

Atomistic Simulation of Hydrogen and Hydrides in Zirconium and Zirconium Alloys

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by

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This thesis is the work of Simon C. Lumley, and details original scientific research in the field of Materials Science and Engineering. All information drawn from the work of others is referenced in the bibliography.

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Abstract

Zirconium alloys are an important material in the nuclear industry, used as a fuel cladding material in water cooled reactors. However, aqueous corrosion of the alloy results in the production of hydrogen at the interface of the cladding with the water. Some of the hydrogen produced may diffuse through the passive oxide layer and be absorbed by the zirconium in solid solution. It has a deleterious effect on the mechanical properties of the cladding alloy, particularly if enough hydrogen is absorbed to cause precipitation of zirconium hydrides. There are multiple different hydride phases that may form, which have complex interactions with alloying additions, hydrogen concentration, stress and temperature. Of particular note is the phenomenon of Delayed Hydride Cracking (DHC), where the interaction of stress fields around crack-tips is believed to bring about the precipitation of hydrides, which promotes further growth of cracks. Overall, the embrittlement and cracking of the cladding by hydride related mechanisms represents a risk for reactor operators, which can be mitigated by a better understanding of the processes at work. This thesis presents an investigation into the mechanisms of hydride formation in zirconium alloys. In order to understand the mechanisms involved, a perspective of the system is has been sought using the *ab-initio*, quantum mechanical, atomistic simulation technique of Density Functional Theory (DFT).

The first component of this study was an examination of the stability of different alloying additions in zirconium. The alloying additions of chromium, iron, nickel, niobium, tin, vanadium and yttrium have been examined, comparing the energy of them existing in a solid solution or in different inter-metallic structures. These intermetallic structures included multiple Laves phase structures, as well as a variety of other configurations. It was found that the thermodynamic driving forces in this system can be correlated with trends in atomic radii and the relative electronegativities of the different species. These same parameters also correlate with the formation energy differences between the different Laves phase polymorphs. Fe and Cr were found to prefer interstitial sites over substitutional locations in the Zr lattice. The Fe atoms had a similar energy of solution in both tetrahedral and octahedral sites, which may have implications for diffusion pathways. Formation energies of Fe, Ni and Sn based intermetallic compounds were found to be negative, and the Zr_2Fe and Zr_2Ni intermetallics were metastable. Most elements displayed neg-

ative energies of solution in β -zirconium but positive energies in the α -phase, with the exception of Sn (which was negative for both) and Y (which was positive for both). Solutions formed from intermetallics showed a similar trend. Incorporation energies onto vacant sites in the Zr lattice were also investigated. It was found that all of the elements investigated showed a driving force to incorporate onto vacancies in α -Zr but some would not incorporate into β -Zr.

Different hydride structures were investigated, including the ζ , γ , δ and ε -phases, and some speculative hydride structures. These were also compared with a large number of structures, which were generated with a random positioning of the H on appropriate sites in the Zr lattice. In α -Zr, inserting a H atom on the tetrahedral site had a more negative solution enthalpy than the octahedral site. This was also found to be true when the Zr was in a FCC lattice structure, and may have been related to the relative size of the sites. The γ and ε -hydrides appear to be thermodynamically stable, while the δ hydride was very close in energy, but not quite favourable and thus, not quite stable. The ζ -phase, and speculative phases containing H atoms on octahedral sites were significantly less stable.

The precipitation reaction was looked at in the context of variations in temperature and pressure. This was done by using phonon density of states data to calculate thermodynamic properties such as heat capacities and vibrational entropies. It was found that at any temperature, the concentration of the initial solid solution had to be at least 300 ppm before precipitation could become favourable. This implies local concentration of hydrogen atoms within a lattice must be significantly greater than the global concentration normally found in experimental results. Increases in temperature were found to drive the reaction towards solution, as would be expected from experimental results. The entropic components of the overall free energy are the main causes of this effect.

Finally, the impact of pressure on hydride precipitation was examined, by applying a range of hydrostatic stresses to the α -zirconium lattice. Importantly, it was found that a tensile hydrostatic Zr lattice has a more favourable hydrogen solution enthalpy than a relaxed or compressed lattice. This implies that hydrogen may prefer to diffuse towards areas of the lattice which are under tension, in agreement with the Diffusion First Model of DHC. Different hydrides were placed under compressive and tensile stress, which demonstrated that the normally anisotropic stiffness of zirconium hydride lattice becomes isotropic for a stoichiometric ratio of around $\text{ZrH}_{1.66}$.

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Dedication

There are three people who have meant so much to me throughout this time.

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Chapter 1

Introduction

1.1 The Challenges of Energy Production

The production and use of energy is one of the most fundamental concerns affecting human quality of life. In pre-industrial eras, the predominant way of producing light and warmth on demand has been by the burning of various combustible fuels. The main ways of producing mechanically useful work were by harnessing the motion of wind, water, and the use of animal or human labour. However, things began to change throughout the 18th and 19th centuries, with the advent of steam power. The initial development of the steam engine by Thomas Savery and Thomas Newcomen, followed by efficiency improvements by James Watt and Matthew Boulton (among others) allowed combustible fuels to be used to provide mechanical work, in far greater amounts than were previously available [1]. This in turn allowed goods to be produced on an industrial scale, bringing down the cost of many products, and transforming a largely agrarian society into an industrial powerhouse. Life expectancy, literacy and quality of life steadily improved due to industrialisation and this was a direct result of the improvements in the ability to produce and use energy. Further advances in energy technology have yielded similarly dramatic improvements to the human experience. One of the most important of these was the discovery and application of electrical energy.

Ever since the discovery of electromagnetic induction by Michael Faraday, in 1821 [2], elec-

tricity has predominantly been produced by the motion of a conducting wire through a magnetic field. Thus an electric current is relatively easily generated using mechanical motion, provided by steam engines and their modern descendant, steam turbines. An electric current is an incredibly useful form of energy, as it can easily be transported and made to perform almost any other form of useful work. As a result of this usefulness, the reliable supply of electrical power is one of the key factors that has allowed civilisation to advance towards post industrial levels of quality of life.

Due to its inherent utility, the global demand for electricity has risen substantially during previous decades and, in all likelihood, will continue to rise for the foreseeable future. Over the past four decades, world electricity consumption has more than trebled, partly due to the industrialisation of developing nations, as well as technological progress in other areas of the world leading to ever more power hungry devices, appliances and processes [3]. There is a strong correlation between the amount of electricity produced or consumed by a nation and the average quality of life of that nation's inhabitants. Thus one of the more effective ways of improving quality of life is to increase access to electrical power, particularly in less developed nations that lack reliable electrical infrastructure. Maintaining and developing supply is also of incredible importance to more developed nations as well. In a modern society, all the basic necessities of human welfare are heavily dependent upon the use of electricity, including light, food preparation, sanitation, water, heating and medical treatment, to name but a few. Thus, an interruption of supply, even if only for a short period, represents a crippling blow to modern society. The negative consequences of a prolonged lack of electrical supply are so significant, that being without electrical power is far more damaging to individuals and society than any negative consequence brought about as a side effect of electricity generation. Thus, maintaining a reliable electrical supply is of paramount importance, both for the UK and the world.

Unfortunately, this task is looking increasingly difficult as humanity has come to the realisation that the supply of combustible fuels is not infinite. The more readily available supplies of oil and gas are already dropping in production, forcing us to use more costly and difficult to exploit resources, such as deep-water reserves, shale gas, and tar sands [4]. This leads to increases in the cost of energy and all the consequences that this entails. If the supply of electricity is to be maintained, it is important that civilisation transitions to using methods of power generation

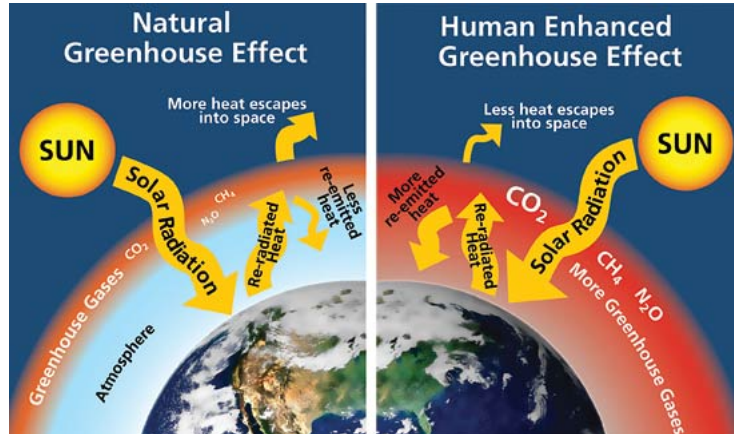


Figure 1.1: A simplified diagram of how man-made emissions of various gasses are thought to be responsible for an increase in global temperature. Reproduced from reference [5].

that are less dependent upon the production of fossil fuels.

As well as maintaining supply, a further challenge has been revealed in the past few decades, which will have a major impact on how electricity is generated and used. This challenge comes in the form of the discovery of Anthropogenic Climate Change. There is strong and growing consensus that the release of man-made CO_2 into the atmosphere is deteriorating the Earth's ability to radiate absorbed solar-radiation back into space (see Fig. 1.1). Thus, as human activities continue to release CO_2 on an industrial scale, the prediction is that much of the climate on Earth will transition to a warmer state [6]. The habitability of many parts of the world depends upon a careful balance of mutually interlinked ecological phenomena, heavily influenced by temperature. Thus, even small rises in temperature could have a significantly detrimental effect on the ecological mechanisms that underpin many aspects of society. In particular, precipitation, food production, sanitation, disease propagation, and wildlife habitability could all change drastically, reducing quality of life in many parts of the world and requiring an immense effort in order to mitigate [6]. A further pressing concern is that a rise in global temperatures could lead to a partial or total melting of polar ice caps and glaciers. Considering that a large volume of water is held in the form of ice, a release of this water could result in a sea-level rise, although there is still debate as to how significant this may be. Considering that over a third of the world's population lives less than 100 m above sea level [7], there is significant capacity for even modest rises of sea level to impact vast numbers of people. A further effect is that de-

structive weather phenomena, such as tornadoes, storms and hurricanes, are largely dependent upon the amount of atmospheric and hydrological thermal energy that they may draw upon. With increased atmosphere and ocean temperatures, these phenomena are predicted to occur more often and with greater severity [6]. Thus the effects of climate change should be mitigated and limited as much as reasonably practicable. As the combustion of fossil fuels is the most significant cause of CO₂ emissions, the most logical way to prevent or mitigate climate change is to curtail the usage of fossil fuels. Some direct uses of fossil fuels, such as burning gas, oil, coal or peat for warming buildings and water can be directly replaced with electrical substitutes. Electrical motors can replace internal combustion engines as a means of providing mechanical power for transport, providing effective batteries can be developed. These measures are already being adopted in many nations around the globe, although this still leaves one final issue. By shifting direct use of carbon dioxide emitting fuels to electricity consumption, there is now the task of providing more electricity, which must also not produce much carbon dioxide.

1.2 Nuclear Reactors

There are a number of different options for providing low carbon electricity, although they generally have a number of disadvantages associated with them. Generally speaking, most low-carbon forms of energy rely on the extraction of energy found in dynamic natural energy flows, such as sunlight, wind, or water-flow and are often referred to as "renewable energy". However, although these technologies are in various states of development and deployment around the world, their drawbacks make them economically unfavourable compared to traditional electricity generation methods. These power sources are normally intermittent, or require specific geological formations in order to be constructed. Mitigation of these flaws often requires expensive distribution of grid assets, or large amounts of (normally fossil fuel based) generation capacity to be ready on standby. Although it is likely that renewable technologies will play some part in future electricity generation, it is doubtful that they will be able to shoulder this load by themselves. However, other, comparatively mature technologies exist, one of the foremost being nuclear power.

The main process for generating nuclear power is the controlled fission of heavy elements. Elements such as uranium or plutonium have multiple different types of atoms which have the same

atomic number (defined by the number of protons), but slightly different masses (determined by the sum of the protons and neutrons in the nucleus). These are known as isotopes. Isotopes of very heavy elements with an even atomic number, but an odd atomic mass are known as "fissile" elements, in that they will split into two or more smaller elements if induced to absorb a neutron. Fissile isotopes include U-235, U-233, and Pu-239. This produces two or more "fission products", lighter than the original atom. Furthermore, the combined mass of these fission products is less than the original mass of the fissile nucleus. As originally predicted by Albert Einstein in 1906, this difference in mass is converted into energy via means of Einstein's famous mass-energy equivalence equation [8]:

$$E = mc^2 \tag{1.1}$$

Where E is the energy m is the mass difference and c is the speed of light in a vacuum (approximately $3 \times 10^8 \text{ ms}^{-1}$). This energy manifests itself as kinetic energy of the fission products, meaning they will fly away from the site of the fission event at extreme speed. If this event takes place within the bulk of a uranium or plutonium containing solid, then these fission products will undergo successive collision with other atoms, until they are at relative rest. This increases the thermal energy of the solid, heating the "fuel" of the reaction.

A fission event will also release one more product: 2-3 additional neutrons. If the fuel is sufficiently dense and the neutrons made to remain in the mass of the fuel long enough, then these neutrons can collide with other fissile atoms before leaving the mass of fuel, causing the reaction to continue. Care must be taken to ensure that the number of neutrons in the fuel is not increasing, thus for every neutron produced by a fission event, only one must go on to create a new fission event, while the rest are removed from the system, by escaping it, or being absorbed by a non-fissile atom. This status is known as maintaining the chain reaction as "critical".

It should be apparent from Eq. 1.1, that the c^2 term is an extremely large number. Destroying a very small amount of mass results in the creation of an extremely large quantity of energy. Although the difference in mass of the reactants and products of the nuclear reaction is small, the amount of energy released is enormous. To put this in perspective, the complete fission of a grapefruit sized lump of fissile uranium, weighing 1 kg, would produce approximately 83.14 TJ

of energy. This is equivalent to about 13,600 barrels of oil, or the approximate lifetime energy needs of 4-8 people, at a modern western standard of living¹. The extreme energy density of fissile materials has always been the greatest promise of nuclear technology, as it potentially offers vast amounts of energy for very small amounts of fuel. This is in comparison with fossil fuel burning technologies where a large coal-fired power-plant can easily burn over 1.5 thousand tonnes of coal *per hour* [10].

The promises of controlling this power initially prompted a large scientific effort to unlock the secrets of nuclear technology. The ability to initiate and sustain criticality was first developed during the second-world-war, as part of the joint American-British-Canadian Manhattan Project. Although the ultimate goal of this project was the initiation of uncontrolled chain reactions for military purposes, a direct result of this technology is the ability to control nuclear reactions for energy generation purposes. If nuclear fuel can be induced to fission in a controlled manner, then the heat generated can be used to boil water and drive steam turbines, just as a more conventional fossil fuel plant.

However, designing a practical plant capable of this is dependent upon overcoming a number of engineering challenges. Initiating a controlled chain reaction requires significant technical capabilities. One of these, is due to the fact that a uranium atom will not simply absorb any neutron. If the neutron is travelling too quickly, it is more likely to elastically scatter off the uranium nucleus than be captured. This leads to the concept of "neutron capture cross-section". U-235 is more likely to absorb a slow moving neutron than a fast neutron. The simplest way to slow neutrons down is to arrange the internal structure of the reactor such that neutrons emitted by fission reactions are likely to interact with nuclei of a low atomic mass. With a low atomic mass, neutrons will elastically transfer some of their momentum to the atom and slow down as a result. This is known as "thermalising" or "moderating" the neutrons, as it brings the energy of the neutrons into thermal equilibrium with their surroundings. The material used to achieve this is called a "moderator". Typically, earlier reactors used high quality graphite as the moderator, or in some cases, deuterated ("heavy") water. The most easily accessible moderator is simply high purity water, although this requires other considerations as will be discussed later on.

One of the most fundamental issues of nuclear plant design, from which many issues stem,

¹Neglecting thermal inefficiencies and assuming energy consumption as given in source [9]

Design	Fuel	Cladding	Coolant	Moderator	Country of Origin
Pressurised Water Reactor (PWR)	Enriched Uranium Dioxide	Zircaloy	Light Water	Light Water	USA
Advanced Gas Cooled Reactor (AGR)	Enriched Uranium Dioxide	Stainless Steel	Carbon Dioxide	Graphite	UK
Reaktor Moshchnostniy (RBMK)	Enriched Uranium Dioxide	Zirconium/Niobium Alloy	Light Water	Graphite	USSR
Liquid Metal Fast Breeder (LMFBR)	Various Pu/U metals or ceramics	Stainless Steel	Liquid Sodium	N/a	Various
Molten Salt Reactor (MSR)	Uranium/Thorium Fluoride salts	N/a	Fluoride Salts	Graphite	USA
Canada Uranium (CANDU)	Unenriched Uranium Dioxide	Zirconium/Niobium Alloy	Heavy Water	Heavy Water	Canada

Table 1.1: A variety of reactor designs from around the world. [11]

is that the fission reaction produces enormous quantities of harmful radiation, of which the fission products are a long-lived emitter. In order to deal with this, the fission products must be contained, normally in a metal cladding, which surrounds the fuel. Further levels of containment exist designed to prevent the egress of radioactive material. These include the reactor pressure vessel, the coolant system, and a large reinforced-concrete containment structure built around all modern reactors.

As the reaction produces an enormous amount of heat, it is important that fuel elements must be kept cool, by means of passing coolant over them. Earlier reactors often used gasses of some description, including inert gasses such as helium, more common gasses such as carbon dioxide, or in the case of some more dubious reactor designs, simple air. However, although gasses are appropriate for high temperature, they tend to have poor heat capacities. Thus, many modern reactors use liquids, the most common example being ordinary water. Some more experimental designs have used more exotic coolants, such as molten metals or salts.

Thus, the main elements of reactor design are now established: the fuel, the cladding, the coolant and the moderator. Table 1.1 shows some of the more common or interesting reactor designs that have been developed around the world.

Some of these reactors experimented with novel or interesting ideas. The Molten Salt Reactor (MSR) development used liquid uranium salts as a fuel, which were circulated through a core for reaction, then allowed to cool externally. It was originally suggested as an aircraft reactor, which would allow air-planes to remain airborne for months at a time, although it was never fully tested in this application. The Advanced Gas-cooled Reactor (AGR) is a unique British design, which

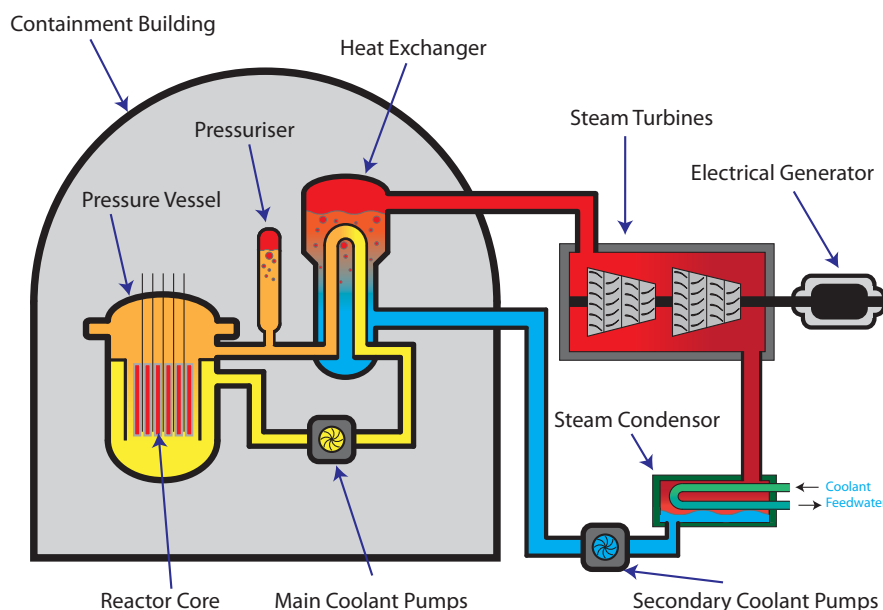


Figure 1.2: A diagram of the various components of a Pressurised Water Reactor. The PWR is currently the most common design of nuclear reactor.

remains the only gas cooled reactor in widespread commercial use. Its high operating temperature leads to impressive thermal-to-electric conversion efficiency, but at the cost of requiring a large core size in order to compensate for the low thermal capacity gas coolant. Some reactor designs, do not moderate the neutrons and are known as "fast" reactors. The premise behind these is that the faster neutron spectrum allows some of the non-fissile components of the uranium fuel to be transmuted more readily into plutonium. This can lead to usage of almost all of the available fuel, instead of the 0.7% of uranium that is naturally fissile. This premise is central to the Liquid Metal Fast Breeder Reactor (LMFBR), which has been investigated in several nations, but yet to be successfully commercialised. Soviet era RBMK reactors used an unusual combination of graphite moderator with water coolant, however this led to the undesirable issue of having increased reactivity at higher temperatures under some operating circumstances. Due to a legacy of poor design, poor construction, poor management and poor operation, this reactor design led to the Chernobyl disaster of 1986. However, despite all of these varied reactor designs, the most prominent reactor design worldwide is the Pressurised Water Reactor, or PWR.

The PWR was initially developed in the 1960's for the U.S. Naval Propulsion Program, under

the direction of Admiral Hyman G. Rickover [12]. The primary goal was to create a reactor small enough to be fit into the engineering section of a submarine, in order to provide systems power and propulsion. A nuclear submarine would have significant advantages over conventional diesel-electric submarines, which could only remain underwater while their batteries had charge before needing to surface for air. With sufficient energy, oxygen and clean drinking water can be produced from sea-water. The immense energy density of nuclear technology means that a nuclear submarine could carry enough uranium to maintain power for years without refuelling. This culminates in the concept of a fast, durable, and difficult to detect vessel which can remain underwater indefinitely. The only limitation to a nuclear-submarine's underwater endurance is the supply of food for the crew.

For the reactor to remain compact, gas based coolant would be out of the question. Thus the PWR uses normal non-deuterated ("light") water as both coolant and moderator. However, in order to keep the water liquid at high temperature, it is maintained at high pressure, in the region of 14-15 MPa. This high-temperature-high-pressure water forms the "primary" coolant circuit of the PWR, as it passes through the reactor and then through one or more heat-exchangers. These heat exchangers consist of a series of fine tubes through which the primary coolant is passed and the secondary coolant water is passed over. The secondary coolant water boils and the steam produced is used to drive turbines. The reactor and associated plant equipment, can be scaled up for larger civil-use power plants[11].

The PWR is currently the world's most common nuclear reactor design. Although it requires significant technological capabilities to construct, it remains a comparatively economical method of generating electricity from nuclear power.

1.3 The Economics of Nuclear Power

Although it is technologically credible to generate electricity from fission, it is important that it is also as economically competitive with other forms of power generation as possible. The economics of planning, building, running, and decommissioning a nuclear power-plant are somewhat unique compared to other forms of power generation. As discussed before, the most defining characteristic of nuclear technology is the vast amount of energy contained in a small amount

of fuel. Thus, for every MWh of electricity produced by a nuclear plant, the fuel will be a very small proportion of the overall costs. However, nuclear reactors are technologically challenging constructions. They require advanced materials and components constructed on a scale not found in many other industries. Compared to fossil-fuel based power plants, large amounts of capital must be spent on high value components, such as complex heat-exchangers, and high specification reactor pressure vessels. The primary driver of this is to ensure that reactors are safe to operators and members of the public. In the nuclear industry this principle is known as ALARP and is expressed as the goal to keep risks "As Low As Reasonably Practical". In other words, this means that it is acceptable to increase spending on the system if it drives risk down further. This means that although the day-to-day running costs of a reactor are small, the construction costs to build the reactor are large [13]. Further profit must be set aside by the operator for end-of-life decommissioning costs and disposal of the radioactive waste products. This means that reactors are extremely long running projects, with many modern reactors expected to take nearly a century, to go from first planning, to the last step of decommissioning. Stretching a project out over such a timespan inherently increases the risk of the project. A change in government policy, serious market fluctuation, construction delay, or accident could be the difference between financial success or failure for a nuclear power-plant operator. Thus, any attempt at decreasing a potential source of risk is one that makes nuclear power more economically viable and cheaper to operate. The main goal of this thesis is to examine one of the sources of risk present in nuclear power plant operation.

1.4 Zirconium and Zirconium Alloys

In PWR type reactors, there is one issue with using light water as a moderator. Specifically, unlike deuterium or carbon, the normal hydrogen in light-water has a comparatively high neutron-capture cross section. This means that a PWR reactor must take steps to ensure that the neutron economy is sufficiently high to counteract the water absorption, or the nuclear chain reaction will not be sustainable. One method of doing this is "enriching" the uranium fuel, such that there is more fissile uranium in the fuel than would be naturally available. This increases the probability that a neutron will lead to a fission event, rather than absorption or escape. However, there

are issues with this, as uranium enrichment is technically challenging and expensive. Furthermore, there is little technical difference in having the ability to enrich fuel slightly for PWR use, or enriching it greatly for the creation of nuclear weapons. Thus, there are political tensions associated with relying heavily on enriched fuels.

Another option is to ensure that the cladding material and internal reactor components have as low a capture cross-section as possible. Importantly, the element zirconium has a very low capture cross-section for thermal neutrons [14]. This improves neutron economy, meaning less fuel enrichment is required. It is also comparatively corrosion resistant, which is important in a high-temperature aqueous environment. Finally, as a metal, it has a good thermal conductivity, for conducting the heat from the fuel into the coolant and adequate mechanical properties. With appropriate alloying agents, most commonly tin, but also iron, chromium and nickel, zirconium provides an excellent choice for light water reactor fuel cladding. The selection of alloying elements and the development of zirconium alloys is covered more in section 2.1.1.

1.5 Hydrides and Failure

Although zirconium is an appropriate material for a cladding material, it is not without limitations. Given its position in a reactor, failure of the cladding can have unfortunate implications in isolated incidents and severe implications in accident scenarios. Should the cladding fail, coolant water can come into direct contact with the fuel. As the surface of the fuel is significantly hotter than the surface of the cladding, the direct exposure of the fuel to coolant will result in flash-vaporisation of the coolant. This can be a violent enough event to further damage the fuel pin and those around it, resulting in a significant release of radioactive material into the primary coolant system. Such an event represents a dangerous risk to a reactor operator. At best, this would mandate the shut-down of the reactor for a complete cleaning, maintenance and fuel replacement session. At worst, this could exacerbate an in-progress accident and result in a release of radioactive material to the outside environment. Being able to understand potential fuel pin failures is an important component of reactor safety and one of the key limitations for how long it is safe to leave a fuel pin in the reactor. There are multiple sources of failure, but one of the most important ones is the phenomenon of hydrogen embrittlement.

