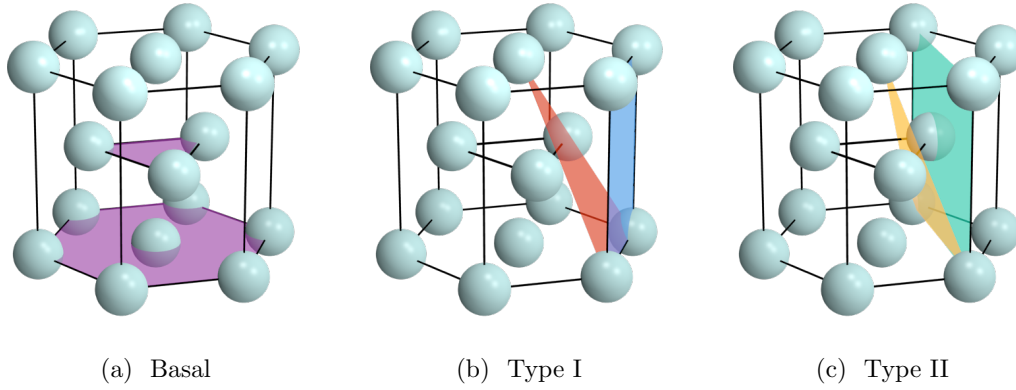


Figure 1.11: Main crystallographic planes of the HCP crystal structure. (a) Purple: basal (0002). (b) Blue: prismatic type I ($11\bar{2}0$). Red: pyramidal type I order I ($11\bar{2}1$). (c) Green: prismatic type II ($10\bar{1}0$). Yellow: pyramidal type II order I ($10\bar{1}1$).

In the case of Zr, dislocations preferentially glide on the prismatic planes but, at temperatures above $\sim 400^\circ\text{C}$, also on the basal planes [91, 92]. For Be, dislocations preferentially glide along basal planes, followed by prismatic slip [93]. Both Be and Zr only exhibit four linearly independent slip systems, which, according to the rule of plasticity of von Mises [94, 95], are insufficient for ductile behaviour. Whilst Be is a notoriously brittle material [80], Zr exhibits high ductility, in contrast to the von Mises criterion for plastic deformation [96]. The discrepancy can be explained by considering twinning deformation.

Twinning often prevails over slip as the predominant deformation mechanism in HCP materials. Twins form by simultaneous displacements of entire planes of atoms by small amounts (fractions of a bond distance) along specific crystallographic directions, as depicted in Figure 1.12. Compared to dislocations, the formation of a single twin may relieve large amounts of lattice strain. This explains the predominance of twins at high deformation rates. However, contrary to a slip system, which may produce dislocations continually in response to an increasing stress, a twin system may be activated only once, thereby providing a limited amount of plastic deformation [97]. Nevertheless, secondary twins have been observed to form within a twinned material, and there is evidence that third and higher order twins also exists in Zr alloys [92, 98]. Furthermore, twins may grow to the size of the entire grain, thereby rotating it with respect to the axis of applied stress and allowing further slip or twin system to activate [92]. These two mechanisms provide extra deformation degrees of

freedom in Zr that are inaccessible with slip alone.

In Zr (and Ti), which are the two most ductile HCP metals, both compressive and tensile twins are observed to form. Compressive twins are $\{11\bar{2}1\} \langle \bar{1}\bar{1}26 \rangle$ and $\{10\bar{1}2\} \langle \bar{1}011 \rangle$; tensile twins are $\{11\bar{2}2\} \langle 11\bar{2}\bar{3} \rangle$ and $\{10\bar{1}1\} \langle 10\bar{1}\bar{2} \rangle$ [92, 99]. In Be, only the common $\{10\bar{1}2\} \langle \bar{1}011 \rangle$ twin is readily observed [99], which is the origin of the brittle nature of Be [100].

Another effect of the HCP structure is that plastic deformation, whether by slip or twinning, is highly anisotropic. This is exploited to great advantages in manufacturing process of Zr alloys (and other HCP metals). During deformation, the grains realign to expose the preferential slip direction (which is the $\langle 11\bar{2}0 \rangle$ in Zr and Be) towards the direction of greatest plastic flow. When cold rolling the material, this results in a preferential alignment of basal planes parallel to the rolling direction (RD) [101]. At higher strain rates, $c + a$ pyramidal slip is also activated [92], so that the the final basal poles of a highly cold and annealed sheet worked material shows a splitting from the normal direction (ND) towards either the transverse direction (TD) or the RD. More precisely, for HCP metals with a smaller $\frac{c}{a}$ ratio than ideal packing (such as Be and Zr), the basal planes (0002) are generally tilted by approximately $\pm 30^\circ$ from ND in the TD, and the $\langle 10\bar{1}0 \rangle$ directions are aligned (post-anneal) with the TD, as can be observed in Figure 1.13.

Zr alloys are often produced as tubes rather than sheets (see section 1.2). When

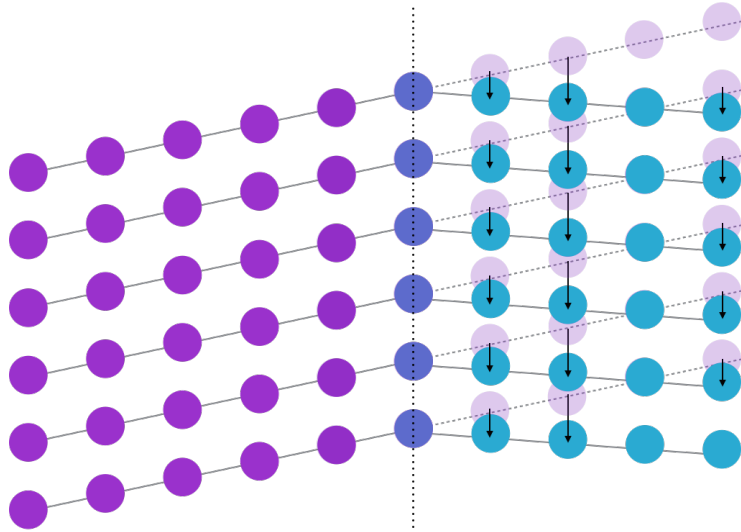


Figure 1.12: Schematic of a twin boundary. Blue and dark purple circles represent twinned and untwinned atoms, light purple sphere represent the original positions of the twinned atoms.

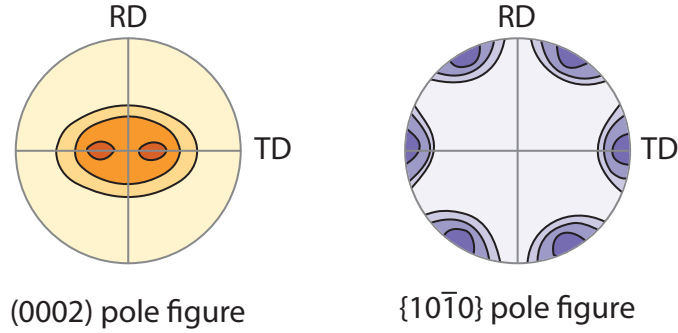


Figure 1.13: Simplified pole figures for sheet rolled and annealed Zr and Be, modified from [80, 101].

extruding tubes, using the process known as pilgering, the plastic flow is restricted to the axial (or rolling) direction only, as the inner and outer diameter are defined by the mandrel and dies, hence deformation in radial and tangential directions is strain controlled. This further reduction in the degrees of freedom of plastic flow implies greater control over the crystallographic alignment of planes. Tailoring of texture is achieved by controlling the ratio of wall thickness reduction to outer radius reduction, as shown in Figure 1.14. Reducing wall thickness more than the outer diameter causes an increased stress (always compressive) in the radial direction, while reducing the outer diameter over the wall thickness increases the stresses in the tangential direction [101].

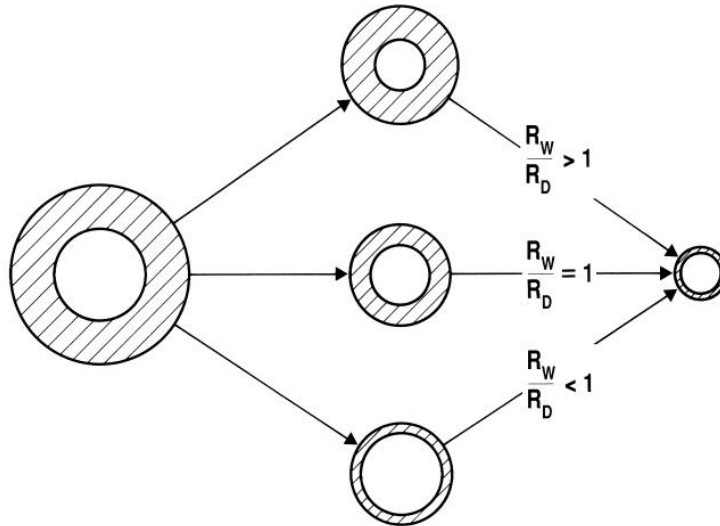


Figure 1.14: Schematic of area and diameter reduction during the pilgering process. R_W and R_D represents wall thickness reduction and outer radius reduction respectively. Reproduced from [101].

With the same argument of crystal rotation as above, the basal plane normals align

parallel to the radial direction if the last stage of deformation is dominated by a reduction in diameter. If, on the other hand, a texture with tangentially aligned basal plane normals is preferred, then the last stage of pilgering should be dominated by a wall thickness reduction. The macroscopic mechanical properties of the material, such as creep, stiffness, strength, and irradiation swelling are affected by texture of the tube, and this may be used to the manufacturer's advantage. For instance: in calandria tubes, which separate the hot coolant from the cool moderator in CANDU reactors, the main concern is to obtain high biaxial strength [102], while in cladding material, although biaxial strength is also a concern, the texture of the tubes is dictated by the necessity to reduce diffusion of iodine (a common and mobile fission product) across the thickness of the tube [103, 104]. Iodine preferentially diffuses along basal planes, therefore Zr cladding is textured with basal plane normals aligned radially.

The HCP structure exhibits a wide variety of interstitial sites of different coordination and size (see Figure 1.15), which are not observed in higher symmetry structures, such as FCC, BCC and simple cubic. The two largest interstitial sites are the octahedral (Figure 1.15a) and the tetrahedral (Figure 1.15b). On the basal face of the octahedron is the trigonal site (red triangles in Figure 1.15c), and on the basal face of the tetrahedron is the hexahedral site (blue triangles in Figure 1.15c). Because of their relationship to the former two sites, these are also known as basal octahedral and basal tetrahedral sites respectively. Another planar defect is found on the remaining faces of the polyhedra (which are shared between octahedra and tetrahedra), this is termed the non-basal trigonal site (blue triangles in Figure 1.15d). Finally, two crowdion or linear interstitial sites exist (also highlighted in Figure 1.15d), one on the basal plane (orange circle), and one across planes (purple circle).

Figure 1.16 shows the spatial relationship between the various interstitial sites, and the possible pathways for interstitial diffusion. Octahedral sites are linked together along the c -axis, through the trigonal (basal octahedral) site. All other faces of the octahedra are shared with tetrahedra, and the common faces host the non-basal trigonal sites. Tetrahedral sites are also linked along the c -axis via the hexahedral (basal tetrahedral) site, however, they are connected only in pairs. Each tetrahedron is also linked to three other tetrahedra by

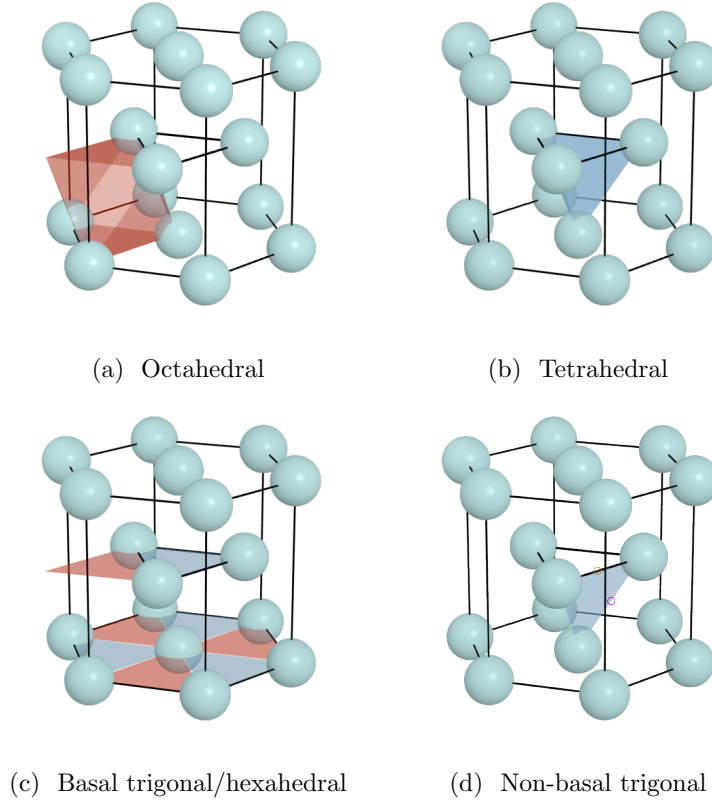


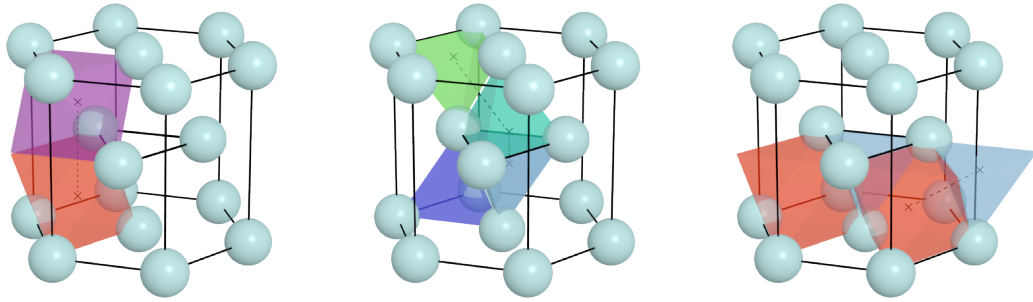
Figure 1.15: Interstitial sites in HCP materials. The sites are defined by the centre of the polyhedra and triangle or by coloured circles.

the non-basal crowdion defect.

Although α -Zr and α -Be exhibit the same crystal structure, Be atoms are much smaller than Zr atoms. In fact, the atomic radius of Be is $r_{\text{Be}} = 1.143\text{\AA}$ [105], which is smaller than most elements of the periodic table. Consequently, only the smaller species (such as H, N, C and O) are likely to occupy interstitial sites in Be. On the other hand, Zr atoms are relatively large compared to most transition elements ($r_{\text{Zr}} = 1.616\text{\AA}$ [106]) and is likely to accommodate many relatively large atomic species in interstitial sites, as will be shown in chapter 4.

1.5 Thesis structure

As outlined above, there is scope for improvements in many aspects of Zr and Be alloys. In particular, the role of alloying additions and SPPs in the H uptake of Zr cladding is



(a) Octahedral to octahedral (b) tetrahedral to tetrahedral (c) octahedral to tetrahedral

Figure 1.16: Diffusion pathways connecting tetrahedral and octahedral interstitial sites.

investigated in chapter 3. SPPs are also known to dissolve with irradiation, which affects the corrosion properties of Zr alloys, but the underlying mechanism for the dissolution is not fully understood. This is investigated at the atomic scale in chapter 4. Regarding Be alloys, the knowledge gap is more fundamental: in chapter 5, the relative stability of SPPs that may form in Be alloys is investigated, and their ability to accommodate other impurities is also studied. Finally, ongoing studies and opportunities for further work are highlighted in chapter 6.

2

Methodology

In this chapter first an historical overview of density functional theory (DFT) is provided. Then methods and parameter selection used in the current work are described. Detailed explanations of DFT, at various levels of complexity, are commonly found in any textbook of quantum chemistry, and is therefore only briefly reviewed here. The main focus, instead, is on the various approximations that are necessarily made to meet the computational requirements, and the practical limitation that those pose to the method. These are discussed in a progressive fashion, from the more fundamental approximations (such as Born-Oppenheimer), to the more practical ones (such as the choice of basis-set and its sensitivity to cut-off energy).

2.1 Density functional theory

In principle, quantum mechanics (QM) provides a framework to simulate solid state matter without the compromise of empirically derived parameters. In reality, the universal portability and exactness of QM simulations are challenged in many ways as will become apparent in this chapter.

All QM computations are based on solving Schrödinger’s equation,

$$E = \langle \Psi | H | \Psi \rangle \quad (2.1)$$

where E is the energy of the system, Ψ is the electron wavefunction, and H is the Hamiltonian operator. H may be expanded in terms of kinetic (T) and potential (U) energy of (and between) electrons (n) and nuclei (N) as follows,

$$H = T_e + T_N + U_{nn} + U_{NN} + U_{nN} \quad (2.2)$$

$$H = - \sum_i \frac{\hbar^2}{2m_i} \nabla_{\mathbf{r}_i}^2 - \sum_i \frac{\hbar^2}{2M_I} \nabla_{\mathbf{R}_I}^2 + \sum_{i,j} \frac{e^2}{2|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I,J} \frac{Z^2}{2|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{I,i} \frac{Z_I e}{|\mathbf{R}_I - \mathbf{r}_i|} \quad (2.3)$$

in which upper-case and lower-case letters refer to properties of nuclei and electron respectively. All other symbols retain their conventional meaning.

Considering the number of terms within H as a function of the number of electrons in the system, it is clear that eqn. 2.1 can be solved only for the simplest systems. For instance H comprises of 10 terms for a single H_2 molecule, 127 for a methane molecule, 861 for a single Zr atom and $\sim 19 \times 10^6$ for a system containing 150 Zr atoms (which is typical of the current work). Consequently, many approximations have been developed to reduce the computational cost of QM simulations. One level of theory in particular — the Kohn-Sham theory or density functional theory (DFT) — has grown in popularity over the past few decades [107]. In the following subsection the main approximations and limitations of this methods are highlighted.

2.1.1 Born-Oppenheimer approximation

The Born-Oppenheimer approximation is widely used at most levels of theory in the field of computational chemistry. It uses the concept that the motions of atomic nuclei and of electrons can be treated separately due to the large difference in mass. Consequently, eqn. 2.1 is solved in two steps: in the first step, known as the “clamped nuclei” approximation, the ions are considered stationary which means that H can be simplified by momentarily ignoring the kinetic energy of ions T_N and the ion-ion interaction potential U_{NN} . The electron-nuclei term U_{nN} is maintained but the nuclei dependence is parameterised. The potential resulting from a clamped U_{nN} is often called the external potential, V_{ext} , as it is externally imposed on the electronic system by the positions of the nuclei.

The simplified Schrödinger’s equation is then solved and fed into the remaining terms to obtain the total energy of the system. By solving the electronic part of Schrödinger’s equation one is defining the shape of the electronic orbitals (including the bonding between atoms) and therefore the total forces acting on the atoms can be evaluated from the electronic distribution. Unless the exact ionic positions are known *a priori*, it is likely that the electronic distribution is exerting some residual forces on the nuclei. Minimising these forces is simply a matter of modifying the atomic positions according to classical laws of inertia [108, 109]. In turn, the updated atomic positions generate a new external potential V_{ext} , which may be fed back into the clamped nuclei approximation. The process may be repeated until the atomic forces — or the difference in total energy between two iterations — are below an arbitrary, externally specified, small threshold.

2.1.2 Hohenberg-Kohn-Sham method

In two publications, Hohenberg, Kohn and Sham [110, 111] outlined the key concepts behind DFT. In the first paper Hohenberg and Kohn [110] proved that the external potential, V_{ext} (and consequently the ground state of a system) is uniquely determined by the electron density of the system, $n(r)$. They further proved that the density functional $F[n(r)]$ follows the variational principle, that is any trial density yields an energy higher than that produced by the ground state density. In other words, they proposed a method analogous to the

Hartree method [112, 113], but that is formulated in terms of the electron density rather than the many-bodied electron wavefunctions. This consideration reduces the complexity of the system from one containing $3N$ variables (the many-body electron wavefunction) to a system with only 3 variables, all pertaining to the electron density, without, in principle, compromising its accuracy.

A similar approach was proposed by Thomas and Fermi [114, 115] but was found inadequate to describe atomic bonding. In light of the Kohn-Sham approach, the Thomas-Fermi method may be considered as a first attempt to define the density functional. Given a functional $F[n(r)]$, solving the set of eigen-equations becomes a trivial task. However, determining the unique functional that describes the energy of the system in terms of its electron density is not an easy task. In fact, to date, there is no exact formulation of $F[n(r)]$, and approximate forms must be used instead.

2.1.3 Exchange-correlation

In the second paper, Kohn and Sham [111] proposed a formulation of the density functional that was consistent with the Hartree and Hartree-Fock methods [112, 113] but also included the correlation term:

$$F[n] = T_s[n] + U_{nn}[n] + E_{xc}[n] \quad (2.4)$$

where $T_s[n]$ is the kinetic energy of *non-interacting* electrons with density $n(r)$, $U_{nn}[n]$ is the Hartree potential (the classical electrostatic potential as presented in eqn. 2.2), and $E_{xc}[n]$ is known as the exchange-correlation term. By definition, $E_{xc}[n]$ contains everything that is not explicitly accounted for in the former two terms, which includes the non-classical electron-electron interactions (i.e. electron exchange and correlation), but also any difference in kinetic energy between interacting electrons and non-interacting electrons. The benefit of the Kohn-Sham formulation, is that two terms may be dealt with simply and with a known physical interpretation. As for E_{xc} , Kohn and Sham proposed to take the exchange-correlation energy of a uniform electron gas $\epsilon_{xc}(n(r))$ with density equal to the local density $n(r)$:

$$E_{xc}[n] = \int d\mathbf{r} \epsilon_{xc}(n(r)) n(r) \quad (2.5)$$

This is known as the local density approximation (LDA). This was shown to work with remarkable accuracy in the limit of slow-varying electron densities [111]. However, real materials often exhibit sharp gradients in the electronic density (e.g. directional or covalent bonds). Metals are amongst the materials with a more uniform (delocalised) electron density, and surprisingly good results have been achieved with the simple LDA.

Various attempts have been made to capture the effect of local gradients in the electronic density, collectively known as the generalised gradient approximation (GGA) [116–120]. In particular the Perdew-Burke-Ernzerhof (PBE) formulation of the GGA [119] preserves the correct features of LDA at slow-varying densities while adding a gradient dependant energy contribution without the addition of empirical parameters. PBE has proved to be enormously successful for a wide range of material types, correcting (although often slightly overcorrecting) the LDA overbinding issue and significantly improving the error associated with the atomisation energy [107, 121–124]; see Table 2.1. Note, however, that both the LDA and the PBE-GGA erroneously find the ω -Zr to be more stable than α -Zr. This is a known limitation of DFT [125–129], sometimes attributed to the pseudopotential approach, discussed in section 2.1.5. The gradient correction of the PBE functional clearly reduces the preference for the ω phase, but not enough. The misrepresentation of the ω -Zr is, however, not strongly relevant to the current work, as the alloys considered in this thesis do not exhibit any ω phase.

Table 2.1: Lattice parameters and atomisation energies (E_{at}) of α -Zr and α -Be. The energy difference (at the ground state) with higher temperature structures is also reported (ΔE). These values do not take into account zero point energy, (see Figure 2.9 and Table 2.3).

		LDA	PBE	exp.	ref.	units
Zr	a^α	3.154	3.234	3.233	[106]	Å
	c^α	5.052	5.163	5.141	[106]	Å
	E_{at}^α	7.477	6.218	6.322*	[130]	eV/atom
	$\Delta E^{\beta-\alpha}$	0.045	0.087	—		eV/atom
	$\Delta E^{\omega-\alpha}$	−0.017	−0.002	—		eV/atom
Be	a^α	2.229	2.273	2.286*	[105]	Å
	c^α	3.522	3.583	3.585*	[105]	Å
	E_{at}^α	4.2251	3.7110	3.358*	[130]	eV/atom
	$\Delta E^{\beta-\alpha}$	0.099	0.102	—		eV/atom

* values from room temperature experiments.

Further attempts to improve the exchange-correlation term were made by introducing

additional exact constraints into $E_{xc}[n]$, according to what is generally known as “Jacob’s ladder” [131–133]. Following LDA and GGA, the third rung of the ladder is known as the meta-GGA [134–140], in which the orbital kinetic energy density is also taken into account. This is only slightly more computationally expensive compared to LDA and GGA, and is able to differentiate between slow-varying densities (where GGA, even LDA, is adequate) and fast varying densities, which are then treated differently. It is also able to remove the spurious self-interaction correlation energy (i.e. it correctly evaluates no correlation in a one-electron system). Some meta-GGA functionals also claim to capture part of the van der Waals interactions [133, 139, 140]. At one rung higher we have hybrid methods [141–145], in which a portion of exact exchange from Hartree-Fock theory (typically 25%) is mixed with the Kohn-Sham exchange and correlation. The fully local nature of the hybrid methods — the second and third rungs are only semi-local — has proved successful in representing small band-gap materials and molecular systems [107, 132, 146]. However, hybrid methods require significantly more computational power than semi-local functionals, thereby restricting the maximum system size that can be simulated, and have been criticised for the presence of at least one (and as many as 40) empirical parameters [133].

In the past three decades, PBE has become the *standard* exchange-correlation functional for DFT simulations of metallic solid state systems (see Figure 2.1 and ref. [107, 147]). The great popularity of the PBE exchange-correlation functional provides a helpful benchmark against which to compare the results of the current work, in addition to a well-established wealth of knowledge regarding the limitations of the current methodology [147]. The ability to estimate (if only qualitatively) the accuracy of the method is a rare advantage in the application of QM computational simulations. This reason — coupled with the moderate computational cost of GGA functionals — is behind the choice of PBE throughout the current work.

2.1.4 A note on spin polarisation

When considering the electron density, a further level of complexity may be added to the system: the spin polarisation. In its simplest form this is included by adding one extra dimension to the three spatial ones. Within this formalism, spin is considered as a scalar

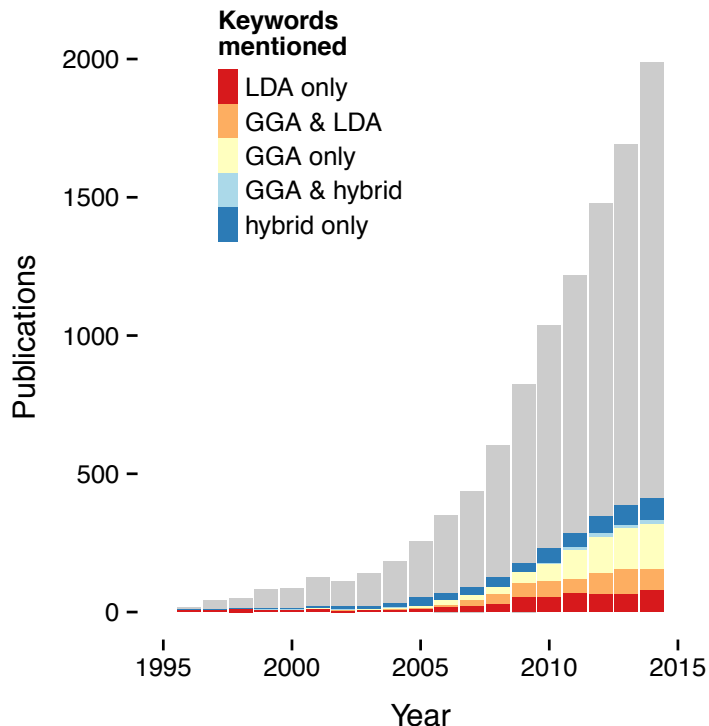


Figure 2.1: In grey is the number of papers found when searching on Scopus the keywords ‘DFT’¹ in the subject area ‘material science’ and with explicit exclusion of the results with subject area ‘chemistry’. In colour are the subset of those papers in which there is at least one mention of ‘LDA’, ‘GGA or PBE’ (for GGA) and ‘B3LYP or HSE’ (for hybrid).

quantity, and provides only one extra degree of freedom (so 4 independent variables in total). When including spin to the level of physics — thereby defining the non-interacting electron-like particles as fermions — the anti-symmetric principle of all fermionic systems should also be correctly described. Preserving anti-symmetry has important implications, the most relevant of which is Pauli’s exclusion principle, but it is also the source of exchange energy. This was first achieved at the Hartree level of physics [112] by using a Slater determinant [148] to define the correct superposition of atomic wavefunctions that form the systems total wavefunction. This method is known as the Hartree-Fock method [113]. A completely analogous method is used at the Kohn-Sham level of physics. In some cases, scalar spin states are insufficient to describe complex electronic interaction; consequently alternative methods have been proposed to include non-colinear magnetic effects and are now routinely

¹The acronym DFT also stands for discrete Fourier transform, therefore the results may include irrelevant publications

implemented in DFT codes, but all are significantly more computationally demanding than simple spin polarised DFT calculations [149–153].

2.1.5 Pseudopotentials

Even within the Kohn-Sham formalism, the computational cost of the simulations is strongly dependant on the number of electrons in the system. Nevertheless, only a fraction of the total electrons contribute to the chemical environment as the electrons that are tightly bound to the nuclei, the *core* electrons, are screened from the surrounding environment by the electrons residing in higher energy orbitals, the *valence* electrons. That is not to say that the core electrons can be disregarded without further consideration; the character of the atom would change substantially if their interactions were removed. Still, it is argued that only the effect that they have upon the valence electrons is relevant. This deliberation leads to the development of the pseudo-potential method [154–158].

In the first instance, the core electrons are *frozen*, that is the dependance of their wavefunction on that of other electrons and nuclei is dropped. Effectively, this means that their presence is felt by the valence electrons as a constant potential, analogous to the external potential caused by the nuclei. Secondly — which is strictly the true pseudopotential approximation — the core electrons are removed all-together, and their static effect on the valence electrons is accounted for by fitting a new, softer *pseudo*-potential to the all-electron potential of the atom (see Figure 2.2). A number of different pseudopotential generation schemes have been developed and the three main types are discussed below.

In all pseudopotential generation schemes, the accurate description of valence electron is guaranteed by ensuring that the pseudopotential overlaps the all-electron potential at distances greater than a radial cutoff r_c from the nucleus. r_c is element dependant, and usually in the order of 0.5 Å–1.2 Å for conventional simulations but may need to be reduced drastically when investigating materials subject to ultra-high pressures[159–161].

- Norm-conserving pseudopotentials [162] impose an additional constraint to the curve fitting process: as suggested by the name, the total charge (norm) of the

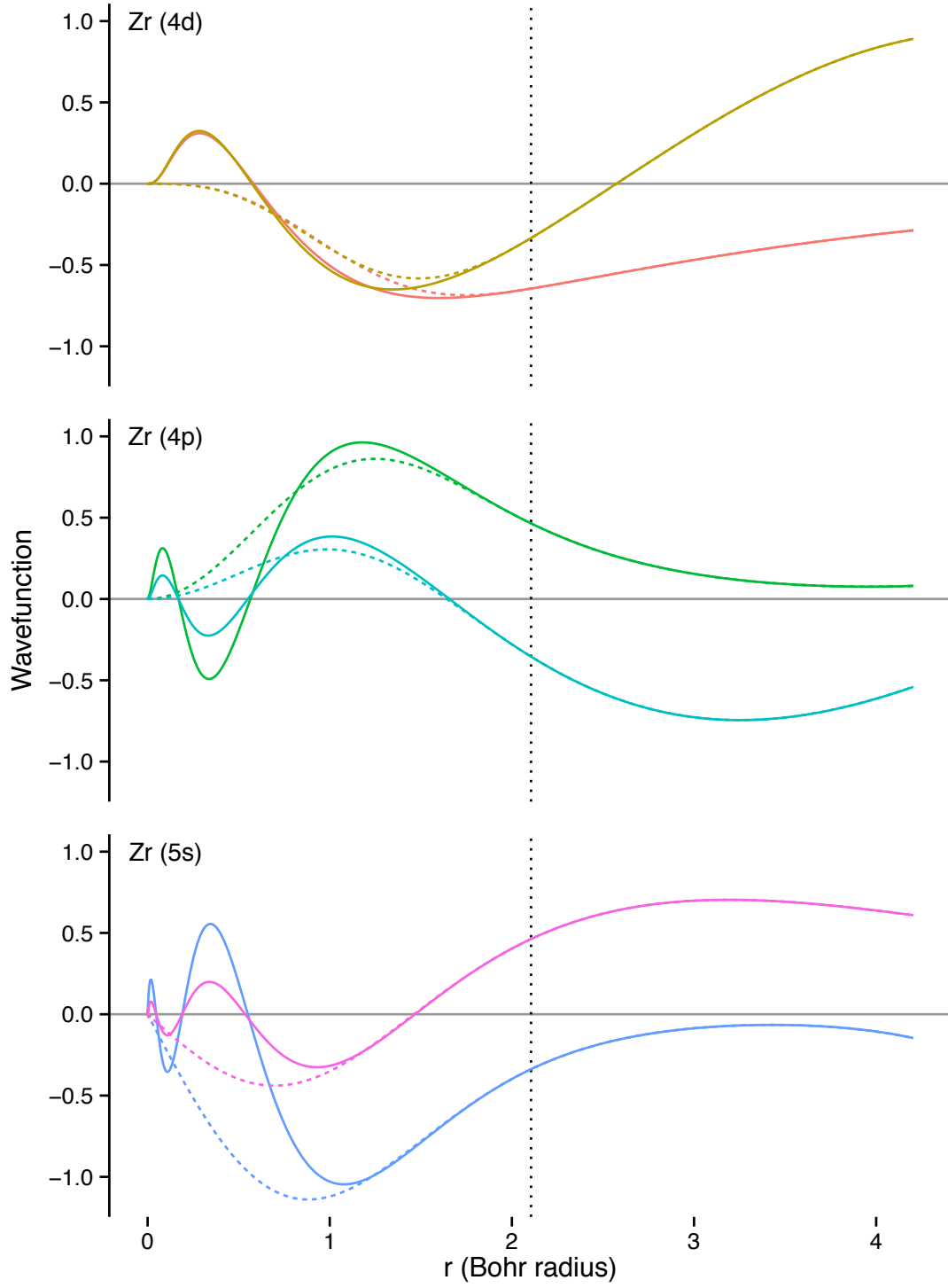


Figure 2.2: All-electron wavefunctions (solid lines) of Zr and the pseudo-wavefunctions (dashed lines) used in the current work (two projectors per angular momentum). The local channel (f -shell) is not shown. The vertical dotted line represents the cutoff radius r_c , beyond which the pseudo-wavefunction is made to match the all-electron wavefunction.

pseudopotential — i.e. the integral of the pseudo-wavefunction inside r_c — must be the same as the total norm of the all-electron potential. Retaining the total charge allows for simpler numerical operations within DFT, especially when involving perturbation theory [163]. However, the additional constraint implies that often harder pseudo-wavefunctions (i.e. ones that requires more terms in order to be described accurately) are produced.

- Ultra-soft (US) pseudopotentials [164] disregard the norm-conservation criteria, and simply fit the softest possible function outside of r_c . This pseudopotential form has proved very successful, partially due to their low computational cost.
- Finally, the projector augmented wave (PAW) method [165–167] combines the pseudopotential approach with the linear augmented-plane-wave (LAPW) method, in an attempt to reintroduce the near-core oscillations of the valence electron wavefunctions. Whilst it is attractive to increase the physical representation in the pseudopotential, and some authors claim that this improves the description of magnetic systems or systems under extreme pressures [166, 168], it is more often observed that the difference between PAW and US pseudopotentials is marginal [169–171].

2.1.6 Periodic boundaries I: k -point sampling

In solid state crystals, the external potential acting on the electron (arising from the atomic positions) must have the same periodicity as the crystal lattice. Therefore

$$V(\mathbf{r} + \mathbf{L}) = V(\mathbf{r}) \quad (2.6)$$

where $\mathbf{L}$ is a multiple of the lattice vectors. Given the Hohenberg and Kohn principle [110], if the potential is periodic, then so is the electron density:

$$\rho(\mathbf{r} + \mathbf{L}) = \rho(\mathbf{r}) \quad (2.7)$$

Since the density is defined as

$$\rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \quad (2.8)$$

then the magnitude of the wavefunction must also retain the lattice periodicity. However, this does not extend to the wavefunction's phase, meaning that there are infinite number of $\psi(\mathbf{r})$, that satisfy the condition of Eqn. 2.7 (see Figure 2.3).