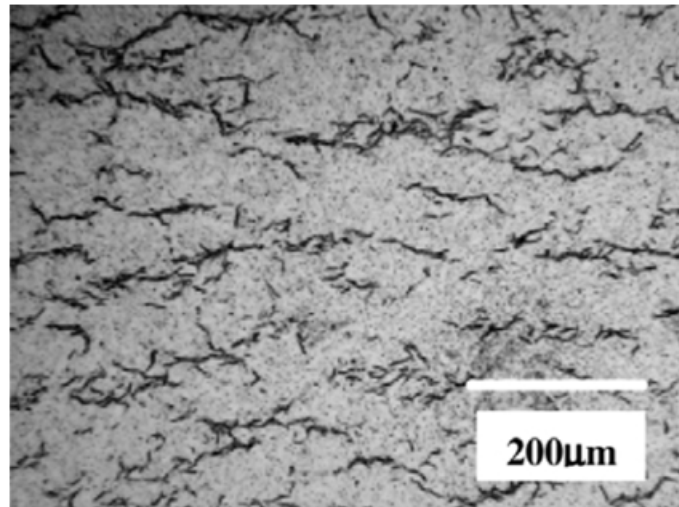
One of the key problems with zirconium, is its propensity for hydrogen uptake. Water reacts with zirconium as shown in equation 1.2:



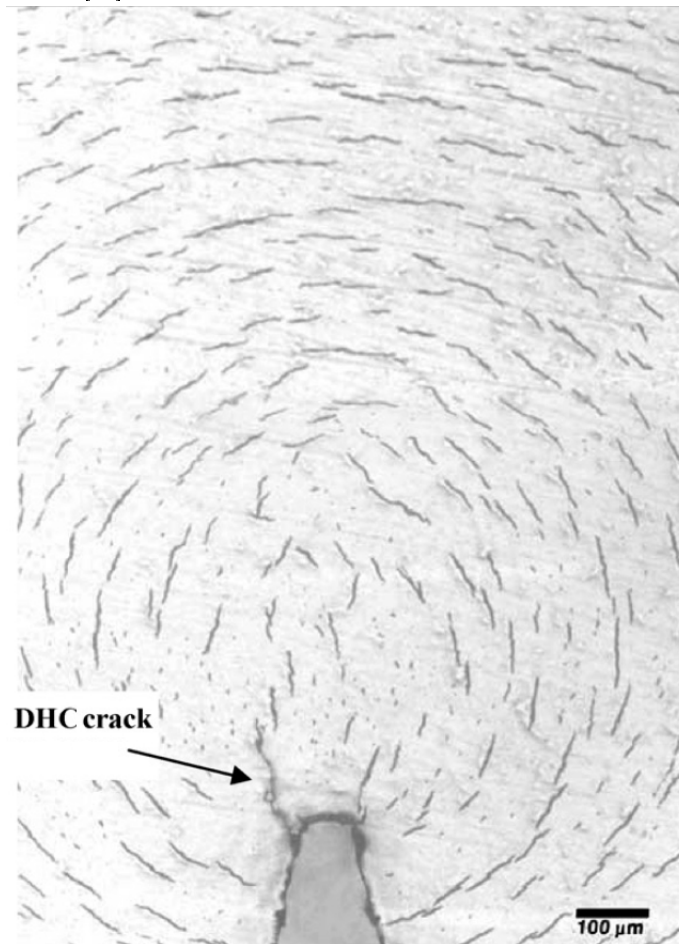
This reaction forms a passive oxide layer on the surface of the cladding, which retards the reaction. Although water cannot move through the oxide layer easily, some quantity of the produced hydrogen will diffuse through the oxide layer and into the metal. Aspects of this reaction remain unknown, it is clear that hydrogen is dissolved in the metal as part of a solid solution. Once in the metal matrix, there are still questions to be answered about how it moves and how it reacts with alloying agents, however it does have a deleterious effect on the mechanical properties of the metal. Furthermore, if the hydrogen concentration is greater than the solubility limit of hydrogen in zirconium, it will form numerous, plate-like, hydride phases (see Fig 1.3a).

This is a particular problem when the reactor is shut down for refuelling or inspection, as the solubility of the hydrogen in zirconium is lower at cooler temperatures resulting in more precipitates forming. The hydrides are known to become orientated in stress fields (Fig. 1.3b). The combination of orientated hydrides and a stress field can give rise to the phenomenon of Delayed Hydride Cracking (DHC), which has the potential to be tremendously damaging to the nuclear fuel pin's integrity. This is particularly a problem at the end of the life of a fuel pin after the cladding has spent a long time absorbing hydrogen [17]. This necessitates careful planning when considering how to store spent fuel pins (such as relying on dry storage) to avoid cladding failure. Considering that few nations have a fully developed long term disposal plan for spent fuel, many of these fuel pins may be held in storage for a long time. Understanding how hydriding mechanisms operate could potentially help with the planning of how to manage these pins, or even lead to new ways of resisting or preventing the formation of hydrides.

There have been a number of different investigations into the interaction of hydrogen with zirconium, although there are still many unanswered questions. Reactor operators tend to rely on empirically derived models to predict safe amounts of hydrogen in the reactor coolant. Thus, if it is possible to understand more about how the hydrogen can be absorbed into the zirconium, how it moves once it gets there, and how it precipitates into hydrides, better models can be developed.



(a) Hydrided Zircaloy-2 sample, showing un-orientated hydrides. This sample contains hydrogen content of approximately 200-ppm [15].



(b) A DHC crack in $\text{Zr}_{2.5}\text{Nb}$, showing hydrides orientated in a stress field [16].

Figure 1.3: Examples of hydrides in Zircaloy. The small dark lines are hydrides.

This necessitates a more precise theoretical understanding of the chemistry and physics behind this process.

1.6 Atomistic Modelling

The purpose of this project is to investigate the evolution of hydrides in zirconium and zirconium alloys. The main tool used to achieve this will be computer modelling at the atomic scale, based upon *ab-initio* methods (such as Density Functional Theory). Computational modelling has a number of advantages and disadvantages when compared with experimental approaches. The most obvious advantage is that computational methods allow us to examine systems under conditions that would be prohibitively difficult to examine experimentally and to look at aspects of systems that could not be observed directly with experimental methods. For example, it can be challenging to examine the atomic structure of a metal at pressures of many, many GPa, however this is normally a trivial scenario to deal with when using computer models. This reason is particularly applicable to nuclear materials, as they are expensive to obtain and extremely difficult to work with after they have been in a reactor. Computer models may also be able to examine systems in time-frames that are not reasonable to look at with conventional experimentation. An example would be that a computer simulation could potentially examine the contribution of many different speculative alloying agents to a metal in the time it would take an experimental set-up to look at very few. This gives computational modelling an excellent prospect as a predictor of results and models, which experimental methods can then go on to confirm. However, a computational model is only as good as the hypothesis it is based on and the initial data it is given. If incorrectly used, computer modelling can give results that are highly misleading. This means that great care must be taken when interpreting the results of computer models and that a modeller needs to have an understanding of the assumptions and mechanisms that underlie any models they are using.

1.7 Overview

The overall structure of this study is set out as follows.

Initially, a study of the available literature is presented. In order to ensure that this research remains relevant and novel, it is important to understand what aspects of this system are already well understood. The key issues are described as related to pure zirconium, zirconium alloys, hydrogen in zirconium, and zirconium hydrides.

With a simulation based investigation, it is of great importance that the strengths and limitations of the simulation method in question are thoroughly understood. The key points of density functional theory are developed, as are some of the practical aspects involved in using it to produce reliable data.

The first key aspect of this study is an investigation into zirconium alloys. In particular, focus is given on secondary phase precipitates and thermodynamic modelling of their formation. Much of the methodology developed here is used in subsequent parts of this work.

Different hydride structures are then investigated, in order to understand the relative stability of both hydrides and of hydrogen when it exists in a zirconium solid solution.

A comprehensive thermodynamic investigation of hydride precipitation is performed. Although studies have examined the thermodynamic aspects of the zirconium-hydrogen system in the past, this approach is aimed at being more rigorous than is common in this field in accounting for as many thermodynamic influences as it is possible to model.

This is combined with an examination of the effect of pressure on this system. As described previously, a stress field is known to have an impact on the precipitation of hydrides. This study examines how DFT can be used to provide information about this aspect of the system.

Finally, some areas for future study and some overall conclusions can be drawn. Although simulation techniques can be very powerful tools, it is often the case that simulators can become divorced from the physical reality of the systems they are trying to simulate. An important theme through this work is the comparison of theoretically derived information to real observations. It is the belief of the author that the linking of empirical engineering with theoretical science is one of the key strengths of this work.

Chapter 2

Literature Review

In order to determine novel areas for research, it is important to have a good understanding of the current status of the field of zirconium alloy research. This is a field that is being actively researched by a number of different groups around the world, due to its scientific and commercial value. Both experimental and simulation based investigations have proven useful in elucidating some of the properties and principles of Zr based systems. Experimental procedures have benefited greatly from increasingly advanced instruments such as high intensity synchrotron X-ray sources and better electron microscopy equipment, as well as improved computer based analytical power. Recent advances in computing power have allowed more advanced simulations to be explored and improved upon, yielding ever more accurate models. Firstly, a brief outline of Zr alloys, will be given, then a more in-depth examination of evolution of the various phases, and their importance to the system will be looked at. As this project is aimed at simulating materials computationally, a focus will be given to atomistic scale results obtained by computation based methods.

2.1 Overview of Zirconium alloys

2.1.1 The Historical Development of Zircaloy

As mentioned previously, the original drive that led to the development of Zr based alloys came out of the US naval development of the nuclear submarine. In order to envisage light water reactor technology, a material was required that would have adequate thermal and mechanical properties, while having good corrosion resistance, and most critically, a low thermal neutron capture cross-section. Initially, Zr was overlooked as a material that could fit these specifications, as experimental results demonstrated that Zr had an infeasibly high neutron capture cross section. However, as Zr was chemically similar to the element hafnium, when the thermal neutron capture cross section of hafnium was shown to be ~ 600 times greater than that of Zr [14], it was theorised that the Zr samples used so far may have had hafnium as an impurity. This discovery allowed new purification methods to be developed, resulting in pure, uncontaminated, potentially useful Zr. Initial experiments alloyed the metal with tin, to improve the yield strength and creep resistance [18], however this made the alloy more susceptible to corrosion. Addition of further alloying elements (iron, nickel, chromium) improved the corrosion resistance substantially, resulting in the development of the first commercially viable Zr alloy for nuclear applications: Zircaloy-2. Further work aimed at enhancing corrosion resistance led to the development of Zircaloy-3 (abandoned due to insufficient yield strength) and one of the current pressurised water reactor industry standard alloys: Zircaloy-4. Modern alloys have also added niobium, although this has been used in Russian alloys for some time. The early work done on Zircaloy focused on obtaining a commercially usable metal via empirical experimentation. Later on, advances in other techniques (such as microscopy, spectroscopy and simulation) have allowed better development of the underlying behaviour from a theoretical perspective as well.

Alloy	Wt%Sn	Wt%Fe	Wt%Cr	Wt%Ni	Wt%Nb	Wt%V
Zircaloy 1	2.5	-	-	-	-	-
Zircaloy 2	1.5	0.15	0.1	0.05	-	-
Zircaloy 3	0.25	0.25	-	-	-	-
Zircaloy 4	1.2-1.7	0.18-0.24	0.07-0.13	70ppm	-	-
Zirlo	0.7-1.5	0.07-0.14	0.03-0.14	0.03-0.14	0.5-2	-
M4	0.60	0.605	0.013	-	0.013	0.325
M5	30ppm	237ppm	32ppm	-	≈ 1	-

Table 2.1: Commercial and experimental alloy compositions. The balance of composition is made up of Zr [18, 19, 20, 21].

The earlier alloys were developed to solve the problem of corrosion in the reactor. However, as resistance to oxidation was improved, the effect of hydrogen embrittlement became noticeable. It was known as early as 1945 that hydride formation effected the mechanical properties of Zr based alloys [22], leading to embrittlement, loss of ductility and a decrease in yield stress. Early approaches towards investigating this phenomenon were centred upon experimental techniques, usually based upon the methodology of charging a Zr based sample with hydrogen and then examining it with a variety of techniques. Much of the early work focused on determining the solid solubility limit of hydrogen in Zr, as this determines the concentration of hydrogen required to form hydride precipitates [23]. Although the early work had less focus on the theoretical framework needed to explain the morphology of hydride formation, it was still well established that the hydride precipitates must play a part in the embrittlement of Zircaloy.

2.1.2 The Production of Zircaloy

Although necessary for PWR type nuclear reactors, Zr alloys are not required for many other major technological endeavours (Zr alloys are sometimes used in some chemical engineering applications). This means that the amount of Zircaloy produced each year (on the order of thousands of metric tonnes) is far below the amount of other engineering alloys such as titanium alloys or steels (respectively, on the order of millions or billions of metric tonnes)[24]. The methods used to make Zircaloy variants in the nuclear industry are proprietary information and thus cannot be revealed accurately in this document, however a rough overview of the general process can be described.

2.1.2.1 Refinement of Ore

Zirconium is normally found in deposits of zircon (Zr silicate), along with other elements such as hafnium [25]. For nuclear grade Zr, it needs to be separated from the hafnium and this can be achieved by processes such as liquid-liquid extraction. Simply put, liquid-liquid extraction, or counter-current exchange is the process of bringing two immiscible liquids together, whereby one has the desired element dissolved in it (normally a strong acid) and the other is an organic solvent with a preferential solubility for the desired element. A quantity of the element will become absorbed by the organic solvent, from which it can be extracted at higher purity [26]. Multiple stages of mixing and extraction are normally necessary. This technique is used throughout the nuclear industry for the purification of various substances, such as extracting uranium from ore, or separating fission products out of radioactive waste [26]. The counter-current exchange process ultimately produces ZrO_2 of the necessary purity (<100 ppm Hf) [27]. This oxide is then used as a reactant for the Kroll process to produce Zr metal. The metal can then be melted, mixed with the necessary alloying agents and cast into ingots. As this is ultimately an industrial process, there are a number of different techniques which may accomplish the same goal. The one detailed above is one of the more straightforward methods.

2.1.2.2 Fabrication of tubes

The general process of producing tubes of Zr alloy is done by a series of anneals and cold drawing stages, known as pilgering. First, the Zircaloy ingot is heated to a temperature of around 1050°C and then quench cooled. This is to make sure that the material structure is locked in the beta BCC phase and remove existing alloy texture [28]. The texture of the alloy is critical to its corrosion resistance and mechanical properties, meaning it is important that the metal have no strong initial texture before the forming process starts. After the β quenching, the tubing normally undergoes a hot extrusion step (information on the temperature of this step tends to be commercially sensitive). Considering that the pre-extrusion billets are on the order of 200 mm across and the final tubes are around 9.5 mm outside diameter, with a wall thickness of less than a millimetre, the amount of strain required to process the material is significant. This means that the entire extrusion process cannot be done in a single step and a hot extrusion process is

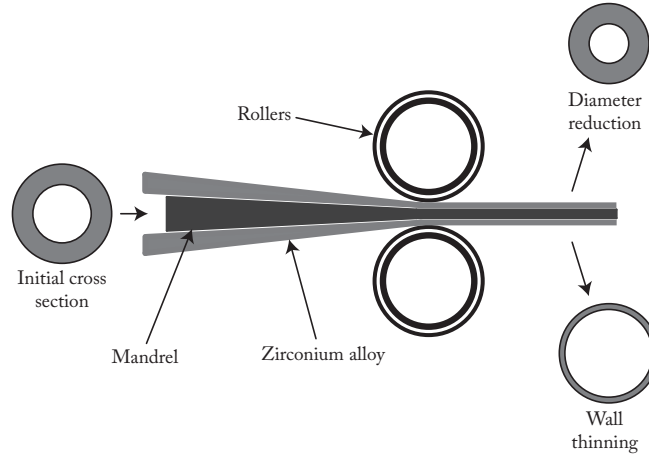


Figure 2.1: Schematic of the Pilgering process.

necessary to start off with to allow an initial high strain extrusion. After this initial process, annealing may be carried out to remove any cold work, caused by the previous step. Following this first annealing, the main forming process can begin. First, the metal is rolled through a pilgering mill around a mandrel. This reduces the thickness of the wall and reduces the tube diameter. (Fig. 2.1)[24].

The process needs to be done cold, as cold working techniques can produce dimensions to more accurate tolerances than hot working methods. After the pilgering, the metal is annealed and the pilgering is repeated. This process of pilger/anneal is repeated a number of times, until the tube is of appropriate dimensions to be filled with fuel pellets, back filled with helium and assembled for insertion into a reactor.

2.1.2.3 Texture Evolution

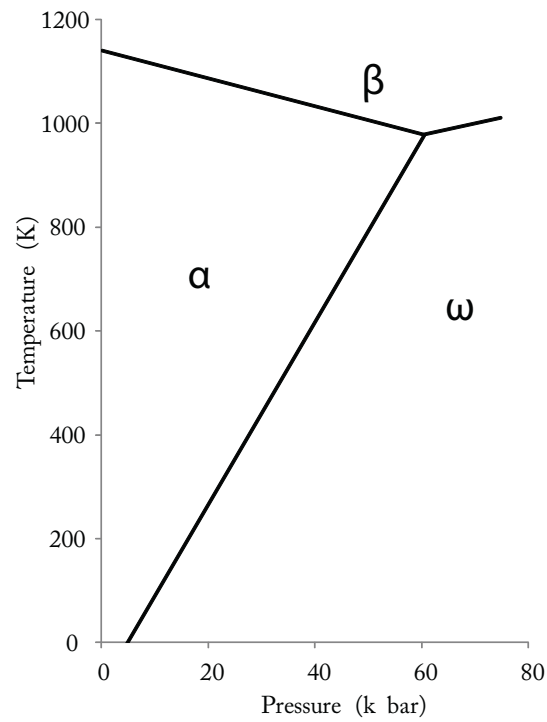
Texture is of critical importance for two reasons. Firstly, as described on page 38, Zr crystals have preferred orientations for deformation, meaning the mechanical properties of a textured tube are anisotropic. Secondly, impurities produced by fission, can diffuse into the Zr lattice and weaken the structure, perhaps the most notable of these being iodine [29]. These impurities have preferential diffusion paths relating to the crystallographic orientations. As the impurities diffuse faster along the basal planes than along prismatic planes, it is important that the crystals are orientated with normal of the basal planes in the tube's radial direction, or it will be subject

to an increased rate of iodine induced stress corrosion cracking [30]. The pilgering process starts with a thick walled, large diameter tube and finishes with a thin walled, small diameter tube. This means that there are two reduction processes working during pilgering: wall thinning and diameter reduction (See Fig. 2.1). If wall thinning has been the dominant forming operation, then the tube wall is strained primarily in the circumferential direction, thus there will be a tendency for the crystals to be orientated with their c-axis in the circumferential direction. If diameter reduction has been the dominant process, then the strain will have primarily been in the radial direction and thus the crystals will be more commonly orientated with their c-axis along the tube radii.

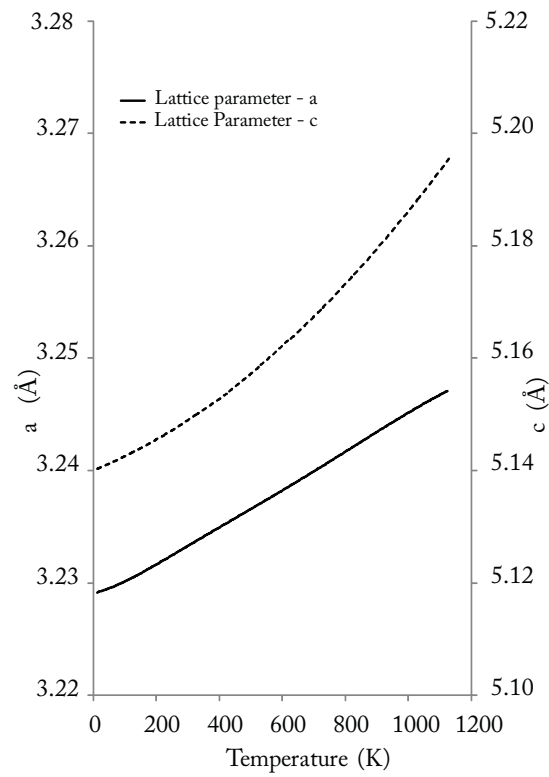
2.2 Pure Zirconium

The room temperature crystal structure of Zr is hexagonal close packed (see Fig. 2.2a). Considering that the operating conditions for a pressurised water reactor tend to be at temperatures of around 300 °C and at pressures of 14 MPa, Zr is stable in the alpha phase and has lattice parameters of $a = 3.238 \text{ \AA}$ and $c = 5.162 \text{ \AA}$, giving a c/a ratio of 1.59 (see Fig. 2.2b). At 853 °C, a body centred cubic phase becomes more thermodynamically stable ($a = 3.5453 \text{ \AA}$) [31]. At high pressures (about 2 GPa at room temperature) a 3 atom hexagonal structure ($a = 5.036 \text{ \AA}$, $c = 3.109 \text{ \AA}$) [32] exists, known as the ω phase, although this changes back to the β phase at extremely high pressures. Crystallographic information on bulk properties is relatively easy to obtain using mature experimental techniques such as X-ray diffractometry. As a result of this, there is a solid quantitative foundation against which to compare computational studies.

Modelling the Zr computationally has been attempted with a wide variety of techniques. Classical molecular dynamics based simulations have had a number of successes at modelling the material. Most notably, a large number and variety of papers used the Embedded Atom Method (EAM) type potential of Baskes and Daw [35] to model Zr metal. For comparison, key materials properties, calculated by molecular dynamics, are presented in Table 2.2. The IKV1991 potential was the first EAM potential to demonstrate any reasonable reproduction of the properties of Zr, although strictly speaking, their potential was of the Finnis-Sinclair type [36]. This was largely due to the fact that EAM type potentials had not previously been found



(a) Temperature and pressure phase diagram for Zr metal [33].

(b) Lattice parameter variation with temperature for α -Zr [34].

that modelled hexagonal close packed crystal structures. Since then, a number of potentials have been generated, of which the most recent are the MA2007#2 and MA2007#3 potentials by Mendelev and Ackland [37]. The MA2007 potentials in particular demonstrate that it is possible to simulate aspects of the Zr system, as the potentials 2 and 3 are able to simulate atomic scale thermodynamic and mechanical properties respectively. Zirconium EAM potentials have been used to simulate various Zr properties and have seen use in investigating dislocations, point defects and radiation damage cascades in Zr [38, 39, 40, 41].

However, it is important to note that the potentials are not always general purpose enough to be able to model multiple aspects of Zr concurrently. Combined with the fact that the functions that describe these potentials are defined with extreme precision, both in terms of the precision of coefficients (with parameters sometimes defined by upto 12 decimal places[37]) and the number of coefficients, this implies that the potential may be somewhat over parametrised. The effect of this is that the potential has exchanged general functionality for over-precision on specifically fitted values. This is, unfortunately, a common problem with many potentials in that they are very good at modelling a single component of a system (such as a phase transition temperature), but fail spectacularly when used to model other aspects (such as defect formation energies). Despite these problems, it is safe to say that the potentials are able to reproduce some of the more straightforward bulk properties. It should be noted that none of the above potentials are fitted to simulate the ω phase of Zr. Doing so would be a significant challenge, as the potential would need to support a 3-atom hexagonal structure, in addition to the HCP and BCC phases.

Ab-initio methods have also been used to model pure Zr. Generally speaking, any published work that deals with an aspect of Zr, or Zr alloys, via *ab-initio* methods will demonstrate that the methods used are viable because they can reproduce the simpler bulk properties of pure Zr. Although this does not necessarily mean that these methods can accurately model more detailed phenomena, it is unlikely that they would be able to examine the more interesting aspects of the system without first being able to reproduce some of the simpler properties. As a result, a large number of published works have given bulk properties of Zr, as calculated by *ab-initio* methods. A few examples are given in Table 2.2. As *ab-initio* methods are not empirically parametrised to fit desired properties, they are capable of producing various discrepancies in the bulk parameters. A most common example is the simulation of the ω phase. Experimental techniques verify that

Method	a ($\text{\AA}$)	c (α) ($\text{\AA}$)	c/a ratio	$a(\beta)$ ($\text{\AA}$)	$C_{11}(\alpha)(\text{GPa})$
Experimental Results[42, 32, 43]	3.23	5.15	1.593	3.5453	155
DFT (GGA US PPs)[44]	3.23	5.18	1.604	-	142
DFT (GGA PAW PPs)[45]	3.23	5.17	1.601	-	156
LMTO (FP GGA)[46]	3.23	5.18	1.604	-	-
LMTO (FP LDA)[47]	-	-	1.583	-	155
EAM Potential (IKV91)	3.23	5.15	1.593	3.644	155
EAM Potential (AWB95)	3.25	5.18	1.594	3.589	160
EAM Potential (PM99)	3.23	5.15	1.593	3.568	146
EAM Potential (MA07 #2)	3.22	5.22	1.621	3.562	165
EAM Potential (MA07 #3)	3.23	5.17	1.601	3.576	147

	$C_{12}(\alpha)(\text{GPa})$	$C_{44}(\alpha)(\text{GPa})$	$\Delta E_{\alpha \rightarrow \beta}$ (meV/Atom)	$T_{\alpha \rightarrow \beta}(\text{K})$
Experimental Results	67	25	40	1135
DFT (GGA US PPs)	-	29	71	-
DFT (GGA PAW PPs)	61	26	78	-
LMTO (FP GGA)	-	-	30	-
LMTO (FP LDA)	65	25	-	-
EAM Potential (IKV91)	67	36	111	1251
EAM Potential (AWB95)	76	36	30	2054
EAM Potential (PM99)	70	32	53	1221
EAM Potential (MA07 #2)	65	48	52	1233
EAM Potential (MA07 #3)	69	44	103	1369

Table 2.2: Comparison of numerical properties of Zr as calculated by a number of different methods. Sample values were chosen to be relevant to bulk structural, mechanical and thermodynamic properties.

the phase most stable at low temperature is the α phase, as can be seen by the phase diagram in Fig. 2.2a. However, *ab-initio* methods tend to predict that the cohesive energy for the α and ω phases are very close together and in some cases, the ω phase is actually predicted to be more stable than the α phase at low temperatures [48, 49]. Although this is contradicted by experimental evidence, it is not a universal conclusion and some work does predict the correct sequence of $\alpha \rightarrow \omega \rightarrow \beta$ phases, with increasing pressure [50]. This highlights the need for care when examining *ab-initio* results, particularly when examining structures involving the ω phase.

Despite these discrepancies, DFT still has much to offer as a method for attempting to simulate other aspects of Zr. A number of different attempts have been made to determine the intrinsic defect energies. Comparison with experimental evidence shows that simulated values fall within the range of experimentally produced values, although there is still some disagreement as to the most stable self interstitial atom (SIA) configuration. Simulations using the VASP DFT code predict the octahedral interstitial ($E_{0f} = 2.84$ eV relative to the energy minimised defect free lattice), whereas experimental work has measured the basal crowdion [51]. Other simulation work has found the basal octahedral configuration to be the most stable based on the trends of values with increasing cell sizes [52].

With regards to deformation, HCP metals have a limited number of close packed slip systems when compared with FCC materials and the viable slip planes and directions are limited still further by the fact that the c/a ratio for Zr is smaller than ideal. A low c/a ratio means that atoms are more closely packed along the prismatic planes than the basal planes, meaning that prismatic slip can be favourable when compared to basal slip. When stress is applied in a direction parallel to the basal plane, then the most favourable slip system is found on the $\{10\bar{1}0\}$ planes in the $\langle 1\bar{2}10 \rangle$ directions, although slip has also been observed in the same direction along the basal plane. At higher stresses, a less favourable ($\{10\bar{1}1\} \langle 1\bar{2}10 \rangle$) system may become active. However, if the stress is applied along the c -axis, there are comparatively less favourable slip systems for dislocations to move on. The most favourable being the first order pyramidal systems of ($\{\bar{1}101\} \langle 1\bar{2}13 \rangle$) and ($\{11\bar{2}1\} \langle 1\bar{2}13 \rangle$) (Fig. 2.3) [53].