This is expressed by Bloch's theorem, which states that in a periodic system a wavefunction $\psi(\mathbf{r})$ may be expressed as

$$\psi_k(\mathbf{r}) = u(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \quad (2.9)$$

such that

$$\psi(\mathbf{r}) = \int \psi_k(\mathbf{r})d^3\mathbf{k} \quad (2.10)$$

and therefore

$$\rho(\mathbf{r}) = \int |\psi_k(\mathbf{r})|^2 d^3\mathbf{k} \quad (2.11)$$

where $u(\mathbf{r})$ is a function with the same periodicity as the simulation cell (i.e. $u(\mathbf{r} + \mathbf{L}) = u(\mathbf{r})$) and k is vector representing the position in reciprocal space. In other words, $e^{(i\mathbf{k}\cdot\mathbf{r})}$ is an arbitrary phase factor that scales the periodic function $u(\mathbf{r})$ in surrounding unit cells (dotted line in Figure 2.3):

$$\psi_k(\mathbf{r} + \mathbf{L}) = u(\mathbf{r} + \mathbf{L})e^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{L})} \quad (2.12)$$

$$= u(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}e^{i\mathbf{k}\cdot\mathbf{L}} \quad (2.13)$$

$$= \psi_k(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{L}} \quad (2.14)$$

This means that the integral of Eqn. 2.11, needs to be evaluated only within the portion of reciprocal space delimited by the reciprocal unit cell, known as the Brillouin zone. Furthermore, $\psi_k(\mathbf{r})$ varies slowly with k , therefore the integral can be approximated as,

$$\psi(\mathbf{r}) \approx \sum_k \psi_k(\mathbf{r}) \quad (2.15)$$

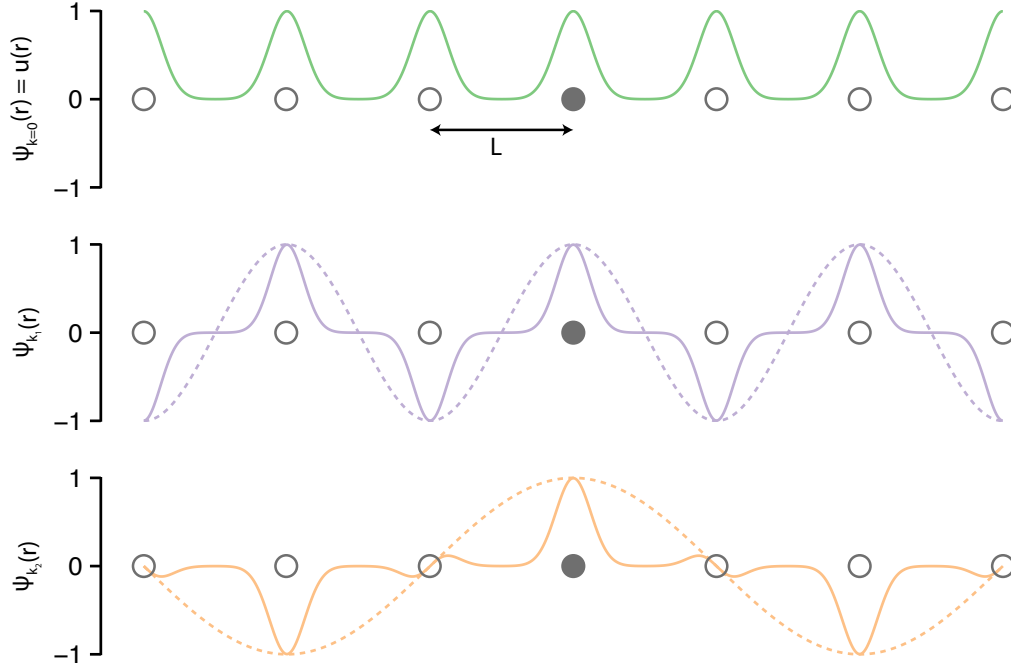


Figure 2.3: Wavefunction solutions (solid lines) that satisfy Bloch's theorem for a model one-dimensional array of atoms (grey circles). Dashed line is the phase factor $e^{ik \cdot L}$.

provided that the weighted k -points used are suitably close together.

It is important to stress that if only one phase factor were considered — for instance that lying on $k = (0, 0, 0)$, known as the Γ point — then only a partial, and therefore inaccurate, description of the system is being described. Take for example silicon (see Figure 2.4); the band structure at the Γ point reveals a band gap of 3.42 eV, but if point X is also considered, then an indirect band gap of width 1.17 eV is found. Even when the weighted average of multiple k -points is taken, particular care should be used to avoid errors associated with the discretisation process. A higher sampling density, of course, yields more accurate results but at a greater computational cost (see Figure 2.5). In particular, when comparing two simulations, the sampling errors may compound if different sets of k -points are employed. Instead, the errors may partially or completely cancel out if the same set of k -points is used.

Since the Brillouin zone is defined by the reciprocal lattice vectors, when larger simulation cells are used, fewer k -points are required to obtain the same (or similar) density. In the current work, every effort was carried out to ensure that a consistent k -point density

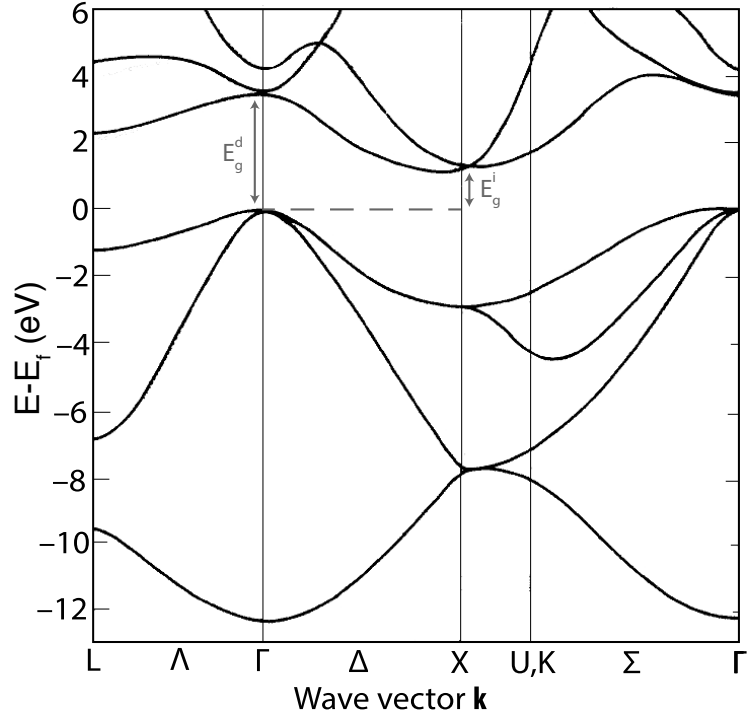


Figure 2.4: Electronic band structure of Si, modified from [172].

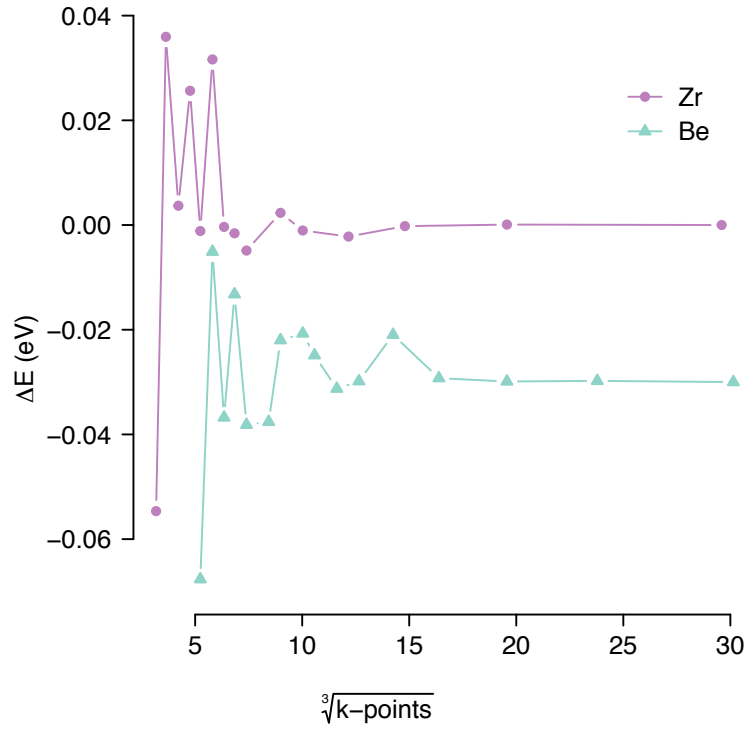


Figure 2.5: Change in total energy of the system as a function of k -point density (calculation parameters provided in section 2.6). The results of the Be system (turquoise) are vertically shifted by -0.3 eV for clarity of viewing.

was used throughout (see section 2.6 for details on the k -point grids used in the current work).

2.1.7 Periodic boundaries II: plane-waves

In principle, any complete basis set may be used to describe the electron density of a system (some DFT codes employ local-orbitals or Gaussian functions [173–176]), but it is expedient to use plane-waves — which are periodic functions — when simulating solid state crystals [177–179]:

$$u_k(\mathbf{r}) = \sum_g c_{g,k} e^{i\mathbf{g}\cdot\mathbf{r}} \quad (2.16)$$

where $c_{g,k}$ are Fourier coefficients and g are wavevectors that satisfy the periodicity (and any additional symmetry operations) of the crystal. The sum should account for all possible plane-waves, $e^{i\mathbf{g}\cdot\mathbf{r}}$, but only a few g vectors have the correct periodicity (i.e. those that are multiples of the reciprocal lattice parameters). In other words, in reciprocal space, the allowed g vectors form a period grid of points with spacing equal to the reciprocal lattice parameters — the reciprocal lattice. In theory, the summation of Eqn. 2.16 is infinite, however, the $c_{g,k}$ coefficients diminish as $|\mathbf{g}|^2$ increases, thereby larger g wavevectors are of less importance. It is conventional to define a cut-off radius in reciprocal space within which all g wavevectors are summed, in terms of the resulting energy,

$$E_{cut} = \frac{\hbar^2}{2m} |\mathbf{g}|^2 \quad (2.17)$$

This can be interpreted as a progressive addition of terms to a Fourier series that describes a wavefunction. Higher order terms contribute by forming progressively smaller ripples in the wavefunction, thereby impacting less and less on the total shape of the wavefunction.

Figure 2.6 shows the convergence of the system’s internal energy (expressed as the $\log_{10}$ of the energy difference with respect to a highly converged value) as a function of E_{cut} . The dashed lines represent the value of E_{cut} used in the relevant chapters of the current work. In order to minimise uncertainty, only simulations with the same E_{cut} are compared. Therefore, for each topic, E_{cut} was chosen as the lowest value that yielded converged results

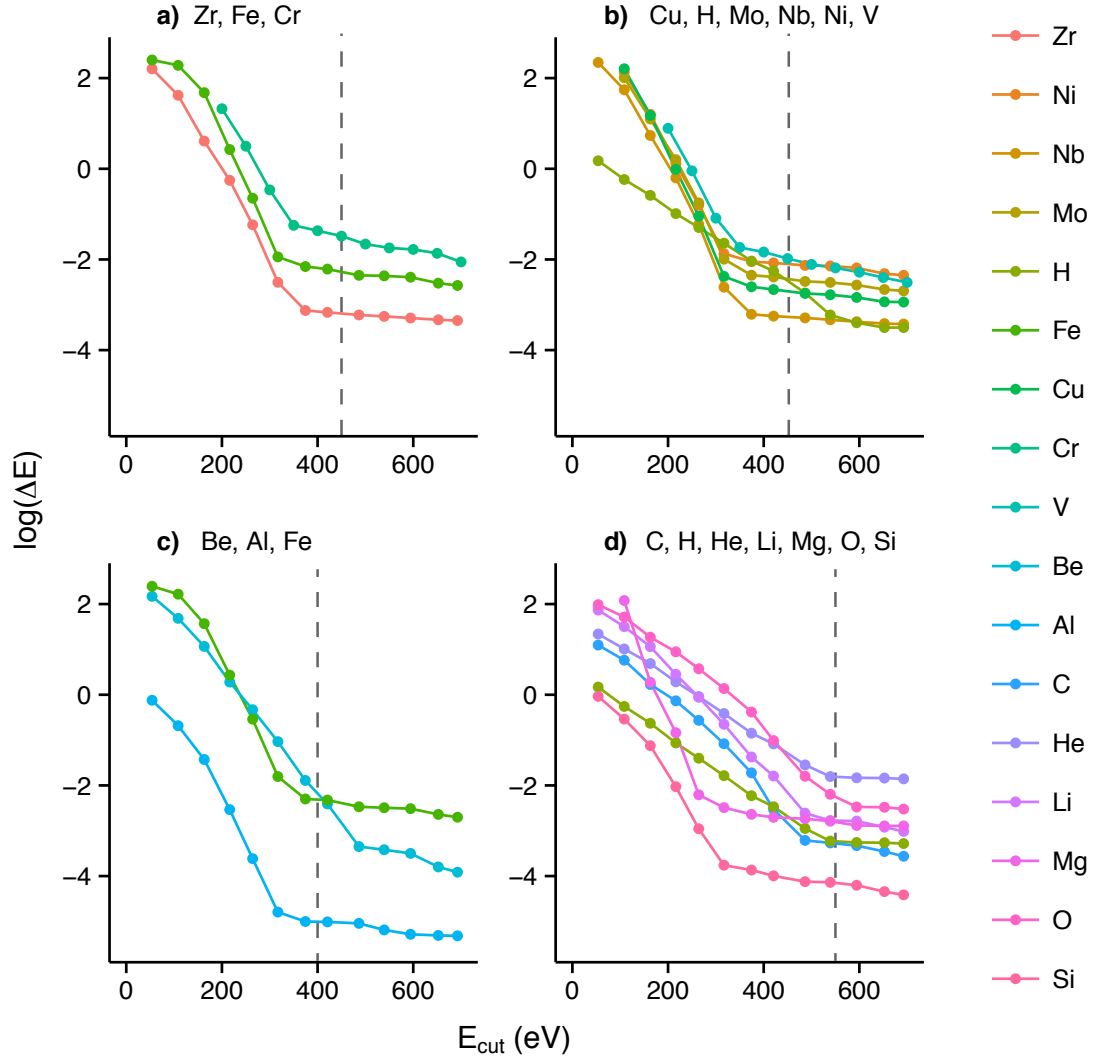


Figure 2.6: Change in systems' total energy ($\log |\Delta E|$) as a function of plane-wave cutoff energy (E_{cut}) calculated for the elements in their standard state. **a)** PP used when investigating Zr-Fe-Cr alloys (chapter 4), **a+b)** PP used when considering the solubility of the intermetallics of Zr (chapter 3), **c)** PP used for the investigation of phase stability in Be alloys (chapter 5, except section 5.7) and **c+d)** PP used to study the accommodation of extrinsic defects in Be intermetallics (section 5.7).

for the hardest pseudo-potential among the ones used in that topic.

2.2 Periodic boundaries III: defects and finite size effects

When describing crystalline materials, it is expedient to use periodic boundary conditions (PBC), which allow the representation of an infinite crystal by computing only its primitive unit cell (or any other cell that obeys the relevant symmetry operations of the crystal). Without the use of PBC, DFT simulations would be limited to describing systems of a few hundred atoms, which are certainly not representative of bulk materials.

The main limitation of PBC are related to the investigation of a non-pristine crystal lattice. For instance, when simulating a point defect in a unit cell of a material with PBC, the defect is replicated *ad infinitum* together with the rest of the unit cell (see Figure 2.7), thereby creating an effective concentration of defects. Furthermore, the defects introduced are arranged in a highly ordered fashion, with the same periodicity as the cell used, which is not representative of a real-life equivalent defect concentration.

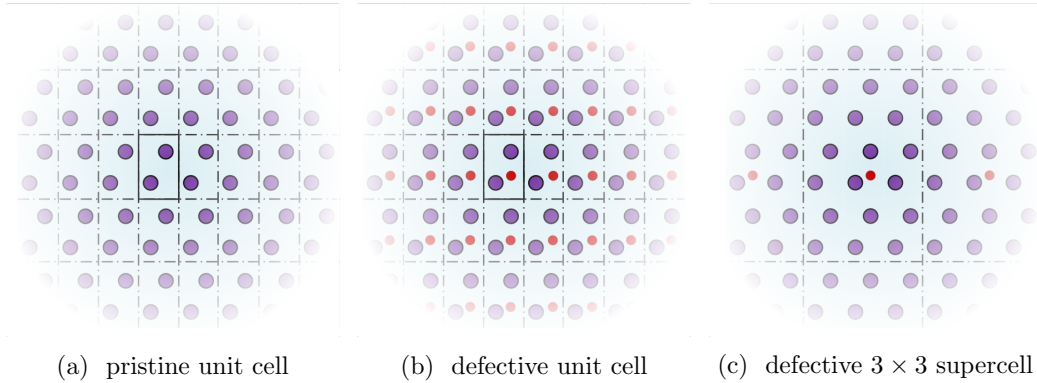


Figure 2.7: (a) The effect of periodic boundaries (dot-dash lines) on a two atom unit cell; (b) the same unit cell with a single defect and (c) a 3×3 supercell with the same defect.

The mainstream solution to this problem is called the supercell approach, in which the replicating unit is a large multiple of the unit cell of the crystal, such that the interaction between a defect in the cell and its periodic images is screened by the surrounding crystal (Figure 2.7c). In practice, the current computational resources allow for the simulation of supercells containing a maximum of 100-300 atoms, depending mainly on the number of valence electrons per atom and the hardness of the pseudopotential. Consequently, some

defects, especially the ones that yield large relaxation volumes, may exhibit a non-negligible interaction energy with their periodic images. To that end, a finite size correction based on linear elastic theory, termed *aneto*, was developed by Varvenne *et al.* [180] to cancel out the self-interaction energy of defects in metallic systems.²

The defect periodic interaction energy (E_{int}) is evaluated from the elastic dipole tensor (P_{ij}) and the strain tensor (ε_{ij}) caused by the point defect

$$E_{int} = -P_{ij}\varepsilon_{ij} \quad (2.18)$$

The strain of the defect is calculated from the summation of the second derivative of the anisotropic elastic Green's function ($G(\mathbf{R}_{mnp})$) multiplied by the local elastic dipole

$$\varepsilon_{ij} = - \sum_{(m,n,p) \neq 0} G_{ik,jl}(\mathbf{R}_{mnp}) P_{kl} \quad (2.19)$$

where $\mathbf{R}_{mnp}$ are the cartesian coordinates of the defect periodic images repeated m, n and p times along x, y and z . Calculating the strain of the defect is a non-trivial task, as the sum in eq. 2.19 is conditionally convergent with respect to system size, which is regularised using the methods of Cai *et al.* [187]. Numerous ways exist to evaluate the elastic dipole [188], but within the *aneto* calculation [180], it is simply taken as

$$P_{ij} = V(C_{ijkl}\varepsilon_{kl} - \sigma_{ij}) \quad (2.20)$$

where the first term is the homogeneous deformation of the cell (if the simulation was performed under $\sigma = 0$ conditions) and the second term is the residual stress on the cell.

Notably, the elastic dipole and Green's function are dependant upon the stiffness constants of the material, C_{ijkl} . Ultimately, E_{int} is calculated to evaluate the degree of self-interaction in the simulated cell; it is therefore logical to use the stiffness constants that are consistent with the elastic properties of the simulated cell, rather than experimentally

²In ionic materials, where point defects may have an associated localised charge, the self-interaction due to PBC tends to be dominated by coulombic repulsion and is generally of much greater magnitude compared to that found in metallic systems. Consequently, correction terms for ionic materials have existed for decades [181–186] but are not applicable to metals.

derived stiffness constants. This was achieved by performing small lattice perturbations from the ground state structures and measuring the resulting stresses. Tools developed by Walker and Wilson [189] were used to automate the process. Ten strain increments were performed in each crystallographic independent direction, between -0.01 and 0.01 .

The *aneto* correction employs two parameters that may affect the quality of the correction term: a real-space radial cutoff for the summation of eq. 2.18 and a Fourier grid size factor for the reciprocal-space part of the calculation of $G_{ik,jl}$. When the *aneto* correction was employed on the Zr lattice, these parameters were set to $15 \text{ \AA}$ with 20 divisions respectively, which yielded energy values converged up to the 4th decimal place. For all other systems, the default values of $40 \text{ \AA}$ with 40 divisions were used, which yielded highly converged results.

Lastly, when comparing solution enthalpies across different phases (e.g. in section 3.4), ideally the supercells of all solids investigated should have the same number of atoms to ensure that the defect concentrations are identical. However, differences in crystal structures means that this is not possible with current cell sizes. In the current work, the spurious effect of periodic defect concentrations were countered by employing the *aneto* correction in conjunction with very large supercells, which were chosen to be as regular as possible, that is, the total lengths of the supercells in the x , y and z directions are roughly equal.

2.3 Defect energies and defect volumes

Defect formation energies E^f were calculated using equation 2.21 or 2.22 if the finite size correction term ($\frac{1}{2}E_{\text{int}}$) from Varvenne *et al.* [180] was included.

$$E^f = E_d^{\text{DFT}} - E_p^{\text{DFT}} \pm \sum_i \mu(i) \quad (2.21)$$

$$E^f = E_d^{\text{DFT}} - E_p^{\text{DFT}} \pm \sum_i \mu(i) + \frac{1}{2}E_{\text{int}} \quad (2.22)$$

where E_d^{DFT} and E_p^{DFT} are the total energies of the defective and perfect DFT cells, μ_i is the chemical potential of all species i that are added or removed from the perfect crystal to form the defect. Since the systems under investigation are metallic, the chemical potential

μ is simply calculated as the DFT energy per atom of the metallic elements in their ground state (e.g. for Zr and Be the ground state is the HCP phase, for Fe it is the ferromagnetic BCC phase, for Cr it is the anti-ferromagnetic BCC phase).

In some cases it is instructive to compare the formation energy of an intermetallic M_xZr_y with that of a dilute extrinsic defect. For this purpose the solution energy (E^{sol}) is defined as:

$$E^{sol}(M_xZr_y) = E^{DFT}(M_xZr_y) - x(E_d^{DFT} - E_p^{DFT} - \mu(Zr)) - \frac{y}{2}E^{DFT}(Zr_2) \quad (2.23)$$

The relaxation volume ($\Delta\Omega$) of a defect is defined as the difference in volume between a supercell containing the defect (Ω_{def}) and the perfect supercell Ω_{perf} :

$$\Delta\Omega = \Omega_{def} - \Omega_{perf} \quad (2.24)$$

When calculating $\Delta\Omega$, mass action is not taken into account, in other words, the number and types of atoms between the defective and perfect cell do not have to be the same. This allows for comparison of defects involving different species. A related quantity often found in the literature is the defect formation volume (ΔV), in which the number of atoms involved in the volumetric change is conserved:

$$\Delta V = \Omega_{def} - \frac{N_{def}}{N_{perf}}\Omega_{perf} \quad (2.25)$$

However, the defect formation volume is only properly defined for intrinsic defects of elemental solids [185], as the reference volume of an isolated extrinsic atom is not a strictly defined quantity.

In certain situations — when competing defects have similar energies, and therefore all of them are likely to occur, all with a different probability — it is instructive to evaluate the *average* effect that multiple defects have on the properties of the material. The average must be weighted by the probability of formation — at thermal equilibrium — of each type

of defect ($c(x)$), given by,

$$c(x) = \frac{n(x) \exp(-Q_x)}{\sum_i n(x_i) \exp(-Q_{x_i})} \quad (2.26)$$

where

$$Q_x = \frac{\Delta E_f(x)}{k_B T} \quad (2.27)$$

and x_i are all possible defect types (or configurations), $n(x)$ and $E_f(x)$ are their multiplicity and formation energy respectively, and all other symbols retain their conventional meaning. Note that the absolute value of $E_f(x)$ is not of importance, instead it is the difference between each $E_f(x_i)$ and the lowest $E_f(x)$ that matters.

The configurational average of a physical quantity (e.g. $\Delta\Omega$) is then obtained following equation 2.28:

$$\langle \Delta\Omega \rangle = \frac{\sum_i n(x_i) \Delta\Omega(x_i) \exp(-Q_{x_i})}{\sum_i n(x_i) \exp(-Q_{x_i})} \quad (2.28)$$

2.4 Harmonic and quasi-harmonic methods

The harmonic approximation assumes that atoms in a crystal reside within an harmonic potential dictated by the surrounding atoms, see Fig 2.8a. At a given temperature, the shape of each harmonic well dictates what portion of space an atom may explore through thermal vibrations (Fig 2.8b). Nevertheless, due to the symmetric nature of harmonic wells, the average position of each atom is unchanged. In other words, the lattice expansion is not accounted for in the harmonic approximation. In addition to the classical harmonic interpretation, it is useful to include the zero-point energy (ZPE), which arises from the quantum mechanical nature of the atoms. A quantum mechanical system is allowed to have only certain discrete energy state, all of which must be greater than the minimum of its classical potential well. Consequently, also at 0 K atoms exhibit some motion.

In the harmonic regime, the vibrational enthalpy $H_{vib}(T, V)$ — which includes the ZPE — and the vibrational entropy $S_{vib}(T, V)$ are evaluated by integrating the phonons density of states (DOS) and the phonons' energy (according to Bose-Einstein statistics). Combined

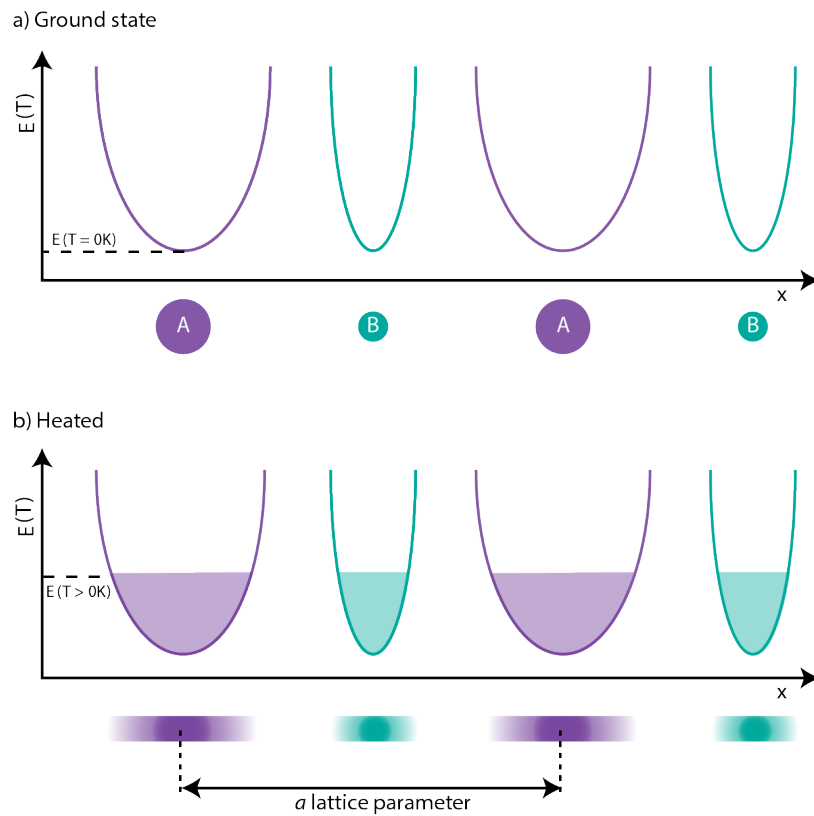


Figure 2.8: Classical harmonic wells of a two-dimensional lattice containing model atoms of species A and B. Injecting the kinetic energy into the system (b) widens the probability distribution of finding the atoms (i.e. increases the standard deviation of the atom's position distribution) without affecting the average position (i.e. the expectation value).

together, these yield the Helmholtz free energy,

$$F_{phonon}(T, V) = H_{vib}(T, V) - TS_{vib}(T, V) \quad (2.29)$$

The quasi-harmonic method is a natural extension of the harmonic method, in which the local potentials are still described by harmonic wells, but their minima are not clamped to the ground state lattice positions. This is achieved by repeating the phonon DOS integration at various unit-cell volumes, then for each temperature an equation of state (EOS) is fitted to the data to determine the lowest energy volume. The third-order Birch-Murnaghan EOS is conventionally used when simulating crystalline solids, expressed in Eqn. 2.30 terms of energy E and volume V .

$$E(V) = E_0 + \frac{9}{16}K_0V_0 \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 K'_0 - 6 \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[\frac{2}{3} \left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\} \quad (2.30)$$

where E_0 , V_0 , K_0 and K'_0 are the equilibrium energy, volume, bulk modulus and its derivative with respect to pressure, respectively.

By allowing volume responses to changes in temperature, the quasi-harmonic approximation describes a system under constant pressure instead of one under constant volume conditions. Therefore, Gibbs free energy $G(T, P)$ is extracted from Helmholtz free energy $F(T, V)$ curves:

$$G_{phonon}(T, P) = \min_V (F_{phonon}(T, V)) \quad (2.31)$$

An example of the procedure is shown in Fig. 2.9 for the case of HCP Be.

2.5 Disordered systems: the Bragg-Williams method

By employing the methodology developed by Bragg and Williams [190–192], it is possible to estimate the degree of order (Θ) of a phase as a function of temperature and potential energy increase (V) caused by an atomic replacement from order towards disorder. The degree of order of a structure may be defined as follows: let N be the total number of atoms in the system, and n the subset of atoms that are susceptible to disordered substitutions.

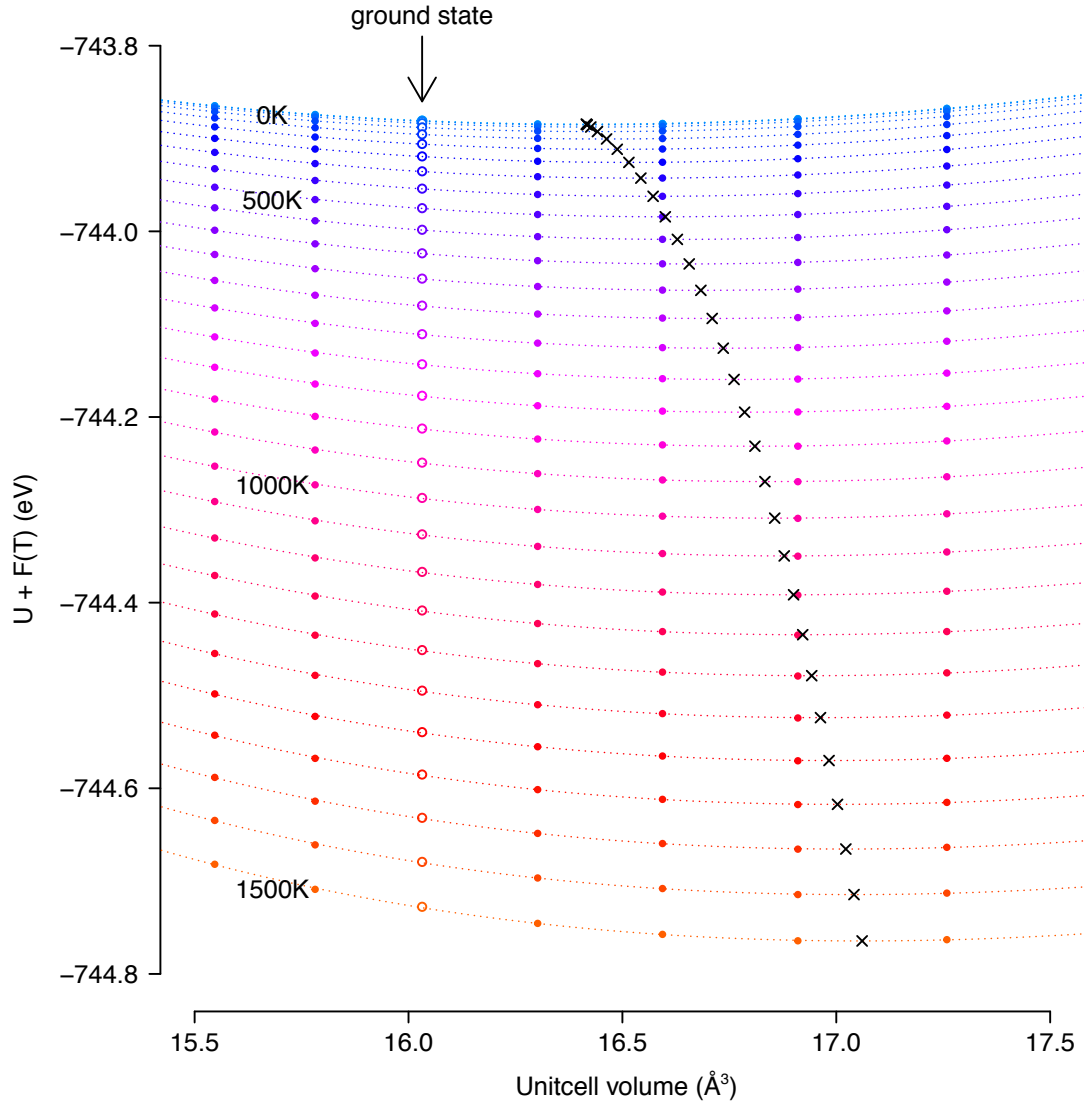


Figure 2.9: EOS of Be at different temperatures. The y-axis represents the sum of internal energy (U) and free energy ($F_{\text{phonon}}(T)$) of the system. Crosses indicate minima of the EOS curves (i.e. the quasi-harmonic approximation). Arrow and hollow points represent the harmonic approximation. Note that the 0K minimum volume is $\sim 0.4 \text{\AA}^3$ larger than the ground state volume due to ZPE.

Further, let there be rn positions of order in the system and therefore $(1 - r)n$ positions of disorder and let p be the probability that an atom is occupying a position of disorder. The degree of order Θ is then defined as:

$$\Theta = \frac{\text{actual value of } p - \text{value of } p \text{ for complete disorder}}{\text{value of } p \text{ for complete order} - \text{value of } p \text{ for complete disorder}} \quad (2.32)$$

$$= \frac{p - r}{1 - r} \quad (2.33)$$

so that in complete disorder (i.e. when $p = r$) $\Theta = 0$, and in complete order (i.e. when $p = 1$) $\Theta = 1$.

Bragg and Williams then consider Boltzmann's distribution formula, and, with suitable substitutions, they obtain the dependency of the degree of order Θ with temperature T and potential energy V of a replacement towards disorder:

$$\Theta(V, T) = \frac{\sqrt{4r(1 - r)(e^x - 1) + 1} - 1}{2r(1 - r)(e^x - 1)} \quad (2.34)$$

where $x = V(\Theta, T)/k_B T$. For the special case of $r = \frac{1}{2}$, equation 2.34, may be simplified to (approximately) $\Theta(V, T) = \tanh(x/4)$.

The energy penalty V is, in turn, dependant on the degree of order Θ . In the Bragg-Williams approach this dependency is assumed to be linear. Furthermore if $\Theta = 0$ (complete disorder), V must also be zero as the positions of order and those of disorder are indistinguishable and substitutions into either site must be equivalent. Owing to the linear relationship, V reaches a maximum value V_0 when $\Theta = 1$ (i.e. in conditions of complete order). Mathematically, that is expressed as

$$V(\Theta, T) = V_0 \Theta(V, T),$$

so that

$$V(0, T) = 0$$

and

$$V(1, T) = V_0.$$

It is acknowledged that local fluctuation of the atomic arrangements in any small sample of crystal will cause a corresponding fluctuation in V , therefore V is to be taken as an *effective average* value of V , representative of the degree of order Θ [192]. Bragg and Williams also recognised that V is almost insensitive to T [190]. In the current work the temperature dependency of V is ignored altogether and V_0 is taken (for all temperatures) as half the average antisite defect formation energy in a completely ordered crystal.

The entropy associated with the degree of disorder may then be included into the total energy of equation 2.29 with the addition of the term $-TS_{conf}$ where the configurational entropy, S_{conf} , is computed using Boltzmann statistics:

$$S_{conf} = k_B \ln(\Omega) \quad (2.35)$$

where Ω is the number of possible states.

2.6 Computational detail of DFT calculations

All DFT simulations were carried out using the CASTEP code [179], with the PBE exchange-correlation functional [119] and ultra-soft pseudo potentials [164]. The plane-wave cut-off energy (E_{cut} , see section 2.1.5) was 450 eV for all simulations of Zr and Zr intermetallics, 400 eV for the study for the Be-Al-Fe system, and 500 eV when investigating the accommodation of extrinsic defects in Be and beryllides. These values are represented by dashed lines in Figure 2.6.

For defect calculations, the scaling factor for the fast Fourier transform (FFT) grid and that for the augmentation charges were set to 2 and 2.3 respectively for all simulations except those concerning defects in Be, where it was found that a value of 1.4 for the FFT grid was sufficient to describe the system accurately provided that the augmentation charges grid was scaled by 2.5, see Figure 2.10. This was a necessary measure in order to perform the large number of calculations on very large supercells. Computational time increases linearly with number of points in the FFT grid, whilst the augmentation charge grid affects the memory requirements but not the computational time. For phonon calculations, the

scaling factors were consistently above 2.0 and 3.0 for the FFT and augmentation charges grid respectively.

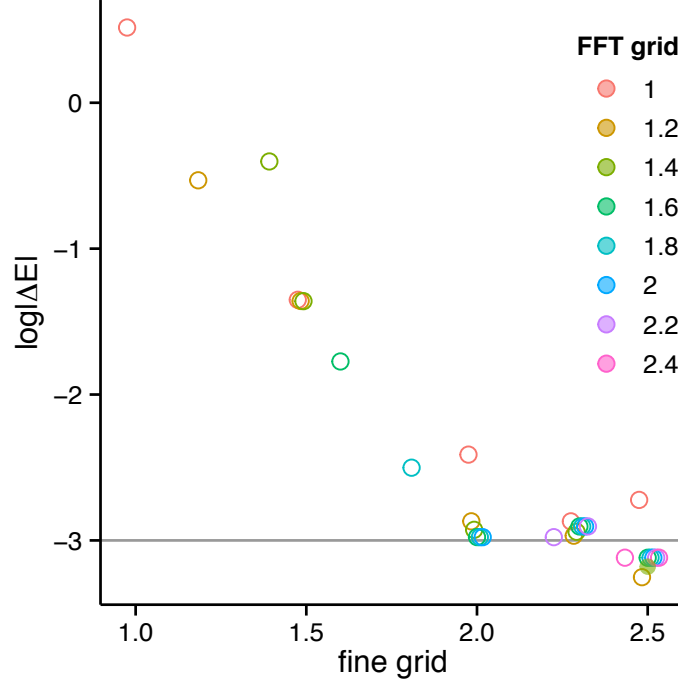


Figure 2.10: Change in total energy of the system ($\log|\Delta E|$) with respect to a highly converged point (FFT grid = 3.0 and fine grid = 3.0) as a function of grid scaling factors for augmentation charges, performed for different FFT grid densities (see legend).

Whenever possible, the same density of k -points was used for different size supercells (e.g. for a $4 \times 4 \times 2$ supercell of a primitive unit cell, the Brillouin zone sampling would consist of a grid with a quarter of the k -points of the primitive cells in the reciprocal a and b direction and half the k -points in the reciprocal c direction). This was not always possible, so a high density of k -points was used throughout to minimise compound uncertainties: the distance between two neighbouring k -points (in reciprocal space) was kept as close as possible to $0.030 \text{ \AA}^{-1}$ and never above $0.035 \text{ \AA}^{-1}$.

Since all systems investigated are metallic, density mixing and Methfessel-Paxton [193] cold smearing of bands were used, with a smearing width = 0.1 eV. No symmetry operations were enforced when calculating point defects. The convergence criterion for self-consistent electronic calculations was set to a difference in the system's internal energy of less than

1×10^{-8} eV for geometry relaxations, and 1×10^{-10} eV when computing spectral, elastic and phonon properties. Geometry optimisation of the structures was carried out using the BFGS algorithm [194] or its memory conservative variant [195]. The convergence criteria for geometry optimisation varied according to the specific needs, but was never set to less than 1×10^{-6} eV energy difference between steps, with forces on atoms smaller than $0.05 \text{ eV } \text{\AA}^{-1}$ and stresses on cells smaller than 0.05 GPa. More commonly these were increased by an order of magnitude or more, especially when calculating elastic and phonon properties.

2.7 Validation of the parameters

The electronic DOS of α -Zr, centred about the Fermi energy (E_f), is presented in Figure 2.11, showing good agreement with those reported in previous DFT literature [196, 197], except for the degree of smoothing adopted by different authors. Aguayo *et al.* [196] employed a full-potential linearised augmented plane waves (FP-LAPW) method, which is computationally more expensive compared to pseudo-potential (PP) approaches — such as the one used in the current work but also by Domain *et al.* [197] and by Olsson *et al.* [198] — but yields a more accurate description of the Zr system. The DOS produced in the current work is in close agreement with the accurate method of Aguayo *et al.* [196] and that of Olsson *et al.* [198], whilst the DOS produced by Domain *et al.* [197] stands out as slightly different, especially in the higher bands (3–5 eV).

Most of the simulations carried out in chapters 3 and 4 are performed within a $5 \times 5 \times 3$ supercell of Zr (containing 150 Zr atoms). It is appropriate then to compare the DOS obtained from the supercell with that of the unit cell. This is shown in Figure 2.12, with projections on the different orbital types (s,p,d). A reasonable overlap is observed between the supercell DOS (shaded areas) and the unit cell DOS (contour lines), thereby providing confidence on the choice of k -point sampling for the supercell. The discrepancy between the supercell DOS and unit cell DOS also provides an estimate of the uncertainty about this type of calculation.

Elastic constants of HCP Be and Zr were calculated and compared to previous work; see Table 2.2. Polycrystalline properties such as the bulk and shear moduli were calculated

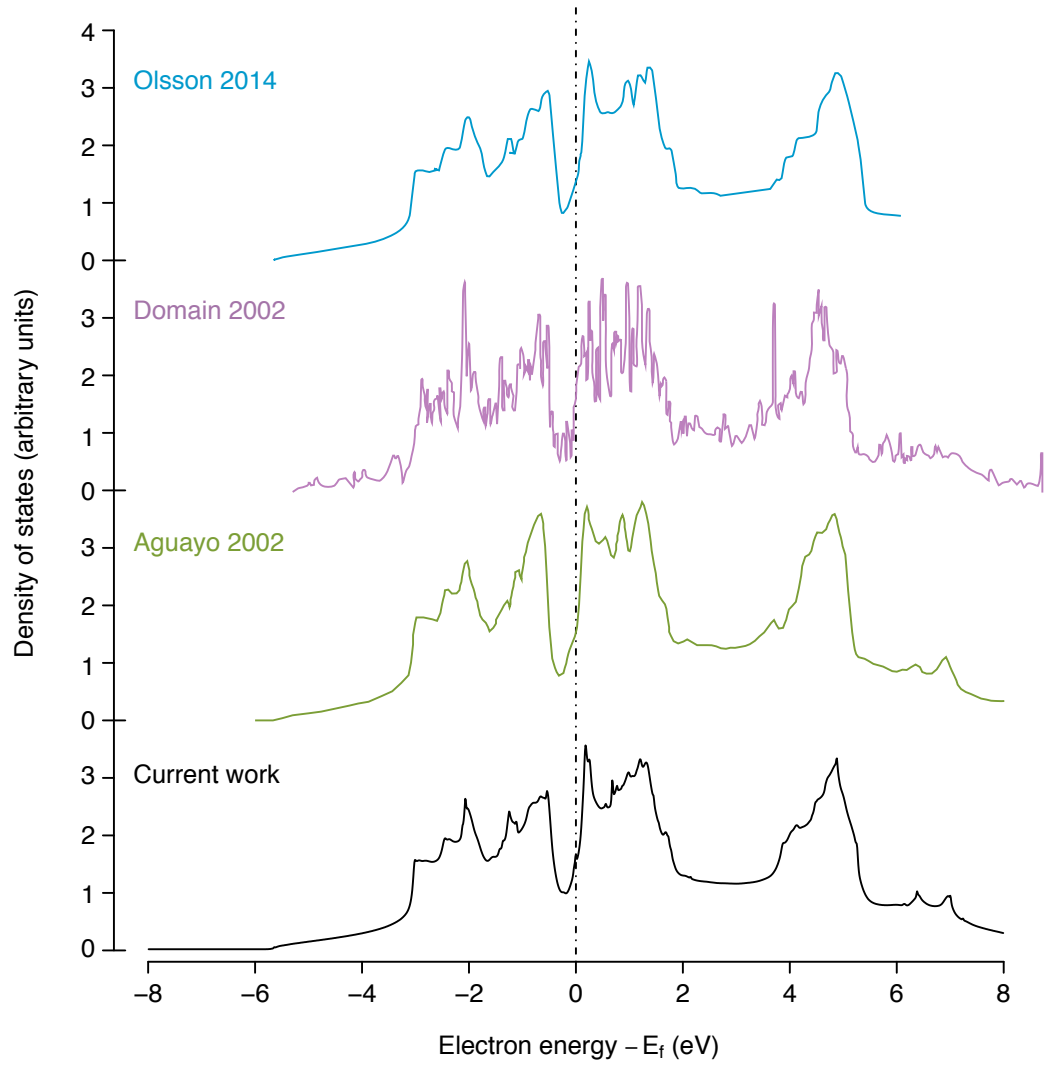


Figure 2.11: Density of states for the electronic structure of Zr compared to that obtained by Aguayo *et al.* [196], Domain *et al.* [197] and Olsson *et al.* [198].

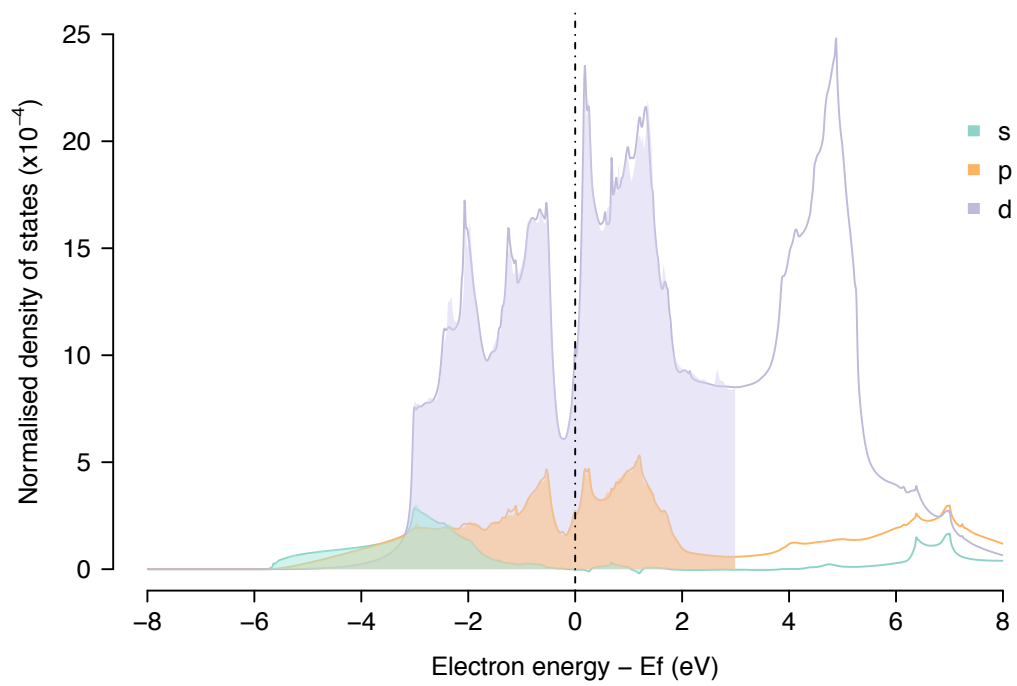


Figure 2.12: Electronic density of states of Zr modelled using a unit cell (lines) and a supercell containing 150 Zr atoms (shaded areas). For computational reasons the supercell calculations were limited to 3 eV, corresponding to 20 % partially occupied or empty bands. The density has been normalised so that $\int_{-\infty}^{3.0\text{eV}} \text{DOS} = 1$.

using the Hill method [199]. This method takes the arithmetic mean of from the Reuss method [200], which assumes uniform loading, and the Voigt method [201], which assumes uniform strain. The current method is generally in agreement with previous work and low temperature experimental measurements, as highlighted by the maximum percentage deviation of 17.4 % and 16.8 % for Be and Zr respectively. In all DFT calculations (current and previous), the stiffness is slightly overestimated for Be, and slightly underestimated for Zr. Experimental data also exhibits considerable uncertainties: between 1 GPa for c_{12} to 5 GPa for c_{13} [202, 203].

Table 2.2: Simulated (with no ZPE contributions) and experimental (low temperature) elastic constants in units of GPa. Mean and maximum percentage deviation from experimental results (δ) are also reported. For hexagonal materials: $c_{66} = \frac{1}{2}(c_{11} - c_{12})$. Bulk modulus K and shear modulus G were calculated using the Voigt-Reuss-Hill average method; see text for details.

	work*	c_{11}	c_{12}	c_{13}	c_{33}	c_{44}	K	G	$\langle\delta\rangle$	$\max(\delta)$
Be	current (PP-PW-PBE)	322.2	22.8	12.7	384.9	188.8	124.8	169.9	6.3	17.4
	PP-PW-LDA [204]	310.9	19.5	19.1	359.5	162.1	121.6	155.3	10.1	73.6
	FP-LMTO-GGA [205]	293.6	26.8	14.0	356.7	166.2	116.8	151.5	5.3	27.3
	experimental [202]	299.4	27.6	11.0	342.2	166.2	115.5	152.4		
Zr	current (PP-PW-PBE)	141.9	65.4	68.0	148.7	30.2	92.8	34.9	-7.3	16.8
	PAW-PW-PBE [129]	141.1	67.6	64.3	166.9	25.8	93.3	33.6	-8.2	28.9
	PP-PW-PBE [206]	139.4	71.3	66.3	162.7	25.5	94.2	30.5	-7.4	29.7
	FP-LMTO-LDA [207]	153.1	63.4	76.5	171.2	22.4	100.7	33.5	-5.5	38.3
	experimental [203]	155.4	67.2	64.6	172.5	36.3	97.3	42.1		
* PP: pseudopotentials, FP: full potentials, PAW: projector-augmented waves, LMTO: linear Muffin-Tin orbitals, PW: plane waves.										

In chapter 5, the harmonic and quasi-harmonic approximations are employed to investigate the temperature dependance of the relative stability of phases. These rely on phonon DOS calculations. The computed phonon dispersion relations and DOS for HCP Be are presented in Figure 2.13, and show a reasonable match with low temperature experimental data (black dots). The largest deviations are observed on high frequency modes, which are also the ones with higher experimental uncertainties [208]. Phonon DOS were calculated using the finite displacement method with supercell extrapolation [209]. Supercells containing 48, 162 and 384 atoms were used to test convergence with respect to supercell size for cubic FeBe₂, see Figure 2.14. There is clearly very little difference between the DOS produced using the 162 and 384 atom cells, indicating convergence already at 162 atoms. Furthermore, the difference in thermodynamical contribution between the 384 atom supercell and the 48 atom supercell was smaller than 10^{-2} eV/formula unit.

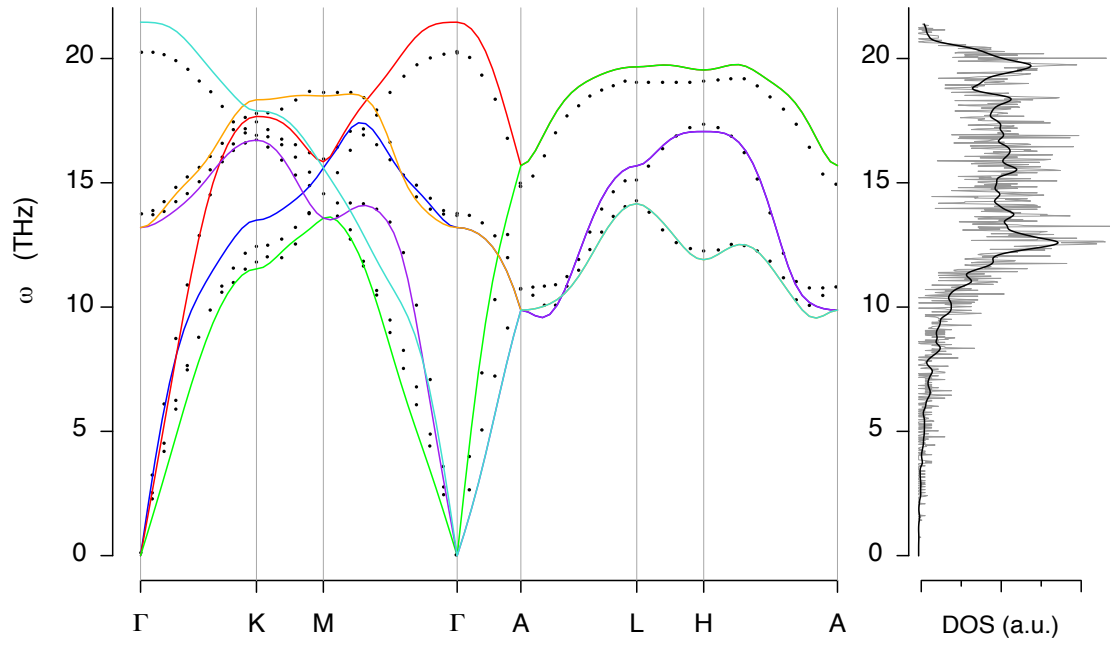


Figure 2.13: Beryllium phonon dispersion relations (left) and DOS (right). Solid lines are from the current work, black dots are experimental points from [208] and the dashed line is a spline smoothing.

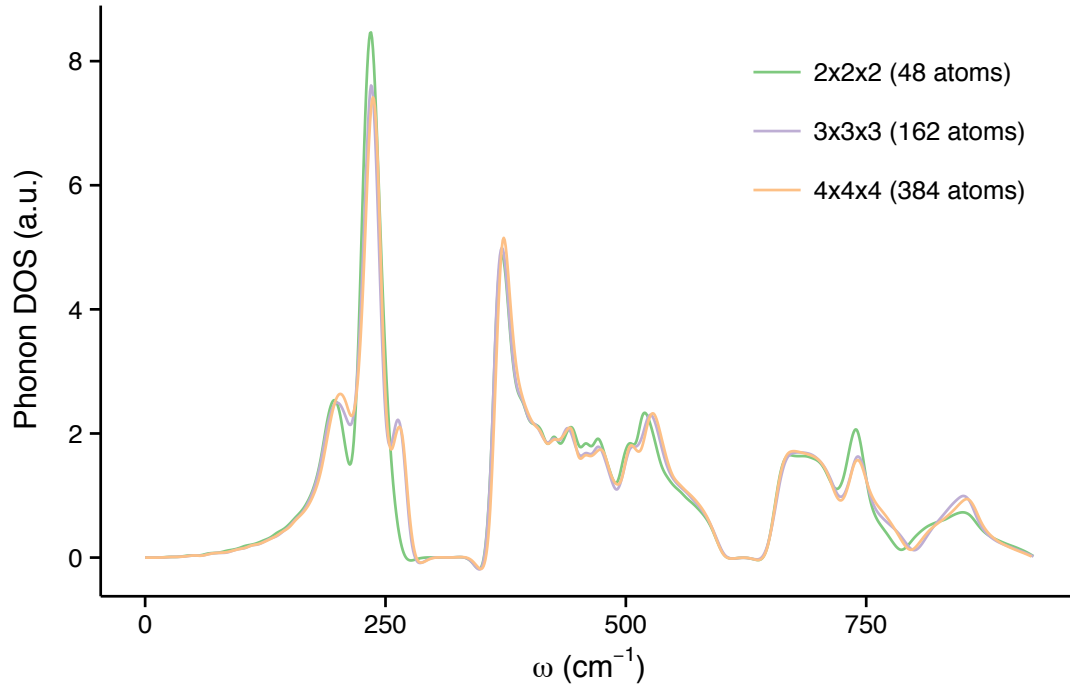


Figure 2.14: Phonon DOS (smoothed with a spline function) as a function of supercell size for cubic FeBe_2 (C15 Laves phase).

To provide confidence on the method used in the current work, Table 2.3 compares the calculated lattice parameters and bulk moduli of three relevant phases (HCP-Be, BCC-Fe and hex-FeBe₂) — with and without the addition of vibrational terms — against experimental measurements. It is clear that the description of the lattice parameters, and more so of the bulk moduli, improves with the addition of vibrational terms from the quasi-harmonic method.

Table 2.3: Simulated and experimental lattice parameters and bulk moduli of Fe, Be, and FeBe₂.

		$a^{0\text{K}}$ (Å)	$a^{300\text{K}}$ (Å)	$c^{0\text{K}}$ (Å)	$c^{300\text{K}}$ (Å)	$K^{0\text{K}}$ (GPa)	$K^{300\text{K}}$ (GPa)
Fe(s)	ground state	2.859	—	—	—	105 ± 5	—
	quasi-harmonic	2.863	2.872	—	—	195 ± 2	186 ± 2
	experimental [210, 211]	2.8550	2.8598	—	—	170.4	166.2
Be(s)	ground state	2.273	—	3.583	—	125 ± 1	—
	quasi-harmonic	2.290	2.293	3.608	3.613	133 ± 2	135 ± 2
	experimental [105][202]	NA	2.286	NA	3.585	133.6	131.2
FeBe ₂	ground state	4.179	—	6.799	—	162 ± 1	—
	quasi-harmonic	4.195	4.209	6.820	6.843	153 ± 2	145 ± 2
	experimental [212]	NA	4.219	NA	6.856	NA	NA

From a computational point of view, the quasi-harmonic approximation is n times more demanding than the harmonic approximation, where n is the number of unit cell volumes that are sampled — commonly between 10 and 20. However, whilst the quasi-harmonic approximation greatly improves the prediction of lattice parameters and elastic constants at temperature, it appears to have little effect on the relative phase stability. For instance, considering the formation reaction for FeBe₂,



the energy of the reactants and the products can be expressed in terms of Helmholtz free energy F (harmonic) or Gibbs free energy G (quasi-harmonic). The difference between F and G is of similar magnitude for each of the reactants and products involved, consequently, the free energy of formation is largely unaffected by the choice of method, see Figure 2.15. Of course, there is no *de facto* guarantee this will be the case for all reactions, but it seems the case in the systems studied here.

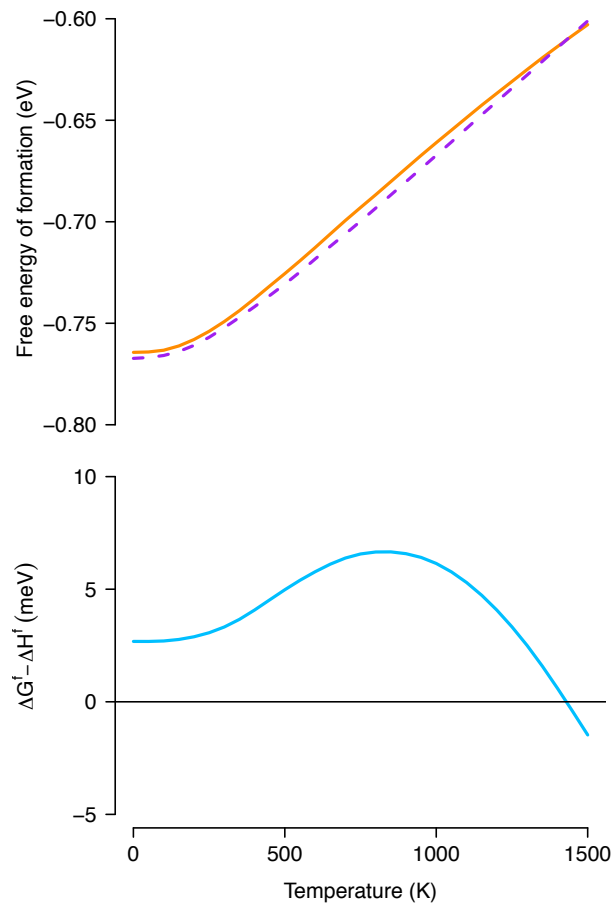


Figure 2.15: Free energy of formation of FeBe_2 calculated using the quasi-harmonic approximation (ΔG^f , orange solid line) and the harmonic approximation (ΔH^f , purple dashed line), both in eV. Below, in light blue is the difference ($\Delta G^f - \Delta H^f$), reported in meV.

3

H in Zr alloys

Part of the work presented in this chapter has been published in:

Burr *et al.* Corr. Sci. **69** (2013) 1–4. Ref [74]

Burr *et al.* J. Nucl. Mater. **443** (2013) 502–506. Ref [73]

3.1 Introduction

One of the limiting factors for a further increase in fuel burn-up is the hydrogen pick-up by Zr alloys. The presence of H in the cladding is of concern for a variety of reasons including dimensional changes, reduced ductility of the metal, and the formation of hard, brittle hydrides, which in turn may increase corrosion rates or cause failure by delayed hydride cracking [213]. New nuclear fuel cycle regulations that take into account hydrogen levels in the cladding are also being considered [214]. It is, therefore, important to develop a deeper understanding of the processes responsible for the H pick-up, in order to deliver improved reactor performance, from both economic and safety standpoints.

That the chemical composition of the Zr alloys affects the H-pickup has been known for decades [13, 19]; testimony of this is the development of Zircaloy 4, an alloy similar to Zircaloy 2 but with reduced Ni to limit HPUF. However, the mechanism or mechanisms by which the alloying additions affect HPUF is still not clearly understood. In this chapter, the solubility of H in Zr and SPPs is investigated and some light is shed on the role of some common alloying elements. First, the simpler case of H in the Zr matrix is presented; following that, a review of the SPP composition, crystal structure and stability is provided; then the solubility of H in the SPPs are considered; finally, the findings are summarised and conclusions are drawn.

3.2 Hydrogen in Zr metal

The solution of H in Zr has been extensively modelled in the past decade [197, 215–217], and provides a good benchmark to validate the current methodology. Due to its small atomic size (0.32 Å covalent radius and 1.10 Å Van der Waals radius [130]) H occupies interstitial sites in the Zr lattice. All interstitial sites of the HCP structure were investigated, but only the tetrahedral and octahedral sites (shown in Figure 3.1) were found to be stable, i.e. when H was placed in a different interstitial site, it spontaneously moved to either of the stable sites during the energy minimisation step. This is in agreement with all previous DFT and experimental literature [30, 197, 218–220].

Table 3.1 compares the values obtained in the current work with values reported in

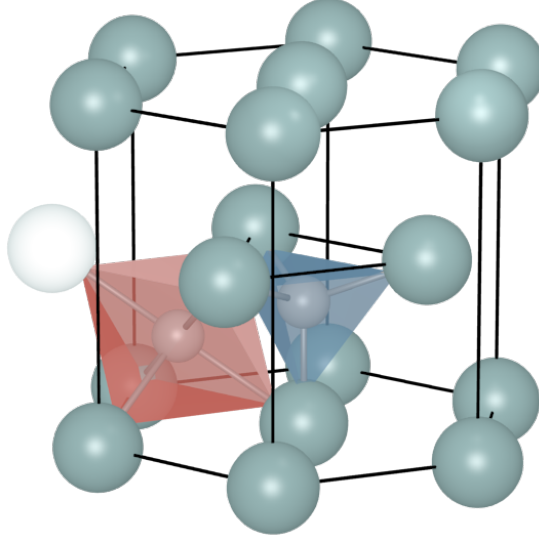


Figure 3.1: Octahedral (red) and tetrahedral (blue) interstitial sites for H accommodation in α -Zr. Translucent spheres represent atoms outside the unit cell (black cage).

Table 3.1: Enthalpy of solution for tetrahedral and octahedral H in α -Zr, and the relative difference.

Refs.	cell size Zr atoms	[H] <i>wt. ppm</i>	$E_{sol}(\text{tet})$ eV	$E_{sol}(\text{oct})$ eV	ΔE_{sol} eV
Current	150	73.1	-0.498	-0.413	0.085
Burr <i>et al.</i> 2013 [73, 74]	150	73.1	-0.464	-0.378	0.086
Domain <i>et al.</i> 2002 (GGA) [197]	96	114	-0.604	-0.532	0.057
Lumley <i>et al.</i> 2013 [30]	96	114	-0.60	-0.56	0.04
Christensen <i>et al.</i> 2015 [218] (electronic only)	48	228	-0.66	-0.60	0.06
Christensen <i>et al.</i> 2015 [218] (quasi-harmonic)	48	228	-0.476	-0.471	0.005
Experimental [222–226]	—	—	-0.34 – -0.66	—	—

the literature. Since the work presented here was published [73, 74], the state-of-the-art methodology for metallic calculations has evolved (see section 2.2), therefore the previous result were revisited and a small change was noted in solution energy values. DFT values reported in Table 3.1 are all within the trends observed experimentally. All DFT studies employed a GGA exchange-correlation functional¹. The recent work by Christensen *et al.* [218] includes a thorough investigation of vibrational contributions using both harmonic and quasi-harmonic models. It is worth noting that the experimental solubility limit of H in α -Zr is 50–60 *wt. ppm* at the operating temperature of a pressurised water reactor of 300 °C, and significantly lower at room temperature [221, 222].

¹The work by Domain *et al.* [197] also used the LDA functional but reported it as less accurate than the GGA approximation.

Tetrahedral sites in hexagonal materials are oriented with one vertex along the c-axis, and the remaining three vertices aligned on a (0002) basal plane (blue volume in Figure 3.1). It was found that the H bonds anisotropically when it occupies the tetrahedral site. More specifically, the H atom is further away from the Zr atom that is directly above or below it, and more closely bound to the remaining three Zr atoms in the basal plane, see Figure 3.2. This is related to the anisotropic nature of HCP materials discussed in section 1.4. That is, bonds between atoms sharing the same basal plane are different to those across basal planes, which results in a deviation from ideal $\frac{c}{a}$ ratio. It is therefore not surprising that H in the octahedral site — which exhibits mirror symmetry with respect to the (0004) planes and consequently has three Zr on the (0002) plane above it and three on the (0002) plane below it — exhibits a more isotropic bonding.

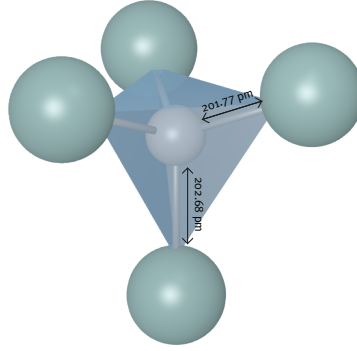


Figure 3.2: Geometry of a hydrogen tetrahedral interstitial defect α -Zr.

The electronic DOS for supercells containing an interstitial H atom, in the tetrahedral and octahedral sites, are presented in Figure 3.4. It is clear that the electronic contribution from the hydrogen atom is restricted to a narrow band ~ 6.5 eV below the Fermi energy. Figure 3.4 also compares the DOS of a Zr near the H atom (solid lines) to that of pristine Zr (dashed lines). The change in electronic character in Zr is observed mainly in the d-band, and is slightly more pronounced when H is located in the octahedral site. However, the variations in the d-band DOS are still within the accuracy of the method (see Figure 2.11), and no further remarks may be drawn from it. More relevant is the energy shift of the localised H band from -6.581 eV below the Fermi level for tetrahedral occupancy to -6.488 eV for octahedral occupancy, see Figure 3.3.

The data presented above, combined with that obtained performing similar analyses on selected Zr hydrides provided by Lumley [217], are being used for the development of a Zr-H tight binding model by colleagues at Aix-Marseille Université and at the “Institut de radioprotection et de sûreté nucléaire” (IRSN), France [227, 228]. The formulation of an accurate tight-binding model that correctly describes the Zr-H interaction under all relevant scenarios (dilute solution, cluster formation and precipitate formation, under tensile and compressive strain fields [188, 229–238]) will allow computation of large-scale systems, such as those relevant to delayed hydride cracking, which is currently too large for Kohn-Sham methods and too complex for simple empirical potential approaches (e.g. pair potentials and embedded atom method) [188].

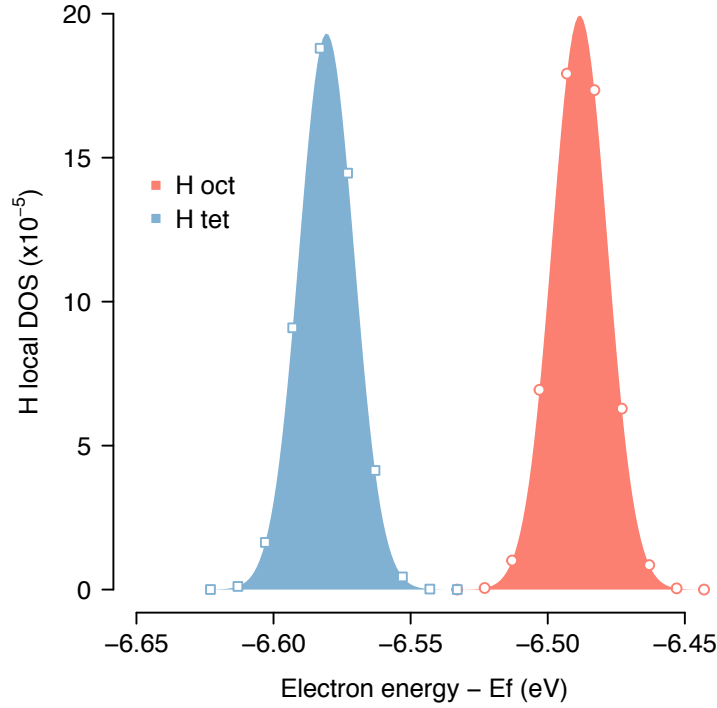


Figure 3.3: DOS of H in the tetrahedral (blue) and octahedral (red) interstitial sites in α -Zr. Detail on y-axis scaling provided in Figure 3.4.