Due to the lack of favourable slip systems for stresses that have a large c component, twinning becomes a viable deformation mechanism. This is of particular importance as although the formation of a twin often results in a relatively small strain, it can re-orientate planes of atoms

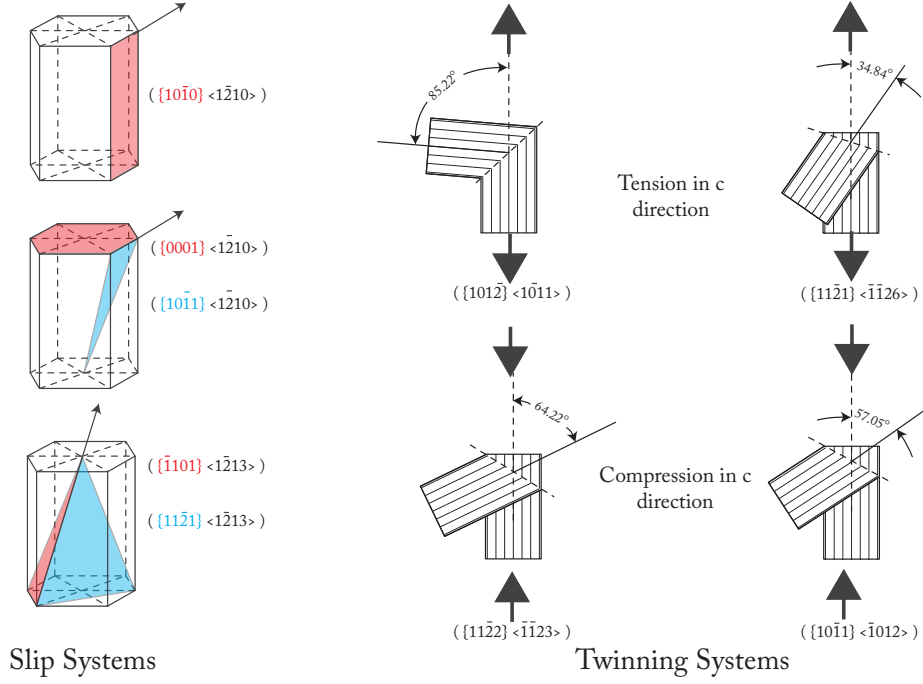


Figure 2.3: Schematic of deformation mechanisms in Zr.[53]

in such a way as to allow previously immobile planes of atoms to lie in a favourable slip direction. A number of different twinning modes can be activated in Zr, depending on whether the load is compressive or tensile. Fig. 2.3 shows these different modes schematically, with the $\{10\bar{1}2\} \langle 10\bar{1}1 \rangle$ mode being the most favourable when the lattice is under tension along the c-axis and the $\{11\bar{2}2\} \langle \bar{1}\bar{1}23 \rangle$ system is the most favourable under compression [53]. So far, only the most commonly activated deformation mechanisms have been discussed. A summary of the different deformation mechanisms, including some of the less favourable systems can be found in Table 2.3 .

Deformation mechanisms have been modelled using the EAM potentials that have already been described. The MA07 potential does demonstrate a number of useful properties, such as predictions of stacking fault energies that are close to those predicted by *ab-initio* results and the ability to predict the relationships between dislocation velocity and applied shear stress, although the model was of infinitely long dislocations [38]. Similar models have been attempted using *ab-initio* methods, however these can show much greater discrepancies with experimental work as

Slip Type	Plane	Direction	Twinning Type	Plane	Direction
Basal	{0001}	<1210>	Tension 1	{1012}	< $\bar{1}$ 011>
Prismatic	{10 $\bar{1}$ 0}	<1210>	Tension 2	{11 $\bar{2}$ 1}	<11 $\bar{2}$ 6>
Prismatic	{11 $\bar{2}$ 0}	<1210>	Compression 1	{11 $\bar{2}$ 2}	< $\bar{1}$ 123>
1st Order Pyramidal - 1	{ $\bar{1}$ 101}	<1213>	Compression 2	{10 $\bar{1}$ 1}	< $\bar{1}$ 012>
2nd Order Pyramidal - 1	{1012}	<1213>			
1st Order Pyramidal - 2	{11 $\bar{2}$ 1}	<1213>			
2nd Order Pyramidal - 2	{11 $\bar{2}$ 2}	<1213>			

Table 2.3: Deformation mechanisms in Zr. Preferred systems relative to the direction of applied stress are emboldened [54].

ab-initio methods are limited in the size of systems they can manage, particularly for metals. The limited results obtained by this method can sometimes only be treated as qualitative, rather than quantitative [55], although it has been pointed out that experimental data or its interpretation may be in error, particularly when dealing with surface relaxations and energies [56]. The key point to note from this is that when good potentials are available, classical mechanics based simulations offer a more appropriate model for deformation mechanisms in this system than *ab-initio* methods, however the caveat of having "good potentials" is a significant one.

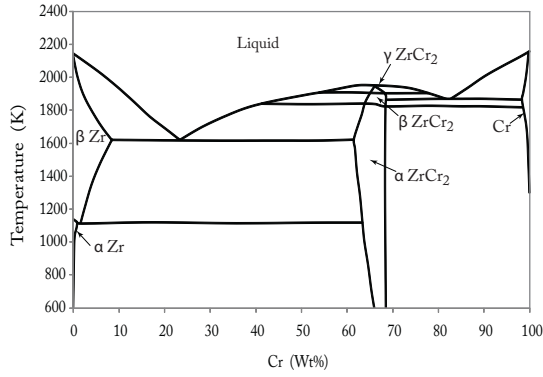
2.3 Zirconium with Alloying Agents

Before taking a look at the behaviour of hydrogen, it is prudent to examine the actual structure of the Zr alloy itself, how the alloying agents used in the metal are arranged and what properties they bring to the alloy.

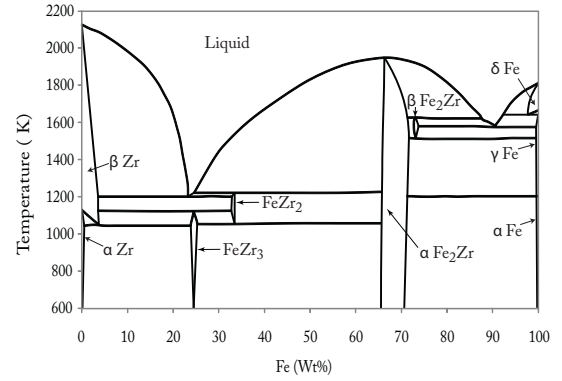
In Zr alloys, there are two possible locations in the lattice where the alloying elements can be considered to occupy. The first of these is that they form addition rich second phase precipitates (SPPs). The other option is that they can remain in the Zr alloy in solid solution as substitutional or interstitial defects. Experimental evidence suggests that the majority of the Fe, Ni, or Cr resides in SPPs (most notably the $\text{Zr}(\text{Fe,Cr})_2$ or $\text{Zr}_2(\text{Fe,Ni})$ intermetallics), while the Sn remains in α -phase solid solution [57, 58, 59, 60]. In the modern alloys containing Nb, the niobium is known to have limited solubility in Zr and form SPPs, however, unlike any iron or nickel SPPs, these are only of a different solid solution phase (β -phase) and are not a specific intermetallic compound as well [61]. However, it has also been noted that Nb may be found in Fe or Cr rich

precipitates if present [62]. Contrary to this picture, Some work has reported that there are still concentrations of Fe and Cr in solid solution, as well as some Sn SPPs [58, 60]. As a result of the various phases in this complex system, it is important to investigate them in the context of the phase diagrams relevant to the system. These are displayed in Fig. 2.4. From examining the relative size of the different phase fields, we can make a qualitative judgement as to which phase is predominately stabilised by the addition of an alloying element. It can be seen that Cr, Fe, Nb, V and Y stabilise the β phase, whereas Sn stabilises the α -phase.

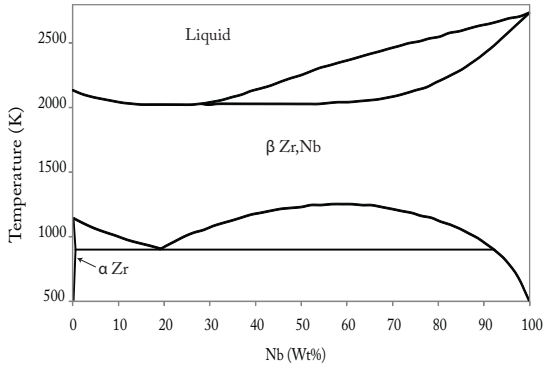
Given the number of different elements that are alloyed with Zr, there are various different crystallographic structures which SPPs can have. Two primary structures of SPPs have been observed via microscopy; these are referred to as the Zr-rich and Laves phase precipitates (see Fig. 2.6). In Zircalloys 2 and 4, the Zr-rich phase contains primarily Ni and the Laves phases consists primarily of Cr, while both precipitates contain Fe [57]. Laves phase precipitates are part of a broad class of intermetallics, with three different structures, known as C14, C15 and C36 [69]. The structures of Zr-Rich and Laves phase precipitates are shown in Fig. 2.6. Precipitates containing only Fe and Zr, with no Cr, are also observed, though rarely [57, 70]. Sn containing SPPs are occasionally observed, often associated with β -quenched samples, or as a result of irradiation [71]. SPPs have been noted to exist either in isolation, or in small clusters with Laves phase precipitates observed to nucleate on existing Zr-rich precipitates (see Fig. 2.5) [57]. Given the processing stages that a Zircaloy tube must go through, there are a number of potential points where SPPs can nucleate and grow. The first is when the Zircaloy is reheated (after casting from melt) to approximately 1050°C and then quenched to manipulate the alloy texture. The second is during recrystallisation, which happens between a series of cold forming operations. A third and final possibility is during reactor operation, which may provide sufficiently high temperatures for precipitate growth, or may induce irradiation assisted precipitation [71].



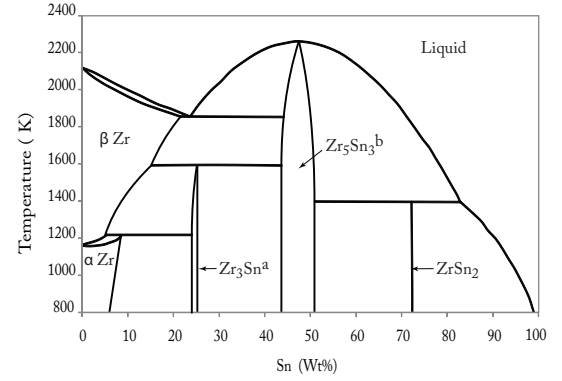
(a) The Zr-Cr Binary Phase diagram [63].



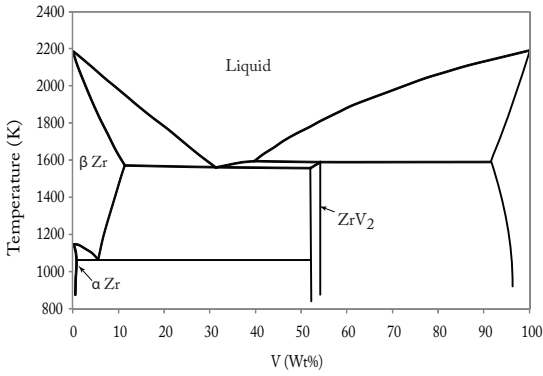
(b) The Zr-Fe Binary Phase diagram [64].



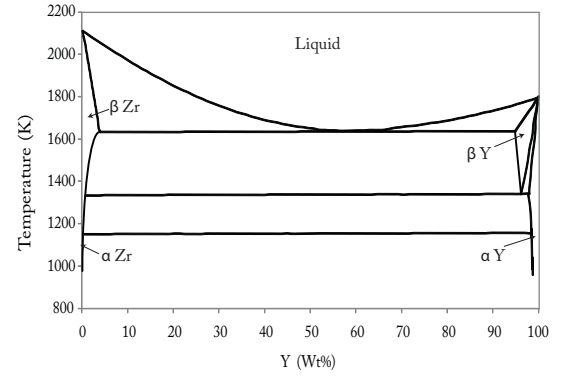
(c) The Zr-Nb Binary Phase diagram [65].



(d) The Zr-Sn Binary Phase diagram. The phases marked "a" and "b" both have a range of stoichiometries [66].



(e) The Zr-V Binary Phase diagram [67].



(f) The Zr-Y Binary Phase diagram [68].

Figure 2.4: Phase diagrams of binary systems investigated in this work.

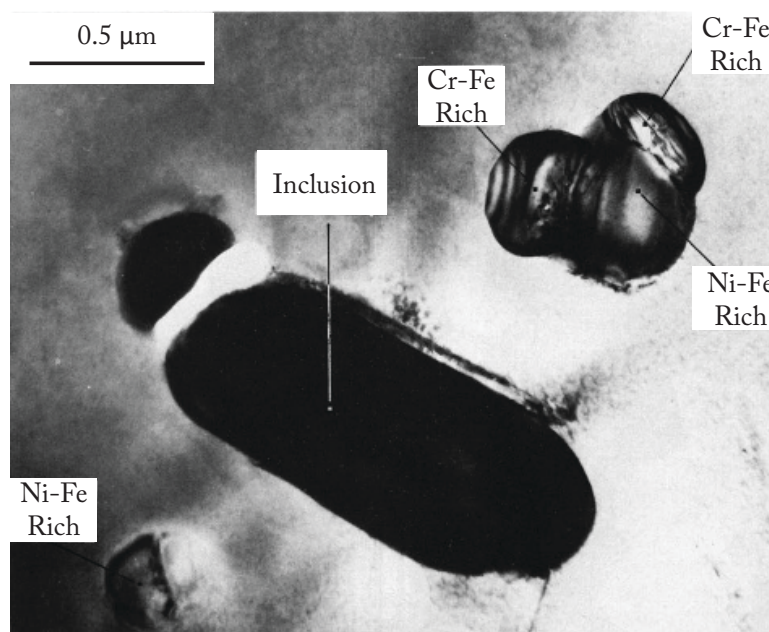


Figure 2.5: Transmission electron micrograph of SPPs found in Zircaloy 2. Reproduced from reference [57]

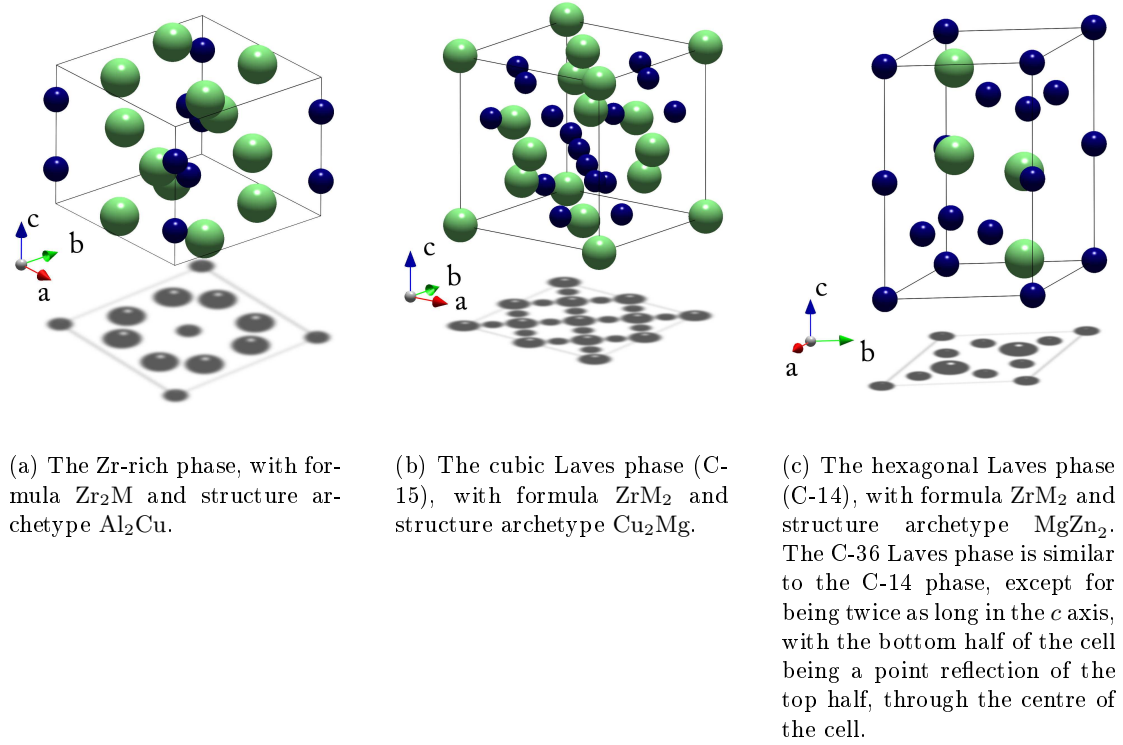


Figure 2.6: Crystal structures of the main precipitates found in Zr alloys. Zr is represented by the larger, light green spheres and the alloying agent by the smaller, dark blue spheres.

It has also been reported that SPPs tend to shrink under neutron irradiation [71]. Different SPPs are known to shrink at different rates, under different fluences and by different mechanisms. Ni rich precipitates show a tendency for Fe to leach out of the SPP until the whole precipitate dissolves into the bulk Zr [71]. Cr rich precipitates are known to amorphise, while both Fe and Cr diffuse out of the SPP [71]. Fe appears to diffuse into the Zr solid solution faster than Cr, which leaves the sluggish Cr atoms to form a Cr enriched zone around the SPP [72]. The phases that these different additions preferentially stabilise are an important component in the mechanisms of dissolution. This process is of particular interest, as the shrinkage of the precipitates is known to correlate with the rate of corrosion and oxide growth, which in turn is thought to correlate to hydrogen uptake [73].

2.4 Hydrogen in Zirconium

As the precipitation of hydrides has such a clear effect on the structural properties of fuel pins, it is important to explain current understanding of how these hydrides form. At the surface of a fuel pin, the Zr is coated in a thin layer of zirconia (ZrO_2). Hydrogen can diffuse through this layer and into the metal, where it remains extremely mobile [74]. Once in the metal, the hydrogen will tend to remain in solid solution while the metal remains at high temperatures (assuming that hydrogen uptake has not been excessive). However, when the reactor is shut down, the solubility of hydrogen in Zr drops and metal hydrides precipitate out of the alloy. It should be noted that even at PWR operating temperatures, the solubility of hydrogen in Zr is still fairly low (80-100 ppm) and lower still at room temperature (60-40 ppm). An idea of the solubility limit of hydrogen can be gained from the phase diagram in Fig. 2.7 and is shown in more detail in Fig 2.8.

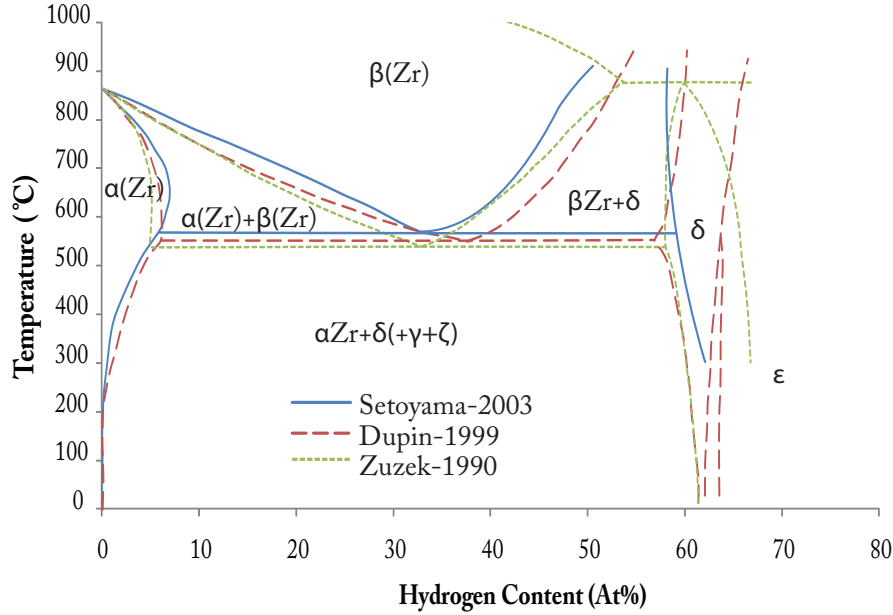


Figure 2.7: The Zirconium-Hydrogen phase diagram [75]. The plots of Setoyama-2003, Dupin-1999 and Zuzek-1990 refer to references [76],[77] and [78] respectively.

Ab initio methods have yielded a number of useful predictions of the Zr-H system to be compared with experimental data. Solution energies are defined as the energy for an atom of

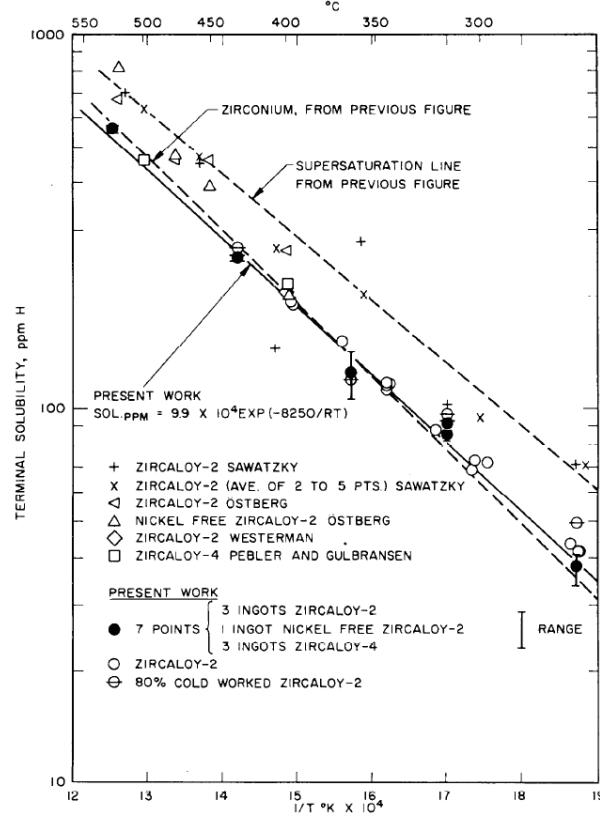


Figure 2.8: The Terminal solid solubility of Zr H is shown here from a variety of works, as compiled by J. J. Kearns [79].

a species in (in this case H_2 gas) to occupy a site in a solid solution. In Zr these energies for tetrahedral and octahedral interstitial sites have been found for hydrogen using VASP and are in good agreement with experimental values. The most favourable site is the tetrahedral interstitial, with an energy of between -0.40 and -0.60 eV, although the energy of a hydrogen atom sitting in an octahedral site is not much greater, implying that both sites will likely be occupied in reality [44, 45]. The data is claimed to be relatively close to comparable experimental results [80]. It has also been found in DFT studies that the vibrational ground state energy of the H atom in the octahedral site is lower in energy than the vibrational ground state energy in the tetrahedral site [81], suggesting that the octahedral site may be preferable at non-zero temperatures. This has yet to be confirmed in other work. The type of bonding between hydrogen and Zr has

also been investigated using DFT. Examining the calculated density of states of Zr atoms in the presence of hydrogen yields a very specific localised state existing 6.5 eV below the Fermi-level. This state appears to show hybridisation between s and d orbitals and is only present in Zr atoms that are adjacent to a hydrogen atom. The implication from this is that Zr-H bonds are extremely localised, with the hydrogen keeping its own electron and then sharing a Zr valence electron with all adjacent Zr atoms [44]. This presents an interesting challenge with regards to modelling as the electron sharing component of the bond presents a partially covalent character, but the way it is shared between multiple atoms has metallic characteristics as well. The distinctive -6.5 eV bonding state has also been seen in experimental X-ray photo-electron spectroscopy studies and lends credence to the findings of this model [82]. Further attempts have also been made to use DFT to simulate larger defects in the Zr-H system in order to examine hydrogen's affinity for and effects on stacking faults and dislocations. As experimental results for the properties of this system are limited, there is little to compare these results against, however, the values appear to be consistent with similar metals, such as titanium. VASP results suggest that hydrogen has a strong affinity for stacking faults in a Zr lattice (0.14 eV - this represents the difference between a hydrogen atom next to a stacking fault and a hydrogen atom far away from a stacking fault). Stacking fault energies are also suspected to be lowered by the presence of hydrogen in the lattice [55]. A possible qualitative explanation for this is that stacking faults in an HCP lattice produce a region with similarities to an FCC structure. As hydride precipitates can have a Face Centered Cubic (FCC) or Face Centered Tetragonal (FCT) structure, it would make sense that the hydrogen would preferentially sit in sites near a stacking fault. However, as mentioned previously, current computational limitations mean DFT is not an ideal method of simulating stacking faults. Molecular dynamics simulations would offer a new perspective on this phenomenon if good potentials can be developed.

Very little has been achieved in terms of using molecular dynamics to produce high quality simulations of the Zr-H system. This is due to the fact that workable potentials for the interaction of hydrogen with Zr have proved difficult to come by. Currently a literature search has revealed few attempts at producing potential that describes the Zr-H system. Ruda et. al. looked at an approach based on the EAM type IKV potential, after being transformed via an "effective pair potential method"[83]. However, it does not correctly predict the preferred sites for hydrogen

to occupy in α -Zr, nor has it been tested on hydride phases. It has not been examined in any papers after its initial publication and reproducing it is made difficult by the omission of key details in the publishing work. A pairwise potential has been developed on the Rose potential [84] and applied to this system [85], however these have gained little use elsewhere and attempts to replicate claimed results have been unsuccessful. A recent attempt has also been made by the Electric Power Research Institute in the USA, based upon fitting the earlier rose-like H potential to the MA2007 potentials with EAM components [81]. However this represents an extremely recent attempt and sufficient time has not been available for an investigation of its accuracy.

2.5 Hydride Precipitation

Perhaps the most critical point in the evolution of hydrides is the initial precipitation of them. Simply put, this precipitation occurs when the local hydrogen concentration in a region is higher than the solubility limit of hydrogen in Zr. How this precipitation occurs is particularly important for determining how the material may undergo failure. Perhaps, the most examined form of failure with regards to Zr hydrides is the phenomenon known as delayed hydride cracking (DHC). In this mechanism, hydrides form in such a way as to allow cracks to propagate through the material, as well as cracks affecting the material in such a way as to promote the formation of hydrides. There are currently two different models for how DHC is initiated, the precipitation first model (PFM) and the diffusion first model (DFM).

PFM suggests the loading of the Zr lattice (due to presence of stress raising defect such as a crack) induces hydride precipitation by locally lowering the solubility limit of hydrogen in α -Zr. When the precipitate forms, hydrogen is removed from solid solution, creating a hydrogen concentration gradient that induces more hydrogen to diffuse towards it, thus growing the precipitate. The DFM assumes that the loading from the crack tip introduces a local difference in chemical potential due to tensile hydrostatic stress, resulting in a diffusion of hydrogen towards the crack tip, up the concentration gradient. When sufficient hydrogen has diffused to the crack tip and the solubility limit is exceeded, precipitation occurs. This model assumes that the solubility limit is not greatly affected by stress. Evidence for this is based on the assumption that diffusion is the limiting step, hence why DHC is observed to show a temperature dependence

which fits reasonably well with standard kinetic models of diffusion [86, 87]. However, there is some debate with regards to which of these models are correct, with the main proponents of PFM being Kim et. al. [88] and the main proponents of DFM being McRae and Puls [87, 86]. The model suggested by Kim is based on the argument that the DFM model assumes precipitation can *only* occur if the hydrogen concentration is greater than the solubility limit. Kim claims that the DFM model predicts samples would only show evidence of DHC if they were heated above the solubility limit and then under-cooled, whereas he reports samples that have not been heated to the solubility limit that still show DHC. McRae has responded to this, stating that should PFM be accurate, then the expected observation would be to see a decrease in the solubility limit of the metal with increasing tensile stress and that no such phenomenon has been seen. Examining this debate in detail would be tangential to the main goals of this project, however a few conclusions on the precipitation of hydrides can still be drawn. We can say that the exact sequence of events leading to the precipitation of hydrides is unknown, although stress has a role in accelerating the precipitation of hydrides and defining the location and orientation of the precipitation. One further note on this debate is that most of the individuals are examining the system from an experimental and thermodynamic point of view. Very little consideration is given to atomic scale phenomena, such as the role of defects and dislocations in the precipitation of the hydrides. Considering that a zone rich in dislocations and stacking faults forms ahead of the crack tip and as previously mentioned, hydrogen has a strong affinity for stacking faults, it is possible that defects may prove to be a driving force in nucleating hydrides if the hydrogen concentration is not yet sufficient to be greater than the homogeneous solubility limit. Investigation into the possible mechanisms could prepare the way towards a synthesis of the different models into a more complete understanding of the precipitation mechanism.