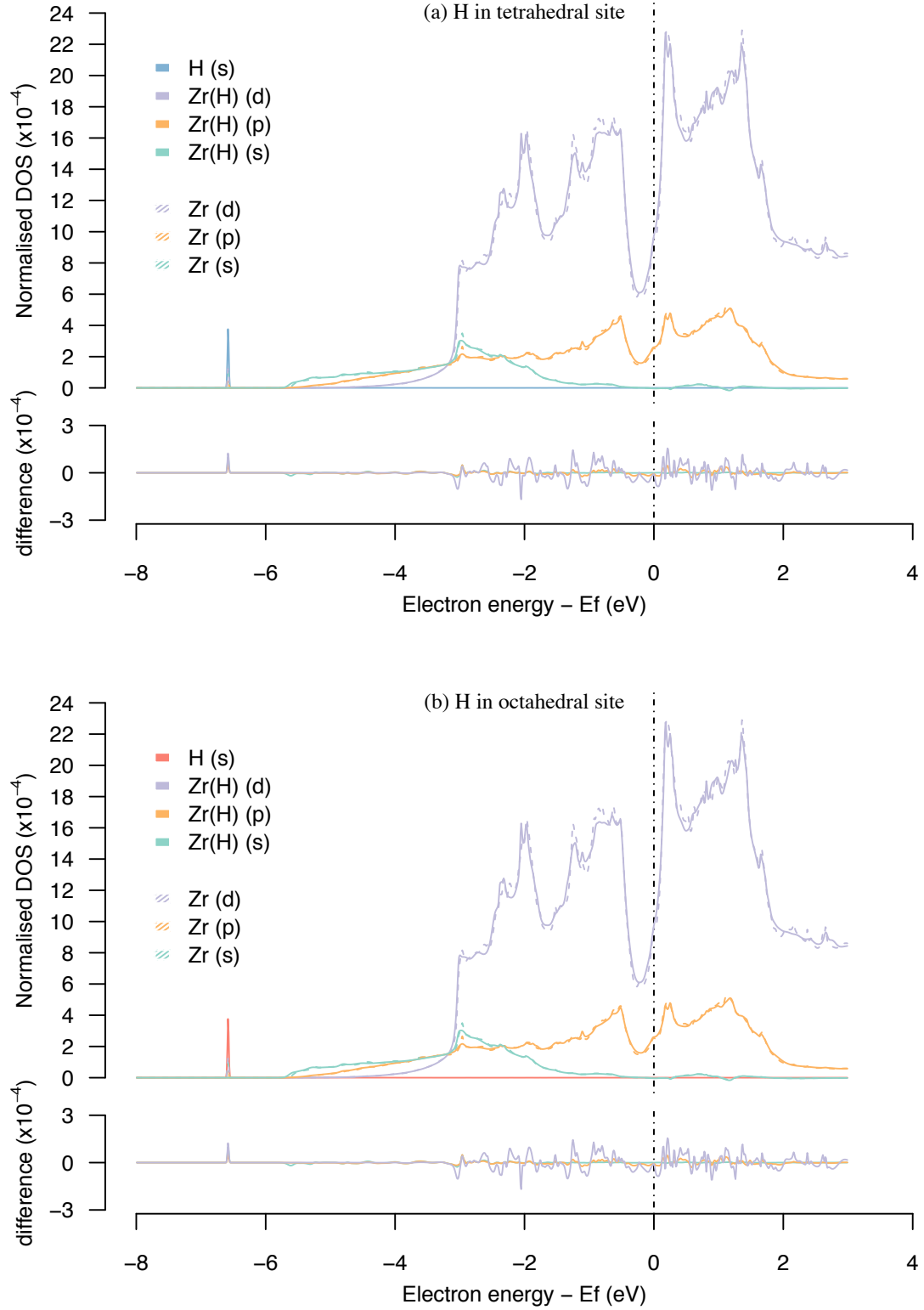


Figure 3.4: DOS of α -Zr supercells containing an interstitial H (solid lines) compared to pristine supercells (dashed lines). The difference in Zr DOS (excluding H DOS projector) is presented in the insets below the main graphs. DOS are normalised such that $\int_{-6\text{eV}}^{\infty} \text{DOS} = 1$

3.3 Review of Zr second phase particles

Most alloying additions, even in small quantities, tend to form intermetallic phases with Zr, see section 1.2. Exceptions are Sn, which shows ~ 3 at % solubility in α -Zr and Nb, which is a β phase stabiliser in Zr and as such, tends to form β -phase precipitates, which are a solid solution of ~ 80 at % Zr and ~ 20 at % Nb. However, if co-doped with Fe, intermetallic $\text{Zr}(\text{Nb},\text{Fe})_2$ and $(\text{Zr},\text{Nb})_2\text{Fe}$ phases are also observed. Limitations in the current methodology do not allow the modelling of solid solutions, therefore the HCP and BCC phases of the pure elements were modelled instead. Similarly, disordered ternary intermetallics were approximated by the binary end members of the solid solution.

Table 3.2 provides a summary of the different types of SPPs that have been reported in the experimental literature relating to Zr alloys.

The crystal structure of selected SPPs is represented in Figure 3.5. In the following paragraphs these are discussed in terms of binary systems, although it is acknowledged that most SPPs are in fact ternary compounds, where the degree of solution of the third element (the minor constituent) is strongly related to the exact composition of the alloy. The most common intermetallic phases observed are the ZrM_2 Laves phases, where $M =$

Table 3.2: Overview of SPPs observed in Zr alloys, together with the size of the largest supercell simulated in terms of the number of atoms (N), distance between the H defect and its replicas (d) and the effective H concentration. For Laves phases, $M = \text{Cr}, \text{Fe}, \text{Mo}, \text{Nb}, \text{V}$.

Phase	Space group	Pearson	Prototype	N	d (Å)	H wt. ppm
α -Zr	$P6_3/mmc$	$hP2$	Mg	150	15.6	74
β -(Zr,Nb)	$Im\bar{3}m$	$cI2$	W	128	14.3	85–86
ZrM ₂ C15	$Fd\bar{3}m$	$cF24$	Cu ₂ Mg	192	14.1	57–81
ZrM ₂ C14	$P6_3/mmc$	$hP12$	MgZn ₂	96	10.0	114–163
ZrM ₂ C36	$P6_3/mmc$	$hP24$	MgNi ₂	96	10.0	114–163
Zr ₃ Fe	$Cmcm$	$oS16$	Re ₄ B	96	11.4	127
Zr ₂ (Fe,Ni)	$I4/mcm$	$tI12$	Al ₂ Cu	96	9.8	131–132
ZrNi	$Cmcm$	$oS8$	TII	96	10.0	140
Zr ₂ Cu	$I4/mmm$	$tI6$	MoSi ₂	96	1.12	128
ZrCu	$Pm\bar{3}m$	$cP2$	CsCl	128	1.31	102
Zr ₃ Sn	$Pm\bar{3}n$	$cP8$	Cr ₃ Si	64	11.3	160
Zr ₅ Sn ₃	$P6_3/mcm$	$hP16$	Mn ₅ Si ₃	128	11.6	78
Zr ₅ Sn _{3.5}	$P6_3/mcm$	$hP17$		136	11.9	74
Zr ₅ Sn ₄	$P6_3/mcm$	$hP18$	Ga ₄ Ti ₅	143	12.0	68
ZrSn ₂	$Fddd$	$oF24$	TiSi ₂	288	17.1	32

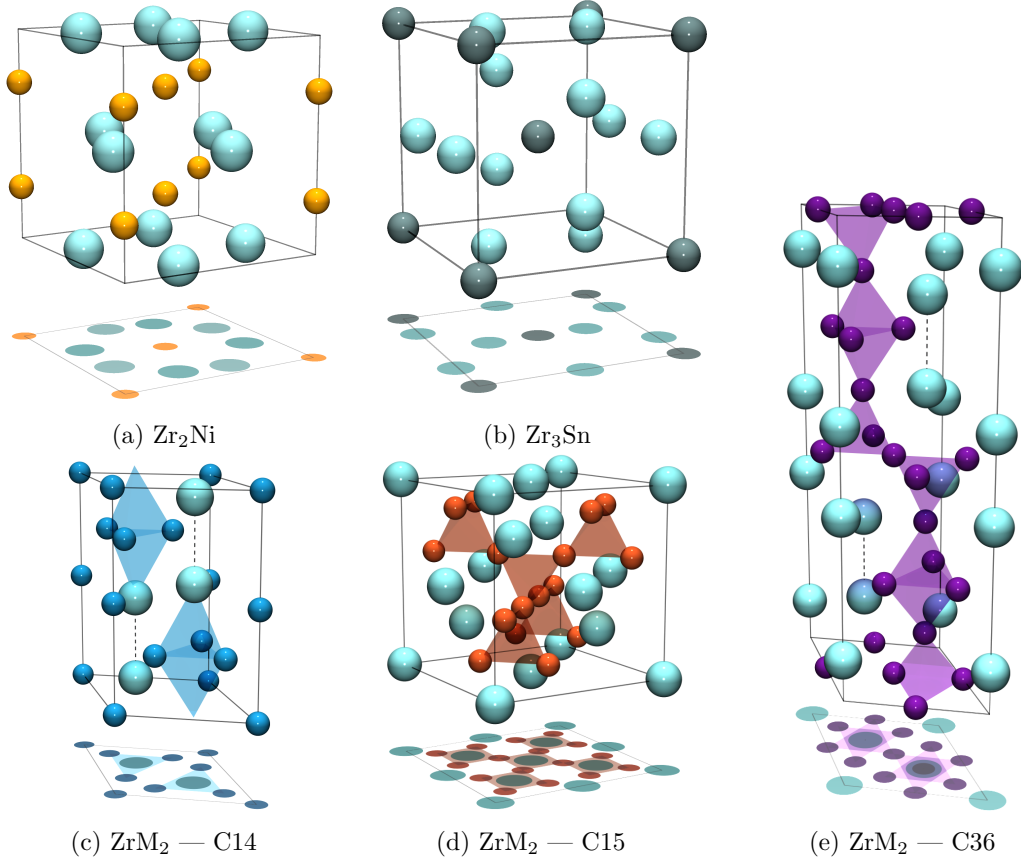


Figure 3.5: Crystal structure of selected Zr intermetallics.

Cr, Fe, Mo, Nb, V; see Figure 3.5 c-e. Among the literature many reports exist of both the cubic C15 [22, 36, 239–242] and the two hexagonal C14 and C36 [22, 32, 34, 240–245] Laves phases. Due to the nominal composition of commercial alloys, these SPPs have mostly been identified as $\text{Zr}(\text{Cr},\text{Fe})_2$ and $\text{Zr}(\text{Nb},\text{Fe})_2$, however, they are also known to form with Mo and V additions [22, 37, 246–248].

The Ni-Zr binary phase diagram exhibits numerous intermetallic compounds [28]. However, Ni containing SPPs tend to be stable as Zr rich phases, typically the body-centred tetragonal Zr_2Ni phase, which — in the presence of Fe — forms $\text{Zr}_2(\text{Ni},\text{Fe})$, commonly found in Zircaloy-2 [31, 34]. For completeness, here we also consider the orthorhombic ZrNi structure.

In addition to the ZrFe_2 and Zr_2Fe phases described above, the Zr-Fe system exhibits an orthorhombic Zr_3Fe phase, which has been observed only sporadically in high Fe, low Ni low Cr alloys [31], β -quenched alloys [33] and irradiated Zircalloys [249]. A metastable Zr_4Fe phase has also been reported [31, 239, 244, 249, 250]. Unfortunately there is insufficient

crystallographic information to conduct a reliable DFT study of Zr_4Fe , therefore it was not considered further. Finally the $Fd\bar{3}m$ structure of Zr_2Fe was also considered, as documented by Buschow [251], but the formation energy of this phase was found to be 0.20 eV greater than the body-centred Zr_2Fe phase described above and is therefore discarded from further investigation.

The stability of binary intermetallic phases described above has been investigated in previous work [30, 217]. Cu additions were not included in that study, and therefore require further analysis. Cu additions in Zr-base alloys tend to be observed mainly as a tetragonal Zr_2Cu phase [252], even though the complete phase diagram presents a large number of possible intermetallic compounds [253, 254]. For completeness, similarly to Ni additions, all reported phases containing $\geq 50\%$ Zr were investigated. Table 3.3 contains a list of the Cu-bearing phases considered, with those that are widely regarded as stable being marked by an asterisk. Enthalpies of formation from standard state (E_f°) and from solid solution (E_f^{sol}) are also reported in Table 3.3, following reaction 3.1 and 3.2 respectively.

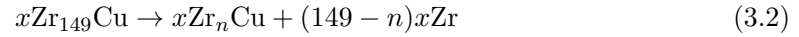


Table 3.3: List of Zr-Cu intermetallic phases modelled in the current work. The standard enthalpy of formation E_f° was calculated from α -Zr and FCC-Cu metals. Whilst the solution energy, E_f^{sol} , was calculated from an isolated substitutional Cu atom in a 150 atoms cell of α -Zr. The quoted enthalpies are per formula unit. * denotes commonly observed structures from literature.

Formula unit	Space group	Pearson symbol	Prototype structure	E_f° (eV)	E_f^{sol} (eV)	Ref.
Zr_3Cu	$P4/mmm$	$tP4$	CuInPt_2	0.29	0.00	[255]
Zr_2Cu^*	$I4/mmm$	$tI6$	MoSi_2	-0.41	-0.70	[256, 257]
Zr_2Cu	$Fd\bar{3}m$	$cF24$	AuBe_5	-0.20	-0.48	[257]
ZrCu^*	$Pm\bar{3}m$	$cP2$	CsCl	-0.21	-0.50	[258, 259]
ZrCu	$P121/m1$	$mP4$	NiTi	-0.25	-0.54	[259]
ZrCu	Cm	$mS16$		-0.26	-0.55	[259]

The Zr_3Cu phase was found to be thermodynamically unstable (positive formation energy). The tetragonal $I4/mmm$ structure of Zr_2Cu was found to possess a substantially more stable formation energy compared to the cubic $Fd\bar{3}m$ structure. On the other hand,

there is little difference in the formation energies calculated for the ZrCu compounds, suggesting that all three phases are likely to form in the Cu-Zr alloy. However, ZrCu is a high temperature phase, which decomposes in a eutectoid reaction at temperatures below 715 °C. Without the explicit calculation of vibrational energy by means of phonon calculations, DFT simulations do not take into account temperature effects, therefore DFT results alone are generally not indicative of the stability of high temperature phases. This is especially true when the differences in formation energy are very small, as in the ZrCu phases. Experimental investigation suggests that the CsCl structure is the most stable at high temperatures [254]. Following the above results, the body-centred Zr₂Cu and the CsCl structure of ZrCu were studied.

Finally, we examine Zr-Sn intermetallic compounds. Although Sn is relatively soluble in α -Zr compared to transition metals, there have been reports of Zr-Sn intermetallic SPPs in irradiated Zircaloy samples [239, 249, 250, 260], suggesting that they form due to radiation enhanced diffusion of the alloying elements. Recent DFT work [30] confirms this from a thermodynamic viewpoint. However, re-deposition of Sn during TEM sample preparation has also been suggested as a possible cause for the formation of Zr-Sn intermetallics [244].

Even ignoring the effects of irradiation and ternary alloying elements on the stability of Sn-SPPs, the equilibrium binary Sn-Zr system is rather complex [261, 262]. At levels of Sn greater than the α -Zr solid solution regime, the stable phases are Zr₄Sn, Zr₅Sn_{3+x} and ZrSn₂. With the exception of the latter, the other phases exhibit a high degree of disorder. Extensive experimental work by Kwon and Corbett [262] subsequently modelled by Baykov *et al.* [263] shows that at equilibrium Zr₅Sn_{3+x} has a large concentration of self-interstitial Sn, up to a stoichiometry of Zr₅Sn₄. These studies also showed that Zr₄Sn is a Zr-substitutional structure, which is derived from Zr₃Sn with one fifth of the Sn sites occupied by Zr atoms, i.e. Zr₃(Sn_{0.8}Zr_{0.2}). Due to limitations in the computational methodology, such complex phases cannot be modelled reliably, instead, their parent phases were simulated: the cubic Zr₃Sn structure, face centered orthorhombic ZrSn₂, and the hexagonal Zr₅Sn₃, as well as two of its interstitial derivatives, an ordered form of Zr₅Sn_{3.5} in which only the 2b Wyckoff sites were occupied, and Zr₅Sn₄, in which all the interstitial sites are occupied (2b and 2a).

It is clear that a great deal of possible SPPs may be found in Zr alloys, and most are found to be ternary compounds. However, these are also disordered and therefore beyond the reach of the current method. Instead, the present work focusses on the binary intermetallics that constitute the end members of the ternary solid solutions described above. Particular attention is drawn to the end members of the $\text{Zr}(\text{Fe,Cr})_2$, $\text{Zr}_2(\text{Fe,Ni})$ and $\beta\text{-(Zr,Nb)}$, as these are the most common type of SPPs found in commercial Zr alloys.

3.4 Hydrogen in Zr second phase particles

Owing to its small size, H may occupy many interstitial sites that are usually too small for common extrinsic elements, but is unlikely to substitute for metal atoms. As shown in Figure 3.5, the crystal structures of the SPPs are more complex than those of simple metals, thereby offering a wide array of possible interstitial sites. Therefore, when investigating the solubility of H in the intermetallic phases, all possible interstitial sites had to be simulated for each structure and each composition. A summary of solution enthalpies for H in the most favourable interstitial site in each of the intermetallic phases, and the comparison with the solution enthalpy in $\alpha\text{-Zr}$, is presented in Table 3.4. A comparison with $\beta\text{-Zr}$ was considered less useful as earlier studies [30, 217] showed that the intermetallics are soluble in the β phase.

As highlighted in section 3.2, H preferentially occupies the tetrahedral site in $\alpha\text{-Zr}$ over other sites. Interestingly it was found that the lowest energy site for H solution in nearly all intermetallic phases also had a tetrahedral configuration. The only exceptions were ZrCu , ZrNi and $\text{Zr}_5\text{Sn}_{3+x}$, which are discussed in greater detail below. Furthermore, it was found that sites with the largest fraction of neighbouring Zr atoms consistently offered the lowest energy for H accommodation. Thus, for most of the intermetallic phases, the lowest energy site is one consisting of 4 neighbouring Zr atoms. For those compounds where, due to stoichiometry, no such sites are present, for example the ZrM_2 phases, H was found to preferentially occupy tetrahedral sites with 2–3 Zr atoms and only 1–2 M atoms, irrespective of the concentration of the M-species. In the case of ZrCu and ZrNi , the most stable interstices are octahedral with coordination of 4 Zr and 2 Cu/Ni atoms. These sites

Table 3.4: Enthalpy of solution for an interstitial H, in the most stable site, for each of the intermetallic phases investigated. $\Delta E_{sol}^{\alpha-Zr}(H)$ is the difference in enthalpy of solution of H in the given intermetallic, compared to the tetrahedral site in α -Zr (favourable cases in bold). The preferred interstitial site for H is indicated in Wyckoff notation, and it is described in terms of its geometry and coordination number with Zr and non-Zr elements X. All values are expressed in units of eV.

Phase	$E_{sol}(H)$	$\Delta E_{sol}^{\alpha-Zr}(H)$	error	H interstitial		
				Position	Type	Zr/X
α -Zr	-0.46			4 <i>f</i>	tet	4/—
β -Zr	-0.62	-0.16		12 <i>d</i>	tet	4/—
β -Nb	-0.46	0.00		12 <i>d</i>	tet	—/4
ZrFe ₂	-0.03	0.50	<0.01	96 <i>g</i> /6 <i>h</i>	tet	2/2
ZrMo ₂	-0.24	0.22	±0.06	96 <i>g</i> /6 <i>h</i>	tet	2/2
ZrCr ₂	-0.31	0.15	±0.03	96 <i>g</i> /6 <i>h</i>	tet	2/2
ZrV ₂	-0.73	-0.26	±0.01	96 <i>g</i> /6 <i>h</i>	tet	2/2
ZrNb ₂	-0.81	-0.35	±0.02	96 <i>g</i> /6 <i>h</i>	tet	2/2
ZrSn ₂	0.28	0.75		32 <i>h</i>	tet	2/2
ZrCu	-0.28	0.19		3 <i>d</i>	oct	4/2
ZrNi	-0.37	0.09		4 <i>c</i>	oct	4/2
Zr ₅ Sn ₃₋₄	-0.38	0.08	±0.14	2 <i>a</i> /2 <i>b</i>	tri/oct	3-6/—
Zr ₂ Fe	-0.45	-0.01		16 <i>l</i>	tet	4/—
Zr ₂ Cu	-0.52	-0.06		4 <i>d</i>	tet	4/—
Zr ₂ Ni	-0.67	-0.20		16 <i>l</i>	tet	4/—
Zr ₃ Sn	-0.64	-0.18		6 <i>d</i>	tet	4/—
Zr ₃ Fe	-0.74	-0.27		8 <i>f</i>	tet	4/—

offer a greater Zr-neighbour fraction compared to the available tetrahedral sites, which have 2 Zr and 2 Cu/Ni neighbours.

In the ZrM₂ phases, little variation in the accommodation of H was observed between the three Laves structures C14, C15 and C36, therefore the results from ZrM₂ simulations have been condensed into a single value for each element and the statistical error is reported. Similarly, the three models of the Zr₅Sn_{3+x} phase were reported as one (the exact values of $E_{sol}(H)$ were -0.56, -0.34, 0.23 eV for $x = 0.0, 0.5, 1.0$ respectively). For the case of Zr₅Sn₄, the lowest energy site was the only unoccupied 2*b* Wyckoff site. It is reasonable to expect a large number of unoccupied Sn self-interstitial sites in this phase, therefore the defect energy was calculated as an interstitial defect into a phase with one unoccupied Sn self-interstitial site, rather than the substitutional H_{Sn} defect in the fully occupied Zr₅Sn₄ structure.

Zr₅Sn_{3+x}, exhibits two preferred sites: the 2*a* site between 3 Zr atoms (white small spheres in Figure 3.6), and, directly above and below it, the 2*b* site between 6 Zr atoms (black

small spheres in Figure 3.6). The relative preference for H in one site over the other changes as a function of Sn content. At a content of three Sn atoms per formula unit, the trigonal $2a$ site is preferred (-0.56 eV against -0.39 eV of the octahedral site). As the Sn content increases to 3.5, half of the $2b$ sites are occupied by the excess Sn. The presence of a Sn atom in the $2b$ site, causes a reduction in space in the neighbouring $2a$ sites, while only marginally affecting the configuration of other (unoccupied) $2b$ sites in the cell. This is reflected in the solution of H in the two sites: the $2a$ site becomes significantly less favourable (-0.27 eV), while the $2b$ provides a similar solution enthalpy as in the previous case (-0.34 eV). In the case of Zr_5Sn_4 all of the $2b$ sites are occupied, consequently the $2a$ sites are compressed by two Sn atoms, one above and one below, reducing the volume available for accommodation of H even further, and the enthalpy associated with accommodating an H atom in that site becomes positive and large (2.06 eV).

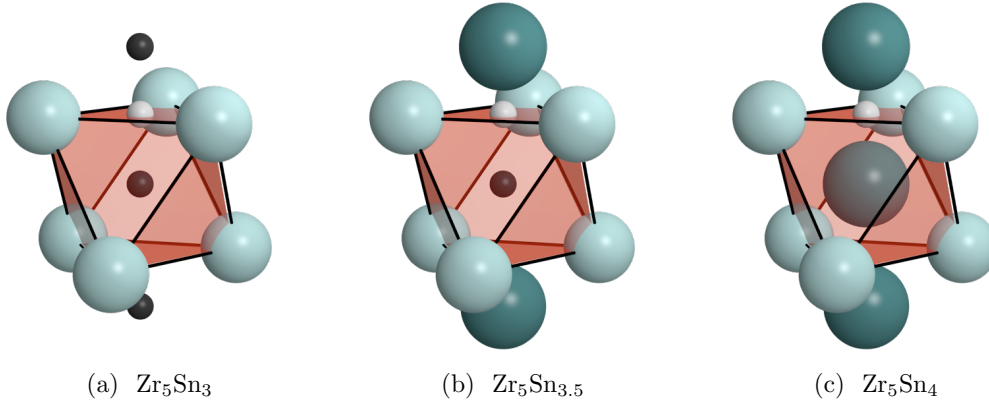


Figure 3.6: Local environment of the $2a$ (light small sphere) and $2b$ (dark small sphere) interstitial sites as a function of Sn content (large dark green spheres).

The current work shows that β -Zr accommodates H more readily than α -Zr (in agreement with experimental data [264]), and that β -Nb exhibits the same value of $E_{sol}(\text{H})$ as α -Zr. This suggests that, if the β -(Nb,Zr) solid solution found in binary Zr-Nb alloys behaves similarly to its two end members, those alloys do not contain any strong sinks for H. Nevertheless, the formation of metastable ZrNb_2 phases may affect this, as discussed below.

Regarding the ZrM_2 Laves phases, the solution enthalpy of H generally decreases with increasing number of d electrons in the transition metal M: from highest to lowest affinity Nb, V, Cr, Mo and Fe. The same trend has been observed with respect to H solution

capacity [69]. Whilst H does not prefer to dissolve in the Laves phases containing the latter three elements (i.e. Cr, Mo, and Fe) compared to α -Zr, the intermetallics formed with either Nb or V offer favourable sites for the accommodation of H. This suggests that if these binary SPPs are present in the cladding, H will likely segregate to them, which may deplete the H content in the zirconium metal. The beneficial effect of the H sinks may, however, be limited to the initial stages of the fuel cycle. At higher burnups, the intermetallic particles are likely to dissolve, amorphise or oxidise (see chapter 4), thereby releasing any stored H.

In addition to ZrNb_2 and ZrV_2 , all Zr-rich phases provided lower $E_{\text{sol}}(\text{H})$ values compared to α -Zr. Furthermore, for each element where more than one stoichiometric phase is present (Cu, Fe, Ni and Sn), those with the largest Zr/M ratio provided the lowest solution enthalpy for H (see Figure 3.7). Zr is known to exhibit higher affinity for H compared to Cu, Fe and Ni (see the extremes of Figure 3.7), therefore a decrease in enthalpy of solution with increasing Zr content is expected. However, from a volumetric standpoint, intermetallic phases have a lower packing fraction compared to the pure metals, offering a larger number of interstitial sites with varying amounts of space. For this reason intermetallic phases are expected to exhibit lower defect volumes (and associated strain fields) when accommodating an H interstice. As a result of the two competing processes — chemical bonding and volumetric effects — the lowest solution enthalpies are found, as mentioned above, for Zr-rich intermetallic phases that provide interstitial sites with 4-fold Zr-coordination.

Unlike other alloying additions, Fe forms a wide range of intermetallic compounds, and their relative stability is greatly affected by other alloying elements: $\text{Zr}_2(\text{Fe},\text{Ni})$ SPPs are commonly observed in the absence of Cr additions, while in Cr-containing alloys, $\text{Zr}(\text{Cr},\text{Fe})_2$ Laves phases become the dominant SPPs [31]. In the presence of Nb, hexagonal $\text{Zr}(\text{Nb},\text{Fe})_2$ Laves phases and cubic $(\text{Zr},\text{Nb})_2\text{Fe}$ phases have been reported [22]. Similarly, the few records of Sn-Zr SPPs also report some Fe solubility into these particles [239, 249, 260]. This suggests that the addition of Fe does not influence which intermetallic phases form, rather it will go into solution in all or most of the SPPs present. Assuming that a ternary phase behaves similarly to its binary end members, solution of Fe in ZrM_2 Laves phases and Zr_2X phases, is expected to reduce their affinity to H, since ZrFe_2 and Zr_2Fe exhibit

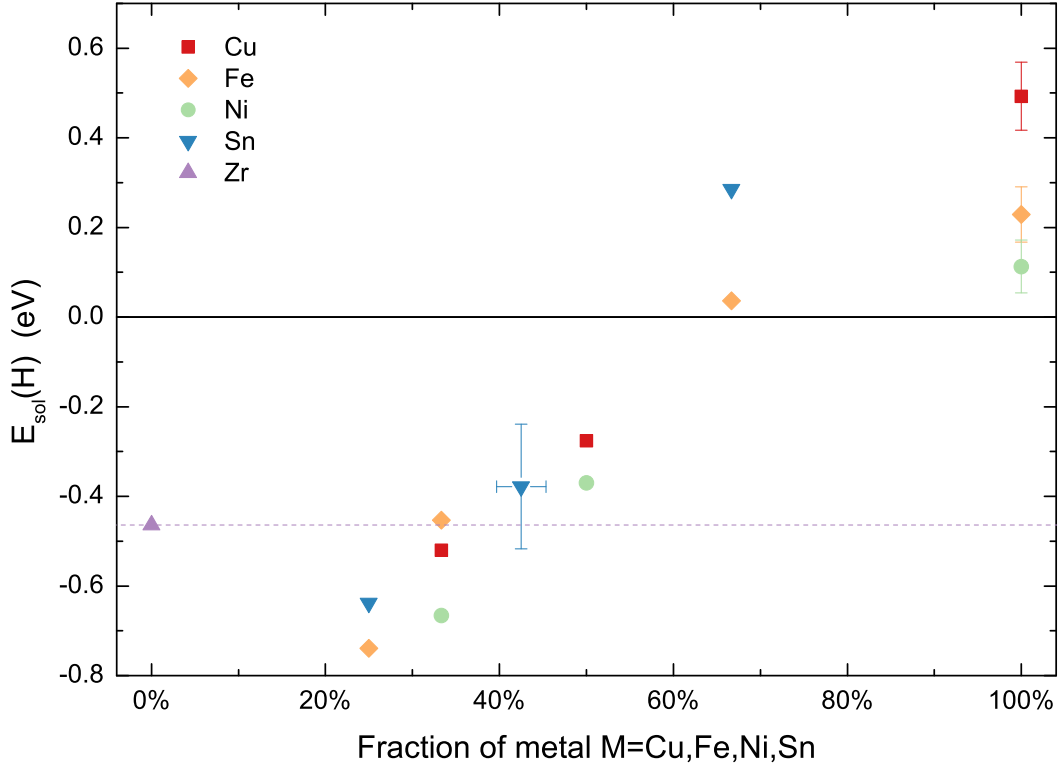


Figure 3.7: Enthalpy of H solution *vs.* fraction of non-Zr metal in compound. The error bars on the $\text{Sn}_5\text{Zr}_{3+x}$ arise from the condensation of different stoichiometries into a single value, as discussed in the text regarding Table 3.4. Values for the pure metals M were taken by averaging previous experimental and previous DFT work [265, 266]. No published results are available for H in Sn.

less favourable $\Delta E_{\text{sol}}(\text{H})$ compared to all other phases with the same stoichiometry and structure (i.e. ZrCr_2 , ZrMo_2 , ZrNb_2 , ZrV_2 , Zr_2Cu and Zr_2Ni). The opposite can be said for the Zr_3Fe -type SPPs.

Owing to the fact that both ZrCr_2 and ZrFe_2 have unfavourable $\Delta E_{\text{sol}}(\text{H})$ values, it is predicted that the ternary $\text{Zr}(\text{Cr,Fe})_2$ phase, found predominantly in Zircaloy-4, does not getter H from the surrounding α -Zr. As for the $\text{Zr}_2(\text{Fe,Ni})$, which is the predominant SPP in Zircaloy-2, both of its binary end members offer favourable solution enthalpies for H. Nonetheless, the difference in affinity to H with respect to α -Zr is rather small (on the order of 0.1 eV), and is expected to diminish with increasing Fe content. Such small differences in energy may easily be overcome by thermal and entropic effects, consequently $\text{Zr}_2(\text{Fe,Ni})$ are not expected to be strong sinks for H in solution.

Whilst it is possible to speculate on the behaviour of ternary phases where both binary end members have either positive or negative $\Delta E_{sol}(\text{H})$ values, it is much harder to predict the H affinity of other ternary SPPs in which one end member favourably accommodates H and the other does not, such as $\text{Zr}(\text{Nb},\text{Fe})_2$ found in ZIRLO alloys. It is possible, however, to expect that the behaviour of such SPPs is strongly correlated with their chemical composition, and more specifically the Nb/Fe ratio of the intermetallic particle. If $\frac{\text{Nb}}{\text{Fe}} \gg 1$ then the SPPs may act as H sinks, whilst with a composition of $\frac{\text{Nb}}{\text{Fe}} \ll 1$ they are not likely to accommodate any H.

Under irradiation, Fe has been reported to diffuse out of the SPPs faster than other elements (see chapter 4). In the case of Laves phases, and especially Nb-containing Laves phases, the current work suggests that this would increase the affinity of the residual SPP for H. However, concomitantly to the dissolution of Fe, the SPPs are reported to amorphise and at present it is impossible to predict how this will affect the interaction between H and the SPP.

3.5 Summary

DFT simulations were performed to investigate the solubility of H in α -Zr and in the second phase particles that may form in Zr alloys. Considering first the H-Zr system, it was shown that the method used in the current work successfully reproduced — and improved on — previous computational work. A large body of electronic structure calculations were performed on the Zr-H system (both dilute solutions and hydride phases), which are being used to develop tight binding potentials for larger-scale simulations. In particular, it was observed that the H-Zr bonding is not isotropic, with a stronger bond forming in the c -axis, which also affects the geometry of the most favourable site for H accommodation in α -Zr (tetrahedral interstitial). Models employing a lower level of theory, such as tight binding and bond order methods, should incorporate such anisotropic behaviour if they are to successfully represent H-Zr interactions.

The solubility of H in the binary SPPs that Zr forms with Cu, Cr, Fe, Mo, Nb, Ni, Sn and V was then considered. H solution in the intermetallics exhibit similar feature to its

solubility in pure Zr (α and β): the most stable site for H accommodation was often an interstitial site with tetrahedral coordination. In addition, the sites with the largest fraction of neighbouring Zr atoms exhibit the lowest solution enthalpy.

The most common type of SPPs are Laves phases with composition Zr_2M ($M = Cr, Fe, Mo, Nb, V$). The presence of Nb or V is predicted to increase the affinity of H to Laves SPPs, whilst the presence of Cr, Mo and Fe will reduce it. $Zr(Cr,Fe)_2$ SPPs found in Zircaloy-4 are predicted to have very unfavourable solution enthalpies for H and therefore not to accommodate any H. It may, however, act as a bridge for fast diffusion of H through the oxide layer. The affinity to H of the $Zr(Nb,Fe)_2$ SPPs, present in ZIRLO alloys, is expected to vary strongly with Nb/Fe ratio: high Nb content SPPs are expected to trap H, whilst high Fe content SPPs will reject it.

Fe is observed to dissolve into most binary SPPs to form ternary phases. $ZrFe_2$ and Zr_2Fe exhibit less favourable solution enthalpy for H compared to all other binary ZrM_2 and Zr_2M phases. The opposite can be said for Zr_3Fe . Cu, Ni and Sn additions may form a number of binary intermetallic phases, but tend to stabilise as Zr-rich phases. All Zr-rich phases, namely Zr_3Fe , Zr_2Ni , Zr_2Cu and Zr_3Sn , provide lower energy sites for H accommodation, compared to α -Zr, suggesting that their presence in the alloy could provide sinks for H. However, the most energetically favourable of the Zr-rich phases, $Zr_2(Fe,Ni)$ found mainly in Zircaloy-2, exhibits an affinity to H similar to that of α -Zr, and are therefore is not expected to strongly getter H from their surroundings.

In addition to the intermetallics SPPs, β -(Zn,Nb) particles have been considered: pure β -Zr exhibits more favourable solution enthalpy for H relative to α -Zr, however the difference is predicted to diminish in the presence of Nb, to the extent that pure β -Nb exhibits the same affinity for H as α -Zr. Therefore, β -(Zn,Nb), which commonly contain $\sim 80\%$ Nb, are also not predicted to be strong sinks for H. Temperature effects and entropy, which are not considered in the current methodology, may play a decisive role in these cases where the enthalpy alone does not provide a decisive picture.

4

Cr and Fe additions in Zr

Part of the work presented in this chapter has been submitted for publication, ref [267]

4.1 Introduction

Zr-alloys commonly contain Fe and other transition metals such as Cr or Ni (see section 1.2). These elements exhibit very limited solid solubility in α -Zr, and therefore precipitate out into SPPs [23–31]. One of the key aspects of the microstructural evolution of Zr alloys under irradiation is the amorphisation and subsequent dissolution of SPPs [244, 260, 268–275]. Consequently, the alloying elements are re-dissolved into the Zr matrix above their solubility limits. In turn, this has an impact on the physical, mechanical and corrosion properties of the alloy. In particular, surface oxidation and hydrogen pick-up fraction are known to be strongly affected by alloy composition and the presence and distribution of SPPs [40, 48, 60, 213, 276, 277].

Recent advances in high resolution techniques — such as ChemiSTEMTM and atom probe tomography (APT) — have shown that clusters of Fe and Cr form in irradiated samples, and that these are found mainly in the vicinity of dislocation loops and other crystal defects [278–280].

The solubility of Fe in Zr — and to a lesser extent also that of Cr and Ni — has also been investigated using atomic scale simulations, but so far, the clustering behaviour of alloying elements has hardly been considered using such methods. Early work by Per   and Weissmann [281] investigated the interaction between Fe and vacancies within a small supercell of α -Zr coating 36 atoms. Their results show the interstitial tetrahedral site to be the favourite site for Zr accommodation, followed by the octahedral interstitial and then the substitutional sites. Confusingly, the text of the publication is in contradiction to the values reported in their tables. The same authors then published another paper in which the possible mechanisms for Fe accommodation in the α -Zr lattice were investigated further and in a slightly larger supercell containing 48 Zr atoms [282]. In particular, they observed that when Fe substitutes for Zr, it occupies a low symmetry configuration that is displaced slightly from the lattice site. More recent studies have employed similar or slightly larger supercells (54 Zr atoms by Lumley *et al.* [30] and 48 Zr atoms by Christensen *et al.* [283, 284]), but only the more conventional interstitial sites (tetrahedral and octahedral) were considered again.