A further interesting effect is that the solubility limit of hydrogen with respect to temperature demonstrates a hysteresis effect. The solubility limit for precipitation on cooling a sample from high temperatures can be over twice that witnessed for re-solution when heating up the same sample from a cooler temperature[87]. The conventional explanation for this is due to work done plastically. Per mole, hydrides have a comparatively greater volume than pure Zr, due to the insertion of hydrogen atoms into the Zr lattice. This means that the Zr matrix must deform (plastically) in order to accommodate the hydride. The addition of new defects during

this process is thought to delay the onset of hydride re-resolution [89, 86, 87].

2.6 Hydride Structures

In terms of basic morphology, hydrides have a tendency to form initially in isolated platelets, on the order of a micron in size along their principle axis. They are known to have preferential forming directions with regards to the orientation of the grain they form in, as shown in Fig. 2.9.

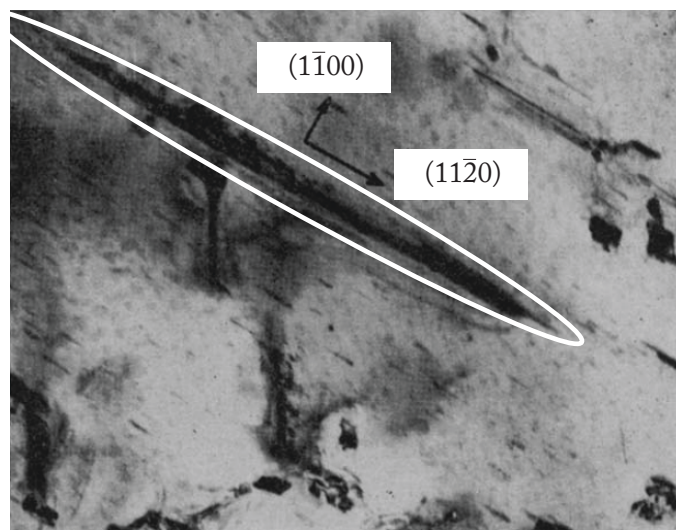


Figure 2.9: An isolated hydride platelet shown by TEM. The hydride is outlined in white. A scale bar was not presented in the original version of this figure, however a magnification of 34000 times was reported. Reproduced from reference [23]

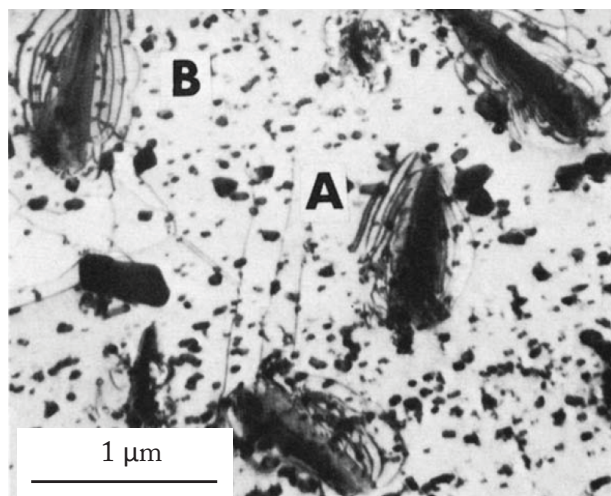
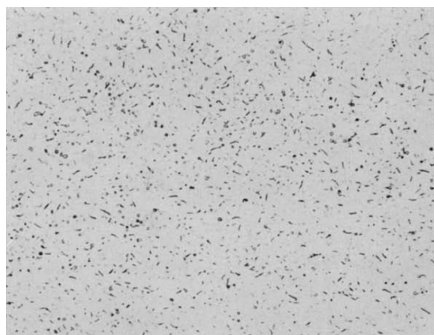


Figure 2.10: A TEM micrograph, showing hydride platelets in Zircaloy-2 which have well developed strain fields, resulting in dislocations being formed. These are visible as a series of lines around the hydrides marked A and B. The smaller black regions are intermetallic phases [90].

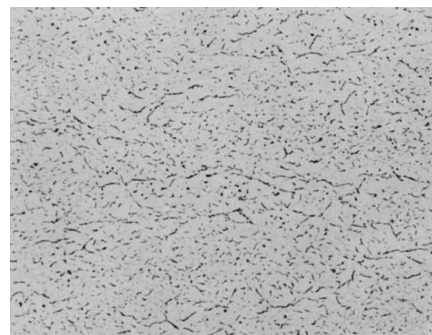
The crystal structure of these hydrides does not typically lend itself to forming a coherent interface with the host Zr matrix. One exception to this is the recently discovered ζ hydride, which will be discussed later. With regards to other hydrides, the interface introduces a significant amount of strain, which is relieved by the creation of dislocations. These are emitted by the hydride precipitate and can form stable loops around the hydride, or could potentially be thrown off into the lattice (see Fig. 2.10). This demonstrates that hydrides are a significant cause of plastic strain on the local crystal lattice.

As H concentration increases, or the solubility limit drops, more hydrides will form. Past experiments have shown the evolution of hydrides over different cooling rates, which will alter the kinetics of the hydride precipitation reaction. This evolution is shown in Fig 2.11. In this experiment, the fast cooling rates show that as hydrides are driven out of solid solution, they will initially form large numbers of small hydride clusters. Each of the darker areas in Fig 2.11 represents a cluster of hydride platelets, as individual platelets would not be discernible under optical microscopy. As the cooling rate becomes less extreme, the size of hydride clusters grows and the distribution becomes less homogeneous until the individual hydrides are found existing in long stringers. Hydrides have been noted to form along grain boundaries when the cooling

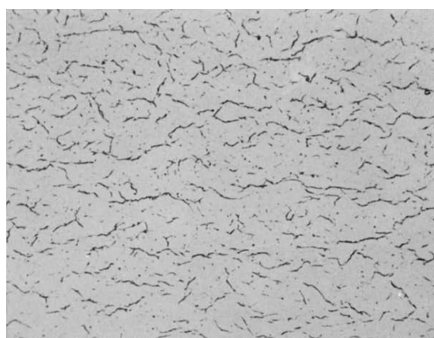
rate is slow, so it is possible that this is what is witnessed in Fig. 2.11d [23].



(a) Cold water quench.



(b) Boiling water quench.



(c) Air cooling.



(d) Furnace cooling.

Figure 2.11: Optical micro-graphs of hydride evolution under different cooling regimes in Zircaloy-2 (200 ppm H). A scale bar was not provided, however magnification of 190 times was reported. Reproduced from reference [23].

So far, large scale morphology of hydrides has been discussed. In terms of an atomistic investigation, the crystallographic structures of hydrides is potentially more relevant for study. The Zr-H phase diagram shows a number of stable phases that play a part in the precipitation of hydrides (Fig. 2.7). As hydrogen intake increases, the dominant two phases to co-exist are α -Zr and δ hydrides. The δ -phase has a non-stoichiometric composition of ZrH_x , with x being less than two and with a typical value of approximately 1.66, but values between 1.3 and 1.7 are commonly quoted [91]. Crystallographically, this hydride is a FCC fluorite structured compound,

with the hydrogen occupying the tetrahedral interstitial sites of the Zr lattice and $a = 4.768 \text{ \AA}$ (Fig. 2.12b). It should also be noted that there is another phase which has been experimentally verified as present in this region - the metastable γ phase, with a composition of around ZrH (some non-stoichiometry is sometimes quoted). This phase is sometimes observed when samples are quench cooled [92]. It has a face centred tetragonal structure ($a = 4.58 \text{ \AA}$, $c = 5.01 \text{ \AA}$) and has hydrogen atoms sitting on interstitial sites on every other (110) plane (Fig. 2.12a) [91, 93]. Finally, should even more hydrogen be taken up, a ϵ phase is observed (although this phase is not reported on the phase diagram of [76], as they were not focusing on the hydrogen rich end of the system). The composition of this phase is ZrH_2 and is face centred tetragonal in structure ($a = 4.99 \text{ \AA}$, $c = 4.45 \text{ \AA}$), again showing similarities to fluorite (Fig. 2.12c) [94]. DFT investigations have predicted that another form of ZrH_2 may be stable, with a $c/a > 1$, however this has yet to be experimentally verified [95]. There is currently little need to look at compositions with a hydrogen content greater than ZrH_2 , as such compositions have not been observed in any prepared samples so far.

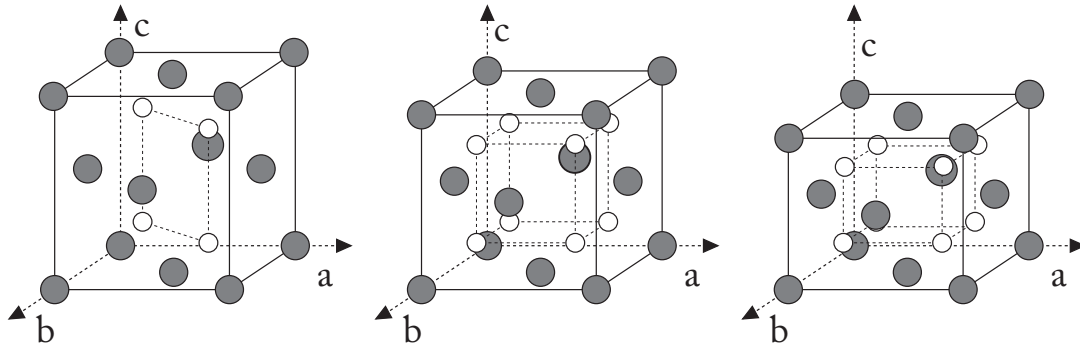
The presence of one hydride or another in a given sample is determined by the complex relationships of these hydrides with temperature and pressure. As discussed, there is a strong relationship between the lattice stress and the precipitate of hydride, although the exact details of this relationship are not fully understood. When hydrides precipitate, there is a positive volume difference between a molar quantity of Zr and a molar quantity of hydride [72]. As a result the Zr lattice and the hydride will be under a local volumetric strain. It has been observed that the elastic strain is larger in the hydride, possibly due to yielding in the Zr lattice [96]. Furthermore, the stress state has been observed to have ordering effects in the different hydride structures. Synchrotron X-ray diffraction has given evidence that for uni-axial strains of around 4% [92], δ -phase hydrides can spontaneously re-order to γ -phase hydrides.

Hydride structures have been simulated using DFT by Domain [44]. Simulations to determine bulk properties have yielded results similar to the experimental data shown previously (Table 2.4). The work done by Domain is well cited in the field, however it does have limitations. As mentioned previously, the δ hydride has a composition of approximately $ZrH_{1.66}$ and a FCC structure. Due to limitations in computing power and the processing cost of DFT simulations only relatively small cells can be simulated by this method. As a result, cells cannot be made

large enough to contain enough hydrogen sites to accommodate the composition exactly. Thus a hydride with a composition of $ZrH_{1.5}$ is studied instead and an explanation for accounting for the different configurations that hydrogen can sit in is not given. Examining Fig. 2.12, it can be seen that there is a clear trend that increasing the hydrogen content decreases the c/a ratio. This suggests that if a hydride with a H content of less than $ZrH_{1.66}$ was simulated, it would be expected to be more stable with a greater c/a ratio. Table 2.4 does not demonstrate this, as the $ZrH_{1.5}$ structure is more stable with a smaller c/a ratio. This may be due to problems with the DFT model used here, or it is possible that the trend described is more complex than outlined here.

As a result of the problems mentioned above, this result may not be representative of an actual physical system. A method of examining this hydride in more detail is developed in chapter 5. Despite these problems, the work is still credible and is mostly able to reproduce experimental data, thus it does provide a workable foundation for future study, as long as its limitations are considered.

A further recent development is the discovery of a new metastable hydride phase in the Zr



(a) The gamma ZrH hydride. (b) The delta $ZrH_{1.66}$ hydride. (c) The epsilon ZrH_2 hydride.
Not all of the hydrogen sites shown above will be occupied.

Figure 2.12: Crystallographic structures of the key hydride phases. Zirconium is represented by grey and hydrogen by white.

Compound	Crystal Structure	a (Å)	c (Å)	E^f (eV)
$ZrH_{0.25}$	FCC	4.61	4.61	-0.119
$ZrH_{0.5}$	FCC	4.66	4.66	-0.305
ZrH	FCC	4.75	4.75	-0.491
	FCT(γ)	4.58	5.04	-0.507
	Diamond like	4.77	4.77	-0.408
	Exp[93]	4.60	4.97	-
$ZrH_{1.5}$	FCT with $c/a < 1$	5.04	4.25	-0.604
	FCC(δ)	4.79	4.79	-0.594
	FCT with $c/a > 1$	4.61	5.14	-0.599
$ZrH_{1.66}$	Exp [94]	4.78	4.78	-
ZrH_2	FCT with $c/a < 1$	5.01	4.44	-0.678
	FCC	4.82	4.82	-0.671
	FCT with $c/a > 1$	4.76	5.13	-0.675
	Exp [94]	4.99	4.45	-

Table 2.4: Lattice parameters and formation energies of different Zr-H structures.[44]

hydride system. This has been verified by a combination of experimental results (TEM) and *ab-initio* calculations of the possible structures of the hydride. Designated as the ζ -phase, this phase is fully coherent with the Zr lattice, has the composition Zr_2H and has lattice parameters $a = 3.3\text{\AA}$ and $c = 10.29\text{\AA}$ [97]. The structure of the ζ -phase is not fully ascertained, however it is likely that it is based on a hexagonal structure. This bears an interesting symmetry, as it would appear that the γ phase is a metastable, ordered form of the δ phase and the ζ phase is a metastable, ordered form of the α phase.

The information provided in this review provides an adequate foundation on which novel research can be developed. The key issues in this system appear to be the diffusion of hydrogen through the oxide layer, the dissolution of hydrogen into Zr matrix, the movement of hydrogen in Zr, the conditions required to bring about hydride precipitation, the structures of hydrides precipitated and impact of intermetallic SPPs on this process, if any. This work will aim to provide insight on the following questions:

- Why do some SPPs form and not others? Is there a thermodynamic basis for SPP formation?
- Why do some SPPs dissolve at a greater rate than others under reactor conditions?
- What is the driving force for hydrogen dissolution in Zr?

- What conditions favour hydride precipitation? Do these conditions determine which type of hydride will form?
- What are the impacts of temperature and pressure on this system? What are the atomic scale mechanisms underlying these effects?

Chapter 3

Methodology

Understanding the processes and mechanisms that occur in materials used inside nuclear reactors presents unique challenges to modern materials science. Fundamentally, this is because the environment inside a nuclear reactor is inherently hostile to all but the most basic observational tools. Sensors have to be designed to withstand extreme temperatures, pressures and radiation fluxes, meaning that it is prohibitively expensive to monitor processes as they occur in real time. Even observations taken after operational use of an in-reactor component are fraught with risk due to radioactive samples, caused by neutron activation and radioisotope contamination.

As a result, the nuclear industry has been a major driver for the use of computer simulation to understand the processes at work in materials. Over the last few decades, there has been an exponential increase in the amount of computer processing power available. This has allowed a wide variety of computational techniques to be developed, ranging from methods that model the motions of individual atoms over a timespan of femto-seconds, to models that examine entire reactors over a timespan of decades. All of these models have different characteristics in terms of complexity, computational cost, flexibility, accuracy and application. In the Zr-H system there are a number of basic phenomena in which the underlying mechanisms are still poorly understood. As a result, the main focus of this work is on atomic scale techniques, aimed at elucidating the underlying mechanisms behind the hydriding process. The main modelling tool used is the *ab-initio* technique of Density Functional Theory (DFT) and the main method of use

is in the form of static calculations, aimed at producing thermodynamic data. Thus, an overview is given, firstly of the use of thermodynamic data, followed by how DFT is used to produce it and finally, some practical considerations for modern DFT codes.

3.1 Thermodynamic Modelling

Fundamentally, the goal is to understand the processes which occur at the atomic scale within a Zr alloy. For example, it would be useful to understand which hydrides will form under which set of circumstances, or where the hydrogen prefers to sit in the microstructure of a Zircaloy. Therefore, the main question is one of stability. Any modelled system will have a variety of variables associated with it and a stability which follows from this set of variables. For example, consider a ball, allowed to roll freely across a smooth yet uneven landscape, under the action of gravity. The important variable is the position of the ball. The totality of all the possible places that the ball could ever possibly be in this system is known as the *configuration space* of this system. Intuitively, if the ball is allowed to roll freely and given sufficient energy, the expectation is for the ball to eventually sit at the lowest point in the landscape. This represents the most favourable state and the lowest energy position within the configuration space.

In an atomic model, these variables are numbers such as the positions of the atoms, or how they are repeated through space to form a crystal. The stability is represented quantitatively as the energy difference between one configuration and another. By comparing the energies of different configurations, and noting which configuration has the lowest energy, it can be seen if there is an impetus for a reaction between the configurations to proceed, or to arrest. As a result, when describing the energy difference between reactants and products, the convention is for a negative energy to indicate that the reaction will proceed and vice versa for a positive energy.

A further consideration is the entropy associated with the different configurations. Entropy is a more difficult concept to apply to the situation and is classically described as the amount of disorder in the system, or how dispersed the available energy is. In the context of the configuration space description, entropy can be thought of as the volume of the configuration space. As is stated by the second law of thermodynamics, the entropy of a closed system can only remain constant or increase. This represents a tendency in nature for systems to become more

disordered and energetically homogeneous over time[98]. The application of this to atomistic simulation is that simulators must have a consideration of the available entropy in mind, when predicting whether a reaction will favour one set of components, or another. It is expected that disordered structures would be more favourable than ordered structures and it is possible that the gain in entropy may drive a reaction forwards, even if the reaction is unfavourable from an enthalpy point of view.

Although entropy can be important, its effects can often be discounted as negligible, particularly with ordered crystals. The two main sources of entropy associated with a crystal are configurational entropy and vibrational entropy. Configurational entropy represents the disorder available in how many different ways the atoms may be configured. Structures that can be organised in a large number of ways, for example, the non-stoichiometric δ -hydride, have a large configurational entropy. Vibrational entropy represents the number of different ways that vibrational modes can be arranged within a crystal. On this scale, vibrations transmitted between atoms are quantised, often modelled as virtual particles known as phonons. As there are a large number of different configurations for how these phonons move and can be positioned, the number and types of phonons available to a crystal has an effect on the entropy associated with it; these considerations increase the volume of the configuration space of the crystal. Published DFT calculations often neglect entropic calculations as a matter of expediency, although this will be discussed in more detail in Chapter 6.

The combination of entropy and enthalpy is referred to as the free energy. Originally, the measurement of free energy was developed from experimental studies and due to variability of experimental conditions there are different formalisation of free energy. Under the conditions most relevant to hydriding, the formalization of interest is referred to as the Gibbs Free Energy, named after its discoverer Josiah Williard Gibbs [99]. This assumes that the temperature and pressure of the system remain constant over the reaction, while the volume may be variable, meaning it is appropriate to slower paced reactions, where pressures have time to equilibrate. The other main formalisation, the Helmholtz Free Energy, assumes that temperature and volume are constant, while pressure is allowed to vary. It is more appropriate to more fast paced reactions where the products may be volumetrically confined by their own inertia or other factors (for example explosives). The change in Gibbs Free Energy is defined as:

$$\Delta G = \Delta H - T\Delta S \quad (3.1)$$

where H represents the enthalpy of the reaction, T represents the temperature, and S represents the entropy. It is important to note that many models are calculated in a purely energy minimised state, meaning that they are treated as existing at 0 K and the entropy is multiplied by zero. If this is the case, the entropic component of the reaction can be discarded and the free energy is equal to the enthalpy. When used, this assumption will be mentioned explicitly.

There is one final consideration before moving onto the descriptions on how enthalpies may be calculated. The thermodynamic component of a reaction describes whether or not there is a driving force for that reaction to proceed. However, thermodynamic calculations say little or nothing about how rapidly the reaction will proceed. It is entirely possible that a reaction is thermodynamically favourable, but it will proceed at such a slow rate that it would not be noticeable during any reasonable time scale. There are a number of factors determining how fast the reaction will proceed within a solid solution, such as how mobile the different species are or the concentrations of the various species. When considering H-Zr reactions, the H is so mobile that it is expected to be able to diffuse to reaction sites very quickly, meaning the progress of the reactions is determined by the availability of the hydrogen. Thus, as long as the necessary hydrogen is present, a reaction should occur, if it is thermodynamically favourable. This is not necessarily the case when examining species that are less mobile.

3.2 Quantum Mechanics Theory

In order to calculate the free energy of the reactions, a model is required of the materials in question. The primary model of this work is quantum mechanical in nature, namely, that the energy of a given configuration uses a quantum mechanical model of electrons and nuclei to derive forces, distances and hence, energies. The starting point of this description is a basic application of quantum mechanical equations (The Schrödinger Equation) to determine the energy of a simple system [100].

3.2.1 The Schrödinger Equation

Fundamentally, particles at the atomic scale possess two forms of energy. These are the kinetic energy of their motion and the potential energy of their interactions with electromagnetic or nuclear forces. In a quantum mechanical model, this energy is discretised, based on the parameters of the system. The quantum mechanical description for the energy of a particle is given by the Schrödinger Equation:

$$E\Psi = \hat{H}\Psi \quad (3.2)$$

where Ψ represents the wavefunction and $\hat{H}$ the sum of the kinetic and potential energy contributions to the system. This important descriptor of the system is known as the Hamiltonian operator. To illustrate its use, an example will be made of one of the simplest useful systems that can be modelled and the methods will be developed there.

Consider the case of describing a single uncharged hydrogen atom, using the framework of quantum mechanics. This is a common case used to illustrate the mathematics of the Schrödinger equation applied to a simple physical system [101]. As a system consisting of only an electron and a proton, interacting through their equal and opposite electric charges, this system makes a useful test case for illustration purposes. If the position of the proton is represented by the Cartesian vector $\mathbf{r}_p$ and the position of the electron by $\mathbf{r}_e$, then the description of the potential between the two of them is given by:

$$V(\mathbf{r}_p - \mathbf{r}_e) = V(\mathbf{r}) = \frac{-e^2}{4\pi\epsilon_0|\mathbf{r}|} \quad (3.3)$$

where the ϵ_0 is the physical constant of the permittivity of free space and e is the fundamental electric charge. If the goal is to apply this system to a hydrogen atom, $\hat{H}$ is replaced with terms to describe the kinetic energies of the proton and the electron, and the potential between the two.

$$E\Psi(\mathbf{r}_p, \mathbf{r}_e) = \left(-\frac{\hbar^2}{2m_p}\nabla_p^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 + V(\mathbf{r}) \right) \Psi(\mathbf{r}_p, \mathbf{r}_e) \quad (3.4)$$

The ∇^2 symbol denotes the sum of second partial derivatives (with respect to x , y and z direc-

tions) of the position of the relative particle, derived with respect to the wavefunction:

$$\nabla^2\Psi = \frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}. \quad (3.5)$$

This operator is known as the Laplacian. The symbols m_p and m_e represent the mass of the proton and the electron respectively. Equation 3.4 now provides a description of the energy of a hydrogen atom from a given $\mathbf{r}_p$ and $\mathbf{r}_e$. If a hydrogen atom is considered, it makes sense to apply two particular transformations, in order to give a more useful description. Firstly, it is noticeable that the proton is substantially more massive than the electron. With respect to an independent frame of reference, both particles are co-orbiting each-other, around a common center of mass (a two-body problem), however, by accepting the proton as the origin of the coordinate system this system can be approximated to an electron orbiting around a stationary proton. Effectively, the frame of reference should be changed to originate at the center of mass of the system. This system is a more sensible model, as it means the only consideration is the motion of the electron. Secondly, following from the concept of a stationary proton at the origin of the system, it is intuitive that the system is spherically symmetrical about the origin. As a result, it simplifies the model of the system to describe the location of the electron in terms of the polar coordinate system (r, θ, ϕ) , instead of Cartesian coordinates (x, y, z) . The transformation from Cartesian to spherical coordinates is accomplished by knowing that $x = r \sin \theta \cos \phi$, $y = r \sin \theta \sin \phi$ and $z = r \cos \theta$. The Schrödinger equation is now transformed to this:

$$E\Psi(r, \theta, \phi) = \left(\frac{-\hbar^2}{2m} \nabla_e^2 + V(\mathbf{r}) \right) \Psi(r, \theta, \phi) \quad (3.6)$$

where only the mass of the electron is considered. The Laplacian of the electron is expanded, via a lengthy algebraic process, to:

$$\nabla_e^2\Psi(r, \theta, \phi) = \frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial \Psi}{\partial r} \right) \right] + \frac{1}{r^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Psi}{\partial \theta} \right) \right] + \frac{1}{r^2} \left[\frac{1}{\sin^2 \theta} \frac{\partial^2 \Psi}{\partial \phi^2} \right]. \quad (3.7)$$

The coordinate system change also highlights a further aspect of the system. Equation 3.7 is broken down into three key components, a radial dependency based upon r , an azimuth

(horizontal angular) dependency reliant on θ and a colatitude (vertical angular) dependency on ϕ . Thus, there is now a differential equation where the overall wavefunction is determined by radial, azimuth and colatitude functions. The wavefunction can be described as a product of these functions: $\Psi(r, \theta, \phi) = R(r)A(\theta)C(\phi)$. These functions must be written such that each is only dependant upon its corresponding variable and no others, meaning that the partial derivatives become ordinary derivatives. Solving this equation will show which values of r, θ and ϕ the electron can occupy and what energies it can have. When separating these variables, constants must be introduced to take into account the components of the other functions that are no longer considered as variables. Thus, separating the variables, the azimuth equation becomes:

$$\frac{1}{A} \frac{d^2 A}{d\phi^2} + K_A = 0 \quad (3.8)$$

the colatitude equation becomes:

$$\frac{1}{C} \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{dC}{d\theta} \right) + K_C \sin^2 \theta = K_A \quad (3.9)$$

and the radial equation becomes

$$\frac{1}{R} \frac{d}{dr} \left[r^2 \frac{dR}{dr} \right] + \frac{2mr^2}{\hbar^2} (V(\mathbf{r}) - E) = K_C \quad (3.10)$$

where the K terms represent the constants introduced by separation. These equations are solvable due to the assumption that there must be no sudden discontinuities in the wavefunction from one angular separation to the next, as this would represent the electron not fitting into its orbital by an integer wave-number. This boundary condition means that only specific solutions to the azimuth equation are viable, hence leading to discrete quantisation of horizontal angular momentum. It should also be noted that the radial equation has had the potential term folded into it, as the energy of this term is dependant upon r_e alone. These equations are normally solved sequentially, as the azimuth equation takes the form of an ordinary second order differential equation with an exact solution. This means valid ranges for K_A can be found, which allow equation 3.9 and then 3.10 to be solved in turn. Once various fundamental constants are taken out, the solution is valid for three different variables known as quantum numbers. An electron

may only occupy values of r, θ and ϕ if the quantum number for the associated function fits the following restrictions.

$$\begin{aligned}
 R(r_e) \quad \text{Principle quantum number:} \quad n &= 1, 2, 3, \dots \\
 C(\phi_e) \quad \text{Orbital quantum number:} \quad l &= 0, 1, 2, 3, \dots n-1 \\
 A(\theta_e) \quad \text{Magnetic quantum number:} \quad m &= -l, -l+1, -l+2, \dots l-2, l-1, l
 \end{aligned} \tag{3.11}$$

Graphically, this gives a complete picture of the hydrogen atom. Ionisation energies can be determined by finding the difference in energies between solutions with different values of n . These functions can even be used to graphically produce electron density distributions and visualise the shape of different configurations of a hydrogen atom, as shown in Fig. 3.1. It is even intuitive to see in Fig. 3.1 that the n value alters the number of radial layers of orbitals, the l value alters the rotational symmetry of the lobes and the m value alters the vertical orientation of the lobes.