It is generally acknowledged that Fe preferentially occupies interstitial sites in α -Zr, as confirmed by diffusivity measurements [285–287]. Previous DFT calculations are in general agreement with the experimental observations, with the exception of the work by Christensen *et al.* [283], in which it is claimed that a high-symmetry high-spin substitutional defect is the most stable defect for accommodation of Fe. Direct comparison of the findings from the literature is made difficult due to the fact that some authors do not report conventional quantities such as formation energies, instead, the difference in energy between each defect and the substitutional defects (Fe_{Zr}) is presented, as in Table 4.1.

Table 4.1: Difference in energy between the interstitial defects (octahedral and tetrahedral) and the substitutional defect from DFT literature. Negative values imply interstitial sites are favourable.

Ref	simulation details*	ΔE_f in eV	
		oct	tet
Per��z and Weissmann [281]	PP-LO-LDA-36	−0.10	−0.98
Pasianot <i>et al.</i> [282]	PP-LO-LDA-48	−0.36	—
Pasianot <i>et al.</i> [282]	FP-LAPW-LDA-48	−0.38	—
Pasianot <i>et al.</i> [282]	FP-LAPW-GGA-48	−0.014	—
Lumley <i>et al.</i> [30]	PP-PW-GGA-54	−0.86	−0.76
Christensen <i>et al.</i> [283]	PAW-PW-GGA-48	0.10	0.63

* PP: pseudopotentials, FP: full potentials, LO: local-orbit, LAPW: linearised augmented plane waves, PW: plane waves, PAW: projector-augmented waves. The number is the cell size in terms of Zr atoms.

A large number of recent DFT studies have investigated intrinsic defects in pure (unalloyed) Zr metal [180, 288–293]. Numerous configurations of self-interstitial atoms (SIAs) were found to be stable with comparable energies, many of which exhibit non-conventional geometries. It was also remarked by many authors [180, 288–291] that finite size effects — that is the interaction of defects with their periodic images — may significantly affect the apparent stability of defects in α -Zr. In particular Varvenne *et al.* [180], showed that supercells containing up to ~ 300 atom may be required to avoid significant artefacts if no correction term is applied. This is significantly more than the number of atoms that has been previously used when simulating extrinsic elements (e.g. Fe or Cr) in Zr, see Table 4.1. It is evident that a state-of-the-art re-evaluation of extrinsic defects in Zr is required.

The chapter is structured as follows: after a brief summary of the computational details (section 4.2), the point defects related to the solution of Fe and Cr in Zr are investigated in section 4.3 and compared to previous work. Then the relaxation volumes of the defects are

considered in section 4.4, and from those, the lattice expansion due to alloying additions is predicted and compared to experimental observations. The dependance of defect energies to external strain is also considered in section 4.4, which leads to the investigation of defect clusters in section 4.5. Finally, in section 4.6, conclusions are drawn and discussed with respect to the microstructural evolution of irradiated Zr alloys.

Much of the value of the work presented in this chapter resides in the synergistic collaboration between simulations and experiments (see [267]). Some of the experimental observations are integral part of the study, and therefore are also reported in this chapter, but at all times it is clearly stated that the experimental work presented here was carried out by others.

4.2 Computational details

To overcome the issue of self-interaction due to periodic boundaries in defect simulations, the *aneto* finite size correction [180] was employed (see section 2.2). Varvenne *et al.* [180] showed that by applying such correction term, supercells containing 200 Zr atoms were sufficient to accurately describe Zr self interstitial atoms (SIAs), and supercells containing only 96 Zr atoms reported yielded errors of only 40–150 meV.

All the defects considered in the current work are significantly smaller than Zr SIAs, providing confident that a supercell contain more than 96 Zr atoms yields converged results. Therefore a $5 \times 5 \times 3$ supercell of the HCP unit cell — containing 150 Zr atoms — was employed. As further evidence that the supercell is sufficiently large, all calculations were repeated at constant volume ($\varepsilon = 0$) and constant pressure ($\sigma = 0$), and the difference in energy between the two approaches was consistently less than 10 meV.

The *aneto* correction is sensitive to the elastic constants of the material, which are supplied by the user. For sake of consistency, the elastic constants of α -Zr, were also evaluated within DFT by performing small lattice perturbations of the unit cell. These are reported in section 2.7 together with experimental values.

4.3 Solubility of Fe and Cr in α -Zr

Many interstitial positions, as well as the substitutional and dumbbell configurations were considered. The resulting formation energies ($E_f^{\varepsilon=0}$), relaxation volumes ($\Delta\Omega^{\varepsilon=0}$) and anisotropic strains on the supercell ($\varepsilon_{11}^{\sigma=0}$, $\varepsilon_{33}^{\sigma=0}$) are reported in Table 4.2 for all stable defects. The relative preferences of the interstitial sites, with respect to the substitutional site, (ΔE_f) are also reported to aid comparison with literature values (see Table 4.1). $E_f^{\sigma=0}$ and $\Delta\Omega^{\sigma=0}$ were within 0.07% and 3.7% of $E_f^{\varepsilon=0}$ and $\Delta\Omega^{\varepsilon=0}$ respectively, and are therefore omitted. $E_f^{\varepsilon=0}$ is also represented graphically in Figure 4.1 by the points lying on the $x = 0$ line (i.e. no applied pressure). Some interstitial positions were found to be unstable, that is, the defects moved to another site upon relaxation; these include the tetrahedral positions, which was reported as a stable site by all previous DFT publications, and the hexahedral position (also termed basal tetrahedral by some authors). The tetrahedral defect appeared stable also within the current work when a smaller supercell (48 Zr atoms) is adopted. If, however, larger supercells are used, the tetrahedral site relaxed into the newly observed crowdion configuration. The substitutional defect consistently relaxed to the off-site substitutional position discussed in [281], therefore the high-symmetry substitutional defect observed by Christensen *et al.* [283] is also considered unstable in the current work. The current work identifies another interstitial site that has not previously been simulated: the off-site octahedral. Mössbauer studies [294] suggested that $\sim 30\%$ of the total Fe in solution is located in off-centre sites such as this. This low-symmetry site is significantly more stable than any other interstitial site for Fe, therefore its identification is of importance to Fe accommodation and diffusion. However, this site is found to be unstable for the accommodation of Cr, which is consistent with the larger atomic radius of Cr.

Regarding the accommodation of Fe, all interstitial sites provide more favourable solution energy than the substitutional site. This is in agreement with experimental diffusivity measurements [285–287], and all previous DFT calculations [30, 281, 282] with the sole exception of the work by Christensen *et al.* [283]. On the other hand, Cr preferentially occupies the substitutional site, however, the difference in energy between that and the interstitial octahedral site is very small, and therefore Cr is expected to exhibit both

Table 4.2: Defect formation energy (E_f) and volumetric properties for all defects that may accommodate Fe or Cr in bulk α -Zr. The energy difference between each interstitial defect and the substitutional (ΔE_f) is also provided to aid comparison with previous literature values (see Table 4.1). ε_{11} and ε_{33} are the strain in the a and c direction respectively.

		substitutional	octahedral	off-site oct	trigonal	crowdion
Fe	E_f (eV)	1.388	1.079	0.941	1.212	1.172
	ΔE_f (eV)		-0.307	-0.445	-0.175	-0.215
	$\Delta\Omega$ ($\text{\AA}^3$)	-10.40	13.70	13.53	13.42	13.52
	$\varepsilon_{11}\%$	-0.15	-0.02	-0.07	0.18	0.10
	$\varepsilon_{33}\%$	0.15	0.27	0.25	-0.26	0.09
Cr	E_f (eV)	1.732	1.882	—	1.968	2.061
	ΔE_f (eV)		0.151	—	0.215	0.318
	$\Delta\Omega$ ($\text{\AA}^3$)	-11.31	15.20	—	13.65	15.41
	$\varepsilon_{11}\%$	-0.03	-0.05	—	0.16	0.15
	$\varepsilon_{33}\%$	-0.21	0.30	—	-0.17	0.08

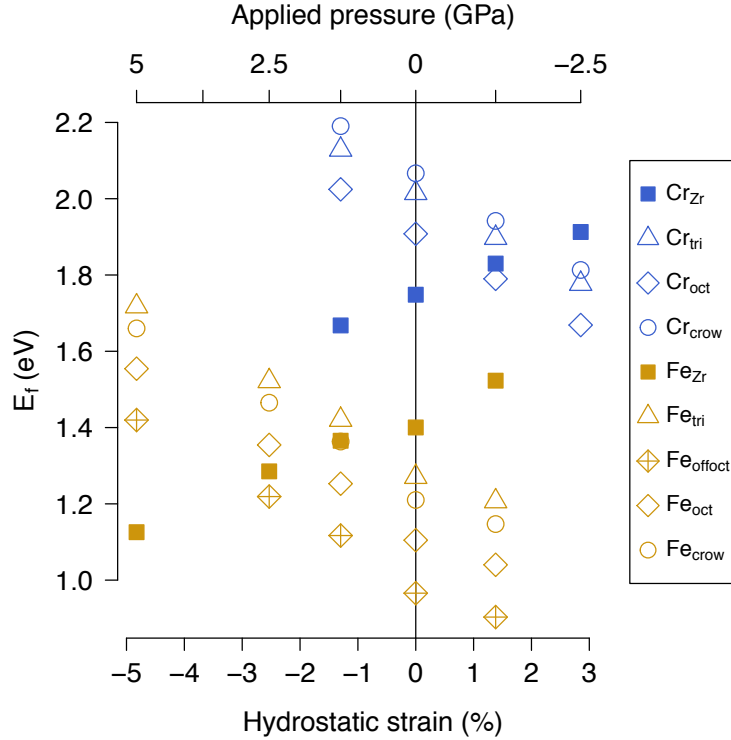


Figure 4.1: Enthalpy of formation of Fe (beige) and Cr (blue) defects as a function of hydrostatic strain. Hollow symbols are interstitial species and filled symbols are substitution species. The simulation cells were strained prior to adding the defect, by applying an external hydrostatic pressure, displayed in the secondary x -axis above (positive = compressive).

substitutional and interstitial accommodation. Experimental diffusivity measurements indicated that Cr diffuses 2–4 orders of magnitude slower than Fe in α -Zr. However, Fe is reported to diffuse 6–9 orders of magnitude faster than for Zr self-diffusion and 9–16 orders of magnitude faster than substitutional solutes [286, 287, 295, 296]. This suggests that the transport of Cr in the α -Zr lattice may yet be mediated by an interstitial solute. Furthermore, APT studies provide substantial evidence of the dual nature of Cr, see [267] and Appendix A.

4.4 Lattice expansion of binary alloys

When mixing two metals, the host (solvent) lattice is expected to expand or contract depending on the difference in atomic radii of between the solvent and the solute. The simplest approximation of such volumetric change is known as Vegard’s law, in which the lattice parameter of a given composition is extrapolated linearly from the end members of the solid solution. Although simple, Vegard’s model is known to provide a reasonable description of various binary FCC and BCC alloys, especially in the dilute regimes, but it has also proved to be inadequate for complex systems [297–300].

Another means of predicting lattice expansion is through the evaluation of defect volumes by means of atomistic simulations. Starting from the defect relaxation volumes presented in Table 4.2, the strains on the cells were calculated (also presented in Table 4.2). The conversion to lattice strains instead of lattice parameters directly, allows for the cancellation of exchange-correlation errors, which would otherwise result in an overestimation of the lattice parameters (see Section 2.1.3). Thermodynamically, the most stable defect is the most likely to form, however, at finite temperatures all defects have *some* probability of occurring. This probability is calculated using an Arrhenius-type equation (see section 2.3) and the predicted defect distribution is presented in Figure 4.2.

By taking the configurational average of all the defect volumes with respect to their probability of occurring (also discussed in section 2.3), the *average* average effect on the Zr lattice is obtained. The resulting strains may be considered as the average strain caused by an alloy concentration of 0.67 at.%, i.e. 1 Fe or Cr for every 150 Zr atoms. Assuming

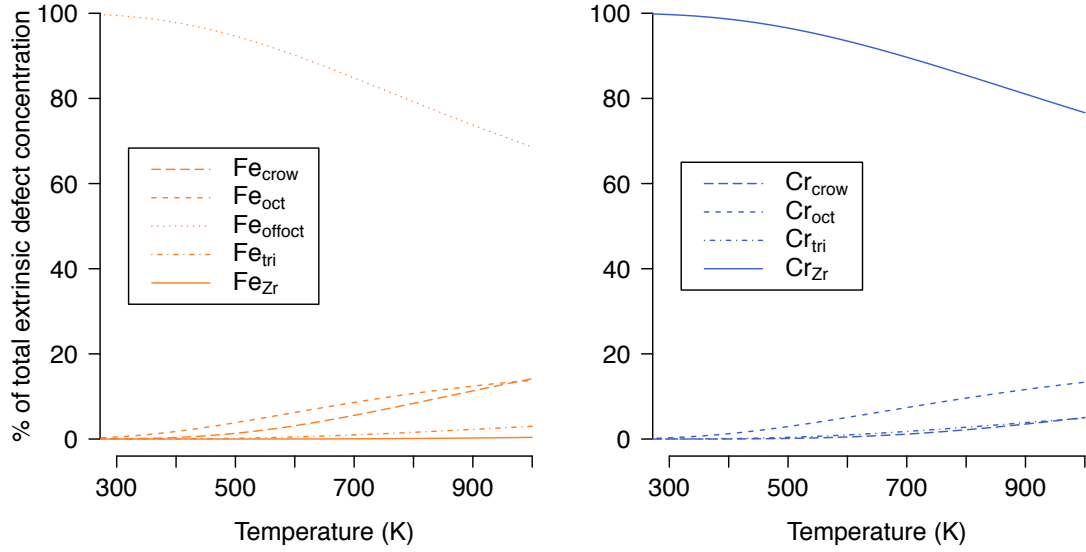


Figure 4.2: Distribution of defect configurations as a function of temperature, assuming dilute non-interacting behaviour and equilibrium conditions.

that within the dilute limit, a small change in concentration yields a locally linear change in lattice expansion, then the lattice parameters of a binary alloy can be estimated for a range of (dilute) compositions. Configurational averaging was performed at 25 K, 300 K and 600 K. This averaging technique does not include other temperature effects such as thermal expansion or phonon scattering. In other words, the model represents a solution that has been homogenised at said temperatures and subsequently quenched, in line with a conventional experiment to measure the lattice expansion. The predicted lattice expansion is presented as dotted lines in Figure 4.3, together with Vegard's Law (dashed line) and experimental measurements carried out by colleagues in Manchester¹.

The experimental procedure used are presented in appendix A and in Ref [267, 301, 302], and summarised thus: samples of binary Zr-Fe and Zr-Cr alloys were triple-melted, punched, and β -quenched at high cooling rates in an attempt to trap most alloying additions in the α -Zr matrix. Lattice parameters were measured by conventional XRD methods with high count rate and long sampling times, to achieve the necessary high accuracy. Nonetheless, the signal-to-noise ratio was too high for accurate prediction of the c -axis. Furthermore, despite the fast quenching procedure, microscopy investigation showed the presence of SPPs in

¹M. Ivermark and M. Preuss [301]

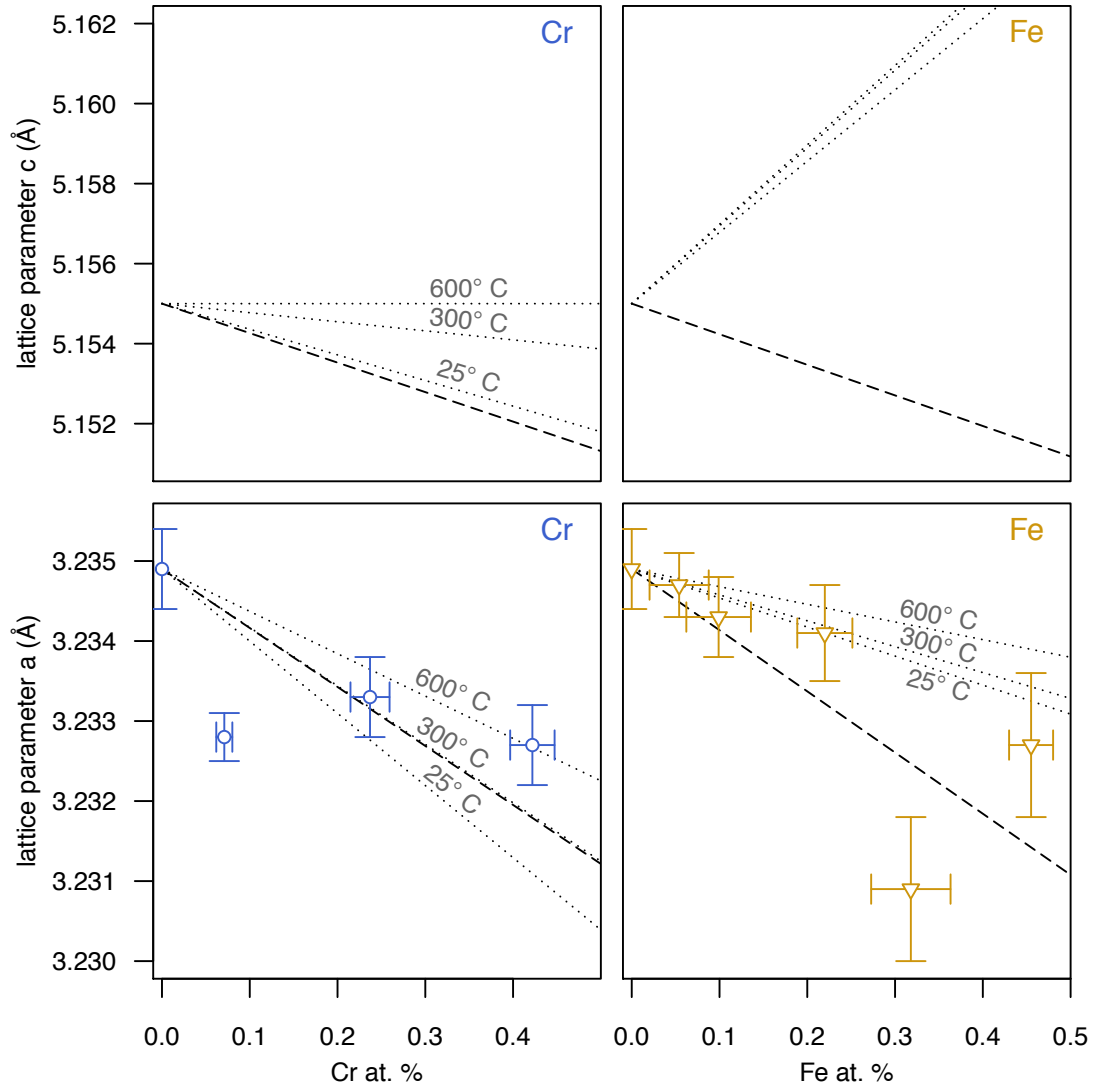


Figure 4.3: Predicted (lines) and experimental (points) lattice parameters a and c as a function of alloying element in solution. Dashed line represents Vegard's law extrapolated from elemental Cr, Fe and Zr; dotted lines represent DFT prediction through configurational averaging of dilute defect simulations.

all binary samples, therefore the nominal composition was not representative of the solute concentration in the HCP matrix. However, thermoelectric power (TEP) measurements indicated that an increasing amount of Fe and Cr were trapped in solution with increasing nominal level of alloying additions. In order to quantify the solute concentrations, TEP measurements were calibrated using APT information obtained for one sample of each binary system by colleagues in Oxford² (calibration procedure outlined in appendix A). The cumulative uncertainties from APT, TEP and XRD measurements are reported as error bars in Figure 4.3.

Figure 4.3 shows that, for Cr-Zr solution, both Vegard’s law and the DFT predictions are in good agreement with experimental observations. However, for the Fe-Zr solution, DFT predictions differ greatly to Vegard’s law: for the a lattice parameter, DFT predictions are in better agreement with experimental data at low concentrations (near the solid solubility of Fe in Zr) whilst Vegard’s law provides a better fit at higher concentrations. For the c lattice parameter, DFT results are in contrast to Vegard’s law in that the lattice is calculated to expand whilst Vegard’s law predicts a contraction of the lattice. Unfortunately, XRD data for the c lattice parameter were inconclusive as the low multiplicity of the c direction caused significant scatter in the data.

When performing the configurational average, it is implicit that the defects are not interacting; therefore, strictly, the average is valid only at the dilute limit. Since the concentrations investigated in Figure 4.3 are beyond the solid solubility limit of Fe and Cr in α -Zr [24, 27], it is reasonable to assume that the alloying atoms are interacting with each other. More specifically, the compressive strain field of an interstitial defect is likely to increase the formation energy of another interstitial defect in its vicinity, whilst reducing that of a substitutional defect (which, due to its negative relaxation volume, produces a tensile strain field). This hypothesis was corroborated by repeating the defect simulations in pre-strained supercells; see Figure 4.1. Under a compressive strain, the stability of substitutional defects (filled squares) increases while that of interstitial defects (hollow symbols) decreases; and the opposite is true under a tensile strain.

As well as affecting the relative formation energies, the strain fields of the point defects

²B. Gault *et al.* [302]

may provide a driving force for diffusion: defects with opposing strain fields may attract each-other at distances of up to a few Angstroms, whilst defects with same-sign strain fields will repel one another. When combined with the extreme mobilities of Fe and Cr [282, 285, 303], this may lead to the formation of defect clusters with a reduced overall lattice strain (and lattice expansion) and consequently a reduced solution energy.

4.5 Cluster formation

To investigate the formation of Fe and Cr clusters, simulations containing two extrinsic species were first considered. The starting positions for the clusters were defined by combining a substitutional defect (M_{Zr}) with and an octahedral or off-site octahedral interstitial defect ($M_{i(oct)}$ or $M_{i(oct')}$), since these are the most stable defects with opposing strain fields for Cr and Fe respectively (see Table 4.2 and Figure 4.1). All such configurations that could fit in a $5 \times 5 \times 3$ supercell of α -Zr (150 Zr atoms) were investigated, leading to defect-defect separations that range from 2.30 Å for the first nearest neighbour (1nn) to 6.97 Å for the 7nn configuration. When considering mixed Fe-Cr clusters, the Cr atoms were placed in the substitutional sites and the Fe atoms in the interstitial sites, $\{Cr_{Zr} : Fe_{i(oct')}\}$, owing to the smaller atomic radius of Fe and its preference for interstitial sites (see section 4.4). The cluster simulations were relaxed to a high level of force convergence ($0.05 \text{ eV \AA}^{-1}$) and the atomic positions were perturbed by small amounts in random directions prior to minimisation. Furthermore, to provide greater degrees of freedom to the simulations, these were repeated under $\sigma = 0$ conditions as well as $\varepsilon = 0$ conditions. This combination of procedures means that the BFGS minimiser [194, 195] is unlikely to trap atoms in local energy minima. In other words, the starting positions are just that, and the extrinsic atoms were expected to explore the energy surface until lowest energy configurations were found.

Figure 4.4 shows the initial and final configurations of some clusters that have moved from their original lattice sites. In all cases, the resulting defect is an elongated or extended defect, often involving one or more Zr SIAs. Most notably the 1nn clusters moved into a split substitutional (or dumbbell) around a Zr lattice site. With regards to the other

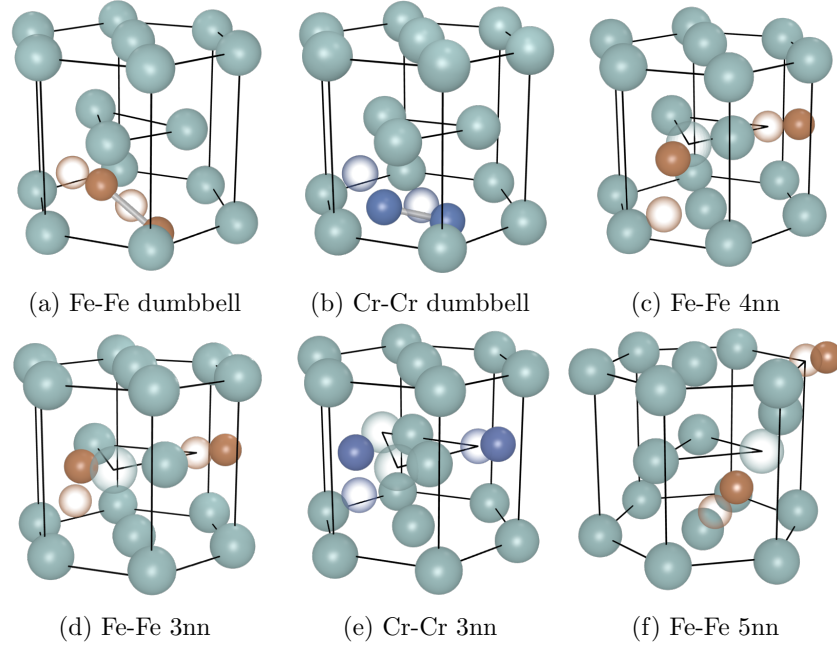


Figure 4.4: Brown spheres represent Fe atoms, dark blue spheres represent Cr atoms, turquoise spheres represent Zr atoms, translucent spheres represent the initial position of selected atoms.

configurations, a general trend has also been observed by which defects that could reach a common basal plane (2nn, 3nn and 4nn), irrespective of the species involved, and the entire cluster was contained within the basal plane with only minor distortions in the c direction.

Dumbbell defects have been reported for Zr SIA [291, 293], but never before for extrinsic elements in Zr. A short description of the dumbbell configuration, and comparison with the SIA dumbbells follows. Here we employ the nomenclature introduced by V  rit   *et al.* [291], to describe the orientation of the dumbbell with respect to the Zr lattice: vertical (S), basal (BS), rotated on prismatic plane type I (PS, PS', PS'', etc. if more than one stable configuration exists at different rotation angles) and rotated on prismatic plane type II (P2S, P2S', etc.).

The Fe-Fe dumbbell is rotated in the prismatic plane type I ($11\bar{2}0$) by a tilt angle of 54.5° from the c -axis, similarly to the PS' defect observed in Zr SIAs (see Figure 4.5). The extrinsic dumbbell exhibited lower symmetry than the intrinsic counterpart: the Fe dumbbell is $\sim 0.25\text{\AA}$ out of plane with respect to the $(11\bar{2}0)$ plane, and also off-centre with respect to the host Zr vacancy so that the one Fe atom is closer to the vacancy than the other (i.e. the centre of the dumbbell is displaced by $\sim 0.005\text{\AA}$ along the direction of the dumbbell). These

simulations were repeated up to five times with different starting configurations and tight force convergence criteria to ensure that such subtle measurements were not artefacts caused by computational parameters. Other potential metastable positions were investigated by rotating the dumbbell with respect to the basal plane (see Figure 4.5). The energy change as a function of rotation angle is shown in comparison to the equivalent property for Zr SIA dumbbells, as reported by V  rit   *et al.* [291]. A metastable position was observed for the Fe dumbbell when rotated so that it would align vertically. Again the dumbbell is preferentially located $\sim 0.40\text{\AA}$ out of plane. This configuration is 0.861 eV less stable than the one described above, and was found to lie on a shallow minima near the transition state for rotation of the dumbbell. Unlike Zr SIAs, no other stable orientations were observed.

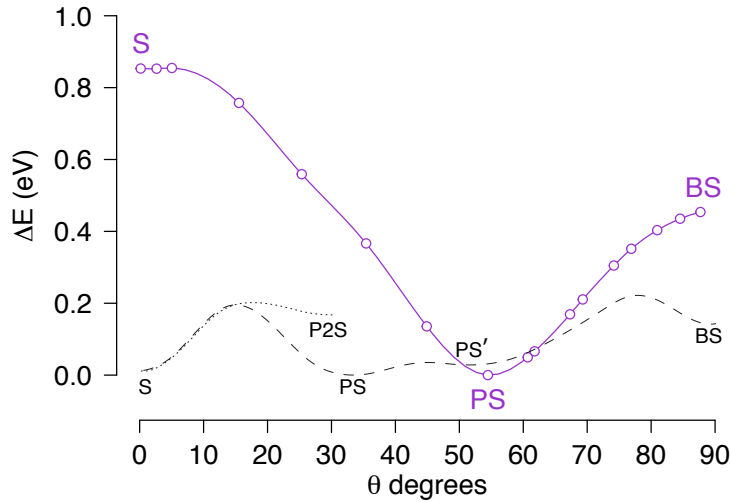


Figure 4.5: Change in energy as a function of polar rotation angle (θ) of extrinsic dumbbells. Purple points are from the current work’s nudged elastic band calculations, black lines show the equivalent energy landscape for Zr SIA dumbbells (from [291]), for rotations in the type I prismatic planes (dashed line) and type II prismatic planes (dotted line).

The Cr-Cr dumbbell exhibits a configuration similar to the P2S defect (as opposed to the PS’ of the Fe-Fe dumbbell), with a large tilt angle of $\theta = 76.4^\circ$. However, the defect is not exactly on the type II prismatic plane ($10\bar{1}0$), instead it exhibits a small deviation angle of $\psi = 8.2^\circ$ from the ($10\bar{1}0$) plane. Furthermore, the centre of the dumbbell is $0.172\text{\AA}$ below the Zr lattice. The mixed element dumbbell exhibits similar properties to the Fe-Fe dumbbell: it adopts the PS orientation with a larger tilt angle of $\theta = 65.9^\circ$, but in this case the dumbbell is in-plane but slightly off-centre (shifted $0.321\text{\AA}$ in the c -direction).

The difference between the dumbbells investigated here and SIA dumbbells is thought to be related to the different ionic sizes and electronegativity of the extrinsic elements. Whilst the differences may appear to be subtle, they are important for the development of accurate larger scale models, such as classical potentials for molecular dynamics, or kinetic Monte Carlo simulations. In particular, all extrinsic dumbbells exhibit only one strongly stable configuration, whilst intrinsic dumbbells exhibit multiple energy minima when rotated (Figure 4.5 and Ref. [291]). This may have implications for the diffusion of the clusters within the Zr matrix.

A summary of the formation energies, binding energies and relaxation volumes of all the 2-atom defects — in their final relaxed positions — are presented in Table 4.3. A graphical representation of the binding energies is also provided in Figure 4.6.

Table 4.3: Normalised defect formation energy (E_f/atom), binding energies (E_b), spin and relaxation volumes ($\Delta\Omega$), for all defect clusters investigated. The spin is the cumulative spin on the extrinsic elements calculated using Mulliken analysis [304]. $c[hkl]$ stands for a crowdion defect along the $[hkl]$ direction. Refer to the main text or to ref [291] for the nomenclature of the dumbbells.

	cluster type	spin ($\hbar$)	E_f/atom (eV)	E_b (eV)	$\Delta\Omega$ ($\text{\AA}^3$)
Fe-Fe					
1nn	dumbbell (PS')	0.00	0.32	-1.69	-2.49
2nn	$\{\text{Fe}_{\text{Zr}} : \text{Fe}_i\}$	1.50	0.79	-0.75	1.00
3nn	$c[10\bar{1}0]$	0.00	0.62	-1.08	-2.39
4nn	$c[11\bar{2}0]$	0.00	0.57	-1.18	-3.59
5nn	$c[20\bar{2}1]$	0.70	0.72	-0.88	-1.95
6nn	$\{\text{Fe}_{\text{Zr}} : \text{Fe}_i\}$	1.64	0.93	-0.47	2.32
7nn	$\{\text{Fe}_{\text{Zr}} : \text{Fe}_i\}$	1.65	0.96	-0.42	2.00
Cr-Cr					
1nn	dumbbell (P2S)	0.00	0.95	-1.95	1.92
2nn	$\{\text{Cr}_{\text{Zr}} : \text{Cr}_i\}$	2.30	1.26	-1.34	7.13
3nn	$c[10\bar{1}0]$	0.00	1.41	-1.03	1.81
4nn	$c[11\bar{2}0]$	2.26	1.31	-1.22	5.52
5nn	$c[20\bar{2}1]$	0.00	1.54	-0.76	2.07
6nn	$\{\text{Cr}_{\text{Zr}} : \text{Cr}_i\}$	2.29	1.37	-1.11	2.96
7nn	$\{\text{Cr}_{\text{Zr}} : \text{Cr}_i\}$	2.29	1.36	-1.11	7.91
Fe-Cr					
1nn	dumbbell (PS')	0.00	0.64	-1.77	-0.42
2nn	$\{\text{Cr}_{\text{Zr}} : \text{Cr}_i\}$	0.00	1.17	-0.70	0.66
3nn	$\{\text{Cr}_{\text{Zr}} : \text{Cr}_i\}$	2.32	0.89	-1.26	6.89
4nn	$c[11\bar{2}0]$	2.14	0.87	-1.31	-0.20
5nn	$c[20\bar{2}1]$	2.19	0.76	-1.52	5.40
6nn	$\{\text{Cr}_{\text{Zr}} : \text{Cr}_i\}$	0.00	1.36	-0.32	2.96
7nn	$\{\text{Cr}_{\text{Zr}} : \text{Cr}_i\}$	2.27	0.90	-1.25	6.34

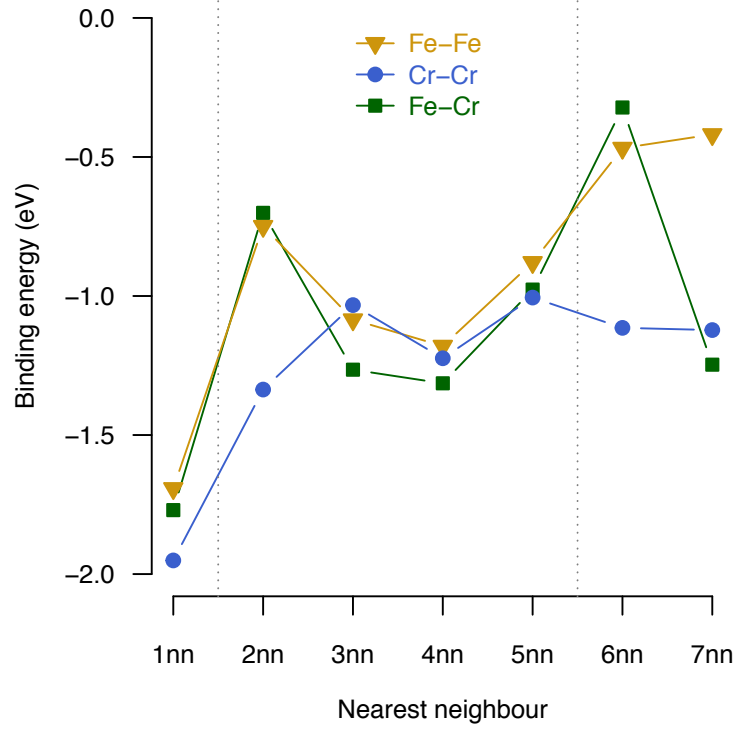


Figure 4.6: Binding energy of two-atom clusters with respect to the dilute counterparts. Vertical dotted lines represents groups at configurations that are a single jump away from the previous group.

In all cases the dumbbell defect (1nn) is consistently the most stable configuration, independent of the species involved, and the relative preference for the dumbbell is as high as 0.5–0.6 eV compared to the next most stable configuration. Importantly, all configurations up to the 5th nn are a single lattice jump away from the dumbbell configuration. Whilst this provides incomplete information about kinetics of cluster formation, it does imply that multiple paths exist for migrating isolated extrinsic species to reach (and be trapped in) the dumbbell configuration.

With regard to the lattice expansion, all two-atom clusters exhibit relaxation volumes that are significantly smaller than those of the single-atom dilute defects (presented in Table 4.2). Furthermore, the sum of the defect volumes for isolated Fe_{Zr} and Fe_i is $3.13 \text{ \AA}^3$, while that of the bound dumbbell is only $-2.49 \text{ \AA}^3$. Similarly for Cr, the sum of the defect volumes for the equivalent isolated defects is $3.81 \text{ \AA}^3$ compared with $-1.95 \text{ \AA}^3$ for the dumbbell. Finally, in the mixed case (in which Cr takes the substitutional site and Fe takes the off-oct interstitial site), the sum of the isolated defect volumes of is again greater

than that of the dumbbell ($2.50 \text{ \AA}^3$ against $-0.42 \text{ \AA}^3$). This suggests that part of the binding energy comes from a reduction of lattice strain.

Notably, many of the other Fe-Fe defect pairs also exhibit negative relaxation volumes, resulting in a tensile strain field, despite the addition of one extra atom in the supercell. In particular, the most favourable configurations (1nn, 3nn and 4nn) exhibit tensile strain fields arising from relaxation volumes of $-2.49 \text{ \AA}^3$, $-2.39 \text{ \AA}^3$ and $-3.59 \text{ \AA}^3$ respectively.

To investigate the stability of larger defect clusters, a third and then a fourth interstitial atom were added to the relaxed dumbbell configurations, as these are the most stable 2-atom clusters. The relaxed structure of these defects is shown in Figure 4.7. Notably, the $\{4M\}_{Zr}$ configuration — a tetrahedron of Fe or Cr around a Zr vacancy — resembles the structure observed in $ZrFe_2$ and $ZrCr_2$ Laves phases. The resulting solution energies (normalised per extrinsic atom) and defect volumes are presented in Figure 4.8. Clusters containing 3 and 4 Fe atoms exhibit similar solution energies to the 2-atom clusters. Furthermore, from Figure 4.8 (top) it is clear that even the least stable 2-atom clusters exhibit solution energies that are similar to the most stable dilute defect. The relaxation volumes of the clusters containing a Zr vacancy shows a fairly linear behaviour, see Figure 4.8 (bottom). As a result, clusters containing 3 Fe or Cr atoms cause a smaller expansion of the lattice than dilute interstitial Fe or Cr defects.

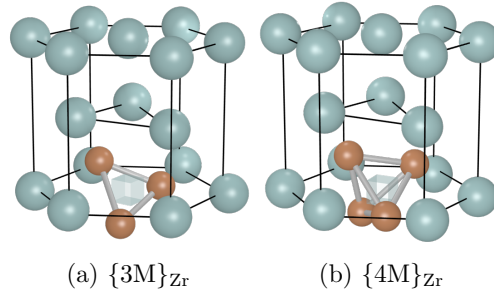


Figure 4.7: Brown spheres represent Fe or Cr atoms, turquoise spheres represent Zr atoms and the translucent cube represents the Zr vacancy.

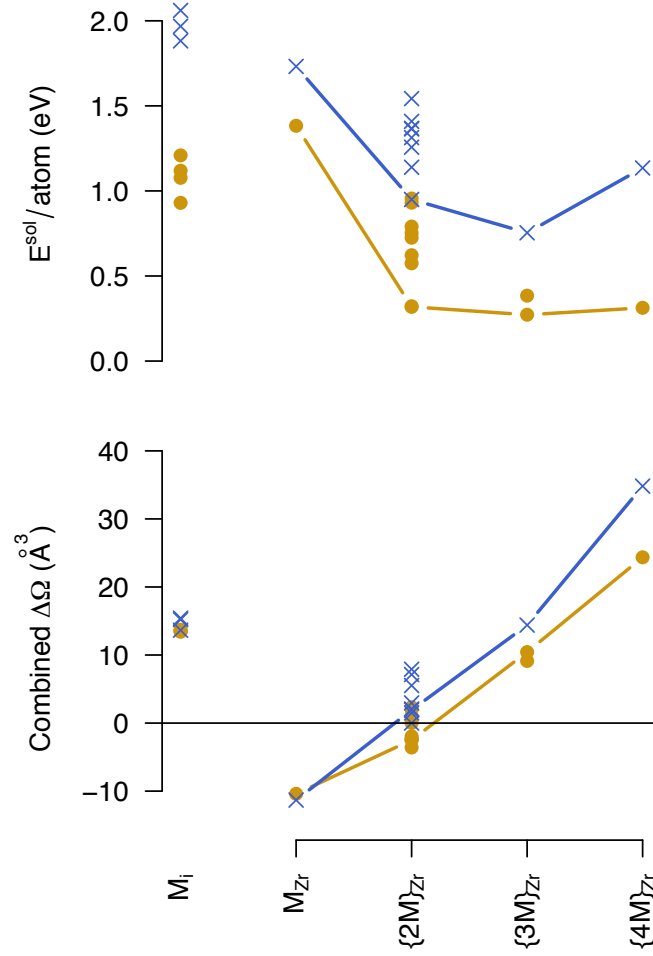


Figure 4.8: Solution enthalpy (top) and relaxation volume (bottom) as a function of cluster size. Blue crosses represent Cr defects, yellow dots represent Fe defects. Dilute interstitial defects are also included for comparison (LHS of the dashed line). Joined points show the lowest energy clusters.

4.6 Summary

Accommodation of Fe and Cr in the α -Zr lattice was investigated by means of DFT simulations. The use of large supercells was found to be crucial to correctly capture the accommodation mechanisms of Fe in Zr. Two new stable interstitial sites were observed – crowdion and off-site octahedral — the latter of which is significantly more stable than all other interstitial sites, which in turn are all more favourable than substitutional accommodation. For Cr, the trend is reversed, with the substitutional site being the most stable, but only by a small margin. Therefore, concomitant accommodation on interstitial and substitutional site is predicted. These prediction were corroborated by APT investigation.

Lattice distortions due to the defects were found to be strongly anisotropic for Fe accommodation: the a lattice parameter decreases with Fe additions (corroborated by experimental observations) while the c axis is predicted to expand. For Cr accommodation, both lattice parameters contract.

The relative preference for one type of defect over the other (interstitial or substitutional) was found to be sensitive to applied stress and/or strain. Local compressive strains of $\sim 3\%$ cause Fe_{Zr} to be more stable than any Fe_i defect, and compressive strains of $\sim 1\%$ sufficed for $\text{Cr}_{i(\text{oct})}$ to become more stable than Cr_{Zr} . Consequently, the strain field caused by the defects themselves may cause a reduction in the formation energy of a defect of the opposite sign. In turn, this may provide a driving force for cluster formation.

Defect clusters containing two extrinsic atoms were investigated and found to be more stable than their constituents as isolated defects regardless of configuration and species. In particular, the most stable configuration for pairs of Fe or Cr or a mixed Fe-Cr pair, is a dumbbell structure across a Zr vacancy. Up to three Cr or four Fe atoms could be accommodated within a single Zr vacancy. Larger clusters are beyond the reach of the current methodology, but it is possible that larger clusters may be more favourable if more than one Zr vacancy is considered.

The DFT calculations provide a strong indication that in the presence of a Zr vacancy, the formation of clusters significantly lowers the solution energy of Fe and Cr in α -Zr,

thereby increasing their apparent solubility. Cluster formation may then be considered as a competing mechanism to SPP formation: during manufacturing, only an equilibrium amount of Zr vacancies are present ($\sim 3.7 \times 10^{-9}$ at the $\beta \rightarrow \alpha$ transition temperature according to the calculated vacancy formation energy of 1.9 eV), thereby limiting the number of potential Fe-Cr clusters, and causing the precipitation of SPPs. On the other hand, upon irradiation the concentration of vacancies and dislocation loops increases by orders of magnitude [249]. Neutron irradiation also causes SPPs to become amorphous and to leach Fe and Cr back into the α -Zr matrix [244, 260, 268–272, 274]. In view of the current results, this re-solution can be explained by the combined effect of SPPs are amorphisation (which is likely to thereby reducing the SPP stability) and the formation of a high concentration of Zr vacancies, which, combined with the significantly faster diffusivity of Fe and Cr compared to Zr, promote the formation of defect clusters.

5

Alloying additions in Be

Part of the work presented in this chapter has been published in:

Burr *et al.* J. Alloy Compd. **639** (2015) 111–122. Ref [305]

5.1 Introduction

Alloying additions and impurity elements can either be retained in solution within the Be lattice, or form SPPs embedded within the grains or at grain boundaries and surfaces (where their presence can be deleterious to the mechanical and chemical properties of the alloy). Here we will be concerned chiefly with the iron (Fe) and aluminium (Al) containing intermetallic phases of Be, as Fe and Al are the most common additions/impurities in Be alloys [306–309].

In a review of the binary Be-Fe system, Tanner and Okamoto [212] argue that, despite the many conflicting reports, much of the phase diagram is now well characterised, as shown in Figure 5.1. This system exhibits solid solutions at either end of the composition range, a metastable BeFe_3 phase and three stable intermetallic compounds: ζ - FeBe_2 , δ - FeBe_5 and an ε Be-rich intermetallic.

Teitel and Cohen [310] first reported the ε phase as hexagonal with composition FeBe_{11}

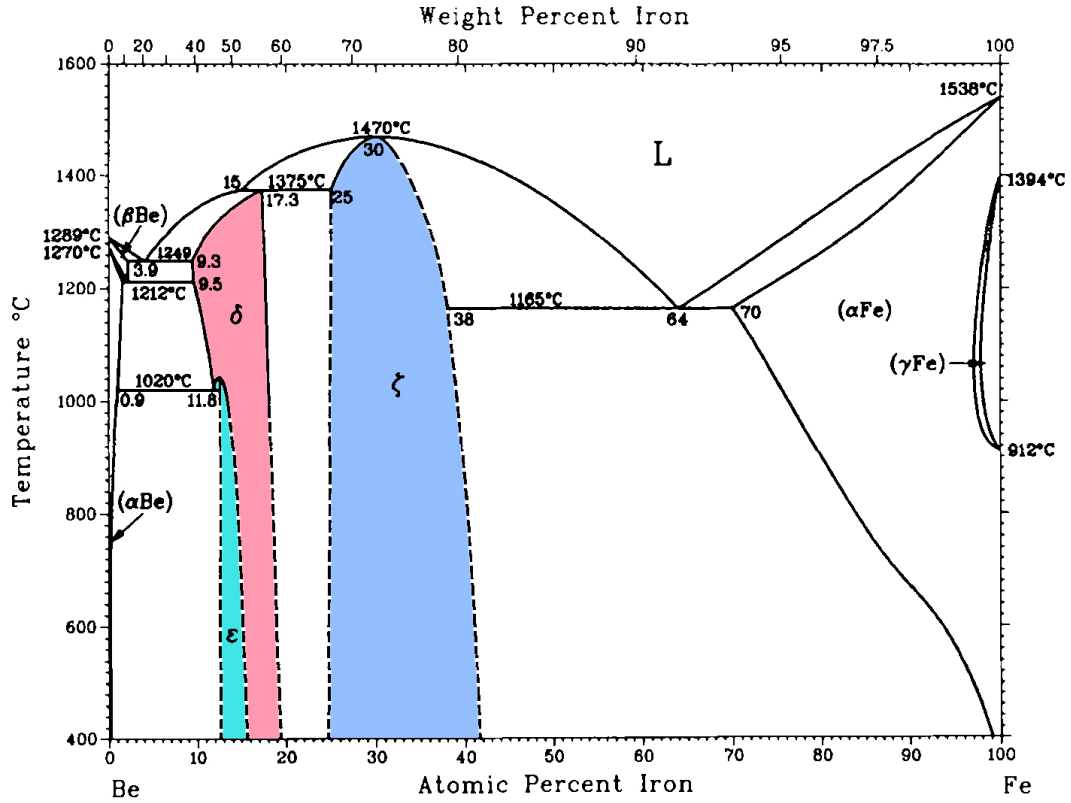


Figure 5.1: Be-Fe phase diagram reproduced from [212]. Intermetallic phases highlighted in colour.

(or potentially FeBe_{12}), which forms only at temperatures below 1065°C and exhibits limited solubility (7.8–8.2 at. % Fe). By means of density measurements, their work shows that a unit cell of FeBe_{11} should contain 18 atoms (i.e. $11/2$ formula units), which remains a peculiar and unexplained result. In subsequent publications, this hexagonal phase is the most commonly reported [212], however there is conflicting information. For example, Von Batchelder and Raeuchle [311] proposed a body centred tetragonal Mn_{12}Th -type structure. Johnson *et al.* [312] reported a new hexagonal phase with unknown composition FeBe_x , but assigned the space group $P\bar{6}m2$ and a basis consisting of 19 symmetrically unique sites, though potentially with partial occupancy. Their x-ray diffraction study reveals many similarities with the FeBe_{11} phase of Tetiel, but accurate density measurements exclude the possibility of a AB_{11} composition. Aldinger *et al.* [313] used the structure reported by Johnson *et al.* [312] but assigned the composition FeBe_7 , yet the compound is still presented with a composition of 8 at. % Fe. Later, Jönsson *et al.* [314] were able to index the same X-ray peaks to another hexagonal structure, with c/a ratio 1.50, rather than the previously reported value of 2.59.

The ternary Al-Be-Fe system is even less well characterised. Raynor *et al.* [315] reported a phase with composition $\text{Fe}_3\text{Al}_7\text{Be}_7$. Black [316] presented an intermetallic with composition $\text{FeAl}_2\text{Be}_{2.3}$, which exhibits a defective form of the cubic C15 Laves structure (prototype MgCu_2) where Fe and Be atoms are ordered on the Cu site (the Be deficiency was not explained). Both studies concentrated on the Al-rich side of the phase diagram and therefore did not identify any low Al, high Be phases.

Subsequent work focused on commercial Be-rich alloys: Rooksby and Green [308] found an intermetallic similar to $\delta\text{-FeBe}_5$ but with a larger lattice parameter, which was initially termed YBe_5 (where Y indicates a transition metal, not yttrium), later identified by Rooksby [317] as $(\text{Al,Fe})\text{Be}_5$, in which the presence of Al on Fe sites results in a larger lattice parameter. Carrabine [318] presented a cubic AlFeBe_4 phase and in an addendum explained how this composition clarifies the results from Rooksby [317]. It is not clear, however, whether the phase is ordered or disordered. Myers and Smugeresky [319] measured the maximum and minimum Al/Fe atomic ratios of AlFeBe_4 (1.4 ± 0.1 and 0.98 ± 0.15 respectively) and noted that the Be-rich ε phase does not accommodate an appreciable

amount of Al and that the stability of this phase reduces with increasing Al content. There is a clear need for further investigation of the Be-rich corner of the Al-Be-Fe system.

This chapter focuses on those phases and conditions that are relevant to Be alloys for fusion applications, that is, with low Al and Fe concentrations. Here DFT is employed in combination with the harmonic and quasi-harmonic approximations of atomic wells to capture temperature effects and the Bragg-Williams approach to include the effect of disorder in the intermetallic phases. After a brief description of the computational details and the crystal structures relevant to this chapter, the results are presented in the following order. First a new structure of the ε phase is reported, which arises from extensive search and refinement of possible candidate structures. Physical properties of the ε phase are calculated using the proposed structure (hexagonal $\text{Fe}_{2-x}\text{Be}_{17+x}$) and compared to experimental results were available, showing that this new structure reconciles diverging experimental observations. Following that, the remaining binary Fe-Be intermetallic compounds are considered and their relative stability is examined as a function of temperature. In subsections the elastic properties, magnetic contributions and the ability to accommodate non-stoichiometry are presented. A brief discussion on the importance of anharmonic contributions follows. Next, the effect of Al additions is considered, yielding solid solutions and a ternary Al-Fe-Be phase. Again, magnetic properties and non-stoichiometry are presented. Following this, the driving force for ordering in each of the intermetallic phases is examined, the lack of ordering of the ternary AlFeBe_4 is demonstrated, as well as an order/disorder transition in $\delta\text{-FeBe}_5$. Finally, the findings are summarised.

5.2 Computational details

All DFT simulations were carried out with the same parameters outlined in the section 2.6, unless otherwise stated. For point defect calculations, a supercell consisting of $2 \times 2 \times 2$ conventional unit cells (containing 192 atoms) was used for the cubic AlFeBe_4 , FeBe_5 and FeBe_2 phases, while a $3 \times 3 \times 2$ supercell (216 atoms) was employed for the C14 Laves hexagonal polymorph of FeBe_2 and a $3 \times 3 \times 1$ supercell for $\text{Fe}_2\text{Be}_{17}$ (171 atoms). All simulations were spin polarised and particular care was taken to ensure that defective cells

reached the lowest energy magnetic state (see sections 5.4.3 and 5.5.3 for further details).

Temperature contributions were included using the harmonic approximation described in section 2.4. Vibrational and configurational entropy were calculated for stoichiometric compositions only.

5.3 Crystallography of Fe-Al-Be intermetallics

The crystal structure of ζ -FeBe₂, δ -FeBe₅ and AlFeBe₄ are closely related; see Figure 5.2. The AlFeBe₄ phase (space group $F\bar{4}3m$), can be described by three face-centered cubic (FCC) sublattices (see Fig 5.9a). The first sublattice, with origin at (0, 0, 0) is occupied by Fe atoms (blue). The second one, occupied by Al atoms (pink), is shifted by $[\frac{3}{4}\frac{1}{4}\frac{1}{4}]$ and has four sites within the conventional unit cell, namely $(\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$, $(\frac{1}{4}, \frac{3}{4}, \frac{1}{4})$, $(\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$. Be atoms (green), which have a multiplicity of 4 compared to Al or Fe atoms, are grouped in tetrahedra, each of which is centred at the lattice points of the third FCC sublattice. The third FCC sublattice is shifted by $[\frac{1}{4}\frac{1}{4}\frac{1}{4}]$, thereby occupying the last four corners of the cube: $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, $(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$, $(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$ and $(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$.

δ -FeBe₅ exhibits the same structure as AlFeBe₄, where all Al atoms have been substituted for Be (Fig 5.2b). If all Al atoms were to be substituted by Fe instead, the structure would become the C15 Laves phase of FeBe₂ (Fig. 5.2c). Experimentally it has been reported that ζ -FeBe₂ exhibits the C14 Laves phase (Fig. 5.2d). Nevertheless, as a check of the validity of the current methodology, the C15 structure was also modelled. Although the two polymorphs of FeBe₂ may look very different, the local atomic coordination is the same: the A atoms (either Fe or Al in the current work) form a diamond structure sub-lattice, where each atom had a coordination number (CN) of 16 (4 A atoms and 12 B atoms). The B atoms (Be) form a network of tetrahedra that intercalate around the A atoms, with a CN of 12 (6 A + 6 B).

5.3.1 The structure of the ε phase

Of the binary Be-Fe phases, the ε phase is the least well characterised: the composition is uncertain, and limited crystallographic information is available, as summarised in Table 5.1.

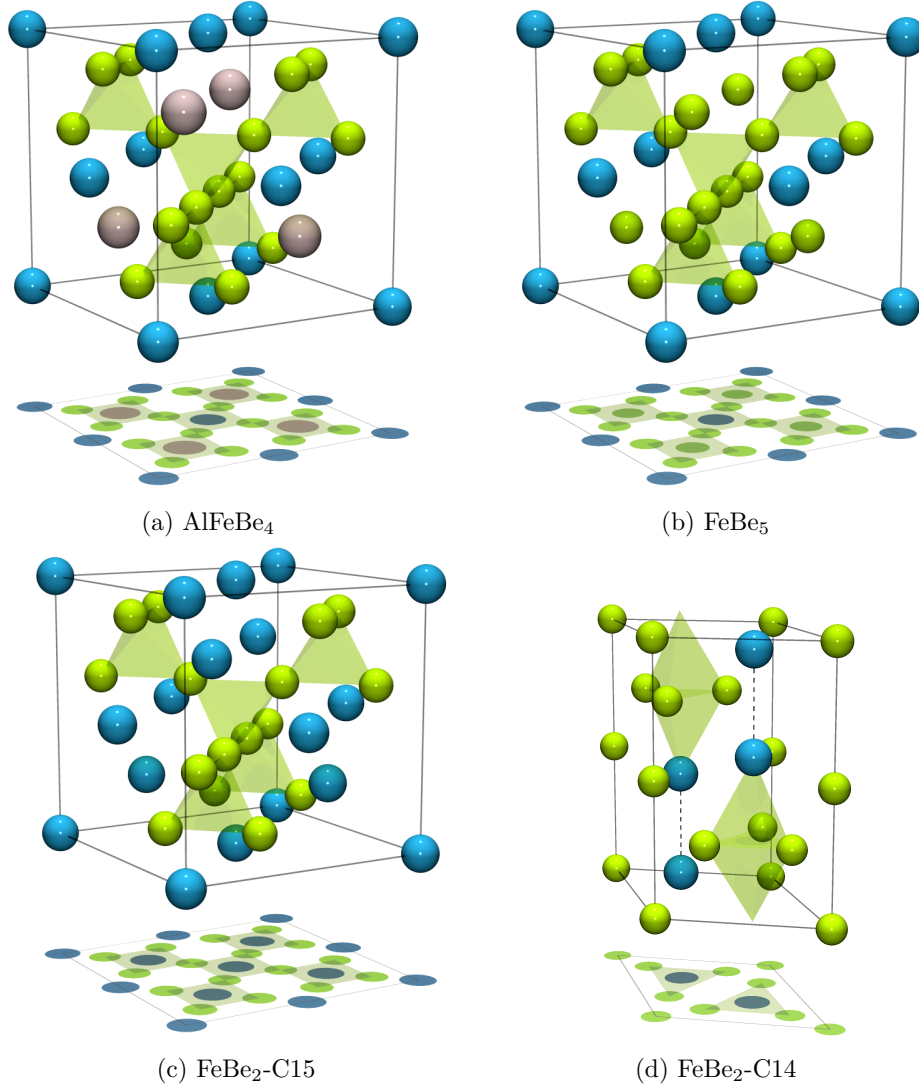


Figure 5.2: Crystal structures of (a) AlFeBe_4 , (b) $\delta\text{-FeBe}_5$, (c) the cubic C15 Laves phase of FeBe_2 , with prototype Cu_2Mg structure and (d) the hexagonal C14 structure of $\zeta\text{-FeBe}_2$, with prototype MgZn_2 structure. Smaller green atoms are Be, the larger blue atoms are Fe and the larger pale pink atoms are Al.

In terms of the basis, Von Batchelder and Raeuchle [311] provide a full set of atomic coordinates for the tetragonal FeBe_{12} structure, but the only information available about the basis of the more commonly observed FeBe_{11} phase of Teitel and Cohen [310], is that a unit cell contains ~ 18 atoms. The structure reported by Johnson *et al.* [312], in a publication that focussed on the structure of $\text{RhBe}_{6.6}$, comprises a list of 9 atomic coordinates which, if fully occupied, would yield composition $\text{Fe}_3\text{Be}_{16}$. However, the exact composition of the compound (FeBe_x) was not provided, and some partial occupancy may be present on

selected Fe and/or Be sites. Interestingly, the phase described by Johnson *et al.* [312] shares similarities with that reported by Teitel and Cohen [310] for FeBe₁₁; this would explain the presence of ~ 18 atoms per unit cell of FeBe₁₁. Aldinger [313] and Jönsson *et al.* [314] report structures with a larger lattice constant but do not give information regarding the crystal basis.

Since the literature provides only limited and incomplete information regarding the structure of the ε phase, our investigation was extended to all the phases with similar composition that are known to form in other Be-Tr systems with (where Tr is any non-Fe transition metal). In these simulations, no symmetry operations were enforced, to provide the system with the maximum number of degrees of freedom. The results are summarised in Table 5.2.

Table 5.1: Summary of crystallographic information available regarding the Be-rich ε phase.

Composition	Crystal class	Prototype structure	Space group	Atoms per unit cell	a (Å)	c (Å)	Reference
FeBe ₉	—	—	—	—	—	—	[310] ¹
FeBe ₁₁	Hex	—	—	18	4.13	10.71	[310]
FeBe ₁₂	Tetr	Mn ₁₂ Th	I_4mmm	13	4.323	7.25	[311]
FeBe ₁₁	Hex	—	—	—	4.13	10.72	[317]
FeBe _{x}	Hex	RhBe _{6.6}	$P\bar{6}m2$	19 ²	4.137	10.72	[312]
FeBe ₁₁	Hex	—	—	—	4.13	10.72	[320]
FeBe ₇	Hex	—	—	—	7.13	10.99	[313]
FeBe ₁₁	Hex	—	—	—	7.15	10.72	[314]

¹ The work of Mish was not published but is indirectly reported in [310].

² While the phase by Johnson *et al.* [312] has 19 symmetry sites, not all are fully occupied.

Most hypothetical phases produced very large and positive (i.e. unstable) formation energies. Some, however, exhibit favourable formation energies. The formation energies of all the passes are represented graphically in Fig. 5.5, in the form of a convex hull. The upward-pointing green triangles represent structures that derive from possible variations of the defective RhBe_{6.6} structure [312]. The orange square represents the tetragonal structure of von Batchelder [311]. The upward-pointing pink triangles represent new hypothetical Fe-Be intermetallics with structures and composition observed in other Be-Tr systems. The point laying on the convex hull (dashed line) represent stable phases, and the distance from the hull may be interpreted as the degree of instability of a phase. This diagram

Table 5.2: Crystal structures modelled to replicate the ε phase. Formation enthalpies H_f are normalised per Fe atom. The most stable structure is in bold.

Composition	Crystal class	Prototype structure	Space group	Atoms per unit cell	a (Å)	c (Å)	H_f (eV)
Fe ₃ Be ₁₆	Hex	RhBe _{6.6}	$P\bar{6}m2$	19	4.08	10.73	−0.61
FeBe ₈ (1)	Hex	RhBe _{6.6}	$P\bar{6}m2$	18	4.09	10.72	−0.13
FeBe ₈ (2)	Hex	RhBe _{6.6}	$P\bar{6}m2$	18	4.10	10.63	−0.20
Fe₂Be₁₇	Hex	RhBe_{6.6}	$P\bar{6}m2$	19	4.10	10.63	−0.97
Fe ₂ Be ₁₅	Hex	RhBe _{6.6}	$P\bar{6}m2$	17	4.15	10.45	0.71
FeBe ₁₇	Hex	RhBe _{6.6}	$P3m1$	18	4.11	10.64	1.20
FeBe ₁₂	Tetr	Mn ₁₂ Th	I_4mmm	13	7.16	4.09	−0.30
FeBe ₁₂	Hex	Fe ₆ Ge ₆ Mg	$P6/mmm$	13	4.15	7.16	0.56
FeBe ₁₃	Cubic	NaZn ₁₃	$Fm\bar{3}c$	28	6.98	—	2.66
Fe ₂ Be ₁₇	Hex	Ni ₁₇ Th ₂	$P6_3/mmc$	38	7.11	7.04	−0.15
Fe ₂ Be ₁₇	Hex	Th ₂ Zn ₁₇	$R\bar{3}m$	57	5.41	—	−0.20
Fe ₃ Be ₁₇	Cubic	Be ₁₇ Ru ₃	$Im\bar{3}$	160	10.99	—	−0.82
Be ₂₂ Fe	Cubic	Al ₁₈ Cr ₂ Mg ₃	$Fd\bar{3}m$	176	11.43	—	0.10

is constructed exclusively in terms of ground state enthalpy, with no considerations about entropic or temperature-dependant contributions, which are considered in section 5.4.2.

The Fe₂Be₁₇ phase appears to be the most stable of the candidate phases. The lattice parameters of Fe₂Be₁₇ are also in good agreement with those reported from experimental work (see Table 5.2). All other variations of the RhBe_{6.6} structures yielded less favourable formation energies and were not considered further. None of the structures replicated from other transition metal beryllides proved to be more stable and were also discounted. The tetragonal phase of Von Batchelder and Raeuchle [311] is also significantly less favourable than hexagonal Fe₂Be₁₇. The full crystallographic basis for the Fe₂Be₁₇ structure is presented in Table 5.3. This includes partial occupancy of the Fe1 site, which is discussed in detail in section 5.4.4.

Table 5.3: Crystallographic basis parameters for ε -Fe_{2− x} Be_{17+ x} .

Atom label	Wyckoff site	x	y	z	Occupancy %
Fe1	$2g$	0	0	0.192	76Fe + 24Be
Be1	$1d$	$1/3$	$2/3$	$1/2$	100Be
Be2	$1f$	$2/3$	$1/3$	$1/2$	100Be
Be3	$2g$	0	0	0.400	100Be
Be4	$2h$	$1/3$	$2/3$	0.131	100Be
Be5	$2i$	$2/3$	$1/3$	0.156	100Be
Be6	$3j$	0.8385	0.677	0	100Be
Be7	$6n$	0.499	−0.499	0.3146	100Be

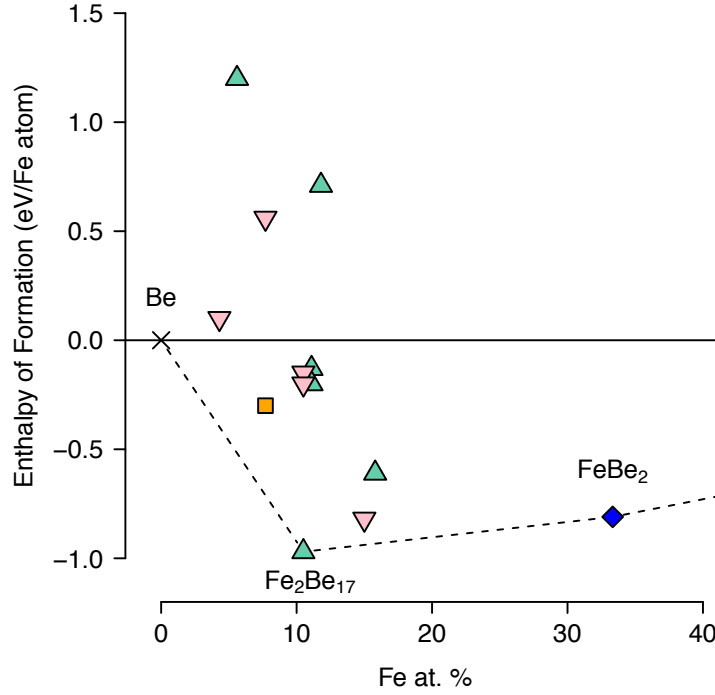


Figure 5.3: Convex hull diagram for the Be-rich side of the Fe-Be system. Orange square and green triangles are variations of previously reported Fe-Be phases. Pink triangles pointing down are hypothetical phases with the structure of other transition metal beryllides.

To confirm the DFT prediction, a theoretical XRD pattern was produced using the data presented in Tables 5.2 and 5.3 (green dashed line in Fig. 5.4). The red solid line represents the XRD data reproduced from Rooksby [317]. A clear correlation can be observed between the two sets of diffraction patterns, however, a slight mismatch is observed in terms of d -spacing. The $1/d$ shift can be attributed to the well-known issues of overbinding/underbinding errors [321, 322] that are associated with all localised models of exchange-correlation functionals — including the PBE used in the current work. To compensate for this, a second spectrum (blue dotted line in Fig. 5.4) was produced by employing experimental lattice parameters of Rooksby [317] and applying them to the modelled $\text{Fe}_2\text{Be}_{17}$ structure.

The excellent agreement between the experimental and theoretical XRD spectra further supports the proposition that the defective $\text{Fe}_{2-x}\text{Be}_{17+x}$ structure is a good representation of the ε phase (see section 5.4.4 for details on non-stoichiometry).

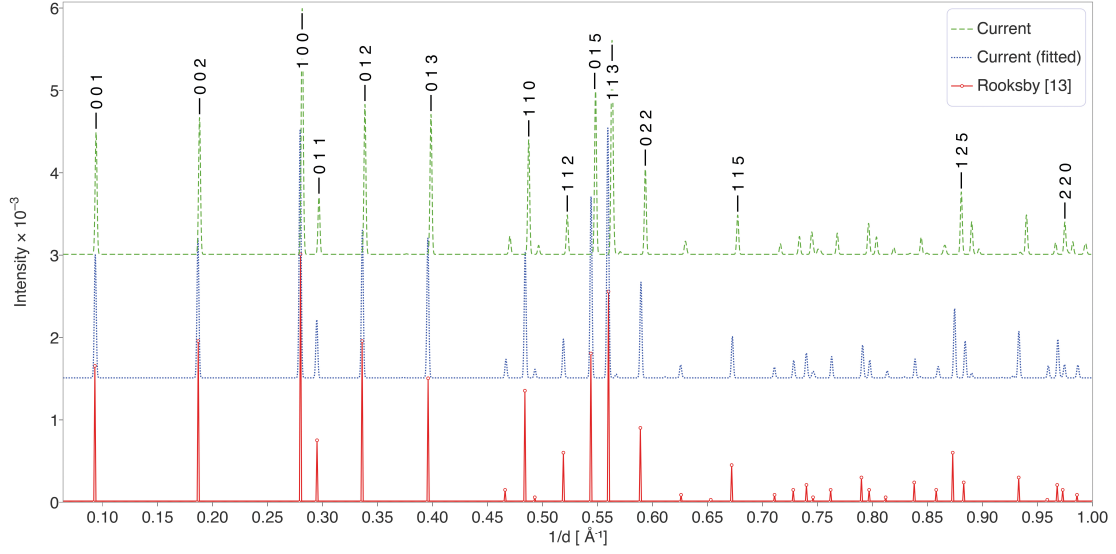
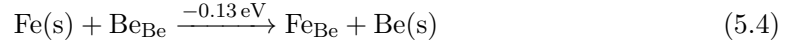
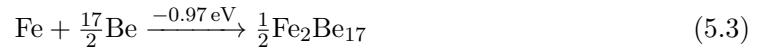


Figure 5.4: Theoretical XRD spectra of $\text{Fe}_2\text{Be}_{17}$ (green and blue) and comparison with the observed spectra of the ε phase (red), reproduced from the tabulated data of ref [317].

5.4 The Be-Fe binary system

5.4.1 Phase stability in the binary Fe-Be system

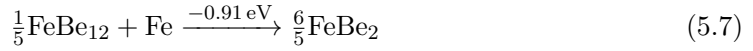
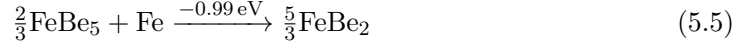
The enthalpy of formation from standard state of each phase under consideration was calculated following the generic reaction $\text{Fe} + x\text{Be} \rightarrow \text{FeBe}_x$; these energies are presented alongside reactions 5.1–5.3. For comparison, the solution enthalpy of Fe into Be metal is also presented (reaction 5.4).



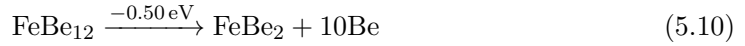
Reactions are normalised per Fe atom. For dilute solution in Be, only the substitutional Fe_{Be} species was considered (in a supercell containing 150 Be atoms), since previous work showed that interstitial accommodation of Fe is less favourable [323].

All phases exhibit favourable (negative) formation enthalpies, and in all cases these

are lower than the enthalpy of solution (reaction 5.4). To better understand the relative stability of the intermetallics, one needs to consider the reactions necessary to proceed from one intermetallic composition to another. For instance, in the presence of excess Fe, ζ -FeBe₂ may form according to 5.5–5.7.



All reactions are exothermic (negative). However, in the framework of Be alloys, the presence of excess Fe is unlikely, therefore reactions 5.8–5.10 should also be considered, in which each phase ejects Be atoms (released into the Be bulk) to form a higher Fe content intermetallic phase.



As mentioned previously, these reactions may be represented more conveniently using a convex hull diagram (see Fig. 5.5). It is apparent that both ε -Fe₂Be₁₇ and ζ -FeBe₂ are stable intermetallic phases. On the other hand, the instability of δ -FeBe₅ is surprising considering this phase is observed experimentally [212, 310, 313, 317]. Note that this analysis is strictly related to the ground state enthalpy of the phases. Temperature effects and the presence of extrinsic point defects may stabilise δ -FeBe₅, as addressed in sections 5.4.2 and 5.5.2, respectively.