It is beyond the scope of this work to show the exact mathematical method that must be followed in order to arrive at this solution. The key point of this treatment of the hydrogen atom is to illustrate that although the Schrödinger equation is a powerful tool and one of the cornerstones of quantum mechanics, it is complex to apply and is reliant on the fortuitous application of various mathematical techniques in order to solve even the simplest system. For example, if the above method was expanded to look at even the simplest of molecules, H_2 , the Schrödinger equation would immediately become incredibly more complex:

$$\begin{aligned}
 E\Psi(\mathbf{r}_{p1}, \mathbf{r}_{e1}, \mathbf{r}_{p2}, \mathbf{r}_{e2}) &= \left(-\frac{\hbar^2}{2m_p} \nabla_{p1}^2 - \frac{\hbar^2}{2m_p} \nabla_{p2}^2 - \frac{\hbar^2}{2m_e} \nabla_{e1}^2 - \frac{\hbar^2}{2m_e} \nabla_{e2}^2 \right) \Psi(\mathbf{r}_{p1}, \mathbf{r}_{e1}, \mathbf{r}_{p2}, \mathbf{r}_{e2}) \\
 &+ (-V(\mathbf{r}_{e1} - \mathbf{r}_{p1}) - V(\mathbf{r}_{e2} - \mathbf{r}_{p2}) + V(\mathbf{r}_{p1} - \mathbf{r}_{p2})) \Psi(\mathbf{r}_{p1}, \mathbf{r}_{e1}, \mathbf{r}_{p2}, \mathbf{r}_{e2}) \\
 &+ (V(\mathbf{r}_{e1} - \mathbf{r}_{e2}) - V(\mathbf{r}_{e1} - \mathbf{r}_{p2}) - V(\mathbf{r}_{e2} - \mathbf{r}_{p1})) \Psi(\mathbf{r}_{p1}, \mathbf{r}_{e1}, \mathbf{r}_{p2}, \mathbf{r}_{e2})
 \end{aligned} \tag{3.12}$$

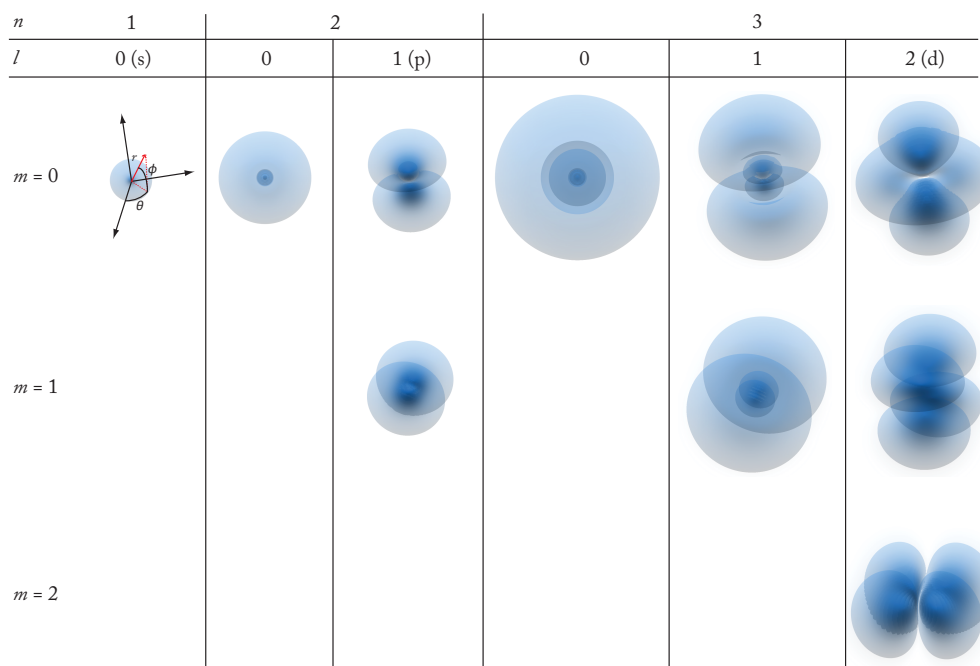


Figure 3.1: A visualisation of the electron probability density around a hydrogen atom and how it varies with quantum numbers. Darker areas mean a greater probability density. Note that this table omits the case where m is negative, which would form a mirror image of this table above the heading, with orbital lobes orientated along the remaining direction. This was omitted for the sake of brevity. These images were generated using "Orbital Viewer" computer software[102].

In this equation it is no longer clear that polar coordinates should be used over Cartesian, nor can the motions of particles be discounted by transforming the coordinate origin. Even if this were not a problem, there is now an issue whereby all of the Laplacians contain variables dependent upon the positions of each and every particle in the system, making it impossible to separate out the variables such that each sub-function contains only one variable. The potential terms also offer difficulties, as any change in the position of one particle would alter the potential energy of every other particle in the system, altering their positions and hence the potential experienced by the original particle. As there is a complex set of interdependent variables, there is what is considered to be an n -body problem where $n > 2$ (or "many body"). Such an issue is not solvable analytically (except in a limited number of specific cases) in order to find the permissible range of unique quantum numbers. However, it may be possible to solve this

using numerical techniques and computation. Essentially, the system will be broken down into a number of variables, numerical values are inserted into this system and an output solution is calculated. The solutions are examined and then the calculations are run again with modified values. Over a series of (possibly many) iterations the model will hopefully converge on an appropriate solution. The mechanism by which the variables are modified and how the solution is determined to be sufficiently converged depends upon the particular numerical method being employed and will be covered in more detail later.

Some simple approximations can be made, given that experimental evidence exists as to what the separation of the protons should be. The parameter of $\mathbf{r}_{\mathbf{p1}} - \mathbf{r}_{\mathbf{p2}}$ can be set to this value (approx 0.74 Å) as an initial guess. Given that protons are substantially more massive than electrons, the assumption can be made that the electrons will move far more rapidly than the protons. Hence the kinetic energy of the nuclei can be neglected (this approximation will be described in further detail later). This partially decouples the proton-electron interaction simplifying the system further still. However, if using the un-approximated Schrödinger equation, there is nothing to be done about simplifying the electron-electron interaction, thus there is no option but to rely on brute force computational power in order to solve this.

Ultimately, a numerical solution to the Schrödinger equation may be able to determine some of the aspects of the H_2 molecule system. This solution will not be as complete as an analytical solution and may only apply to certain situations, however it is the only solution which is currently available. Other mathematical techniques based on the Schrödinger equation have been developed and may also be applicable to this problem, but are beyond the scope of this investigation. Even with appropriate techniques, the hydrogen molecule is still a very small and limited system. If the goal is to expand the horizon of the model to encompass systems of crystals comprising of many septillions of atoms, all of which have far more electrons than hydrogen, insurmountable computational difficulties quickly become apparent. As each electron effects every other electron, the number of interactions between electrons scales with the triangular number of the number of electrons. Thus if required to model a full HCP unit cell with just 6 Zr atoms containing 40 electrons each, there would be 28920 unique electron-electron interactions. This very quickly grows to be impractical for any number of atoms that could reasonably approximate a crystal. Thus, a new model is needed, which avoids this many-body problem.

3.2.2 Hartree-Fock Methods

Hartree and Hartree-Fock methods are a solution to the many body problem suggested originally by Douglas Hartree in 1926 and expanded upon by John Slater and Vladimir Fock in the late 1920's and early 1930's [103, 104, 105]. To describe this approach, the first step is to return to the concept of the difference in mass between nuclei and electrons. As described previously, the mass of even the smallest nucleus is many of orders of magnitude greater than the electrons surrounding it. Thus, we can treat the nuclei as effectively stationary with respect to the electrons and possessing negligible kinetic energy. The electrons are treated as moving within the combined potential wells of the nuclei. This is referred to as the Born-Oppenheimer approximation [106]. Thus for a system containing n electrons:

$$E_{\text{BO}} \Psi = \left(\sum_i^n -\frac{\hbar^2}{2m_e} \nabla_{e_i}^2 + \sum_j^n V_{\text{nuclear}}(\mathbf{r}_{e_i}) + \frac{1}{2} \sum_{i \neq j}^n U(\mathbf{r}_i - \mathbf{r}_j) + E_{\text{nuclear}} \right) \Psi \quad (3.13)$$

where the $U(\mathbf{r}_i - \mathbf{r}_j)$ term in this equation is the most computationally expensive as it represents the many-body electron-electron interactions. The Hartree method approximates the many body term by assuming that electrons do not directly interact with each other and the electronic wavefunction containing n electrons is given as:

$$\psi(\mathbf{r}_{e_1}, \mathbf{r}_{e_2}, \mathbf{r}_{e_1}, \dots, \mathbf{r}_{e_n}) = \psi_{e_1}(\mathbf{r}_{e_1}) \psi_{e_2}(\mathbf{r}_{e_2}) \psi_{e_3}(\mathbf{r}_{e_3}) \dots \psi_{e_n}(\mathbf{r}_{e_n}) \quad (3.14)$$

where each individual $\psi_{e_1}(\mathbf{r}_{e_1})$ is normalised such that the integral of the square of $\psi_{\text{electronic}}(\mathbf{r}_{e_1}, \mathbf{r}_{e_2}, \mathbf{r}_{e_3}, \dots, \mathbf{r}_{e_n})$ is unity. This is known as the Hartree product. However, it is still clear that electrons must somehow influence each-other. Thus rather than interact directly with each-other, they interact with a general electron potential computed from the average charge density found using the wavefunctions. This mean field, or "Hartree Potential" as experienced by electron i out of n electrons (assuming each electron experiences a straightforward Coloumbic repulsion) is given as :

$$U_{\text{Hartree}}(\mathbf{r}_i) = \int \frac{\rho(\mathbf{r})e^2}{4\pi\epsilon_0|\mathbf{r} - \mathbf{r}_i|} d\mathbf{r} \quad (3.15)$$

where the average density at $\mathbf{r}$ is given by the function:

$$\rho(\mathbf{r}) = \sum_j |\psi_j \mathbf{r}|^2. \quad (3.16)$$

To clarify, it can be seen that this potential is represented as an interaction between e_i and the total charge density given acting at the mean position of all the electrons (excluding e_i itself). The Hartree potential is determined by the collection of individual electron wavefunctions and the electron it is acting on, meaning the expectation for the wave-function can be calculated for the system. The Hartree potential is now substituted into 3.13 to get the description of the expectation value of the Hamiltonian, $\langle \hat{H} \rangle$:

$$E_{\text{BO}} \Psi = \left(\sum_i^n -\frac{\hbar^2}{2m_e} \nabla_{e_i}^2 + \sum_i^n V_{\text{nuclear}}(\mathbf{r}_{e_i}) + \sum_i^n U_{\text{Hartree}}(\mathbf{r}_i) + E_{\text{nuclear}} \right) \Psi \quad (3.17)$$

The expectation value for the Hamiltonian represents an upper limit on the energy of the system. This is effectively a set of single electron calculations, meaning there is 1 equation for each electron, rather than one for all the electrons. For each electron equation, the starting point is an initial estimation of the wave-function of each of the other electrons. The solution to the various equations is then calculated, in order to get the expected wavefunction for each electron. If the expected wavefunction is approximately equal to the initial guess, then the calculation is self consistent and the permitted wavefunctions have been found. If not, the expected values for the electron wavefunctions are taken and fed back into the equations as the new "initial" guess. The results of one calculation of the Hartree equation will always be lower in energy than the initial state fed into the equation. The reason for this is due to the variational principle, in that the system is more stable in its lowest energy state. For example, imagine a cloud of electrons that have been densely packed together. When calculating the Hartree potential, any given electron will have a large potential energy, as each is close to the location that the mean field originates from. Hence, the expected output of the Hartree equation is to give the electron cloud a more spread out probability distribution than was originally fed into it, lowering the overall potential. When the parameters which gives a self consistent wavefunction have been found,

the electronic structure has been determined via the Hartree method. This algorithm is shown in Fig. 3.2. If desired, the initial positioning of the ions can be modified and the calculation re-run, in order to determine if the atoms are at the lowest energy state. It is important to note that in reality, the output of the Hartree equation is not simply taken as the input of the next iteration. The reason for this is that the progression of iterations is often numerically unstable from a practical point of view and may oscillate wildly between near-stable states. Instead, it is common to "mix" the old guess with the new answer, in order to retard any instabilities.

However, Hartree simulations do not necessarily give correct properties of simulated structures, due to their simplification of electrons to non-interacting particles. There are two key properties that a Hartree method by itself will not take into account. These are known as the effects of "exchange" and "correlation". Firstly, a description will be given of how the Hartree approach can be modified to deal with exchange.

It is a basic principle of atomic physics that a fundamental particle of a given type is indistinguishable from any other particle of that type, e.g. all electrons are identical. Thus, it is intuitive to expect that the exchange of two identical particles would not alter the state of the system in any way. However, although electrons are identical, they do have external properties imposed upon them by the surrounding system, for example the quantum numbers n , l and m in a hydrogen atom. One of these properties that has been neglected so far is the quantum spin of the electron. A fundamental principle of quantum mechanics is that no two fermions, such as electrons, can occupy the same quantum state at the same time. If one electron has a given set of values for n , l and m , then another electron cannot have that same set, unless it differs in another way. This difference is that the spin of the electron, which can be thought of as the angular momentum vector intrinsic to each particle. If two electrons have the same n , l and m , it is said that one is "spin up" and the other is "spin down". This fundamental principle of quantum mechanics is known as the Pauli exclusion principle [107], named after Wolfgang Pauli and is ultimately responsible for many of the phenomena seen arising from electron interactions (such as chemistry).

Without alteration, the Hartree method does not account for spin. As a result, if two electrons were exchanged between different orbitals, a forbidden configuration could be produced with two electrons having the same quantum state. Hartree calculations can be made to distinguish

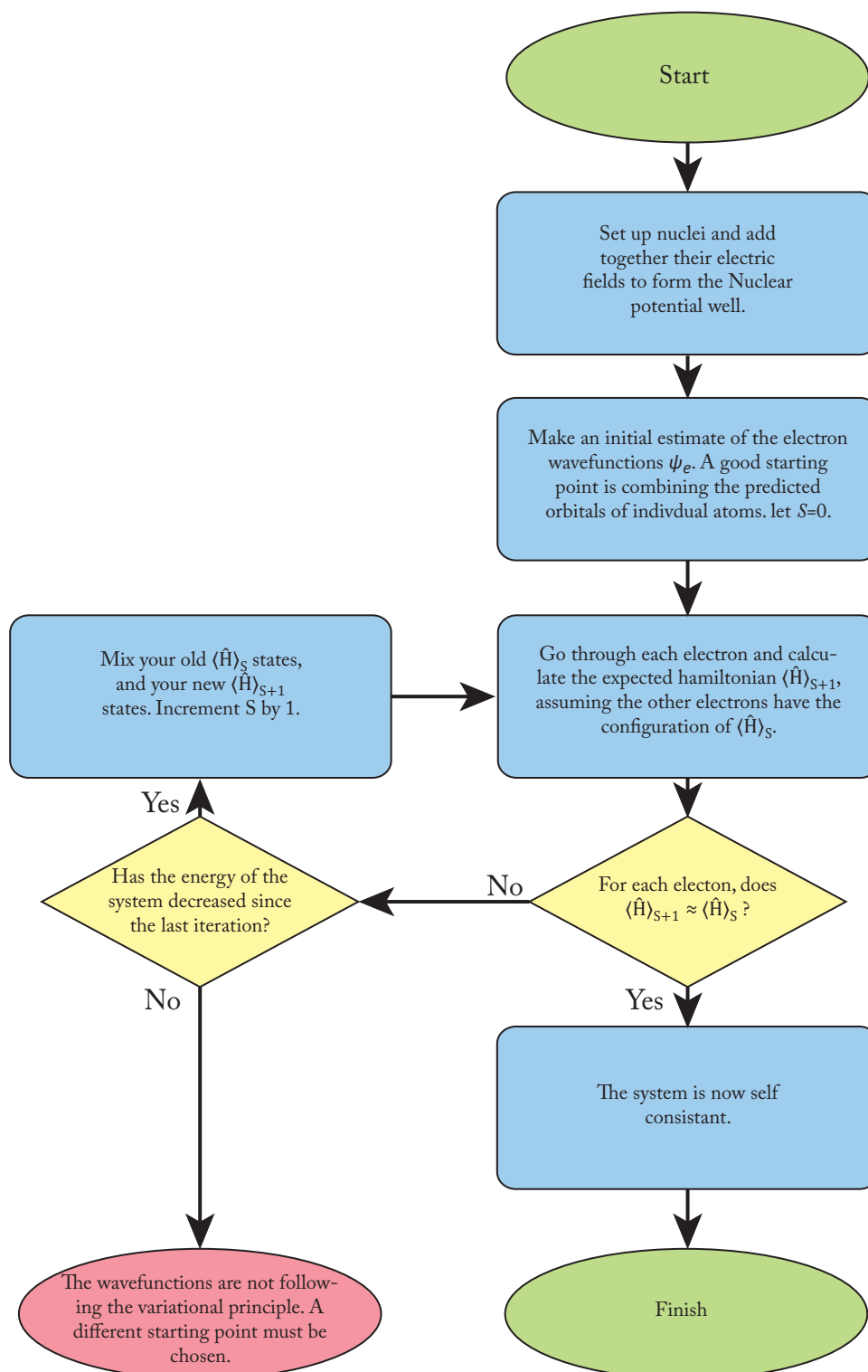


Figure 3.2: This flowchart demonstrates the basic algorithm behind any Hartree computer program. Other methods such as Hartree-Fock or DFT use similarly designed loops, modified to include their different mathematical formulations.

between spin up and spin down electrons by creating two sets of wavefunctions, one for each spin direction. For example, in a two electron system, electron one could be in a spin up orbital and electron two in a spin down orbital:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_{up}(\mathbf{r}_1)\phi_{down}(\mathbf{r}_2) \quad (3.18)$$

where ϕ represents the spin orbital. However, if this is reversed:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_{up}(\mathbf{r}_2)\phi_{down}(\mathbf{r}_1) \quad (3.19)$$

there is a distinguishably different description. This creates the issue that spin up electrons are now intrinsically distinguishable from the spin down electrons [108]. In order to correct for this, a new approach must be created; the Hartree method must be modified into a Hartree-Fock form. In the two electron example, this would be done by taking both eq. 3.18 and eq. 3.19 and combining them linearly:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}(\phi_{up}(\mathbf{r}_1)\phi_{down}(\mathbf{r}_2) - \phi_{up}(\mathbf{r}_2)\phi_{down}(\mathbf{r}_1)) \quad (3.20)$$

where the first term on the right hand side is a normalisation term. The minus sign means that the overall wavefunction is antisymmetric, such that exchanging the position of electrons causes the wavefunction to change sign. If there are more electrons than the above example, it is easier to describe the combination of spin orbitals in the form of the determinate of an antisymmetric matrix. This is known as Slater determinate [105]:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \cdots & \phi_1(\mathbf{r}_n) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \cdots & \phi_2(\mathbf{r}_n) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_n(\mathbf{r}_1) & \phi_n(\mathbf{r}_2) & \cdots & \phi_n(\mathbf{r}_n) \end{vmatrix}. \quad (3.21)$$

Now the model takes into account exchange, there is only the issue of correlation. Correlation is one of the phenomena arising directly from the interactions of individual electrons. For example, consider two electrons in an electron gas containing a large number of electrons, there

is an expectation for e_1 to experience a repulsive coulombic force away from e_2 and vice versa. If e_1 and e_2 are now placed very close together, the true force between them would increase substantially, however the force each would experience from the mean field would alter by a negligible amount, skewed by the large number of unaltered electrons. The forces experienced by each electron are said to be correlated and thus the mean field approach is a limited approximation. Hartree-Fock methods still provide a useful starting point and there are a number of Post-Hartree-Fock methods which attempt improve the description of electron correlation with varying degrees of success, although they will not be not discussed in further detail here.

These models are universally computationally expensive, as they must embody some element of the intractable many-body issue. Slater determinates must be found for a matrix containing many electrons. Even with efficient algorithms, this tends to scale with the cube of the number of electrons in the system. Post Hartee-Fock methods add yet more complexity. Such techniques are often limited to single atoms or small compounds and clusters, even with modern computers. In order to correctly model solids with vast numbers of particles and still capture enough of the physical processes such that the model is reasonable, a more computationally efficient technique is required.

3.2.3 Density Functional Theory

Density Functional Theory is a reformulation of the electron many body problem, developed by Pierre Hohenberg, Walter Kohn and Lu Sham in the 1960's [109, 110]. It is one of the most well used tools in computational chemistry and materials science and is considered such a significant development, that Walter Kohn was awarded the Nobel prize for chemistry in 1998. Currently, the wavefunctions have been formulated out of an explicit description of the interactions of each of the particles, with approximations as necessary. The methods described so far all demonstrate that the external potential of the system determines the boundary conditions that the electrons interact within. At any given point, the system will have an electron density $\rho(\mathbf{r})$, which can be calculated by an integration of the normalised wavefunction's probability density of the system with respect to the volume of the system:

$$\rho(\mathbf{r}) = n \int |\psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_n)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 \dots d^3\mathbf{r}_n \quad (3.22)$$

The key reformulation used in DFT is that this relationship can be reversed. If the system is in its ground state configuration (Ψ_0), then the wavefunction and any observables based on the wavefunction such as the expected energy, can be related to the density via a functional:

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_n) = \psi[\rho_0] \quad (3.23)$$

The square bracket notation denotes a functional. A functional represents a function of a function. It is an expression that takes in a function (in this case a description of the electron density) and maps it to a scalar value, such as the system energy. This expression forms the underlying backbone of DFT. The fundamental statement of DFT can be put as "*The electron density uniquely determines the Hamiltonian operator of the system*". It follows that if the Hamiltonian is given by a functional of the density, then the constituents of the Hamiltonian must either be density functionals as well, or be invariants. The three terms that make up the Hamiltonian are the kinetic energy $\hat{T}$, the nuclear potential $\hat{V}$, the electron-electron interaction $\hat{U}$:

$$E[\rho_0] = \langle \hat{H} \rangle[\rho_0] = \int \psi \left(\hat{T} + \hat{V} + \hat{U} \right) \psi d^3\vec{r}_1 \dots d^3\vec{r}_n \quad (3.24)$$

The nuclear potential of any system is unique to each configuration of atoms. The potential can be formulated explicitly in terms of the density. However, the kinetic and the interaction terms are universal to any system. They can always be considered as a functional of the density, regardless of which system is being modelled. In order to model their behaviour, the Kohn-Sham theorem models this as a collection of fictitious non-interacting particles with a density identical to the electrons. Thus the wavefunction of electron i in the system of Kohn-Sham particles is given as:

$$\left(-\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 + V^{KS}[\rho](\mathbf{r}_i) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (3.25)$$

Where $V^{KS}(\mathbf{r}_i, \rho(\mathbf{r}_i))$ is the potential experienced by the non-interacting particles. From the wavefunction here, the Kohn-Sham particle description of the density is

$$\rho(\mathbf{r}) = \sum_i^n |\psi_i(\mathbf{r})|^2. \quad (3.26)$$

This density is then used to find the potential experienced by the actual electrons in the system, by adding on the Hartree energy and a functional term which describes the missing interactions of exchange and correlation:

$$V^{KS}[\rho](\mathbf{r}) = V(\mathbf{r}) + U_{Hartree}(\mathbf{r}) + f_{XC}[\rho(\mathbf{r})] \quad (3.27)$$

Thus a model as to how DFT is used to find the ground state of the system can be developed. The starting point is an initial guess of $\rho(\mathbf{r})$, which is used to find the potential experienced by the electrons in the system. These potentials are then used to create a new density and the calculation is solved iteratively as before.

What DFT has done is effectively rearranged the initial problem such that the many body issue is hidden inside the final term of equation 3.27 is known as the "Exchange-Correlation" function. With a rigorous description of the $f_{XC}[\rho]$ DFT would give a solution which is identical to a many-body solution of the Schrödinger equation (fig. 3.3). In this way, DFT is often described as an *ab-initio* approach. However, no such rigorous description exists and approximations are necessary. The first approximation, known as the Local Density Approximation or LDA was formulated by means of a description of a uniform electron gas, unperturbed by any external potentials. The only input to an LDA function is the density an electron experiences at a given point. As a result, LDA has a tendency to produce estimations which can differ significantly from real observables. For example, the enthalpy of vaporisation will typically be underestimated. More sophisticated approximations for $f_{XC}[\rho]$ do exist, such as GGA, Meta-GGA and Hybrid functionals [111]. In this study the primary tool will be the Generalised Gradient Approximation. The GGA approach goes a step ahead of LDA by using not just the density of the electrons, but also the gradient of the density at that particular point. It is more computationally expensive than the LDA approach, but strikes an appropriate balance between accuracy and cost and will be discussed in more detail later[112].

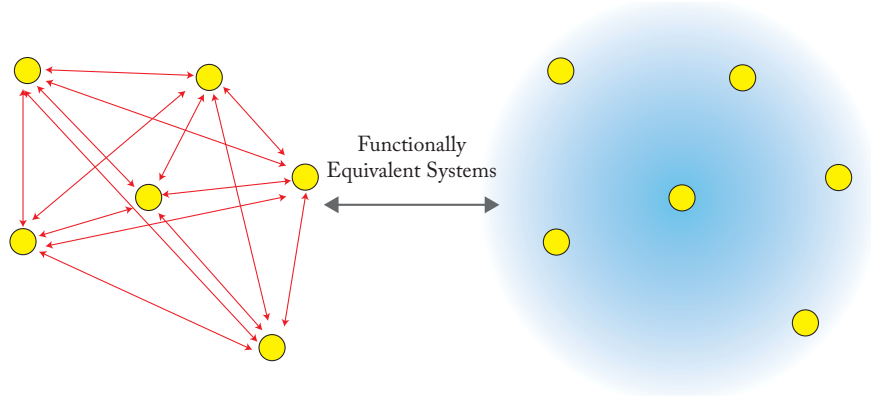


Figure 3.3: DFT replaces an intractable many-body problem with a functionally identical system of non-interacting particles which only influence each other via the particle density

3.3 Practical Considerations

So far, the discussion has been focused on modelling methods in a somewhat abstract sense. Unfortunately, as with all engineering and science, there is often a gap between the theoretical description of a method and practically implementing it in a useful manner. Running a modern DFT computer code requires careful consideration of a number of different parameters. Incorrect specification of these parameters will, at best, give misleading results and at worst, simply produce no results at all. The work in this study has relied heavily on use of the CASTEP computer code [113], although some work has also been carried out using the VASP code [114]. Both of these codes are referred to as plane wave, pseudo-potential codes. The rationale for using this type of code stems from their efficient modelling of bulk crystallographic materials. The main parameters of the simulations will now be discussed, as the specification of these is an important component of generating reproducible results.