5.4.2 Temperature effects of the thermodynamics of Fe-Be intermetallics

The effect of temperature was considered using the harmonic approximation (where the potential well of each lattice site is described by an harmonic function). Here we re-evaluate the same reactions as before (5.1–5.4), but instead of adding and subtracting changes in

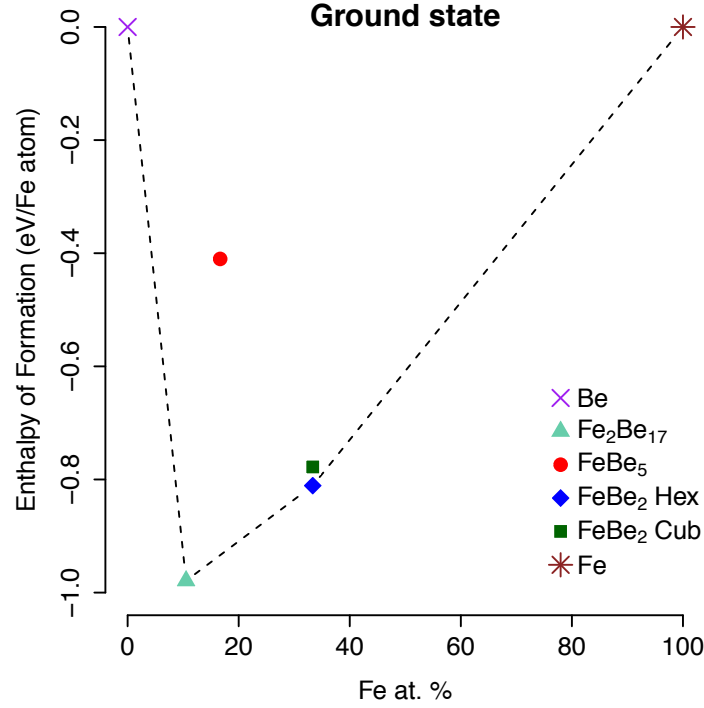


Figure 5.5: Change in formation enthalpy with increasing Fe content. The line represent the convex hull and determines those phases that are expected to form.

enthalpies, we consider Helmholtz free energy changes $F(T, V_0)$, which are a function of temperature.

When integrating over the phonon DOS, there is no theoretical limit to the applied temperature. However, for computational reason, liquid phases are not considered in the current work. This imposes a limit of validity of our method to temperature at which the liquid phase is not competing against the solid phases of interest (i.e. below their melting temperatures).

A further limitation arises from the fact that the harmonic approximation becomes progressively less reliable at higher temperatures; however, as shown in section 2.7, including non-harmonic contributions does not affect the stability of the phase in this system. Additional temperature contributions not considered in these calculations (including configurational entropy due to large deviations from stoichiometry and pressure effects) may lower the energy of the solid solutions, particularly disordered phases and phases with partial occupancy [216].

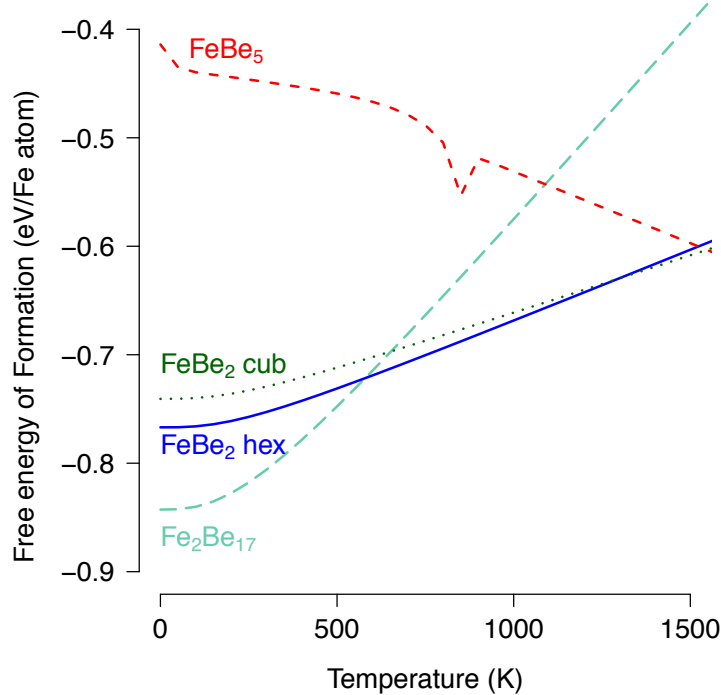


Figure 5.6: Helmholtz free energy of formation versus temperature for Fe-Be binary intermetallics. The values are normalised per Fe atom.

The most striking feature of Fig. 5.6 is that with increasing temperature, the stability of the δ -FeBe₅ phase increases, while those of the other phases decrease. Thus, δ -FeBe₅ is stabilised at higher temperature, although it is not expected to form at low temperature under equilibrium conditions. The dip observed at ~ 750 K is caused by an order/disorder transition, discussed in section 5.6.

At ~ 1200 K, the δ -FeBe₅ curve crosses the ε -Fe₂Be₁₇ curve. This is a condition necessary but not sufficient for the spontaneous decomposition of ε -Fe₂Be₁₇ into δ -FeBe₅, as the reaction energy also depends on the Fe content. Therefore, 1200 K may be considered as the lower bound for the formation of δ -FeBe₅ in Be-rich compounds. Experimental phase diagrams, although tentative and based on limited data [212, 310], show a first order transition from ε to δ at ~ 1450 K.

Secondly, we observe a hexagonal to cubic transition of the FeBe₂ phase at high temperature. This is a common feature in many Laves phase systems [30, 73, 248, 324]. Nevertheless, the predicted difference in free energy between the two phases is very small

and never exceeds 0.01 eV/atom, which is below the level of confidence that the current methodology offers (see section 2.7). Based on these Helmholtz formation energy values convex hull diagrams were created at 0 K (including ZPE), 500 K, 1000 K and 1600 K (see Fig. 5.7). The ζ -FeBe₂ phase lies on the convex hull across the entire temperature range. On the other hand, ε -Fe₂Be₁₇ and δ -FeBe₅ are only expected to be stable at low and high temperatures, respectively. At intermediate temperatures the two phases are predicted to co-exist (Fig. 5.7c).

5.4.3 Elastic and magnetic properties of Fe-Be intermetallics

The complete stiffness matrices were calculated for all the intermetallic phases in the Fe-Be system (see Table 5.4). For completeness the hypothetical FeBe₁₂, which this study predicted to be unstable, was also considered. These were obtained by performing small lattice perturbations from the ground state structures, and measuring the stresses, while keeping all relative atomic positions fixed. Bulk moduli (K) and shear moduli (G) were evaluated using the Voigt-Reuss-Hill method (Hill average) [199].

Table 5.4: Elastic constants of binary intermetallic phases. In all cases $C_{11} = C_{22}$, $C_{13} = C_{23}$ and $C_{44} = C_{55}$. All values are expressed in units of GPa. Uncertainties are below 1.5 % unless otherwise stated.

Phase	C_{11}	C_{33}	C_{12}	C_{13}	C_{44}	C_{66}	K	G
FeBe ₁₂	345.0	319 ± 7	20 ± 1	41 ± 2	131.7	109.2	134.7	133.8
ε -Fe ₂ Be ₁₇	318.6	377.8	66.8	25.8	107.0	125.9	139.1	125.8
δ -FeBe ₅	285.2	285.2	69.3	69.3	138.6	138.6	141.3	125.4
ζ -FeBe ₂	361.7	378.3	61.4	57.3	160.2	150.2	161.5	155.8

ζ -FeBe₂, δ -FeBe₅ and ε -Fe₂Be₁₇ may exhibit one of a range of magnetic orders, as illustrated in Figure 5.8 as summarised in Table 5.5. In all cases ferromagnetic (FM) ordering is the most favourable, followed by a high spin antiferromagnetic configuration (AFM-2) in δ -FeBe₅ and ζ -FeBe₂. Conversely, the ε -Fe₂Be₁₇ phase only shows a slight preference for magnetic ordering, indicating that the order should be lost quickly with increasing temperature.

The reported energy differences correspond to a conventional unit cell. This non-negligible contribution to the energy of the system should be considered when computing

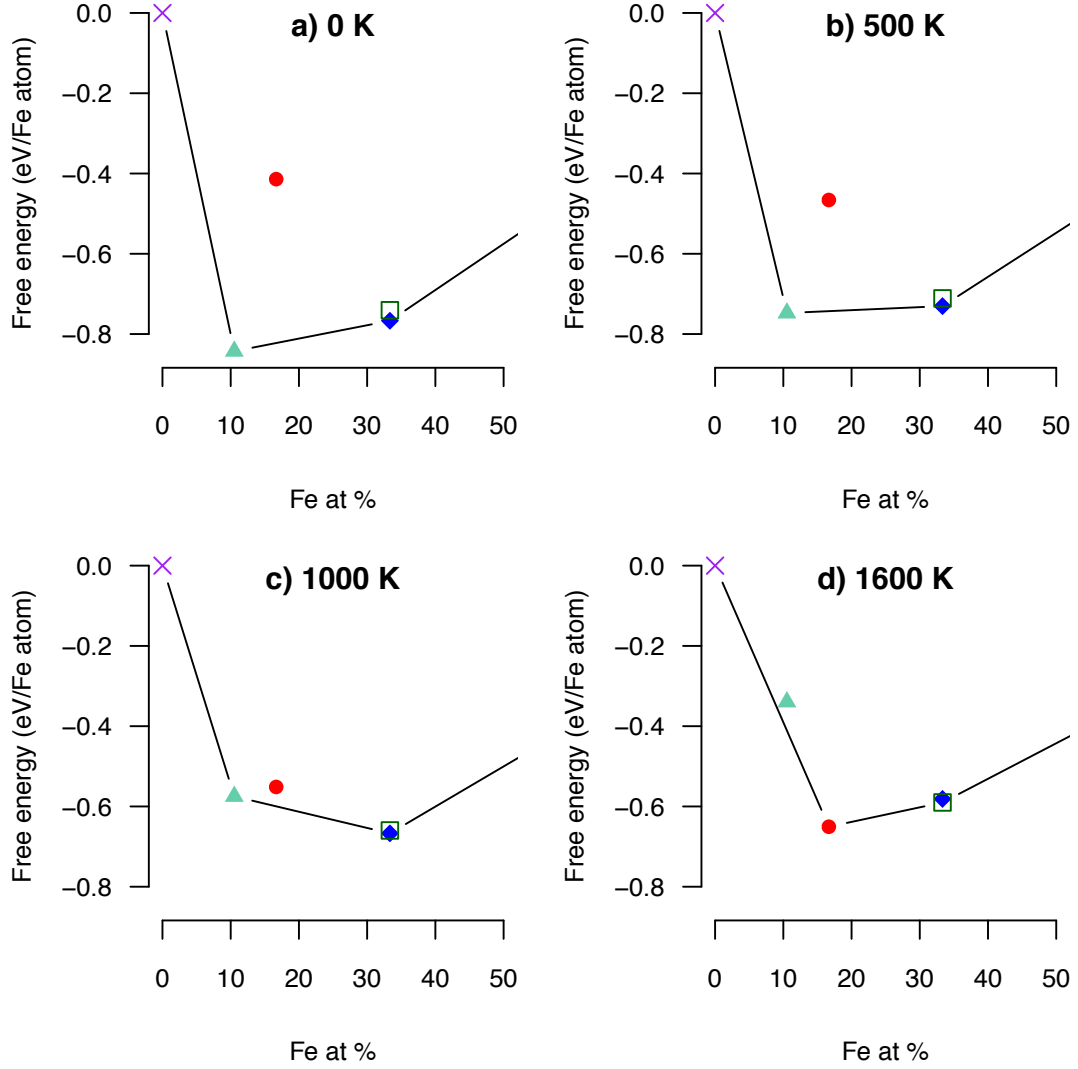


Figure 5.7: Convex hull diagrams for the Fe-Be system at 0 K, 500 K, 1000 K and 1600 K. For the legend see Fig. 5.5. The values have been normalised as in reactions 5.1–5.4. For clarity the x-axis was truncated at 50 at. % Fe.

Table 5.5: Energy difference between non-spin polarised calculations (NM), and possible stable magnetic configurations. Values are reported in eV and normalised per conventional unit cells.

	NM	AFM-1	AFM-2	FM
$\text{Fe}_2\text{Be}_{17}$	0.00	—	—	−0.04
FeBe_5	0.00	−0.49	−0.59	−0.67
FeBe_2	0.00	−0.01	−1.24	−1.66

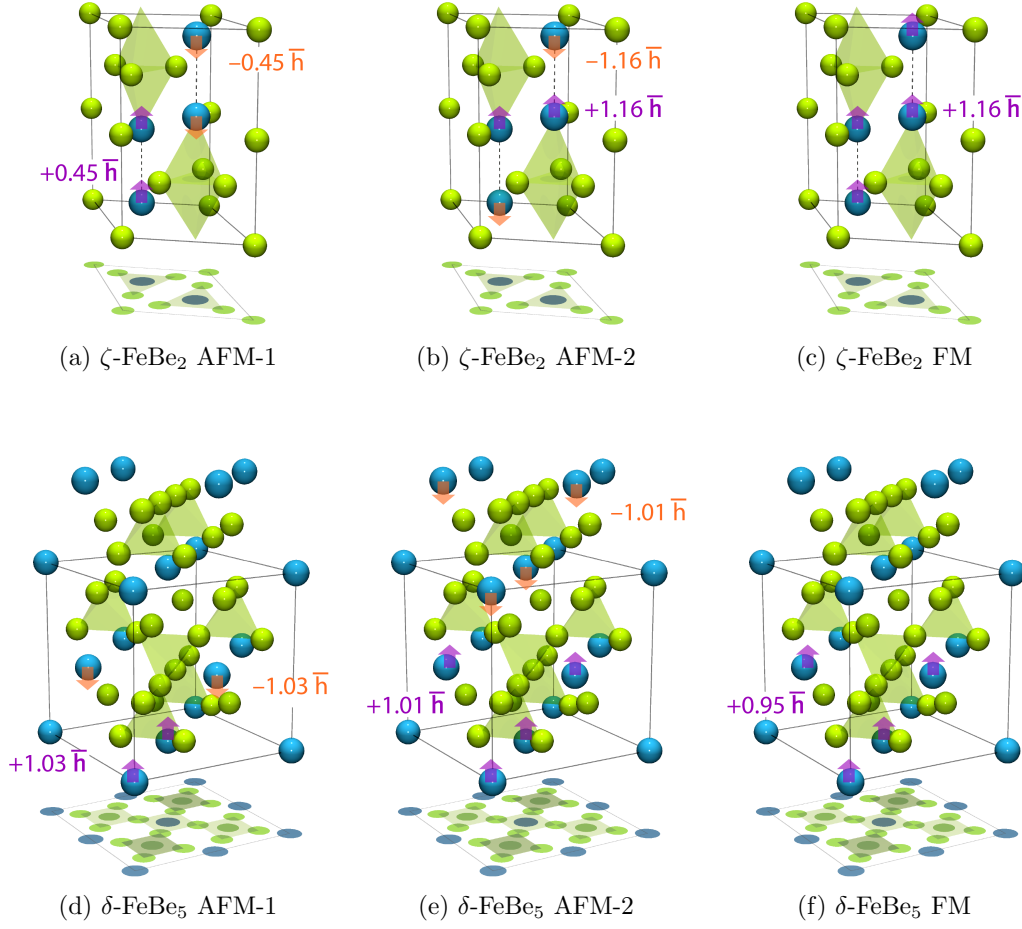


Figure 5.8: Schematic diagrams of spin order in ζ -FeBe₂ and δ -FeBe₅.

isolated defects. In such simulations, the presence of a defect may cause the minimisation algorithm to converge into a shallow minima with a metastable spin state. In the current work, no constraints were added to the spin while performing an energy relaxation to allow localised changes of the spin near a defect, but great care was taken to ensure that the overall spin state of the system was unchanged after the introduction of a defect. When this did not occur, the simulations were restarted with a slightly different initial spin state and tighter electronic convergence criteria, to help the minimiser overcome local barriers and find the lowest energy minimum. In all cases, it was found that the ferromagnetic solution was the lowest energy configuration.

5.4.4 Non-stoichiometry of binary Fe-Be phases

To investigate the accommodation of non-stoichiometry in the intermetallics, the formation enthalpies of intrinsic defects were calculated; in particular, the Fe and Be vacancies, Be substituting for Fe and vice versa. Interstitial Be atoms were also considered. In Kröger-Vink notation these are V_{Fe} , V_{Be} , Be_{Fe} , Fe_{Be} , and Be_i , respectively. Fe interstitial defects were considered unimportant. However, to check this, the energies of Fe_i in $\zeta\text{-FeBe}_2$ were calculated and values typically greater than 5 eV were found, which are much higher than for equivalent substitutional related process.

The formation enthalpy of the defects that may lead to non-stoichiometry are presented in Table 5.6. These are evaluated from Be-excess conditions, and therefore may not correspond to *standard* formation enthalpies. In those cases, standard formation enthalpies are reported in parenthesis. The *standard* formation enthalpy is calculated from the ground state of the constituent elements. This implies that both Be(s) and Fe(s) are present at equilibrium with the product of the reaction, a situation not found in commercial Be alloys. Here, intermetallics only occupy a minute volume fraction, in the form of nano-to-micron sized SPPs surrounded by metallic Be. Most of the Fe present in the alloy is retained in these SPPs, with a small portion of Fe left in solution in the Be matrix, and virtually none in elemental form (see reactions 5.1–5.4). In practice this means that there is a readily available reservoir of Be atoms and mass action is achieved by adding or subtracting atoms from bulk Be (reactions 5.11, 5.12). The formation enthalpies resulting from defects on Be sites correspond to the *standard* defect enthalpies of formation. On the other hand, the only reservoir of Fe atoms are the intermetallics themselves. Therefore when forming Fe defects, a unit of intermetallic must decompose into free Fe and Be. Fe will react to form the defect and the Be atoms are released into the bulk (reaction 5.13). Similarly, defects occupying the Fe site will cause the displaced Fe to react with bulk Be to form one formula unit of the pre-existing intermetallic phase (reactions 5.14–5.15). The enthalpies arising

from reactions 5.13–5.15, do not correspond to *standard* defect formation enthalpies.

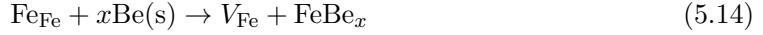
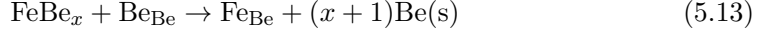


Table 5.6: Defect formation enthalpies in ζ -FeBe₂, δ -FeBe₅ and ε -Fe₂Be₁₇ (reactions 5.11–5.15). All energies in eV. In parenthesis are the *standard* formation enthalpies, when these do not coincide with defect formation energies in excess-Be conditions. Defects on Be sites are presented in order of increasing multiplicity. Details of the interstitial configurations are presented in the last column.

	Be depleted		Fe depleted		Be_i	interstitial configurations
	Fe_{Be}	V_{Be}	V_{Fe}	Be_{Fe}		
ζ -FeBe ₂	1.88 (1.07)	1.95	2.53 (3.34)	0.30 (1.11)	5.99	1c
	2.11 (1.30)	2.10			4.45	3j($x = 0.488$)
					3.67	6m($x = y = 0.282$)
					3.52	6n($x = 1/2, z = 0.467$)
δ -FeBe ₅	-0.67 (-1.11)	2.39	1.29 (1.74)	-0.42 (0.25)	8.29	4b
	1.07 (0.63)	1.84			7.28	4d
					1.82	<111> dumbbell on 4c
					2.31	24f($x = 0.726$)
ε -Fe ₂ Be ₁₇	0.90 (-0.08)	1.56	1.79 (2.76)	-0.15 (0.82)	2.69	<001> dumbbell on 2a
	1.82 (0.84)	1.48			1.74	4f
	0.89 (-0.08)	1.58			1.89	6h($x = 0.459$)
	1.88 (0.90)	2.67			2.30	12k($x = 1/6, z = 0.938$)
	2.08 (1.10)	2.02				
	0.84 (-0.14)	1.74				
	0.79 (-0.19)	1.94				

Note that a number of defects exhibit negative formation energy in the ε and δ phases. This is an indication that those structures, as modelled in the current work, are predicted to be unstable. In the case of ε -Fe₂Be₁₇, this is due to the presence of partially occupied atomic sites, as reported by Johnson *et al.* [312]. Due to computational limitations, when modelling the structure of the reference material (undefective) we consider a perfectly ordered and stoichiometric compound. The defect calculations reveal that the nature of the partially occupied sites is not one of vacancies, as vacancy formation energy are highly unfavourable on both the Be and Fe lattice sites. Instead, the Be_{Fe} and Fe_{Be} substitutions exhibits

negative formation energy in Be rich conditions and Fe rich conditions, respectively. ε -Fe₂Be₁₇ is unlikely to form in Fe rich-conditions (see section 5.4), therefore we shall only consider the Be-rich scenario. The presence of Be_{Fe} defects that form under this condition would reduce the Fe content of the compound from 10.5 at. % for stoichiometric Fe₂Be₁₇ to a value closer to the observed 8 at. % value. Therefore, we propose that the ε phase is best represented by the chemical formula Fe_{2-x}Be_{17+x}, where $x \sim 0.48$.

In the case of δ -FeBe₅, the negative values are associated with the predicted instability of this phase at low temperatures, as reported in section 5.4.2. δ -FeBe₅ is predicted to dissociate into a Be-rich phase and a Fe-rich phase. It is, therefore, expected that deviations from stoichiometry are favourable. For instance, the substitution of Fe onto an FCC-Be site, effectively creates one primitive unit cell of the very stable FeBe₂ (C15 polymorph) within the δ -FeBe₅ structure. Experimentally, the solubility range of δ -FeBe₅ is recorded to be large (8.33–16.55 at. % [325]). Here we propose that this is achieved by a substitutional mechanism on both sides of the stoichiometric composition (i.e. FeBe_{5-x} and FeBe_{5+x}).

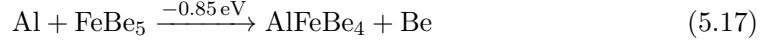
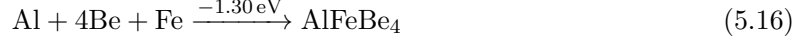
In the case of ζ -FeBe₂, substitutional and vacancy defects have significantly lower formation enthalpies compared to the interstitial defects. Defects producing FeBe_{2+x} (reaction 5.15 proceeding with 0.30 eV) are markedly easier to accommodate than those that form FeBe_{2-x}. Vacancy mediated accommodation is evidently less favourable but again the defects that lead to the accommodation of excess Be (V_{Fe}) are more stable than those that accommodate excess Fe (V_{Be}).

5.5 Ternary Al-Fe-Be system

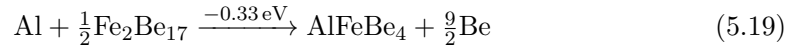
5.5.1 Formation of AlFeBe₄

The binary Al-Be system exhibits no intermetallic phases, and the mutual solid solubilities (Be in Al and Al in Be) are very limited [326]. A binary Al-Be alloy would therefore only contain single element phases of HCP-Be and FCC-Al. A recent DFT study [323], showed

that in the presence of Fe, Al can react to form AlFeBe_4 following reactions 5.16 or 5.17.



The enthalpies of reaction calculated in the current work (above) are in close agreement with the previous study (-1.30 eV vs -1.42 eV and -0.85 eV vs -0.89 eV , respectively). The small differences are probably related to the choice of pseudopotential method (ultra-soft vs PAW in [323]) and the degree of ionic convergence. Following the results of section 5.4, which suggested that $\zeta\text{-FeBe}_2$ and $\varepsilon\text{-Fe}_2\text{Be}_{17}$ are the stable phases at low temperatures, the reactions between Al and these phases were also found to be exothermic (reaction 5.18 and 5.19):

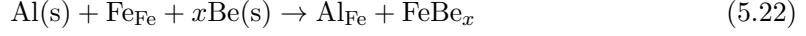
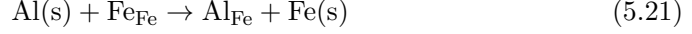
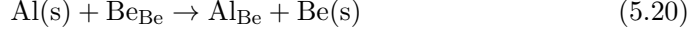


The implications are that in the presence of excess Al, the ternary phase is thermodynamically stable.

5.5.2 Accommodation of dilute Al additions in the Fe-Be system

The incorporation of Al as a dilute point defect into binary Fe-Be intermetallic phases was investigated to model dilute Al-content conditions. Since the addition of Al may act as a stabilising agent for some of the metastable intermetallic phases, all binary Fe-Be phases were considered. Al atoms (calculated metallic radius $r_{\text{Al}} = 1.425\text{ \AA}$) are significantly larger than Be and Fe atoms ($r_{\text{Be}} = 1.109\text{ \AA}$, $r_{\text{Fe}} = 1.238\text{ \AA}$) and therefore unlikely to occupy interstitial sites. Instead, substitution onto each of the symmetrically unique Be

sites (reaction 5.20) and the Fe site (reactions 5.21 and 5.22) were considered.



The solution enthalpies from reactions 5.20–5.22 are reported in Table 5.7, together with the formation enthalpy of (ordered) ternary AlFeBe_4 (following reactions 5.16–5.19). Once again, we are interested in the Be-excess conditions, so the standard formation enthalpy (relevant if excess Fe and Al are present) are presented in parenthesis.

Table 5.7: Solution enthalpy of Al into Fe-Be binary phases together with the formation enthalpy, E_f , of AlFeBe_4 . Value in parenthesis are the *standard* formation enthalpies (equation 5.21), when these do not coincide with defect formation energies in excess-Be conditions. Defects on Be sites are presented in order of increasing multiplicity. All values in eV.

	Al_{Fe}	Al_{Be}	$E_f(\text{AlFeBe}_4)$
$\zeta\text{-FeBe}_2$	−0.31 (0.50)	0.79 0.95	−0.49
$\delta\text{-FeBe}_5$	−0.66 (−0.22)	−0.73 0.94	−0.85
$\varepsilon\text{-Fe}_2\text{Be}_{17}$	−0.07 (0.90)	0.08 0.09 0.27 −0.50 0.84 1.09 1.26	−0.33
FeBe_{12}	1.04 (1.34)	1.94 0.77 1.21	−1.00

Comparing the solution enthalpy with the formation enthalpy of AlFeBe_4 , it is clear that AlFeBe_4 is preferentially formed over dilute Be-Fe-Al ternary intermetallics if sufficient Al is present. Nevertheless, the dilute incorporation of Al in $\zeta\text{-FeBe}_2$ and $\delta\text{-FeBe}_5$ yields large and negative solution enthalpies, therefore a degree of solid solution is expected. On the other hand, the solution of Al into the Be-rich phases is highly unfavourable, in agreement with experiment [317, 319].

The solution energies in Table 5.7 show that solution of Al in $\delta\text{-FeBe}_5$ is significantly

more favourable than in ζ -FeBe₂. This suggests that Al may stabilise δ -FeBe₅. Interestingly, the preferred site for Al accommodation in δ -FeBe₅ is the FCC-Be (2a Wyckoff site), which is nominally occupied by Al in the AlFeBe₄ phase (see Figure 5.2). Accommodation on the FCC-Be site is more favourable than the Fe site, suggesting that the (Fe,Al)Be₅ ternary phase originally predicted by Rooksby [317], is unlikely to form. This agrees with the work of Carrabine [318]. If the incorporation of Al onto the FCC-Be site continued (unchanged) until Al/Fe = 1, then the AlFeBe₄ phase would be formed. However, the accommodation energy onto the Fe site is only 0.07 eV more positive, therefore, as the reaction progresses, it is expected that some of the Al will occupy the Fe site and some the FCC-Be site. The combined reactions, together with the fact that the displaced Fe will either form one extra formula unit of FeBe₅ or substitute for an FCC-Be (see section 5.4.4), leads to the formation of disordered (Al,Fe)Be₂ instead of ordered AlFeBe₄ (see Figure 5.9). The disordered structure retains the higher symmetry of the Laves phase instead of the $F\bar{4}3m$ space group of AlFeBe₄. The sparse literature available for the ternary Al-Fe-Be phase is inconclusive regarding order/disorder [308, 317, 318].

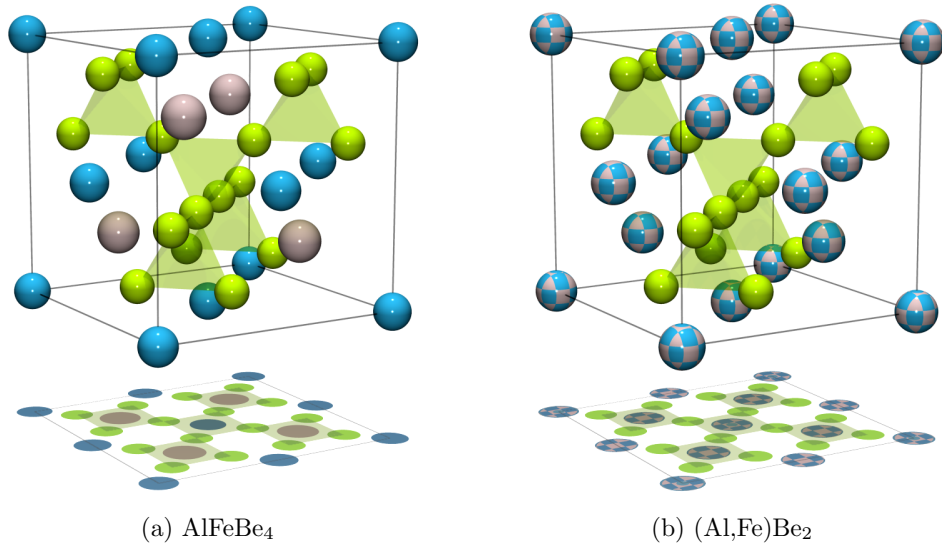


Figure 5.9: Crystal structure of the (a) ordered and (b) disordered structures of the ternary Al-Fe-Be compounds.

Regarding ζ -FeBe₂, the only favourable solution energy is found for substitutions onto the Fe site. Similarly to the previous case, as the incorporation reaction progresses, the host

intermetallic ζ -FeBe₂ tends to become disordered (Al,Fe)Be₂. Therefore, in the presence of Al, both ζ -FeBe₂ and δ -FeBe₅ will react with any Al in the system and tend towards (Al,Fe)Be₂.

There is a consideration to be made: the calculated solution energies are strictly valid only at the dilute limit. This limits our scope of prediction to small Al/Fe ratios. Nevertheless, the change in solution energy with Al concentration is likely to be a smoothly varying function, therefore it is reasonable to speculate that since the solution energy at the dilute limit is favourable, and the formation energy of AlFeBe₄ is favourable (reactions 5.16–5.19), then the incorporation reaction is likely to be favourable at intermediate compositions.

5.5.3 Elastic and magnetic properties of AlFeBe₄

Possible magnetic configurations that the ordered form of AlFeBe₄ may exhibit are reported in Table 5.8. It was found that AlFeBe₄ exhibits similar, yet significantly less pronounced, magnetic ordering to δ -FeBe₅ phases (see Figure 5.8d–5.8f).

Table 5.8: Energy difference between non-spin polarised calculations (NM) and possible stable magnetic configurations of AlFeBe₄. Values are reported in eV and normalised per conventional unit cells.

NM	AFM-1	AFM-2	FM
0.00	−0.08	−0.14	−0.16

As will become apparent in section 5.6, disorder plays an important role in AlFeBe₄. long range magnetic ordering, both FM and AFM, cannot be maintained if the Fe and Al atoms are randomly distributed in the FCC sublattice, therefore, the disordered form of AlFeBe₄ is expected to be paramagnetic. The preference for disorder (see section 5.6 for further details) is observed *despite* the energy penalty associated with the loss of magnetic ordering. Comparing the small differences in energy between the various magnetic configurations of AlFeBe₄ with the much larger changes observed in ζ -FeBe₂ and δ -FeBe₅, it is clear that the lack of strong spin polarisation is a contributing factor to the formation of the disordered phase.

Elastic constants for ordered AlFeBe₄ are presented in Table 5.9. The elastic constant of the disordered phase could potentially be very different from the values reported for

the ordered structure. However, because a large inter-solubility range is predicted between AlFeBe_4 and $\delta\text{-FeBe}_5$ (section 5.5.2), it is instructive to compare physical properties of the two ordered compounds.

The Al-bearing compound is predicted to be stiffer than binary $\delta\text{-FeBe}_5$ in all regards, except under shear loading σ_{12} . Small additions of Al in the $\delta\text{-FeBe}_5$ lattice may also lead to similar mechanical stiffening but due to altogether different reasons: Al atoms are significantly larger than either Fe or Be atoms, and therefore are likely to locally expand the lattice considerably. In turn, these localised defects, which are also not likely to be as mobile as Fe or Be for the same volumetric reasons, may act as pinning points for dislocations motion through the intermetallic. The resulting increase in stiffness would also cause a reduction in ductility.

Table 5.9: Elastic constants of AlFeBe_4 (and $\delta\text{-FeBe}_5$ for comparison). Values in GPa. $C_{11} = C_{22} = C_{33}$, $C_{12} = C_{13} = C_{23}$ and $C_{44} = C_{55} = C_{66}$. Uncertainties are below 1.5 %.

Phase	C_{11}	C_{12}	C_{44}	K	G
AlFeBe_4	349.8	54.2	142.2	152.7	144.4
$\delta\text{-FeBe}_5$	285.2	69.3	138.6	141.3	125.4

5.6 Order/disorder in the intermetallic phases

The discovery of the negative formation energies for some substitutional defects in Fe-Be phases (explained in section 5.4.4), lead to an in-depth investigation of substitutional defects, including defect clusters. The driving force for ordering can be investigated by computing antisite defect energies. Here, both dilute (non-interacting) and bound antisite defect pairs were studied. In a $2 \times 2 \times 2$ supercell of AlFeBe_4 , containing 198 atoms, bound antisite pairs on the Fe and Al sublattices were considered at separations ranging from 2.55 Å, as the first nearest neighbour (1nn), to 7.66 Å (4nn) (see Fig. 5.10). Equivalent simulations were carried out for $\zeta\text{-FeBe}_2$ and $\delta\text{-FeBe}_5$, where only FCC-Be were considered for antisite pairs as these most easily accommodate Fe atoms, as shown previously in Table 5.6. The results are presented in Table 5.10.

For the ternary phase, the defect formation energies are negative for the bound defects,

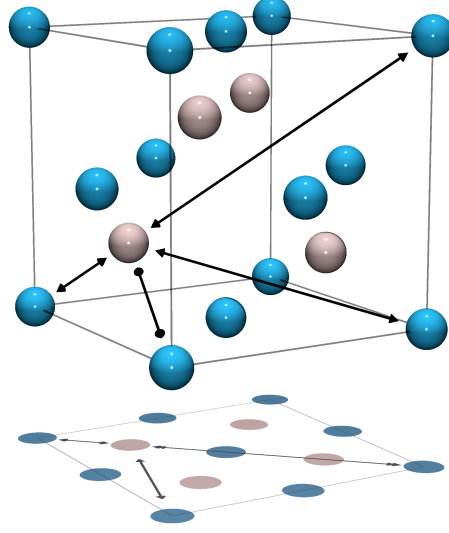


Figure 5.10: Antisite configurations (up to 4nn) in a unit-cell of AlFeBe_4 , where the Be tetrahedra have been removed for clarity. The two FCC sublattices (blue and light pink) are equivalent.

Table 5.10: Formation energy of antisite defects in binary and ternary intermetallic phases of Be-Fe(-Al). All values in eV.

Phase	defect pair	1nn	2nn	3nn	4nn	Unbound
AlFeBe_4	$\text{Fe}_{\text{Al}}\text{-Al}_{\text{Fe}}$	-0.08	-0.05	-0.07	-0.11	0.00
$\zeta\text{-FeBe}_2$	$\text{Fe}_{\text{Be}(2a)}\text{-Be}_{\text{Fe}}$	1.99	2.13	2.22	2.14	2.18
$\delta\text{-FeBe}_5$	$\text{Fe}_{\text{Be}(4c)}\text{-Be}_{\text{Fe}}$	0.67	0.65	0.64	0.66	-1.09

and zero for the dilute case. This is a strong indication that ordered AlFeBe_4 is unstable and that there is no driving force for ordering in this phase. Therefore, we expect the Al-Fe bearing intermetallic phases of Be to exhibit the $(\text{Al,Fe})\text{Be}_2$ Laves structure (see Figure 5.9b), where the two FCC sublattices are indistinguishable. This agrees with Rooksby [317], but applied to the correct stoichiometry reported by Carrabine [318] and Myers *et al.* [319].