3.3.1 Basis Set and Pseudopotentials

The previous sections demonstrate the need for a model of the wave-function, which is refined by the DFT code. An initial guess of the wave-function must always be made and there needs to be an overall framework for the numerical description of the wave-function. This is known as the basis set. There are a number of ways in which a code can formulate a basis set. One of the most common methods is to have a set of wave-functions which model the individual atomic orbitals, which are then combined together. This is often used in chemistry and related fields, where atomic orbital models can be used to give insight into how atomic bonds form. However, this model is not necessarily the most convenient choice when trying to replicate bulk materials, as the ideal scenario is to simulate crystals which are practically infinite (when viewed from an atomic scale). Instead, the selected DFT codes model electrons as a series of plane waves. Just as a function can be decomposed into a series of periodic functions by means of a Fourier transform, a 3-dimensional wavefunction can be decomposed into a series of plane waves by the same method. Each of the individual plane waves is multiplied by an expansion coefficient, C_{ij} such that they can be summed together by different amounts in order to model the different orbitals. These are known as Bloch waves [101] and are discussed in more detail in section 3.3.2.

A further approximation can also be made when dealing with how the electrons interact with the nuclear potential well. When considering the formation of atomic bonds, it is clear that only the most exterior electrons are contributing to the formation of a bond. This may even be limited only to the outermost shell of electrons, with the inner shells contributing nothing to atomic bonds. Thus approximation can be made whereby the nuclear potential "drops off" as the distance to the nucleus decreases (see fig. 3.4) . The "core" electrons are considered frozen with respect to the valence or conduction electrons, which are modelled explicitly by the DFT code. This reduces the effective number of electrons and greatly reduces the computational cost of a simulation, with little or no reduction in accuracy. It is important to note that there are circumstances where this model can break down, such as systems under high compressive stress, where core-core interactions become more important.

There are various different ways of generating a pseudopotential. The first developed method is referred to as "norm-conserving" in that the charge in the core is required to be the same as

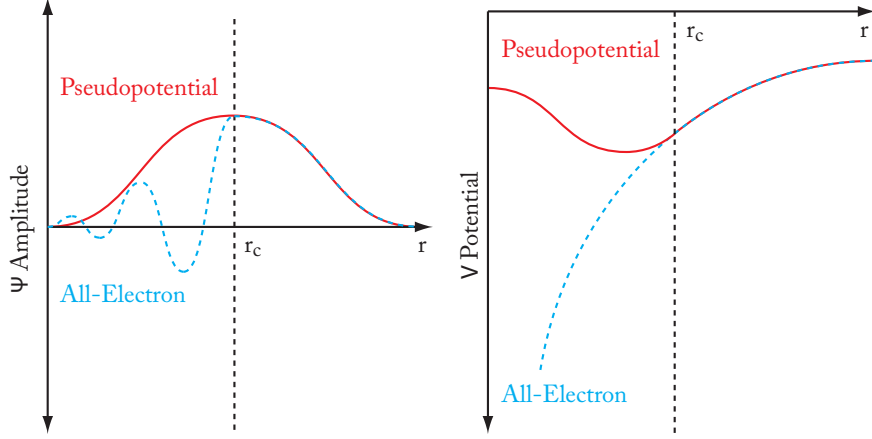


Figure 3.4: The difference between a Pseudopotential and an all-electron model. The pseudopotential becomes simpler to model below a core radius, r_c

an all electron description. As a result of this, norm conserving pseudopotentials often require high cut-off energies (see section 3.3.3) in order to function properly. Another option is to use "ultra-soft" potentials in which the norm conservation criterion is relaxed in order to produce a less computationally demanding pseudopotential[115]. Ultrasoft pseudopotentials often sacrifice some degree of transferability and will often need to be tested in different reference cases in order to ensure that they produce the correct behaviour in different environments. Other types include projector augmented wave pseudopotentials, which aim to approximate some aspects of core electron behaviour. In this work, ultrasoft potentials are used for their relatively low computational cost. CASTEP aims to reproduce some of the features of an all-electron DFT code by performing a brief, isolated all-electron calculation of the individual atoms before the run through of the main simulation. Data from this all-electron simulation is then used to generate an ultrasoft pseudopotential, which is used when the main algorithm commences. This is referred to as an on-the-fly pseudopotential in the CASTEP documentation, where more information on this process can be found[116].

3.3.2 K-point Grids

Even with modern computers and efficient DFT codes, there are still limits in the number of particles that can be simulated. Generally speaking, in this system, it is challenging to simulate more than about 100 atoms. In real terms, any system is effectively infinite compared to the number of atoms that can actually be modelling. This raises the problem that in order to simulate infinite crystals, it would be necessary to have an infinite number of electrons. When using a plane-wave based DFT code this problem is overcome using Bloch's theorem. At 0 K, it can be considered that the ion cores in a crystal will exist in a perfectly periodic array. As previously discussed, it follows that rather than describing the nuclear potential as a finite number of wells, it can be described as a periodically varying potential. The Bloch theorem states that the wave-function of an electron can be expressed as the product of two functions, one describing their wavelike nature and the other describing the system's periodicity:

$$\psi_{j,k}(\mathbf{r}) = u_{j\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \quad (3.28)$$

where $u_{j\mathbf{k}}(\mathbf{r})$ is a function that has the same periodicity as the primitive cell of the crystal, j represents the band index and $\mathbf{k}$ is the wave-vector, confined to the first Brillouin Zone (a unique volume described by the primitive cell in reciprocal space). As $u_{j\mathbf{k}}(\mathbf{r})$ is a periodic function, it can be expanded into a fourier series. Substituting this into the full equation gives us:

$$\psi_{j,k}(\mathbf{r}) = \sum_{\mathbf{G}} \mathbf{c}_{Gk} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad (3.29)$$

where $\mathbf{G}$ are reciprocal lattice vectors defined such that $\mathbf{G} \cdot \mathbf{R} = 2\pi m$, with $\mathbf{R}$ being a real space lattice vector and m being an integer. The term, $\mathbf{c}_{Gk}$, represents plane wave expansion coefficients as mentioned previously. Essentially, this treatment means that for a given periodic system, there is no need to explicitly consider all the electrons throughout an infinite system, the wave-function of any electron in the system can be described at a given $\mathbf{k}$ vector. The points defined by these vectors, are known as "K-points". This transforms the problem of having an infinite number of electrons into having an infinite number of K-points. Although this does not seem like the problem has been solved, there is no need to consider every single K-point as

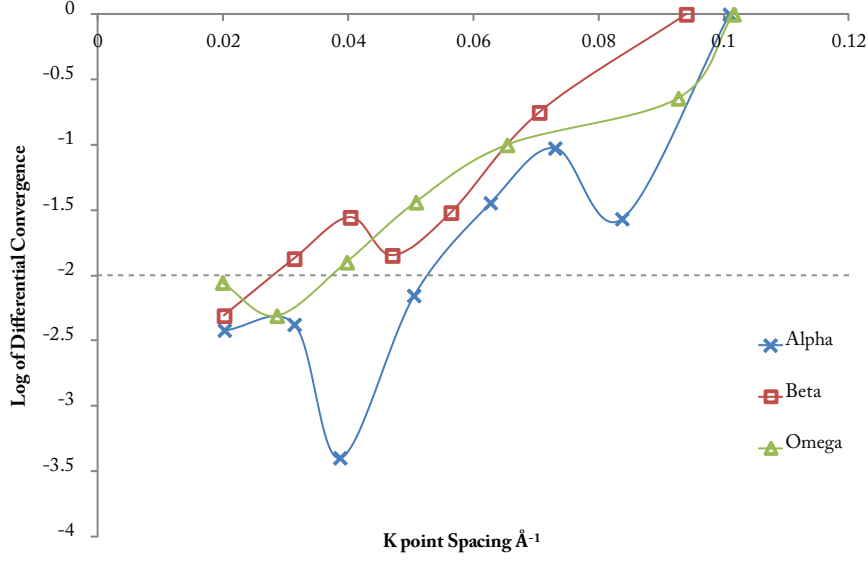


Figure 3.5: The relationship between K-point spacing and simulation precision for the different Zr crystals examined in this work.

K-points next to each other will be almost identical.

From a practical point, this means that any simulations done via DFT needs to have the arrangement of K-points specified. The more K-points used, the more accurate the simulation will be and the more computationally intensive. This means that for any given simulation, the consideration must be made of how many K-points are necessary in order to achieve the desired level of accuracy. It can be said that a system has an appropriate K-point density when increasing the number of K-points does not alter the energy of the system by more than the desired level of precision (0.01 eV). Fig. 3.5 shows a plot of the log of the energy difference of successive runs against the K-point spacing in that system. Energies are not plotted as relative to the most accurate value, as K-point convergence is not variational (unlike cut-off energy convergence). Unlike cut-off energy variance, which depends only on the pseudopotential, the effect of K-point density upon precision also depends upon the size and shape of the simulated cells. For every type of cell run, it is important to perform a K-point study. For the sake of conciseness, fig 3.5 only includes Zr structures, although the study has been performed on all cells used throughout this work. It is visible that the different runs display the desired precision for an approximate

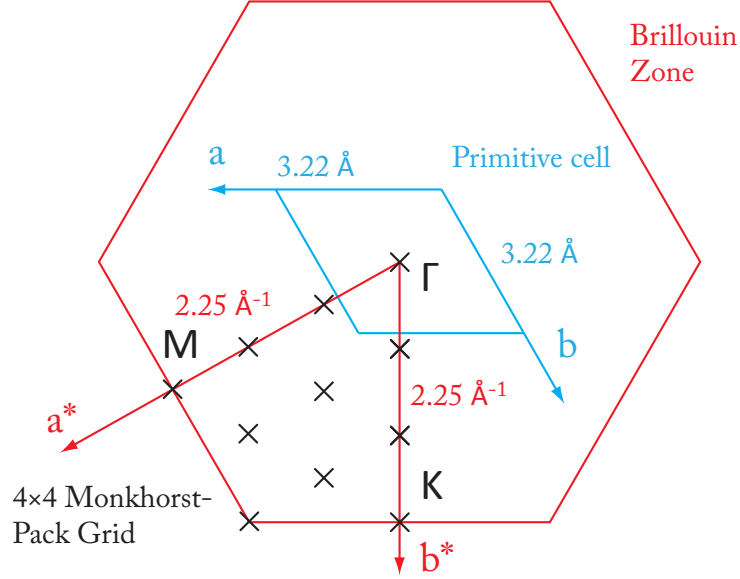


Figure 3.6: An illustration of the relationship between a real hexagonal lattice and the reciprocal hexagonal lattice in 2 dimensions.

K-point spacing of $0.03 \text{ \AA}^{-1}$, which is used throughout the remainder of this work.

Consideration must also be given as how the K-points are arranged in reciprocal space. The most common arrangement is a simple grid constructed of K-points spaced along multiples of reciprocal lattice vectors, known as a Monkhorst-Pack grid [117]. This system is also used in this study. In a repetitive structure, it is also important to note that some locations are points about which symmetry operations are based. In the Brillouin Zone, these are referred to as "special K-points" or "high symmetry K-points" and are normally given specific symbols, corresponding to reciprocal vectors. The gamma (Γ) point is always the central point. Constructing K-point grids so as to contain these high symmetry points is necessary for producing electronic or phonon band structures and simulations with grids centred on the Γ point tend to converge more quickly, particularly for hexagonal structures. It is also important to make sure that multiple simulations that are meant to be compared, or used in conjunction with each other to calculate important values, have comparable K-point grids. As a consequence of this grid arrangement and the fact that K-space is reciprocal, it is important to note that larger axes require fewer K-points. In anisotropic cells this may lead to small differences in the K-point spacing in one direction over

another (less than about $0.015 \text{ \AA}^{-1}$). Throughout this work, the aim is to keep K-point density as consistent as possible, as small variations in K-point density will not impair the accuracy or reliability of results.

3.3.3 Bands and Cut-off energy

When an attempt is made to calculate the energy of electrons in a material (via whatever means) there is the consideration that the electronic structure of the system is defined by a series of bands. Any system modelled in this way could only be described perfectly by an infinite number of these energy bands. The number of occupied bands modelled is closely related to the kinetic energy term of the electron equations. Electrons with a larger energy will be found in higher bands. As electrons with extremely high kinetic energies are likely to be rare, it can be said that the contribution of high energy bands in the system would be negligible. As a result, only a fixed number of bands are simulated. In order to ensure that a sensible number of bands is used, the simulation is always checked to ensure that the highest energy band is unoccupied.

A further distinct issue is the cut-off energy of the plane-waves. As previously discussed, electron wavefunctions are modelled as a Fourier series comprising of many plane waves, each necessarily multiplied by a coefficient of c_{Gk} , where the planewave is perpendicular to $\mathbf{G}$. This series would perfectly describe the wavefunction for an infinitely large number of increasing values for $\mathbf{G}$, corresponding to increasing the kinetic energies of the individual planewaves. However, as the kinetic energy becomes larger and larger, the term c_{Gk} would become smaller and smaller, as the contributions of excessively high energy planewaves become less important.

The kinetic energy cut-off term is variational, in that a higher cut-off *will* result in a lower final energy and a more accurate simulation. However, increasing cut-off energy yields diminishing returns with regards to accuracy, for an increasing computational cost [111]. Thus the most sensible course of action is to initially run a series of trial simulations with different cut-off energies and find the cut-off that the drop in system energy becomes negligible. As will be discussed in section 3.3.5 the target precision for this work is 2 decimal places. Thus in Fig. 3.7, the cut-off energy is compared with the log of the difference between a given run and the most precise run available. If the plot dips below -2, then an appropriate cut-off energy has been

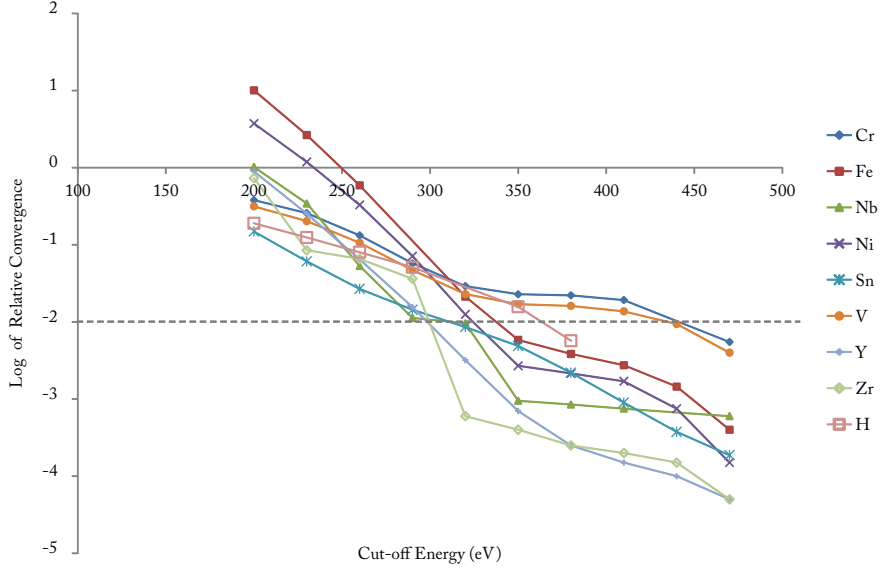


Figure 3.7: How cutoff energy effects the calculated energy of a variety of elements used in this study.

reached. In order to ensure compatibility across results, it is important that all the simulations have the same cut-off energy. For this reason, 450 eV has been used across all simulations, as below this value, not all elements have reached the required 2 d.p level of precision.

3.3.4 Cell Configuration

As the previous section demonstrates, when a bulk material is simulated, a cell containing a given number of atoms is effectively repeated throughout space with an infinite number of images. If if this is meant to represent a bulk material with no defects, then this means materials can be simulated using relatively small simulation cells. However, if the simulation is of a defect of some description, then the material is no longer entirely homogeneous. If the goal is to find out the energy associated with forming that defect, it is important to consider the fact that the defect may be interacting with defects in adjacent images. There is also the fact small cells will effectively contain more defects for a given number of host atoms, than larger ones. This is illustrated in Fig. 3.8.

Effectively, this means that if simulation cells are too small, then the energy difference between

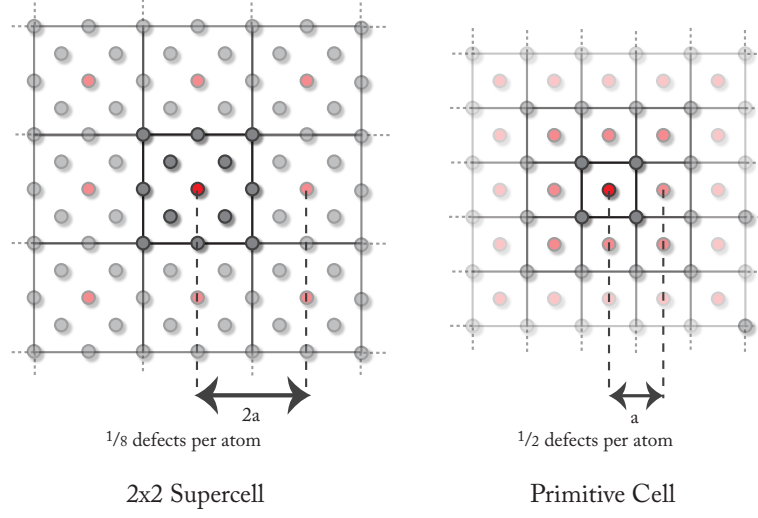


Figure 3.8: A 2 dimensional depiction of the differences between using large cells and small cells when simulating defects.

a defect containing cell and a defect free cell will contain contributions from both the formation energy of the defect and the interaction between nearby defects. This interaction energy is not necessarily what is being looked for in some cases, hence tests must be performed at a number of different cell sizes in order to make sure that the defects are not interacting with each other. It was found that a $5 \times 5 \times 4$ super-cell for α -Zr was the largest super-cell that could be reasonably simulated (containing 200 atoms), although smaller cells can often be used. Smaller super-cells of $2 \times 2 \times 1$ and $2 \times 2 \times 2$ dimensions demonstrated convergences to within 10^{-3} eV, however these were still small enough that defect-defect interactions were probably making a significant contribution to the overall result, hence larger super-cells (e.g. $3 \times 3 \times 3$ or $3 \times 3 \times 2$) were used where-ever possible. Either way, this suggests that the effect of hydrogen on a Zr lattice tends to be quite localised.

3.3.5 Energy Minimisation

As with any numerical method, convergence criteria are important parameters. During a DFT simulations, the start is an atomic configuration that is suspected to be near a global minimum, then the code will perform successive iterations of solving the DFT equations, in order to converge

towards the lowest energy solution. The simulation will only stop when successive iterations produce energy results with a change smaller than the convergence criteria, as selected by the user. This means that results obtained by DFT codes can be treated as being no more accurate than their convergence criteria (taking into account systemic errors inherent in DFT and in the code itself).

During a DFT run, there are multiple different levels of iterative convergence. The one discussed so far has generally been the electronic convergence (also known as Self Consistent runs), effectively determining if the system's electronic structure is in its ground state. In the simulations run in this work, electronic convergence is considered achieved if the difference in energy between successive iterations is less than 10^{-6} eV.

A further form of convergence is that of geometry optimisation. As discussed, DFT provides information on the forces and energies present in a given atomic configuration. However, the goal often is to determine what the actual atomic structure of a crystal is. To do this, the initial configuration is input as the atomic positions of an experimentally determined crystal structure. After the electronic convergence has been achieved, the system's ions will be moved via a method specified in the DFT package. A number of different methods are available, including the conjugate gradient method, the quasi-Newtonian method and the damped-dynamics method. All of these methods represent a method for finding the geometrical configuration with the lowest energy. The work here uses the quasi-Newtonian scheme (the movement of the ions between steps is proportional to the force they would experience). The actual formalisation implemented in this DFT code is known as the Broyden-Fletcher-Goldfarb-Shanno algorithm [118]. Over successive iterations, ions are gradually moved to occupy the lowest energy state available, as defined by the geometry optimisation convergence criteria. This is a key tool in simulating materials, as it allows DFT codes to predict lattice parameters, symmetry groups and to examine how atoms move when influenced by nearby defects. Like electronic convergence, a system is considered converged when successive changes produce only a small variation in energy. For this study, a structural convergence criteria of 10^{-3} eV was considered acceptable, although convergence criteria were also based on the force between atoms, the displacement of atoms between iterations and the overall stress tensor. More specific details on what these parameters are set to is discussed with the relevant simulations.

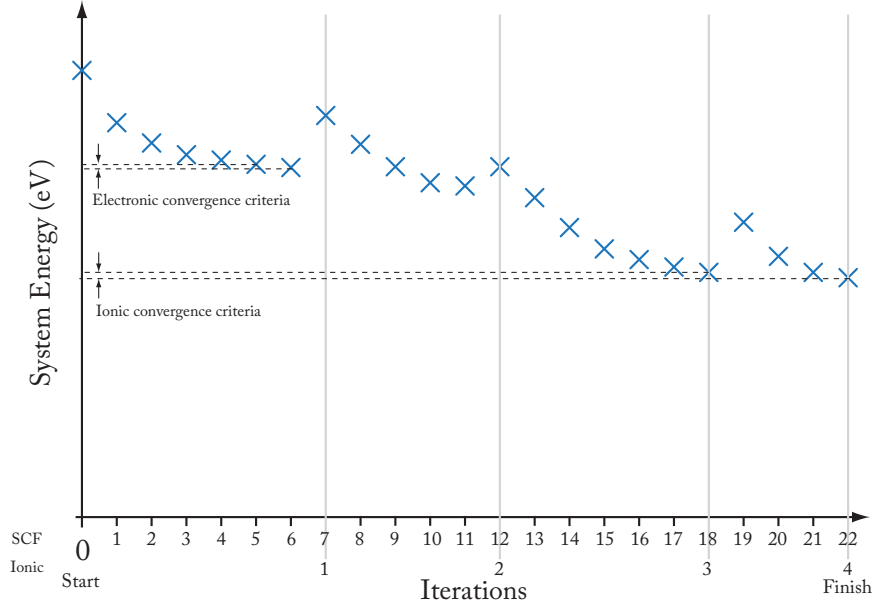


Figure 3.9: An illustration of how the energy of the system is expected to converge as further iterations are performed.

As a result of these criteria, it is important to note that all relaxed criteria are at the most thermodynamically favourable ground state. This is something that must be taken into account, particularly if predicting phenomena that would be expected at reactor operating temperatures, as the distribution of states (as defined by the Boltzmann distribution) would not necessarily be the ground state.

The term convergence has been used throughout this section. For clarification and summation, the main forms of convergence as applicable to the work here are summarised below.

- *Electronic Convergence:* The phenomenon of how subsequent iterations of DFT calculations approach the lowest energy (ground) state for the system's electronic configuration.
- *Ionic Convergence:* The phenomenon of how Electronically Converged systems can have their geometry iteratively improved, such that their ionic configuration approaches its lowest energy state. This is sometimes referred to as a “relaxed” structure.
- *Convergence with respect to plane wave cut-off energy:* The phenomenon of how a system with a higher cut-off energy will be more accurate in representing a system (excusing the

deficiencies of DFT in general). The system is considered converged to within a given tolerance when increasing the cutoff energy does not alter a specified value by more than that tolerance.

- *Convergence with respect to K-point number:* The phenomenon of how a system with more K-points will be more accurate in representing a system (excusing the deficiencies of DFT in general). The system is considered converged to within a given tolerance when increasing the number of K-points does not alter a specified value by more than that tolerance.

This section should have provided an explanation of how DFT can be used to model solid materials and some of the considerations that must be taken on board when doing so. Thus, this thesis can now move onto the more important matters of what results have been found from an application of DFT to Zr alloys and the Zr-H system.

Chapter 4

Alloying Additions in Zirconium Alloys

4.1 Overview

As discussed in chapter 2, a variety of different alloying elements are added to Zr in order to improve its resistance to creep, corrosion and its yield strength (see Table 2.1). This has produced a number of different commercially used alloys. All the Zr alloys used exhibit the low temperature, hexagonal-close-packed α -phase. β -phase Zr, with a body-centred-cubic structure is stable above 863°C, although metastable β -phase Zr does exist below this temperature [33]. The β -phase, although not the primary component of in-reactor alloys, is still important as an intermediary phase during alloy processing and in Zr-Nb alloys as SPPs.

The alloying additions used will either form SPPs or remain in solid solution. The abundance, size and properties of all of these precipitates have a significant impact on alloy corrosion resistance, mechanical properties and the tendency of the alloy to absorb hydrogen [119, 57, 71, 72, 70].

In order to understand the formation and dissolution of precipitates, a grasp of the various thermodynamic driving forces at work is essential. A knowledge of the relative stabilities of the different phases may allow prediction of aspects of the life-cycle of these precipitates and by extension, the properties that they affect in the host alloy. In this study, the alloying elements Cr,

Fe, Nb, Ni, Sn, V and Y are examined in Zr using DFT simulations. Atomistic scale techniques in general and DFT simulations specifically, have demonstrated a degree of success when modelling alloys [120]. The thermodynamic driving forces for the formation of various intermetallic phases containing these elements are examined, as well as the solubilities of these elements and their intermetallic compounds in both α and β -Zr. This allows examination of the relative stabilities of various different phases in Zr alloys.

The work described in this chapter was published in June 2013 by the peer reviewed *Journal of Nuclear Materials* [121].

4.2 Specific Methodology

It is important to discuss the specific parameters used in this simulation set. Various different structures and phases have been simulated using the CASTEP 5.5 simulation package [113]. It is important to select which electrons are modelled as non-interacting core electrons and which are modelled explicitly (valence electrons) by the DFT software. Here, the electrons considered as valence are:

- Cr - $3s^2 3p^6 4s^1 3d^5$
- Fe - $4s^2 3d^6$
- Nb - $4s^2 4p^6 5s^1 4d^4$
- Ni - $4s^2 3d^8$
- Sn - $5s^2 5p^2$
- V - $3s^2 3p^6 4s^2 3d^3$
- Y - $4s^2 4p^6 5s^2 4d^1$
- Zr - $4s^2 4p^6 5s^2 4d^2$

The pseudopotential scheme used is "on-the-fly" generation, in which an isolated all-electron calculation is carried out before the main calculation and used as a starting point to generate a pseudopotential. This was carried out for all pseudopotentials except Cr and V, as the default

on-the-fly pseudopotentials for these elements required a much higher cut-off energy. Instead, standard ultrasoft pseudopotentials, as found in the CASTEP pseudopotential library, were used for Cr and V. All pseudopotentials (both on-the-fly and library) are of the ultrasoft type [115] and so are compatible with each-other. Exchange-correlation was modelled using the Perdew, Burke and Ernzerhof formalisation of the Generalised Gradient Approximation [112].

A series of simulations were run to establish an appropriate basis set cut-off energy and the density of sampling in the Brillouin zone. The results were converged to within two decimal places for a cut-off energy of 450 eV and a k -point spacing of $0.03 \text{ \AA}^{-1}$. The k -points were arranged in a standard gamma centred Monkhorst-Pack grid [117]. In these simulations, the energy of the electron wavefunctions was considered converged to a minimum value when the difference between successive iterations was below 10^{-6} eV/atom . Integration of the Brillouin zone was achieved using a cold smearing scheme (2nd order, Methfessel-Paxton) [122], with a smearing parameter of 1 eV, in order to account for partial occupancies in the band structure. Simulations that varied this value by up to 0.9 eV found negligible difference in the final state of the system, so a higher value was chosen to speed convergence.

The simulations are static calculations, that is, they identify the minimum energy positions for atoms in a given structure and as such relate to zero temperature. As a result, any entropic terms are ignored and the free energy of any reactions here is considered the same as the enthalpy (as is the internal energy under relaxed geometry). Thus the two terms may be used interchangeably.

When modelling cells, in order to find useful enthalpies and structural properties the starting structure was selected from literature values and the geometry of the system was allowed to relax, via a Broyden-Fletcher-Goldfarb-Shanno algorithm [118]. The positions of the ions and the size and the shape of the cell boundaries are all allowed to relax. This is an appropriate scheme of relaxation, as the goal is to approximate a system with a limited concentration of alloying additions, after it has been allowed to reach equilibrium. The criteria for a successful iteration were selected as a balance between computational cost and numerical accuracy and are shown below:

- Energy derivative $< 0.001 \text{ eV}$
- Force on ions $< 0.1 \text{ eV\AA}^{-1}$

- Displacement of ions derivative $< 0.001 \text{ \AA}$
- Total stress derivative $< 0.1 \text{ GPa}$

When modelling defects, a $3 \times 3 \times 3$ supercell was used. In the case of α -phase Zr, this was created from the primitive hexagonal cell and in the case of β -phase Zr, the conventional unit cell. Both supercells contained 54 atoms. Although this choice introduces some anisotropy into the dimensions of the hexagonal system, it means that α and β -phase cells have an identical number of atoms and hence identical alloying addition concentrations of 1.85 at%. This concentration is useful, as the weight percent composition is appropriate to commercial alloys, particularly in the case of Sn, although it is still relevant with other alloying additions.

It is important to note that magnetic effects can have a substantial impact on overall lattice parameters and energies. Consequently care must be taken to ensure that the correct final magnetic state is converged upon. For all simulations carried out, this was achieved by setting the initial spin state of the system to the sum of individual formal spins of each of the present atoms and performing a spin polarized calculation. This produced reasonable magnetic configurations in most cases, with the exception of pure Cr. In order that the known magnetic state of Cr (anti-ferromagnetic) was achieved, it was necessary to specify the spin states of each atom individually, prior to convergence.

4.3 Results

4.3.1 Perfect Crystals

It is important that the current calculations are able to reproduce experimental data concerning basic bulk properties, to provide confidence in simulated data for properties where there is little or no experimental data. Parameters calculated for the three polymorphs of Zr, are reported in Table 4.1, while the relevant intermetallic phases have their parameters reported in 4.2. Most results are in excellent agreement with the available literature, especially those for Zr. These results also agree well with other relevant ab-initio results [44, 45].

Phase	Space Group	Present Work				Experimental			
		a (Å)	b (Å)	c (Å)	Stability (eV)	a (Å)	b (Å)	c (Å)	Stability (eV)
αZr	P6 ₃ /mmc	3.22	-	5.20	0	3.23	-	5.145 [34]	0
βZr	Im $\bar{3}$ m	3.59	-	-	0.07	3.61[32]	-	-	0.071[44]
ωZr	P6/mmm	5.06	-	3.12	-0.01	5.03	-	3.11[32]	± 0.007 [44]

Table 4.1: Properties of pure of Zr phases. Stabilities are given relative to the α phase.

There is one issue with the stability of the α phase with respect to the ω -phase. The ω -phase is only stable under high pressures of over 500 MPa (at 0K). However, the values here report it stable under conditions where the volume is allowed to relax, corresponding to zero external pressure. This is not a new problem, in that multiple DFT simulations in the past have reported this issue [48, 46, 44]. Unfortunately, this is most likely a limitation of the DFT methodology used. As a high pressure phase, the bonding ω -Zr will be more likely be stabilised by electrons which are regarded as core and therefore non-interacting. This is confirmed by the fact that all-electron simulations of Zr typically handle this phase transition better [46]. As a result, a small portion of the underlying physics is not captured in this model, being taken out by the approximations necessary in order to run simulations of a reasonable size and in a reasonable time-frame. Given the fact that a lot of properties produced by these simulations agree well with experimental data, it is believed that this one discrepancy over a phase, which has little impact on this study, can be overlooked as a necessity.

Species	Space Group	Present Work			Literature			Refs
		a (Å)	b (Å)	c (Å)	a (Å)	b (Å)	c (Å)	
C15 Laves ZrCr ₂	Fd $\bar{3}$ m	7.12	-	-	7.20	-	-	[123]
C14 Laves ZrCr ₂	P6 ₃ /mmc	5.05	-	8.14	5.11	-	8.31	[123]
Zr ₂ Cr (speculative)	I4mcm	6.57	-	5.37	-	-	-	-
Zr ₃ Fe	Cmcm	3.30	1.09	8.85	3.32	1.10	8.83	[124]
Zr ₂ Fe	I4mcm	6.25	-	5.63	6.38	-	5.59	[125]
C15 Laves ZrFe ₂	Fd $\bar{3}$ m	7.02	-	-	7.06	-	-	[126]
C14 Laves ZrFe ₂	P6 ₃ /mmc	4.98	-	8.11	-	-	-	-
Zr ₂ Ni	I4mcm	6.49	-	5.29	6.48	-	5.27	[125]
ZrNi	Cmcm	3.32	9.84	4.07	3.27	9.93	4.11	[127]
C15 Laves ZrNi ₂	Fd $\bar{3}$ m	6.96	-	-	6.92	-	-	[128]
C14 Laves ZrNi ₂	P6 ₃ /mmc	4.92	-	8.04	-	-	-	-
Zr ₃ Sn	Pm $\bar{3}$ n	5.64	-	-	5.64	-	-	[129]
Zr ₅ Sn ₃	P6 ₃ /mmc	8.48	-	5.88	8.45	-	5.77	[66]
Zr ₅ Sn ₄	P6 ₃ /mmc	8.83	-	5.99	8.77	-	5.93	[66]
ZrSn ₂	Fddd	5.70	9.65	10.00	5.64	9.57	9.93	[66]
Zr ₂ V (speculative)	I4mcm	7.46	-	5.68	-	-	-	-
C15 Laves ZrV ₂	Fd $\bar{3}$ m	7.38	-	-	6.92	-	-	[128]
C14 Laves ZrV ₂	P6 ₃ /mmc	5.23	-	8.47	-	-	-	-

Table 4.2: Lattice parameters of the various intermetallic phases studied in this work. Where available, literature values have been provided for comparison [130]. Ideally experimental values were drawn from the literature, however if none were available, simulation results are shown instead.

It is important to note that when discussing intermetallic phases, magnetic effects are important and in some cases, resulted in differences of over 1 eV per atom in formation energies, between the most favourable magnetic state and a converged state when magnetic effects were not taken into account. As would be expected, Fe and Ni demonstrated strong ferro-magnetism, as well as all forms of Laves phase Fe intermetallics. Pure Cr, C14 and C36 Cr Laves phase intermetallics appear to be anti-ferromagnetic, while the C15 Laves phase and the Zr₂Cr intermetallics are weakly ferrimagnetic. The same is true of the Zr₂Fe precipitate, although it has been noted in other work that this phase has a somewhat complicated magnetic structure [70]. Aside from this, all other simulation cells displayed no magnetic ordering.

4.3.2 Formation of Intermetallics

The formation energies of different intermetallic phases provide a measure of their relative stability. Here, formation energies are defined as the enthalpy of forming a quantity of intermetallic compound from one unit of a composition weighted mixture of its constituent elements. Thus, the energy is given by:

$$E_{formation} = \frac{1}{x+y} E(Zr_xM_y) - \left(\frac{y}{x+y} E(M) + \frac{x}{x+y} E(Zr) \right) \quad (4.1)$$

where $E(Zr_xM_y)$ is the energy of a cell simulating the intermetallic. The terms $E(M)$ and $E(Zr)$ represent the energies of a single atom from cells containing only the alloying agent and Zr respectively. In Fig. 4.1, the formation energies of various intermetallic phases are plotted against the composition of the intermetallic.

The plot of composition vs. formation energy is a useful representation, which will be used again in other investigations. Thus, it is important to explain some of the aspects of this plot. Looking at Fig. 4.1, a series of lines is drawn, which connects some points, but not others. The lines drawn are known as a convex hull. A hull is a mathematical description of a shape which encloses a set of points. For example, the hull of 3 points on a two dimensional surface would most likely be a triangle (unless the points were in a single line, or on top of each other). In this case, the hull must obey the convex principle that any line drawn through the hull must cross the hull in no more than two locations. All internal angles of the shape must be less than 180° . This is an important tool as for any given mixture of the two constituents, the convex hull represents the lowest energy and therefore most stable configuration. If the composition is that of a phase on the convex-hull, then it is expected that that phase would be the one which forms. If composition lies above a line segment, then the most stable configuration is a mixture of the two phases which terminate that line segment. The mixture of phases would be weighted as could be calculated via the lever rule. As an example, consider a mixture of 75 At% Zr and 25 At% Sn. According to Fig. 4.1, for this composition, an intermetallic phase with the formula Zr_3Sn does exist, but it rests above the convex hull by approximately 0.04 eV. This means that a mixture of Zr and Zr_5Sn_3 would be more preferable, in a ratio of 4 parts Zr for every 1 part Zr_5Sn_3 . Thus, the value of the convex hull and formation enthalpy plot can be seen.

The convex hulls for Sn and Fe have been drawn on Fig. 4.1. Convex hulls have not been drawn for Cr and V due to the intermetallics displaying positive formation energies. The convex hull for Ni was not drawn as Ni forms a large number of different intermetallic phases in the Ni-rich portion of the Zr-Ni binary phase diagram, which were not modelled due to their irrelevance to Zr alloy compositions [131]. A convex hull for Ni intermetallics would not be reliable, without modelling these phases.

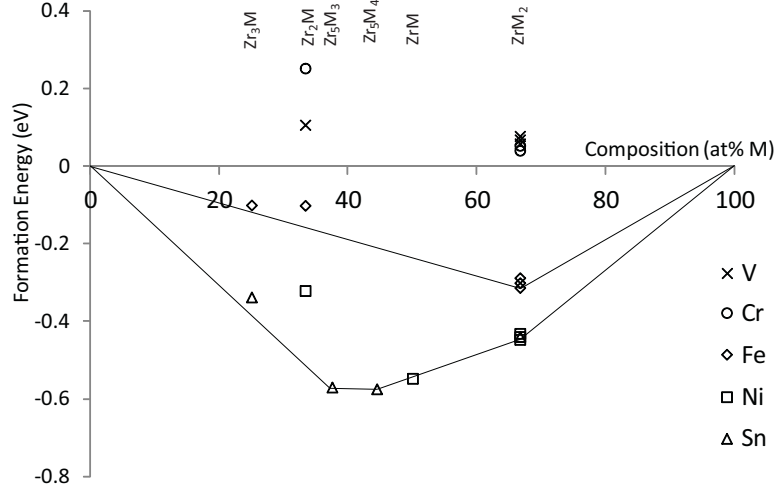


Figure 4.1: Formation energy of different intermetallic phases, from their low temperature, single element phase constituents. Calculated using equation 4.1.

Fig. 4.1 shows that Fe, Ni and Sn based intermetallics all have negative enthalpies of formation, with the most favourable intermetallics being: C15 $ZrFe_2$, $ZrNi$ and Zr_5Sn_4 . When Laves phase structures were modelled, Cr, Fe and Ni all favoured the C15 structure, followed by C36 and finally C14. For V based Laves phases, this order was reversed. Relative stabilities between C14 and C15 Laves phases are presented in Fig. 4.2. These were calculated by subtracting the formation energy (per formula unit) of the C14 variant from the C15 variant. A negative relative stability indicates a preference for the C15 structure, whereas a positive number indicates a preference for C14. These values are correlated with the metallic radius ratio between the two elements (R_{Zr}/R_M) and the valence electron concentration (VEC). The VEC is modelled as the number of valence s and d electrons (as modelled in the pseudo-potential) divided by the volume of a single formula unit of intermetallic. Previous studies of Laves phases have taken the VEC

to be the number of s and p electrons per formula unit, however, this approximation does not accurately predict Laves phase stabilities for transition metal based Laves phases [69]. Instead, s and d electrons have been chosen, due to their importance in transition metal bonding and a volume component has been added to account for the importance of electron density.

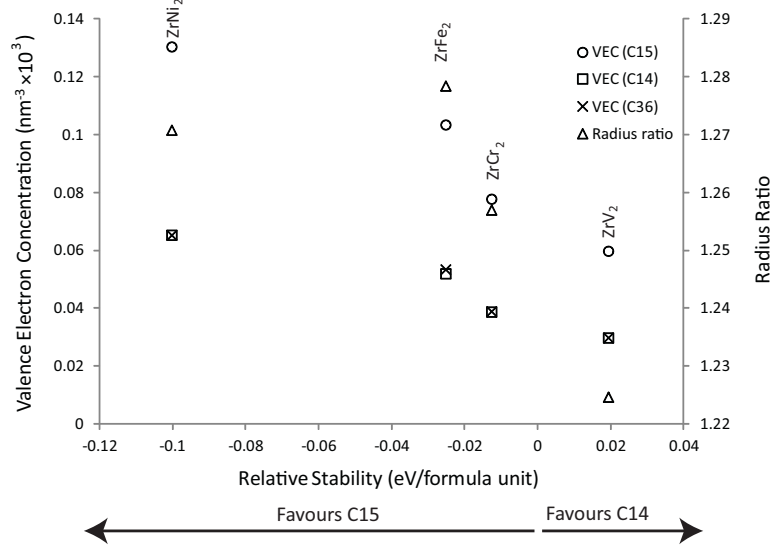


Figure 4.2: Relative stabilities of two different ZrM_2 Laves phases, plotted against values representing the geometric (radius ratio, $R_{\text{Zr}}/R_{\text{M}}$) and electronic (valence electron concentration) components of Laves phases stability. Radius ratio is plotted on the secondary axis, while VEC is plotted on the primary. The VEC for the C36 Laves phase is almost identical to that of the C14.

4.3.3 Solutions from Single Element Phases

Solution energies of alloying elements in Zr are presented in Fig. 4.3. This energy indicates whether there is a thermodynamic driving force for either the element to segregate from Zr (positive values), or dissolve into the host matrix (negative values). For all elements, substitutional solution is examined, in which atoms of Zr are replaced by atoms of the alloying addition, with the Zr atoms forming new host lattice. For elements with a small metallic radii, that is Cr, V, Fe and Ni, interstitial solution was also considered, where the alloying additions occupy interstitial sites in the host matrix. Only the tetrahedral and octahedral interstitial sites are examined, as the other sites are too small to be viable; atoms placed at such sites will relax to tetrahedral or

octahedral sites. Large atoms, such Nb, Sn and Y, were not considered for interstitial solution. The energy of solution for a substitutional site is given by the equation:

$$E_{solution} = \left(E(\alpha\text{Zr}_{53}\text{M}) + \frac{1}{54} E(\alpha\text{Zr}_{54}) \right) - \left(E(\alpha\text{Zr}_{54}) + \frac{1}{x} E(\text{M}_x) \right) \quad (4.2)$$

and the equation for interstitial solution is given by:

$$E_{solution} = E(\alpha\text{Zr}_{54}\text{M}_i) - \left(E(\alpha\text{Zr}_{54}) + \frac{1}{x} E(\text{M}_x) \right). \quad (4.3)$$

It is important to ensure that balancing α is on both sides of the equation, as this ensures that the equations remain reversible under different concentrations. Solution calculations were carried out for α and β -phase Zr and compared (see Fig. 4.3). Most elements have a positive energy of solution in the α -phase and a negative energy of solution in the β -phase. Sn has a negative energy of solution in both the α -phase (-1.07 eV) and the β -phase (-1.54 eV). Conversely Y has a positive solution energy in both the α -phase (0.26 eV) and the β -phase (0.40 eV). Fe and Cr have lower solution energies in the α -phase when occupying an octahedral interstitial site, rather than a substitutional position (by 0.86 eV and 0.09 eV respectively). It should be noted that the solution energy of Ni on a tetrahedral site in the α -phase is not reported because it relaxed into the octahedral site. All the elements for which an interstitial site in the β -phase was investigated exhibit a preference for interstitial solution. The energy of substitution for V in the β -phase, -0.02 eV, is so small it is not readily apparent in Fig. 4.3.

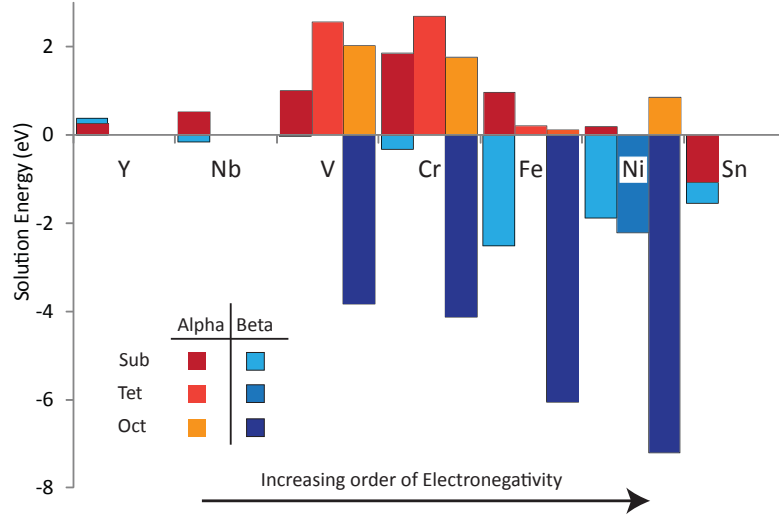


Figure 4.3: Solution energies of different single phase elements, on different sites in α and β -Zr, as calculated by equations 4.2 and 4.3. Elements are arranged in increasing order of electronegativity, although the horizontal axis is not scaled. The electronegativity of Zr sits between Y and Nb [132].

The volume associated with each defect was also calculated and is presented in Fig. 4.4. The self interstitial volumes for Zr are also shown. Defect volumes are simply the difference in volume between a defective cell and a Zr supercell. As such, they correspond to volumes per atom but at a specific defect concentration of 1.85 at% (as do the solution energies). These values are plotted against the metallic radii of the different elements. The metallic radius for each element was calculated from its single element phase, as simulated in this study (assuming a simple contacting sphere model). As this investigation involves two different phases of Zr, the appropriate metallic radius for each phase is different and has been plotted as such. Linear regression trend lines are displayed in Fig. 4.4 for all defect types. These display a positive linear relationship. The trend lines for substitutional defects in the α and β -phase cross the x axis at 1.59 Å and 1.55 Å, which are respectively the calculated metallic radii for α and β -phase Zr. All interstitial defects show much greater defect volumes than in substitutional alloys. The elements Sn and Nb have similar metallic radii, hence they are difficult to distinguish in Fig. 5 (the results for Sn lie above those for Nb).

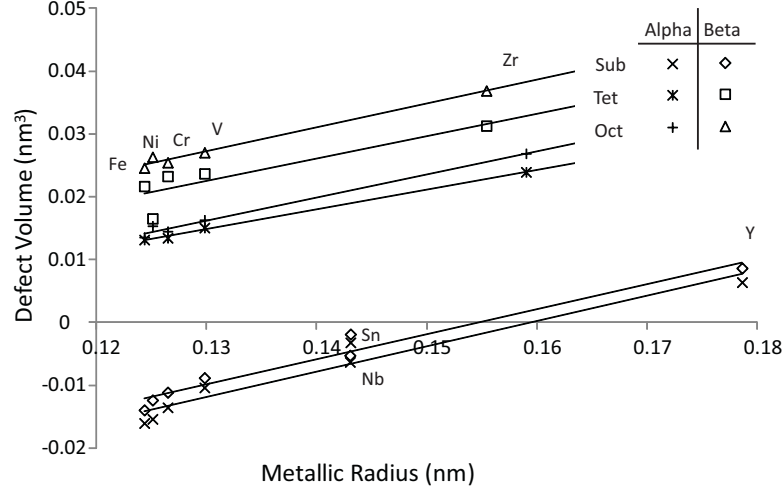


Figure 4.4: Defect volumes of the different elements in various different sites of α and β -phase Zr. Metallic radii were calculated from the relaxed, single phase element.

4.3.4 Solutions from Intermetallics

When considering a real alloy system, it is important to appreciate that it may not be a single element phase that is dissolving into the host matrix. As discussed above, most of the elements investigated here form intermetallic phases, consequently the reaction of interest is not necessarily between a pure species and a solution but between an intermetallic phase and a solution.

The solution energy of a general intermetallic phase onto a substitutional site in the host lattice is given by:

$$E_{solution} = \left(E(\alpha\text{Zr}_{53}\text{M}) + \left(\frac{y}{x} + 1\right) E(\alpha\text{Zr}) \right) - \left(E(\alpha\text{Zr}_{54}) + \frac{1}{x} E(\text{M}_x\text{Zr}_y) \right) \quad (4.4)$$

or if the solution is interstitial:

$$E_{solution} = \left(E(\alpha\text{Zr}_{54}\text{M}_i) + \frac{y}{x} E(\alpha\text{Zr}) \right) - \left(E(\alpha\text{Zr}_{54}) + \frac{1}{x} E(\text{M}_x\text{Zr}_y) \right) \quad (4.5)$$

The solution energies of Cr, Fe, Ni, Sn and V dissolved from their intermetallic phases are presented in Fig. 4.5. The solution energy of the most favourable site in each phase is used, as

determined from Fig. 4.3. The trends in Figs 4.3 and 4.5 are similar; that is, elements displaying a positive solution energy from a single element phase into α -Zr, will display a positive intermetallic solution energy. The same follows for β -phase Zr. Sn has a comparatively low solution energy in the α -phase and a comparatively high energy in β -phase; it is the only element where an intermetallic possesses a negative solution energy in α -phase Zr.

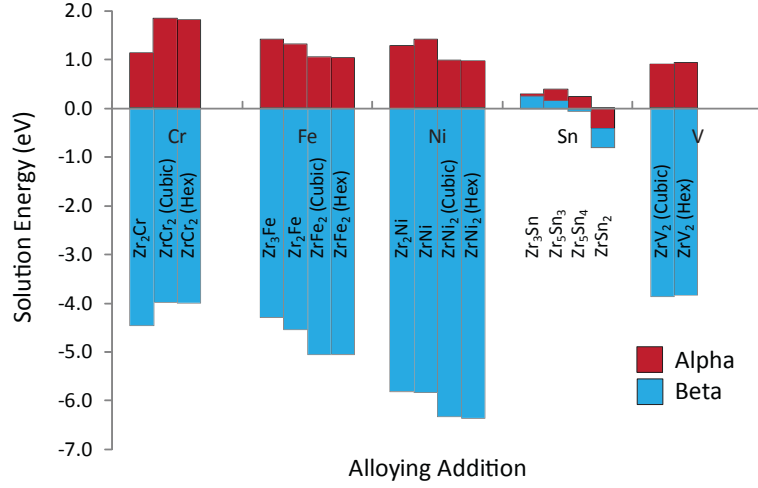


Figure 4.5: Solution energies of different intermetallics in Zr, as calculated by equations 4.4 and 4.5. The site chosen for solution was based upon the most favourable site, as shown in Fig. 4.3.

In Fig. 4.6 a different scenario is considered. In these graphs, the energy of incorporating an atom of alloying addition onto a zirconium site that was previously occupied by a vacancy is plotted. As all formed solution energies are substitutional, interstitial solutions are irrelevant. Thus, the energy of incorporation in the α -phase is given by:

$$E_{incorporation} = (E^f(\alpha Zr_{53}M) + (y/x) E^f(\alpha Zr_{54})) - (E^f(\alpha Zr_{53}v_{Zr}^x) + \frac{1}{x} E^f(M_x Zr_y)) \quad (4.6)$$

Unlike Fig. 4.5, Fig. 4.6 shows generally negative solution energies in α -phase and positive energies in β -phase. The energy associated with the incorporation of an alloying addition onto a vacant zirconium site becomes important when discussing the effect of radiation damage on

SPPs.

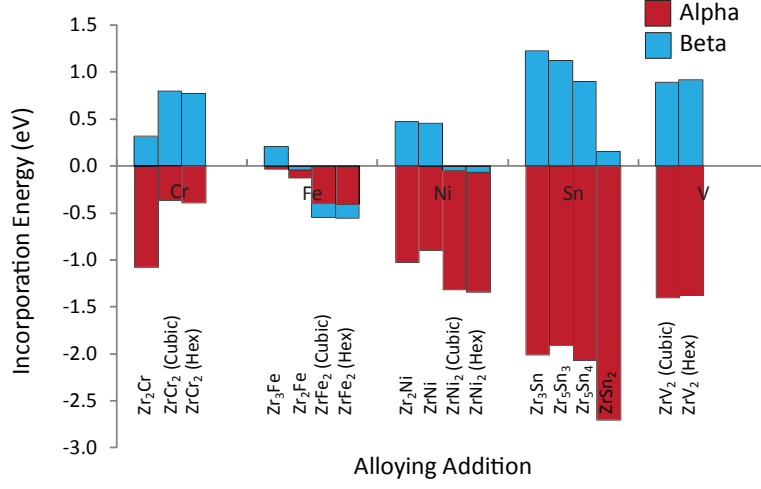


Figure 4.6: Incorporation energies of different intermetallics in zirconium, as calculated by equation 4.6. The assumption underlying this is that vacancies are created during neutron irradiation, that may present sites which alloying additions from intermetallic phases may be able to occupy.

4.4 Discussion

4.4.1 Intermetallic Formation

Fig. 4.1 indicates that the general order of increasingly negative intermetallic formation energy (excluding Zr_2Cr and Zr_2V for reasons discussed below) is V, Cr, Ni, Fe and finally, Sn. With the exception of Fe and Ni, this is consistent with the Hume-Rothery rules, that is, the greater the difference between the two elements' electronegativities, metallic radii, or native crystal structures, the greater the likelihood of intermetallic compound formation rather than a solid solution [133]. The positions of Fe and Ni in this order are reversed, possibly because they have very similar electronegativities (and metallic radii), suggesting that another factor is contributing. In fact, single phase Fe, Ni and some of their associated intermetallics display distinct magnetic structures. Magnetism stabilises some phases over others and magnetic effects are not referred to in the Hume-Rothery rules. Other than Fe and Ni, the greater the difference in electronegativity between an alloying addition and Zr, the more stable the intermetallic.

In this study, two speculative intermetallics have also been investigated; Zr_2Cr and Zr_2V . Although Cr and V form ZrM_2 Laves phases, they are not known to form Zr_2M Zr-rich precipitates, despite the fact that this structure is commonly formed with Fe and Ni. The formation energies for Zr_2Cr and Zr_2V were found to be substantially positive (0.75 eV and 0.31 eV respectively) suggesting that they are not stable and the absence of these structures in existing phase diagrams and commercial alloys is due to thermodynamic instability, rather than poor kinetics during formation.

It can be seen in Fig. 4.1 that the Cr and V based Laves phase intermetallics have slightly positive energies of formation. This would suggest that these phases are not stable, however, it does not necessarily rule out their formation. The binary phase diagrams of Cr and V with Zr show that the Laves phase is particularly non-stoichiometric [63, 64]. As a result, the system configurational entropy will increase considerably, when moving from two pure substances, to a single non-stoichiometric intermetallic phase; such an increase in entropy could be sufficient to drive the reaction as temperature increases. This is particularly important when considering the actual SPPs, as a $\text{Zr}(\text{Fe}, \text{Cr})_2$ intermetallic is observed. It is possible that the more stable Fe based Laves phase stabilises its Cr counterpart to some degree.