A competing contribution to the disorder of the phase is the ferromagnetic behaviour found in AlFeBe_4 , discussed in section 5.5.3. Whilst the disordered material may not have any long range magnetic ordering, it may still maintain some local spin polarisation around the Fe atoms and/or clusters of spin polarised material surrounded by non spin-polarised species, as observed in other materials [327]. To quantify the contributions of magnetic moments to the driving force for ordering, the difference between FM and non-magnetic (NM) configurations provide the upper bound: this is calculated to be 0.16 eV per unit

cell. This is commensurate with the defect formation energy of a single antisite pair and is therefore not sufficient to promote an ordered structure.

Regarding δ -FeBe₅, all bound configurations exhibit a small yet positive defect formation energy (~ 0.64 eV), suggesting that the defect concentration will be temperature dependant (i.e. the ground state phase is ordered) although some disorder is may occur at higher temperatures. This is a often an indication of radiation tolerance in the material [328–330]. Conversely, the dilute antisite pair in δ -FeBe₅ (which is evaluated by considering the effect of accommodating Fe_{Be} and Be_{Fe} in two spatially separated sites with no interaction between them) has a strongly negative formation energy, which is related to the predicted instability of the phase at low temperatures and its ability to accommodate non-stoichiometry (see section 5.4).

Employing the Bragg-Williams approach (section 2.5), the degree of order in ζ -FeBe₂, δ -FeBe₅ and AlFeBe₄ intermetallics was predicted as a function of temperature between 0 K and 1700 K (see Fig. 5.11). Of course, beyond the melting point of the compounds, this analysis becomes meaningless, and should thereby be ignored. The Al-bearing compound exhibits no order across the entire temperature range, due to the zero formation energy for antisite pairs. In contrast ζ -FeBe₂ exhibits a high degree of order up to its melting point, while δ -FeBe₅, though ordered at low temperatures, exhibits a decrease in ordering at ~ 700 K and complete disorder at temperatures above 950 K. These predictions could be tested experimentally through measurements of the specific heat, since a spike in specific heat should be observed in the vicinity of the critical temperature for ordering [191].

5.7 Solubility and partitioning of extrinsic species in Be SPPs

The solution enthalpies of common impurities in intermetallic phases of Be were calculated and compared to the accommodation enthalpies of the same impurities in bulk Be. Extrinsic species can be accommodated onto one of the occupied sites via a substitution mechanism, or, for relatively small species such as C, H and O, onto an interstitial site (see Table 5.11, where a dash indicates a site that is unstable or significantly less favourable — by a few

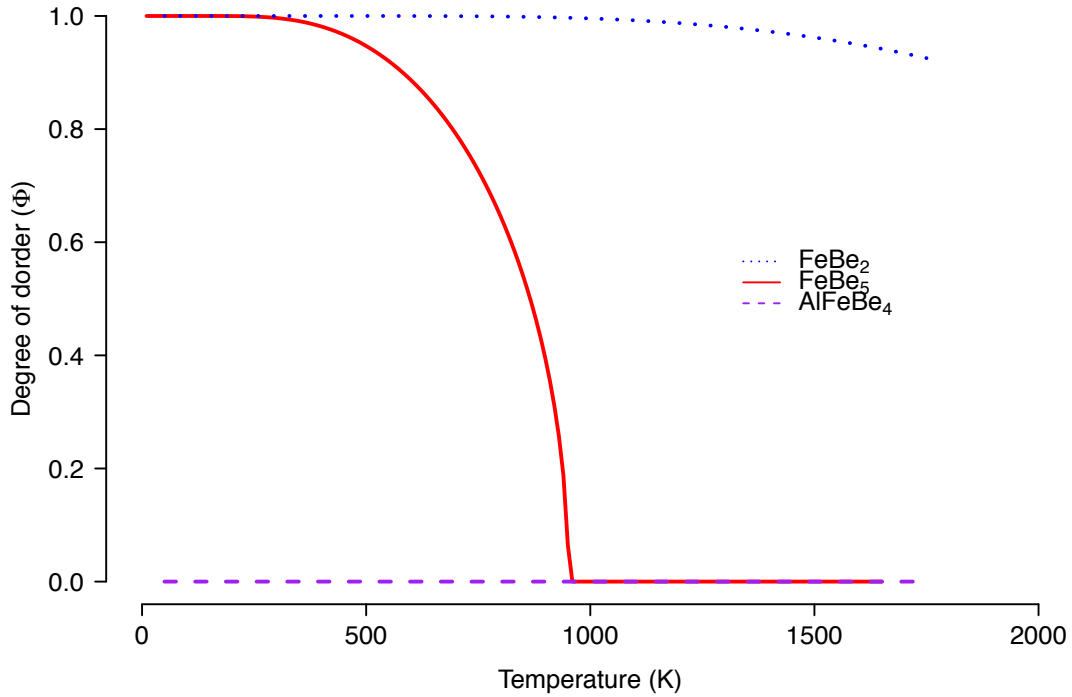


Figure 5.11: Degree of order as a function of temperature for ζ -FeBe₂ (blue, dotted), δ -FeBe₅ (red, solid) and AlFeBe₄ (purple, dashed).

eV — than other accommodation sites). For the larger atoms, substitution onto a Be-tetrahedron (e.g. Al_{4Be}) was also considered, but this was found to be consistently much less favourable than conventional substitution mechanisms, and are therefore not reported.

Whilst Be alloys are best represented by excess Be conditions (see section 5.4.4), in the current work all solution enthalpy values are reported from the standard state to aid comparison. In this framework, a negative values does not necessarily imply a favourable solution mechanism, as it merely implies that it is more favourable than the standard state, but does not take into account other competing processes (formation of intermetallic compounds or partitioning into other phases). Instead it is the smallest (or most negative) value that is the thermodynamically most likely incorporation mechanism.

When calculating the solution energy of the extrinsic elements in bulk Be, only the lowest energy sites reported by refs. [323, 331, 332] were recalculated in the current work and reported in Table 5.11. No prior work considered Li accommodation in metallic Be, therefore all potential accommodation sites were considered and the solution energies were

Table 5.11: Solution enthalpy (in eV) of impurities in ζ -FeBe₂, δ -FeBe₅ and AlFeBe₄, compared to those in bulk Be. Only the lowest energy interstitial configuration is presented for each element.

Phase	site	Be	Al	Fe	C	H	He	Li	Mg	O	Si
ζ -FeBe ₂	Be(2a)	—	0.79	1.07	2.09	2.43	5.18	1.65	3.21	0.46	-0.14
	Be(6h)	—	0.95	1.30	1.95	2.27	5.39	1.88	3.25	0.61	-0.17
	Fe(4f)	1.11	0.50	—	4.97	3.59	5.25	1.66	1.85	0.58	0.58
	<i>i</i>	3.52	—	5.03	2.78	0.64	5.19	—	—	-0.18	—
δ -FeBe ₅	Be(4c)	—	-0.73	-1.11	4.72	3.68	4.47	0.85	—	1.63	-0.67
	Be(16e)	—	0.94	0.63	—	2.21	5.00	1.92	3.33	0.27	—
	Fe(4a)	0.02	-0.22	—	3.60	0.81	3.38	0.60	0.84	-0.18	-0.11
	<i>i</i>	1.82	—	—	2.33	0.80	—	—	—	—	—
AlFeBe ₄	Al(4c)	0.98	—	-0.19	5.59	4.45	4.94	1.40	1.40	2.40	-0.03
	Be(16e)	—	0.81	0.58	1.74	2.15	4.70	1.54	3.03	-0.50	-0.33
	Fe(4a)	0.37	0.21	—	3.85	3.05	3.67	0.70	1.27	0.05	2.45
	<i>i</i>	3.24	—	4.77	2.39	0.40	4.20	—	—	-1.53	—
Be ₂ C	Be(8c)	—	2.49	4.04	8.06	3.03	5.20	1.17	2.85	2.02	4.23
	C(4a)	5.25	8.91	8.48	—	6.09	7.59	7.90	12.06	-0.87	5.00
	<i>i</i>	5.85	10.29	5.99	6.48	3.10	3.28	3.35	9.00	4.38	12.75
Be(s)		—	1.56	-0.13	4.00	1.85	3.29	1.01	2.34	-2.09	2.50
SPP formation		—	—	ζ -FeBe ₂ -1.30	Be ₂ C -0.68	—	—	—	MgBe ₁₃ 0.06	BeO -6.06	Be ₂ Si 0.70

calculated to be 1.01 eV for Be substitution, 6.34 eV for octahedral interstitial, 6.25 eV for hexahedral interstitial and 5.75 eV for trigonal interstitial.

Whilst it is predicted that lattice disorder plays an important role for AlFeBe₄ (section 5.6) and — at high temperatures — for δ -FeBe₅, calculating the energy associated with point defects within disordered phases is computationally impractical, hence the current work concerns only with the ordered structures. Nevertheless, a statistical distribution argument may be applied to consider the current results as an upper limit for the range of solution energies in the disordered structures: on average, the entropic contribution due to disorder may increase or decrease the stability of point defects with equal probability; however, over any period of time, those sites with increased stability are more likely to be occupied with respect to those with decreased stability; therefore the effect of disorder should — on average — reduce the formation energy of extrinsic defects.¹

¹Note: whilst the defect formation energy is the main thermodynamical driving force for the accommodation of the defects, the presence of disorder may affect other aspect related to the accommodation of extrinsic elements, such as the kinetics of migration. Investigation of those processes is computationally very demanding and may be a potential subject for future work.

5.7.1 Hydrogen and helium

All Fe-bearing intermetallic phases show a higher affinity to H compared to the Be matrix. Therefore, if a sufficiently large volume fraction of SPPs is present, these may act as H sinks, thereby degrading the tritium retention properties of Be alloys, a high degree of purity with respect to Fe may be desired for Be-based plasma facing materials. This is in contrast to the mechanical properties, which are predicted to benefit from small amounts of Fe, as it acts as a getter for Al (section 5.5). On the other hand, Be_2C does not provide strong trapping sites for H, therefore the presence of C impurities should not degrade the tritium retention performances of Be. Similarly to what is observed in Zr SPPs (chapter 3), H exhibits a strong preference for interstitial over substitutional accommodation in these intermetallic phases. This suggests that H may retain the high mobility that it exhibits in the Be metal [323, 331, 333].

Conversely to H, He exhibits a higher solubility in Be metal over the Fe-bearing intermetallics; and a comparable solution energy between Be_2C and Be. Various studies have shown that multiple H and He atoms may be trapped by a single lattice vacancy in metals (including Be) [333–336]. Consequently, further work should be carried out to investigate the clustering behaviour of H, He and vacancies in the intermetallic phases.

5.7.2 Carbon, oxygen and magnesium

The formation energies of Be_2C , BeO and MgBe_{13} are more favourable than the accommodation of dilute C, O or Mg in Be metal or Be intermetallics. Be_2C and BeO exhibit negative formation energy, while MgBe_{13} exhibits a positive yet small formation enthalpy, which is within the bounds of certainty of the current methodology. This suggests that entropic contributions not included here (such as thermal vibrations or configurational disorder) may play an important role in the stabilisation of MgBe_{13} . The difference in energy between the formation of a formula unit of MgBe_{13} and the solution of Mg in the intermetallics is 0.8–1.8 eV, so some solubility is expected; whilst the difference in energy between the formation of Be_2C and dissolution of C in intermetallics is 2.4–3.0 eV, and that between the formation of BeO and dissolution of O in Be metal is ~ 4.0 eV, therefore only limited solubility of C

and O is predicted. Mg and C exhibit a more favourable solution enthalpy in the Fe-bearing intermetallics rather than bulk Be, whilst the opposite is true for O.

5.7.3 Silicon and lithium

Si, like Al, has detrimental effects on the mechanical properties of Be alloys [309]. Also similarly to Al, Si exhibits strong preferential dissolution in the Fe-bearing intermetallics rather than bulk Be. Whilst elemental Si precipitates have been observed in some Be alloys [308], it is expected that the presence of Fe-bearing intermetallics may provide strong sinks for Si dissolution, and therefore act as Si getters if suitable heat treatment is provided. This is in agreement with observations by Rooksby and Green [308] that in some Fe-containing samples Si was detected by chemical analysis but no elemental Si was found through XRD analysis. The existence of a Be_2Si phase, with Be_2C -like anti-fluorite structure, was proposed by recent DFT work [337], yet it has not been observed experimentally [308, 309, 338]. Our calculation found that the formation enthalpy of Be_2Si was found to be large and positive, in agreement with the lack of experimental observations. Li, like Si and H, also favours dissolution in Fe-bearing intermetallics. However, the degree of preferential Li dissolution (0.2–0.3 eV) is significantly less than that of Si (2.7–3.2 eV) or H (1.0–1.4 eV).

5.8 Summary

As discussed in section 1.3, Be is the plasma facing material of choice in current fusion reactor designs. Fe and Al are common elements found in Be, either as alloying additions or as unintentional impurities, and their influence on the performance of Be will depend upon which phases are present. While it is well established that Be rich intermetallics are formed in the presence of Fe and Al, there is conflicting experimental data. Here DFT simulations were used to predict the structures and energies of various intermetallics and these have been compared with the solution energies of Fe and Al in Be metal. While previous simulations have focused on enthalpies alone, here by calculating the phonon DOS of the various phases, temperature effects are included by determining both vibrational

enthalpy and entropy contributions — and hence discussion is based around the Helmholtz free energy.

A commonly observed intermetallic is the so-called ε phase, however, its stoichiometry and structure are not well established. Of the 13 candidates considered in this study, a $\text{Fe}_2\text{Be}_{17}$ phase, exhibiting a hexagonal $\text{RhBe}_{6.6}$ structure with space group $P\bar{6}m2$ is identified as the lowest energy, with potential Fe deficiency as highlighted below. The intermetallics $\zeta\text{-FeBe}_2$ and $\delta\text{-FeBe}_5$ are better characterised experimentally, although we find that $\delta\text{-FeBe}_5$ starts to become disordered around 500 K and is completely disordered by ~ 1000 K, whereas $\zeta\text{-FeBe}_2$ exhibits little disorder until at least 1500 K. In terms of phase stability, convex hull diagrams indicate that below ~ 1250 K only $\zeta\text{-FeBe}_2$ and $\varepsilon\text{-Fe}_2\text{Be}_{17}$ are predicted to form at equilibrium; above ~ 1650 K only $\zeta\text{-FeBe}_2$ and $\delta\text{-FeBe}_5$ are observed; and at intermediate temperature all three phases co-exist.

Point defects are calculated for all the phases in order to identify the likely extent of deviations from stoichiometric compositions. $\delta\text{-FeBe}_5$ exhibits considerable non-stoichiometry with both Fe and Be excess compositions. Conversely, in $\varepsilon\text{-Fe}_2\text{Be}_{17}$ substitution of Be for some Fe is energetically favourable and thus ε will be Fe deficient ($\text{Fe}_{2-x}\text{Be}_{17+x}$), while defects in $\zeta\text{-FeBe}_2$ are high in energy and this phase will remain much more stoichiometric.

While the binary Al-Be system exhibits no intermetallic phases, Al is readily incorporated into Fe-Be intermetallics with Al substitution for Be in $\delta\text{-FeBe}_5$ leading to the AlFeBe_4 phase. Disorder is also apparent in this ternary system with no driving force for ordering, so that AlFeBe_4 should more accurately be reported as $(\text{Al,Fe})\text{Be}_2$, where the Fe and Al sublattices are indistinguishable.

Fe-bearing intermetallics are found to getter H, Li, Al and Si. The high affinity to Al and Si is thought to be beneficial in Be alloys, as it may counter the detrimental effect on mechanical properties caused by the precipitation of Al and Si SPPs at grain boundaries. On the other hand, the ability to absorb H may have a negative impact on the tritium retention of plasma facing components. Conversely, Be_2C does not exhibit strong interactions with any of the extrinsic elements considered.

6

Ongoing and further work

6.1 Zr alloys

The work presented in Chapter 3 shed light on the solubility of H in binary Zr SPP. The interaction between H and ternary SPPs, such as the commonly observed $\text{Zr}(\text{Cr},\text{Fe})_2$ and $\text{Zr}_2(\text{Fe},\text{Ni})$, is extrapolated from their binary end members. A possible avenue for improvement is to perform direct calculations of H solubility in ternary compounds. The first step of this investigation should be to identify whether specific compositions are more favourable than others. Taking for instance the example of Nb-Fe-Zr intermetallics, where Nb may substitute for Zr or Fe in ZrFe_2 Laves phases, further work should identify which Fe/Nb or Zr/Nb ratios yield higher stability ternary phases. Once that is determined, it would be instructive to measure the change in H solution energy as a function of Nb or Fe content. This would clarify whether these particles may act as trapping sites for H during uptake and/or may release H in later stages of life of as a consequence of particle dissolution or oxidation. As highlighted in Chapter 4, the effect of Fe/Nb ratio is particularly relevant to high burn-up fuel cladding, where neutron irradiation causes the preferential dissolution of Fe and Cr over other, slower diffusing, species such as Nb and Zr.

Diffusion of alloying elements in Zr is also a key aspect that deserves further investigation. In particular, the finding of novel interstitial sites for Fe and Cr may open diffusion paths that were previously not known. Furthermore, literature on Cr diffusion in Zr (both experimental and DFT) is particularly scarce. Further work may also be carried out to understand the role of defect clusters (intrinsic and extrinsic) on the diffusivity of Fe and Cr. Considering larger length-scales, not accessible by DFT, the diffusion of alloying additions along dislocations and grain boundaries may also prove insightful. Embedded atom model (EAM) potentials have proved to be suitable for the study of pure Zr metal [339–345], therefore, it would be logical to extend the currently available sets of potentials to include the alloying additions. Some such models have been developed [283, 346–349] but all have some limitation. For instance, many potential sets are restricted to Zr-Ni interactions [346–349]. The EAM potential set developed by Christensen *et al.* [283], which includes Fe, Cr, Ni, Nb, Sn and O, was fitted to substitutional point defects in α -Zr using 64 atoms supercells. As highlighted in section 4.1, point defects simulations in such small supercells are subject

to large artefact energies, which severely alter their relative stability, defect volumes and geometrical configurations. These spurious effects are then expected to be translated into the EAM potentials. Furthermore, the potentials were derived only from substitutional defects, whilst all of the above elements also occupy interstitial positions in the α -Zr lattice [30, 267, 281, 282, 285–287] and in some cases — notably Fe and Ni — interstitials are the dominant accommodation sites in Zr. Ongoing work is also being carried out to develop tight binding potentials to describe the Zr-H systems [228]. The aim is to obtain a model that is able to capture the complex chemical changes involved in the precipitations of hydrides (which are not accurately described by EAM potentials [188, 350]) whilst still being significantly less computationally demanding than DFT.

A natural extension of the current work is also to investigate the behaviour of H with the Zr oxide, as H must diffuse through the protective oxide layer before dissolving into the metal. For Zr oxidation to occur, the electrochemical circuit must be closed either by electron transport from the metal/oxide interface to the oxide/water interface, or by proton transport in the opposite direction. Consequently, significant efforts are being carried out to investigate the effect of electrical conductivity of ZrO_2 on the hydrogen diffusion kinetics through the oxide [38, 76, 351, 352]. However, H may not only diffuse through the bulk material but also through the grain boundaries, which may be hydroxylated [64, 75, 353]. Here atomistic modelling may provide insightful knowledge in an area where experimental observation is meagre and difficult to obtain. The tight binding Zr-H potential that is currently being developed may be further extended to include oxygen, so that the $\text{ZrO}_2/\text{ZrO}/\text{Zr}$ boundaries may be studied. The effect of alloying additions at the metal/oxide interface — in the form of SPP or in solution — may also be subject of further work if a consistent set of tight binding potentials are developed. Alternatively, information from DFT calculations (e.g. preferential charge states of alloying additions as a function of stress, clustering tendencies of intrinsic and extrinsic defects, diffusion kinetics, etc.) may feed into numerical models that evaluate the ionic (oxygen vacancies), electronic and protonic conductivity of the oxide.

6.2 Be alloys

Disorder is predicted to play an important role in the Al-Fe-Be system (see chapter 5), therefore it is logical to extend the investigation carried out for ordered structures (such as intrinsic point defect calculations, elastic constants predictions, accommodation of extrinsic elements) to disordered structures. This is a non-trivial task as significantly larger simulation cells must be adopted and a large number of local environments must be sampled for each point defect to obtain reliable statistical information. Furthermore, the role of other common impurities such as C and Si may be explored further. For instance, ongoing work is investigating the self-diffusion of C and Be in Be_2C .

Other beryllium intermetallics that are of high importance to the fusion industry are MBe_{12} ($\text{M} = \text{Ti}, \text{V}, \text{Mo}$ or W), $\text{Ti}_2\text{Be}_{17}$ and ZrBe_{13} . These are potential candidates for neutron multiplier components, as they contain a high Be density, exhibit a high melting temperature and good corrosion resistance. Understanding their ability to accommodate non-stoichiometry is especially important as the Be/M ratio will decrease with time as the Be is consumed by the $(n,2n)$ reaction. Further work should also be carried out to understand their interaction with He (from the coolant and from α particles), Li (from the breeder material) and O (also from the breeder material but also potentially from the coolant).

Similarly to the Zr alloys, a promising avenue for the investigation of larger and more complex systems is to derive computationally cheaper models (such as EAM, bond order or tight binding potentials) [354–363]. Ongoing work is aiming to expand some of the currently existing potential of Be to Be-Ti, Be-W, Be-V, Be-Mo and Be-Zr systems. When a lower level of physics is employed, inevitably some transferability of the method is lost. It is therefore crucial to fit the potentials to those properties that are relevant for the study in question. For the case of plasma facing components, some of the necessary physical properties that should be correctly described are: the interaction with H and He from the fuel and C and W from potential substrates, the thermal conductivity (phonon and electrical), the elastic properties, the ballistic collision behaviour, the defect formation energies and the relative phase stabilities.

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Details of experiments on Fe-Zr and Cr-Zr alloys

A.1 Materials and sample preparation

Binary Zr-alloys were melted in an arc furnace in a water cooled copper crucible under an argon atmosphere at Western Zirconium, USA. The Zr starting material was in the form of chips while Cr and Fe were small beads. All alloying elements were standard materials used by Western Zirconium for their production of zirconium alloys. The 125 g buttons were triple melted to ensure chemical homogeneity. The chemical composition of the alloys was analysed using induced coupled plasma-atomic emission spectroscopy and combustion analysis at Western Zirconium, is presented in Table A.1. Notably, the alloy containing 0.05% Cr also contains large amounts of Fe and Sn impurities and is close in composition to commercial Zircaloy 2. All other alloys exhibit a high degree of purity.

The as-cast buttons were cross rolled at 540 °C with an intermediate recrystallisation

Table A.1: Chemical composition of the binary alloys in wt. ppm. Hf and Nb were consistently less than 23 and 20 ppm respectively. Si and any other potential impurities were always below the detection limit.

Sample name	Cr	Fe	Cu	N	O	Sn
Zr-0.1Fe	< 20	1049	10	NA	NA	< 8
Zr-0.2Fe	< 20	1927	11	NA	NA	< 8
Zr-0.4Fe	< 20	4298	< 10	44	810	< 8
Zr-0.6Fe	< 20	6226	22	NA	NA	< 8
Zr-0.8Fe	< 20	8943	19	NA	NA	< 8
Zr-0.05Cr	475	217	11	NA	NA	1155
Zr-0.15Cr	1608	37	< 10	NA	NA	< 8
Zr-0.30Cr	2869	41	< 10	43	849	< 8

anneal at 600 °C to a final thickness of 3 mm. Subsequently, $3 \times 3 \times 40 \text{ mm}^3$ matchstick samples were cut and β heat-treated for 10 minutes at 1000 °C in a vertical furnace flushed with argon, followed by water quenching, in an attempt to maintain most of the Fe and Cr into α -Zr solution. Scanning and transmission electron microscopy investigation showed that complete solid solutions were not obtained even at these very high cooling rates. Instead a significant number of small SPPs had formed [301].

A.2 Atom probe tomography

Atom probe tomography (APT) carried out by colleagues¹ on a Cameca LEAP 3000 X Si, with a flight path of 90 mm. The experiments were conducted at a base temperature of $-213 \pm 5^\circ\text{C}$, in laser-pulsing mode ($\sim 10 \text{ ps}$, 532 nm , spot size $< 10 \mu\text{m}$ diameter). Throughout the analysis, the DC voltage was increased to keep a detection rate of 5 ions per 1000 pulses. Specimens were prepared by means of a FIB lift-out procedure, from a mechanically polished sample of the Zr alloys, using a Zeiss Auriga and an electropolished Mo grid as support [364].

The samples containing 1.30 at.% Fe and 0.26 at.% Cr were chosen for APT analysis. The datasets were reconstructed using state-of-the-art algorithms [365], resulting in the tomogram shown in Figure A.1. Fe and Cr are either found within small particles or atmospheres along grain boundaries, or are randomly distributed within the matrix.

¹B. Gault and M. Moody at the University of Oxford

The total composition calculated using APT is in excellent agreement with the nominal composition of the alloys (1.34 ± 0.026 at.% Fe and 0.25 at.% Cr respectively). Selecting volumes that contained no SPPs or grain boundaries, the concentration of alloying element in solution was calculated to be 0.42 ± 0.015 at.% Fe and 0.21 ± 0.01 at.% Cr.

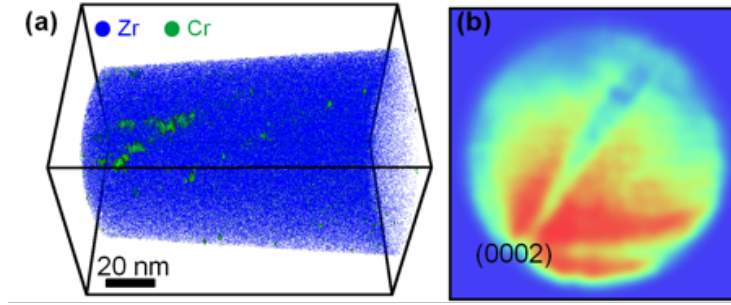


Figure A.1: a) Three-dimensional reconstruction of the dataset from the Zr-Cr sample. The green surface encompasses regions containing above 2 at.% Cr. b) Top-down projection of the dataset shown in (a), with red representing regions of higher density and blue of lower density. The six-fold symmetry in the lower left corner of the projection is indicative of the (0002) pole. Reproduced from [366].

Experimental evidence of the dual nature of Cr accommodation in Zr is provided by our APT work. The dataset of the sample is shown in Figure A.1(a). A $10 \times 10 \text{ nm}^2$ subset of the data centred on the (0002) pole indicated in Figure A.1(b), and going down the whole length of the dataset, was exported. Advanced species-specific spatial distribution maps were applied to this subset and the resulting data are plotted in Figure A.2. The Zr-Zr distribution exhibits broad peaks corresponding to the (0002) atomic planes. The slight and progressive shift away from the expected location of the peaks can be attributed to distortions in the tomogram, as discussed in [367]. The Zr-Cr distribution, which measures the average distribution of Cr atoms relative to Zr atoms along this crystallographic direction, exhibits peaks that are in-between the main peaks of the Zr-Zr distribution. This is consistent with a significant fraction of the Cr atoms being located at interstitial sites. This is the first evidence of interstitials provided by APT. A similar procedure was attempted on the Fe-containing sample, but the large volume fraction of SPPs in the sample [302] made it extremely challenging to achieve a sufficient signal-to-noise ratio to generate definitive results.

Two distinct analyses were performed to investigate the distribution of distance between

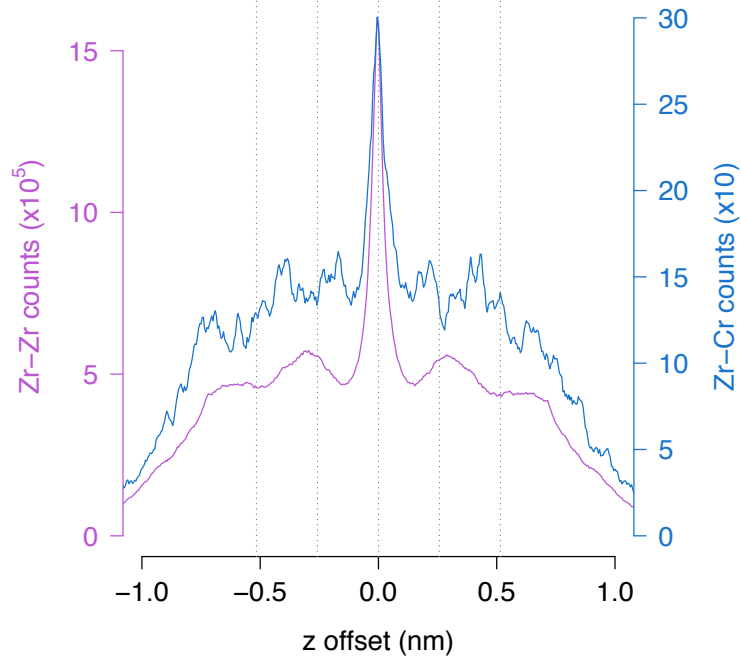


Figure A.2: In-depth spatial distribution map showing the Zr-Zr distribution (in purple) and the Cr-Zr distribution (in blue). Dashed lines indicate $d_{(0002)}$ spacings from XRD data.

each Cr atom and their first nearest neighbour Cr: first considering the whole dataset, and second considering a subset of the data that excludes the regions delineated by an isoconcentration surface similar to the one displayed in Figure A.1, with a threshold of 1 at%Cr. The latter allows for an analysis of the matrix. The two graphs, shown in Figure A.3, exhibit a different behaviour: for the complete dataset, there is a clear tendency for neighbours of shorter distances compared to random, while Cr in the matrix are close to a random distribution, which was expected based on visual inspection. The closer distances in the subset containing the clusters, is in agreement with the DFT predictions that closely bound clusters (those in 1nn configuration) are more stable than clusters in which the Cr atoms are further apart and compared to dilute defects.

A.3 Thermoelectric power measurements and calibration

TEP experiments measure the Seebeck coefficient (S), which is the electric potential difference that arises when two metals in tight contact form a thermocouple with two junctions held under a temperature difference. Previous work has shown that the Seebeck

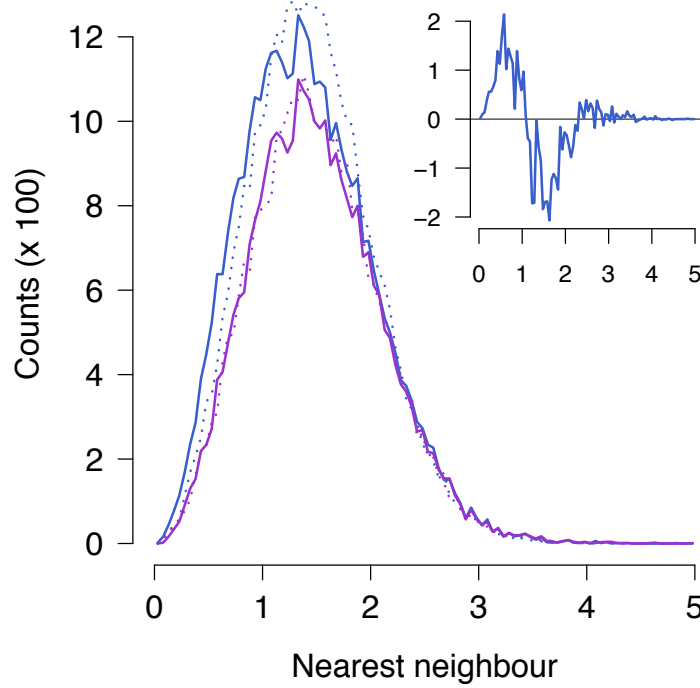


Figure A.3: Cr first nearest neighbour distribution (solid lines) compared to randomised datasets (dotted lines) for the whole dataset (blue) and for the matrix only (purple). Inset is the difference between the experimental and random that highlights the clustering tendency of Cr in the full dataset.

coefficient of zirconium alloys is sensitive to solute concentration, texture and cold work, but is not affected by the presence of small volume fraction of SPPs [368–374]. All samples were prepared using the same procedure to minimise variations in texture and microstructure, therefore any change recorded in TEP can be attributed to variations in solute concentrations.

The measurements were conducted at INSA, Lyon, France using a TechMetal Promotion instrument and a Cu reference. The temperature of the clamping Cu blocks was held at 15 ± 0.2 °C and 25 ± 0.2 °C. In order to stabilise the thermo-electricity, each specimen was left for 1 min after mounting before measurement. Each measurement had a duration of 20 s in which the initial value and the variation from this value were recorded. Each surface of the matchstick specimen was measured twice to give an average value from eight measurements per alloy concentration.

Figure A.4 shows the change in Seebeck coefficient as a function of Fe and Cr content.

It is observed that the Seebeck coefficient decreases with increasing content of Fe or Cr, indicating that, despite the formation of SPPs, an increasing amount of alloying element was trapped in solution with increasing nominal composition of the samples.

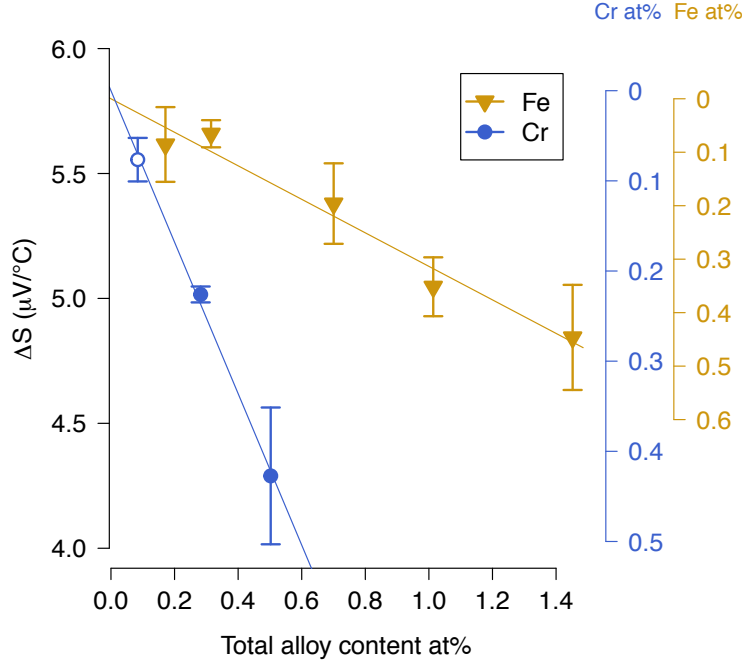


Figure A.4: TEP measurements (Seebeck coefficient) against nominal composition of the binary alloys. Right-hand side axes are the calibrated concentrations of Cr and Fe dissolved in solution. Error bars express the standard deviation of eight samples per datum. The hollow symbol represent the low purity alloy.

To obtain quantitative concentrations for the α -Zr matrix, it is necessary to establish a datum by calibrating at least one TEP point that has a known alloy concentration in solution. Since all of the samples exhibited some segregation of Fe/Cr to SPPs, APT results of matrix content in volumes containing no SPPs was employed. New linear scales (right-hand side axis of Figure A.4) were defined by assigning the following two values:

- zero at the intersection between the left-hand side y-axis and the linear best fit line of the TEP results (i.e. extrapolated change in Seebeck for pure Zr)
- 0.42 at % Fe and 0.21 at % Cr for the fifth and second point of the Zr-Fe and Zr-Cr series respectively.

The errors arising from the APT matrix content were added to the deviation from linear

best fit to obtain total uncertainty about the matrix content.