The Zr_2Fe phase, does not lie on the Zr-Fe convex hull. Consequently this phase is metastable and would decay into a mixture of Zr_3Fe and ZrFe_2 under equilibrium conditions. A similar finding has been reported previously and typically, the Zr_3Fe phase is only observed in Fe rich alloys [70]. The Zr_2Fe phase is readily observed as a component of $\text{Zr}_2(\text{Fe}, \text{Ni})$ precipitates, in alloys containing Ni. Thus, two mechanisms are suggested that may play a role in its stabilisation. First, that the phase cannot decompose due to kinetics. This is reasonable as the alloy is quench cooled. Second, the corresponding Ni based intermetallic has a lower enthalpy of formation and may assist in stabilising the Zr_2Fe phase. If Ni stabilises the Zr_2Fe phase, (or even vice versa), the expectation is that bringing the two intermetallics together would have a significant enthalpy of mixing, in order to offset their individual metastabilities. This mechanism is consistent with experimental results published by Barbaris *et al.* [70], who observed that Zr_2Fe is significantly more common in alloys containing Ni. Further work on mixed intermetallic phases may allow development of these ideas. The formation of one intermetallic in preference of another has significant impacts in terms of the hydride formation resistance of the alloy, as the $\text{Zr}_2(\text{Fe}, \text{Ni})$

phase has been noted to provide preferential solution sites for hydrogen [134] .

The formation of a Laves phase and the preferential stability of a particular Laves phase have two main predictive aspects. The first is a geometric component relating to the difference in size between the two atoms, while the second is an electronic component, relating to the concentration of valence electrons, the VEC as discussed earlier [135]. With regards to the geometric component, Laves phases tend to be more stable as the radius ratio between the two elements approaches 1.225 [136]. In Fig. 4.2, the Laves forming additions have ratios between 1.21 and 1.29. V is the only element which preferentially forms a C14 structure and this element has a ratio below the ideal value. With regards to the electronic component, Fig. 4.2 shows that as the VEC decreases, there is a tendency for C14 structures to be favoured over C15. The implication is, that for this system C14 is more suitable for large and electrically diffuse alloying additions. However, the relative stabilities of different Laves phases are notoriously difficult to predict from first principles [69], consequently, the previous statement is probably not a rule that can be reliably applied outside this system.

4.4.2 Solution Energies

4.4.2.1 Solutions from Single Elements

In the α -phase, Cr and Fe prefer to occupy interstitial sites, while all other atoms occupy substitutional sites. This is not surprising as Cr and Fe are the smallest atoms considered. The octahedral interstitial site is predicted to be the most favoured, most likely because it is the largest site by volume in which to insert an atom. In a simple contacting-spheres model, the tetrahedral and octahedral sites in α -phase Zr have radii of 0.35 Å and 0.65 Å respectively [137]. The metallic radii of Cr and Fe are 1.25 Å and 1.24 Å [132], however as both are slightly more electronegative than Zr (respectively, 1.66 and 1.83 Pauling units, compared to 1.33 of Zr), these additions will be "larger" still, due to having gained electrons at the expense of Zr. Therefore, Cr and Fe atoms can only fit into the interstitial sites with a significant volume change of the cell, as shown in Fig. 4.4. This volume change is an important consideration with regards to the solution energy, as demonstrated in a comparison of the values determined during this study and the values given by Christensen *et al.* [138]. Unlike the present study, Christensen *et al.* did

not allow the boundaries of the periodic cells to relax, constraining the cell volume and aspect ratio. As a result, the present study finds a lower solution energy for Fe in α -phase Zr, as well as finding that Cr, prefers an interstitial, over a substitutional site. As this investigation centres on the impact of a given concentration of an alloying addition in a Zr lattice, it is necessary to allow the lattice to accommodate the strain caused by the defect.

In the β -phase, all the elements for which interstitial sites were considered showed preference for an interstitial site over a substitutional site. Unlike HCP, the BCC structure is not close packed and therefore its interstitial sites are larger. To compare, the octahedral site in α -Zr is 1.30 Å across, while in β -Zr it is 1.93 Å across in the ab plane, though only 0.48 Å along the c -axis. This is because the four atoms in the ab plane are in $[110]$ directions whereas the two in the c -axis are in $[001]$ directions. During relaxation, these two atoms are pushed out along $[001]$ directions, while the cell experiences a slight contraction in the other two directions. Overall, this is responsible for the large defect volumes shown in Fig. 4.4.

Except for Sn, all elements exhibit positive solution energies in α -phase Zr, in-keeping with observations that these elements do not remain in solid solution under equilibrium conditions [70]. Sn is the only element that exhibits a negative solution energy and the only element in this study that forms an α -phase Zr solid solution. Sn is known to stabilise α -Zr and this effect can be seen clearly on the Zr-Sn binary phase diagram [66], as the phase boundary between the α and β -phase Zr increases in temperature as Sn content is increased. A similar observation can be made with Nb. The Zr-Nb binary phase diagram shows that Nb exhibits complete solid solubility in the β -phase and little solubility in the α -phase [65] (although metastable solubility under irradiation has been reported [71]). The results here show a positive solution energy in the α -phase, but a negative energy in the β -phase. The Nb case is particularly clear, because Nb does not form intermetallic compounds with Zr in a binary system, hence intermetallic reactions do not need to be considered when examining solubility.

As in the case of formation energies, the difference in electronegativity between Zr and a given alloying addition gives rise to a correlation in how stable the alloying addition is in solution. In Fig. 4.3 for the β -phase, the trend is that a greater difference in electronegativity results in a greater energy of solution, with the exception of Sn. As the only non-transition metal in the selection of elements here, the difference in behaviour can be ascribed to the different bonding

character.

Some correlations with behaviour under irradiation can also be noted. It has been observed that Fe-Cr SPPs tend to dissolve more quickly than Fe-Ni SPPs and in the latter case, the Fe leaches out of the SPP before the Ni [73]. With Fe and Cr both occupying interstitial sites, there are more readily accessible sites for them to occupy in the Zr matrix, thus Fe and Cr can dissolve into Zr faster than an addition that requires a substitutional site to become available, such as Ni. Nevertheless, Cr dissolves slower than Fe [72]. As Fe has a lower solution energy in the α -phase than Cr (by 0.98 eV), there is a greater driving force for Fe to dissolve. It may be that Fe atoms, given their large defect volume, block adjacent sites from being occupied by other interstitial solutes due to the associated lattice strain field, thus slowing the solution of Cr. It is also notable that the tetrahedral and octahedral sites for Fe are very similar in energy, whereas those for Cr are not. If the lowest energy diffusion pathway involves both sites, this may be consistent with a lower migration activation energy for Fe than Cr, although it would be necessary to calculate the actual migration barrier energy before a definitive statement can be made.

With regards to the defect volumes shown in Fig. 4.4, atoms with a greater difference in size, with respect to Zr, distort the lattice more when substituted into a Zr lattice. The relationship between metallic radius and defect volume is linear, with each defect site showing near parallel trends. The α -phase Zr defect volumes are always lower than the corresponding β -phase values. The α -phase is a stiffer structure, with higher elastic constants, so it is reasonable to expect the α -phase to resist volume change more than the β -phase [32]. As would be expected, the metallic radius predicted when the defect volume equals zero is the same as the metallic radius of Zr in the host lattice. That most elements show good agreement with the linear relationships is consistent with geometrical factors being dominant in determining lattice strain in this system due to single alloying additions.

Fig. 4.4 shows that Sn lies slightly above the trend lines in α and β -phase Zr. This is an indication that bonding effects, or electron transfer is making the Sn atom appear "bigger" than would otherwise be expected. This could be due to the fact that Sn is the element in this study with the greatest electronegativity difference with respect to Zr. Fig. 4.4 also indicates that Ni has an unusually low defect volume when it occupies a tetrahedral site in β -Zr, which coincides

with a comparatively high solution energy for Ni on this site. It is not clear why Ni exhibits this behaviour specifically on the tetrahedral site, however, as this is not the most favourable site (by a significant margin), it will not have any impact on conclusions drawn.

4.4.2.2 Intermetallic Solutions

Fig. 4.5 indicates that most intermetallic phases have positive solution energies in α -Zr. Conversely, the extremely negative solution energies in β -Zr, suggest that these intermetallics would not coexist with the β -phase at the concentrations examined here, instead favouring solution. The implication of this is that the formation of SPPs will be critically dependent on details of the $\beta \rightarrow \alpha$ phase change during processing, as is well known.

Sn intermetallics demonstrate much lower solution energies into α -Zr than those of other alloying additions, ranging from 0.45 eV (favouring intermetallic formation) to -0.41 eV (favouring solid solution). Thus, even when the enthalpy for intermetallic formation is favourable, it is small. Therefore, at temperatures where the material is processed (and used) configurational entropy will likely drive solid solution formation. However, under substantial irradiation, some Sn based precipitates have been reported [71, 139]. If sufficient Sn could diffuse together, (via radiation assisted migration) then this study is consistent with these precipitates being stable at lower temperatures.

4.4.2.3 Incorporation onto vacancies

Incorporation energies shown in Fig. 4.6 could potentially have implications for mechanisms of SPP dissolution, by irradiation damage. The negative solution energies onto a vacant site in α -phase zirconium, suggests that the addition of vacancies could potentially increase the solubility of various different intermetallic phases. Considered as a simple equilibrium reaction, this suggests that as more vacancies are added to the system, an equilibrium system that formerly favoured a segregation of most intermetallic phases from pure zirconium, will move to one that favours a solid solution. Radiation induced damage cascades produce large numbers of vacancies. Even after the damaged area is allowed to recover, empirical simulations have demonstrated that vacancies can persist for long time-scales. It has been found that damage cascades can produce both highly mobile small clusters or isolated vacancies [39] and large sessile clusters containing

upwards of 30 defects [40].

Although some of these vacancies will encounter self interstitial atoms and annihilate, the values shown in Fig. 4.6 suggest that a vacancy encountering an intermetallic phase will provide an opportunity for solution. They also show that the reverse reaction (the formation of an intermetallic phase at the expense of creating a vacancy) is not favourable. As the process of vacancy assisted dissolution is reliant on the diffusion of vacancies, this process would be strongly controlled by kinetics. It has been previously noted that the temperature of an irradiated sample has a strong impact on the rate of dissolution, with higher temperatures favouring more rapid dissolution of SPPs [71]. It is important to note that vacancy assisted dissolution is unlikely to be the only pathway to SPP shrinkage. Atoms in SPPs will be knocked into the zirconium matrix by fast moving neutrons and primary knock-on atoms, as well as other mechanisms. In β -phase zirconium, vacancy assisted dissolution does not appear to be particularly favourable. This is due to the preference for dissolution onto more favourable interstitial sites, as available in the more open BCC lattice.

4.4.2.4 Implications for Hydriding

Currently, this investigation has focused purely on the thermodynamics underlying the precipitation of SPP phases, without regards for hydrides. However, the work necessary to investigate intermetallic phases has resulted in a spin-off investigation into the solubility of hydrogen in different intermetallic phases. This work was largely carried out by P. A. Burr, with some collaboration with the author of this thesis. This work was published in April 2013, by the journal *Corrosion Science* [134]. A short overview of some of the implications is presented here.

A selection of the stable intermetallics, as discussed previously, were investigated for possible sites of hydrogen sequestration. The intermetallics selected were the three laves phase structures of ZrCr_2 and ZrFe_2 , as well as Zr-rich structures based on Zr_2Fe and Zr_2Ni . Hydrogen was inserted into each of these structures and the whole cell was allowed to relax. The energy of inserting hydrogen into these structures was compared and it was found that hydrogen will always preferentially occupy tetrahedrally coordinated interstitial sites. The energies associated with this solution were compared with the solution energy in pure Zr. The solution energy of H_2 gas in Zr is calculated as described in Chapter 5 and is similar to equation 4.3, except the alloying

element is replaced by H. It was found that the energy of solution in laves phase intermetallics was greater than the energy of solution in α -Zr. The differences were between 0.1 eV and 0.19 eV for Cr based Laves phase intermetallics and 0.5 eV for Fe based Laves phase intermetallics. However, for Zr-rich intermetallics, the solution energy was 0.01 for the Fe containing phase and -0.2 eV for the Ni containing phase.

There is speculation in the Zr community about the role that intermetallics play in the formation of hydrides. It is possible that SPPs both help and hinder hydride formation. It is possible they assist hydride precipitation, as hydrogen is extremely mobile in metals and intermetallic SPPs are found inside the ZrO_2 oxide layer. This means they could potentially form bridges for accelerated hydrogen diffusion through the oxide barrier, allowing easier hydrogen ingress into the cladding. On the other hand, it is possible that SPPs may provide sinks for hydrogen accumulation in the metal. If the H atoms preferentially sit in SPPs rather than Zr, then precipitation may be delayed. Of course, the total volume of SPPs is smaller than the volume of the Zr matrix, meaning that SPPs acting as "H sponges" may do nothing more than concentrate H atoms for easier precipitation. In whatever case, it is clear that this is a complex system with multiple interactions, none of which are understood to a satisfactory level [140].

The implication for these results is that Laves phase structures are poor candidates for H sinks. However, Cr based laves phase SPPs do have a lower solution energy than their Fe based counterparts. Thus the possibility remains that Cr rich intermetallics may provide a better H absorber than ZrO_2 , but a worse absorber than bulk Zr. It is possible that Cr-rich intermetallics have a part to play as hydrogen "highways" through the oxide barrier. This is particularly important, as Cr is well known for its corrosion resistance, meaning Cr based SPPs often become trapped in the oxide layer as the Zr around them oxidises. However, there is some doubt about this hypothesis, as the oxide layer is significantly thicker than the size of SPPs.

However, when Zr-rich SPPs are being discussed, a different picture emerges. The lower solution energy with respect to bulk Zr indicates these may be potential sites for H sequestration. The Ni based intermetallic has the distinction of being the one one with a negative solution energy, meaning that it is the best candidate for a hydrogen sink. Furthermore, the work done previously suggests that this type of precipitate is stabilised by the presence of Ni, meaning it would be more common in Ni containing alloys. This has an interesting correlation with Zircaloy-2, which

both contained Ni, yet had to be abandoned due to its high hydrogen pick-up fraction. The Ni content was lowered for Zircaloy 4, which seemed to improve the situation. This potentially supports the idea that Ni containing SPPs play a part in hydride formation.

4.5 Conclusions

The simulations support the following conclusions.

- Overall, much of the behaviour of this system can be understood in terms of simple trends in energy and defect volume as a function of the electronegativities, metallic radii or valence electron concentrations of the alloying elements.
- Formation energies for intermetallic phases show that some compounds are stable, while others are metastable. In particular, Zr_2Fe and Zr_2Ni are metastable, although Zr_2Ni has a more negative formation energy. It may be that the presence of the Zr_2Fe phase in Zr alloys is a result of kinetics rather than thermodynamics. It is also likely that the corresponding Ni and Fe phases stabilise each other to some degree.
- Speculative Zr_2Cr and Zr_2V intermetallics have substantially positive formation energies, implying they are not stable.
- There is an energetic preference for Cr and Fe to reside on interstitial sites, rather than substitutional sites. With all additions, an interstitial alloy produces a significant, anisotropic lattice strain.
- Defect volumes for the different elements correlate well with metallic radii, with some anomalies regarding Sn (which has a larger volume than expected) and Ni (which shows a smaller volume than expected when on the less stable tetrahedral interstitial site).
- Most alloying additions show limited solubility (from their single phase metals) in α -Zr, but much greater solubility in β -Zr. The same is true for solutions from corresponding Zr intermetallics.
- Sn shows solubility in both α and β -Zr. However, most Sn intermetallics, show only

a marginally positive solution energy, meaning they are likely to be soluble at elevated temperatures.

- Y, which does not form a stable intermetallic with Zr and has little equilibrium solubility in both α and β -Zr.
- Nb does not form a stable intermetallic and has little equilibrium solubility in α -Zr. However, unlike Y, Nb is soluble in β -Zr.
- Alloying additions from intermetallic phases have a negative incorporation energy onto vacant sites in α -phase zirconium. This reaction may play a role in the dissolution of SPPs under neutron irradiation.
- Work done in collaboration with P. A. Burr suggests that Ni containing SPPs may have a part to play in encouraging hydride precipitation.

This has hopefully added to the picture of zirconium alloys. The following chapters will look in more detail at the solution and precipitation of hydrogen in these alloys.

Chapter 5

Zirconium Hydrides

5.1 Overview

Some of the key questions that should be studied are "What conditions promote hydride formation?", and "What kind of hydride will form?". In order to understand this, a basic thermodynamic understanding of hydrides and their relative stabilities is a logical place to start. In order to do this, models are required for how the hydrides are structured, so they can be investigated via DFT. As chapter 3 explained, DFT confers some limitations on the scope of the investigation. One of the most prominent of these is that the DFT methodology forces the simulation of a limited number of atoms in an isolated void, or a limited number of *crystallographically unique* atoms in the context of an infinitely repeating structure. The code this investigation uses is focused solely upon the latter of these two scenarios.

As discussed, many hydride structures are disordered. In a solid solution between Zr and H, containing H atoms placed interstitially in a Zr lattice, it is unknown if a specific ordering is preferable. Further considerations exist when thinking of the hydrides themselves. If a primitive cell of the delta hydride is considered, it contains one Zr site and two H sites. However, experimental results have shown that typical delta hydrides have a formula of $\text{ZrH}_{1.66}$, meaning the sites have partial occupancy. It is not known if there is any pattern to which sites go filled or unfilled in a δ -hydride crystal. Thus techniques are necessary to investigate this partial oc-

cupancy. The γ and ε hydrides are more ordered, but any real system would still differ from a crystallographically perfect model. The hydrides in question are compared by composition on the Zr-H phase diagram in Fig 5.1.

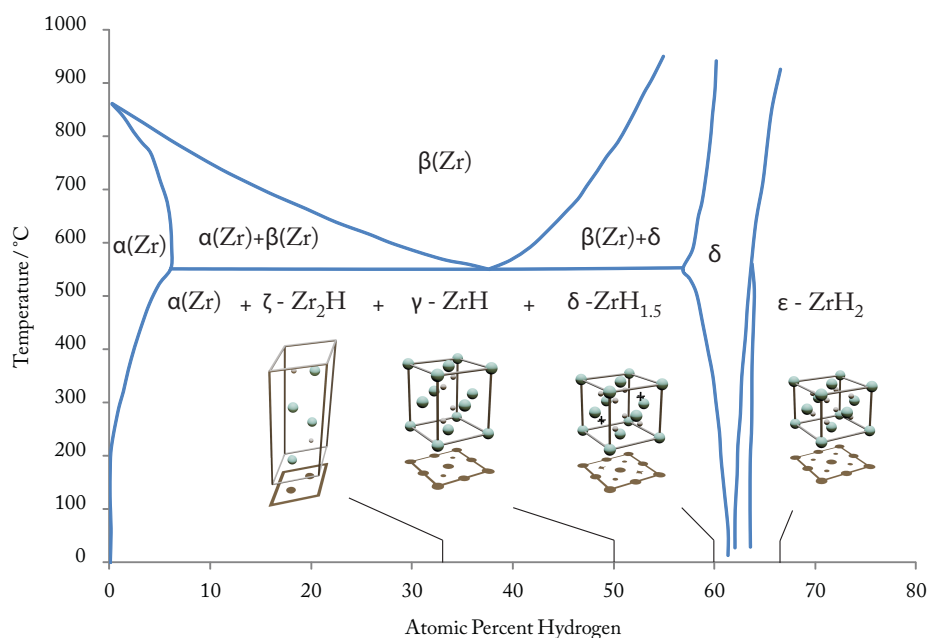


Figure 5.1: Structures and formulae of different hydrides found in the Zr-H system. The Zr and H atoms are represented by the larger and smaller spheres respectively. The δ Hydride shown here is as commonly simulated ($\text{ZrH}_{1.5}$, while real δ -phase hydrides have a formula of $\text{ZrH}_{1.66}$ and have H atoms arranged randomly across all tetrahedral sites, including the black crosses shown in the diagram. The phase diagram has been reproduced from [76].

This chapter will primarily explore the basic tools necessary to ensure these structures can be studied with DFT. Initially, modelling solid solutions containing hydrogen atoms on interstitial sites is investigated. Afterwards, the study will move onto hydrides, and explore some different options for modelling the disorder possible.

5.2 Methodology

5.2.1 Simulation Parameters

Simulations are similar to those given previously, using CASTEP [113]. As a plane-wave pseudopotential code, it is particularly appropriate for modelling crystals, although considerations must be made about how it can be used to approximate disorder. The pseudopotentials used are of the "on-the-fly" generation, where an isolated all-electron calculation is carried out before the main calculation and used as a starting point to generate a pseudopotential. This generation takes place under the ultrasoft formalisation of pseudopotential type [115]. Valence electrons for Zr have been modelled as $4s^2 4p^6 5s^2 4d^2$. Convergence with respect to basis-set cut-off energy and K-point grid density was tested in a series of electronic self consistency calculations. It was found that the simulations were accurate to 2 d.p. for a cut-off energy of 400 eV and a K-point grid spaced at $0.03 \text{ \AA}^{-1}$. K-points were arranged in a gamma-centred Monkhorst-Pack grid [117]. As the system displays metallic characteristics, the sampling of the Brillouin zone is achieved via a Methfessel-Paxton smearing scheme, with a smearing width of 1 eV.

These are static calculations, in that all cells used in this work have had their geometry relaxed in order to ascertain their most stable state. Cells were considered relaxed when the difference between two successively modified iterations were below the following criteria:

- Energy derivative $< 0.001 \text{ eV}$
- Force on ions $< 0.01 \text{ eV \AA}^{-1}$
- Displacement of ions derivative $< 0.001 \text{ \AA}$
- Total stress derivative $< 0.1 \text{ GPa}$

Relaxation of atomic positions was carried out under the quasi-Newtonian BFGS scheme [118]. Initially, cell boundaries were only allowed to relax volumetrically, such that the ratios of lattice parameters were constrained. However tests showed that cells maintained sensible aspect ratios even when this constraint was removed, thus the results reported here are fully relaxed. This allows the system to more truly approximate the volumetric factors available in a bulk hydride. Temperature effects are not modelled here (but will be discussed in Chapter 6),

meaning these can be thought of as 0 K results. This means that the energy change of a reaction is approximated as identical to the latent enthalpy of a reaction.

5.2.2 Cell Configurations

In order for hydride phases to be stable as a structure, there must be some driving force for H atoms to congregate and order themselves. Thus, it can be said that there is an interaction between H atoms (e.g. they exert some force on each other), which must logically extend some distance away from the H atom, however small that distance may be. Therefore, two scenarios can be conceived, of which any models used must belong to. One in which H atoms are too distant from each other to be interacting noticeably (dilute) and one in which the H atoms are close enough to interact in some way (non-dilute). The former is the typical scenario in a solid solution (below a threshold concentration) and the latter is more relevant in all other cases. If the goal is to model a solid solution, a zirconium lattice is constructed, and a H atom simply inserted on an interstitial site. The interstitial site is defined by the arrangement of zirconium atoms around it, and the individual site chosen is unimportant. The size of the cell simulated must also be considered, as discussed in chapter 3. In this investigation a number of different cell sizes are investigated, from those containing only 8 atoms of Zr, up to those containing 96 atoms. Properties of the cells investigated are shown in Table 5.1.

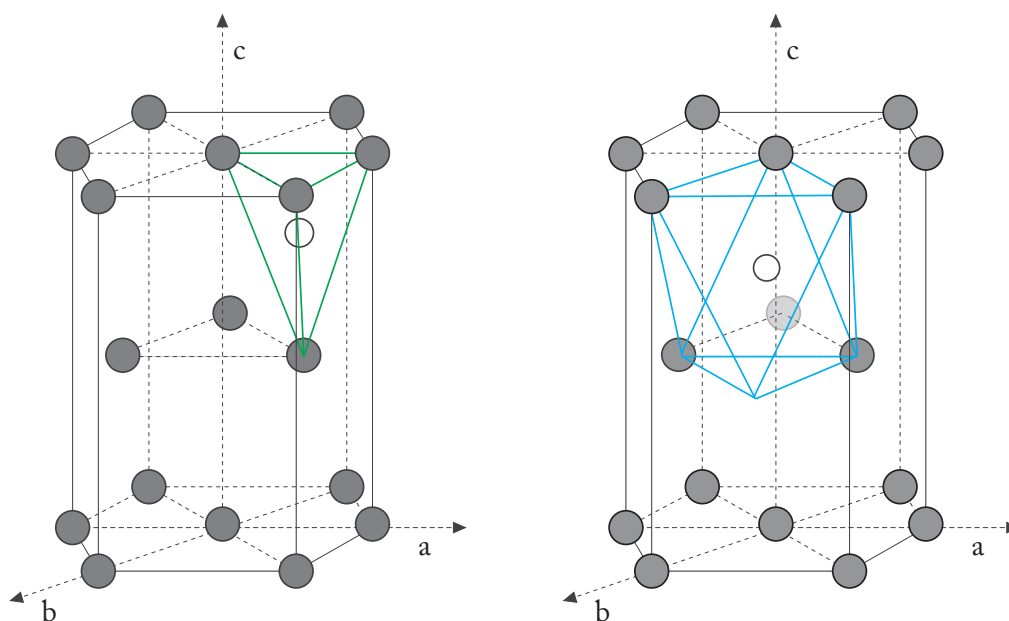
Supercell size	Number of atoms	Zr	Atomic Fraction H	Weight H	PPM	Shortest distance between H atoms ($\text{\AA}$)
$2 \times 2 \times 1$	8		0.11	1371		5.24
$2 \times 2 \times 2$	16		0.06	686		6.48
$3 \times 3 \times 2$	36		0.03	305		9.71
$4 \times 4 \times 3$	96		0.01	114		12.93

Table 5.1: Properties of Zr Solid solution cells

The size of the cell determines the distance between proximal H atoms, and hence the level of interaction between them. In α -Zr, there are two main sites of interest, the tetrahedral site, and the octahedral, as shown in Fig. 5.2.

It is in the non-dilute case that different configurations become important. It is comparatively easy to model ordered hydrides, simply by specifying the experimentally determined structure.

All of the currently determined hydride structures consist of H atoms occupying varying fractions of tetrahedral sites in a HCP or FCC Zr matrix. However, as found in a number of investigations [44, 45], the difference in solution enthalpy between the octahedral site and the tetrahedral site is relatively small. The difference is small enough that other arrangements of H atoms could potentially alter the stability of the preferred interstitial solution and it has also been suggested that zero-point motion contributions may favour the octahedral site [81]. Considering that new phases have been found in this system as recently as 2008 [97], it is not inconceivable that there may be more undiscovered metastable phases, which only manifest themselves at particular pressures or temperatures. With this in mind, a number of speculative hydride structures are created, in which HCP and FCC Zr lattices are occupied by H sitting on octahedral sites. If these



(a) The tetrahedral site is bounded in green, with a H atom occupying it.

(b) The octahedral site is bounded in blue, with a H atom occupying it. An atom positioned slightly out of the plane of the page is omitted for clarity.

Figure 5.2: H occupying both tetrahedral and octahedral sites. The H is shown in white, and the zirconium in grey.

speculative hydrides are treated as ordered with a repeating pattern the size of the unit cells of their respective Zr matrices, then there are two obvious HCP structures (with stoichiometries of Zr_2H and ZrH) and two obvious FCC Structures (with stoichiometries of Zr_2H and ZrH). The structures parallel the conventional FCC hydrides, in that the Zr_2H hydride has H atoms on alternate planes (like the γ -hydride), while the ZrH structure has all of the available sites occupied (like the ε -hydride). Unfortunately, when disorder is considered, or ordering based on a larger cell size, then the number of possible structures begins to balloon towards infinity. However, it is worth examining these structures, on the probability that they reveal an interesting avenue of study. These structures are shown in Fig. 5.3

Now, thought must be given to disordered hydrides. In order to examine these, a statistical approach has been developed. To start with, a δ hydride structure is built, formed from a $2\times 2\times 2$ supercell of the primitive cell, with all potential H sites occupied (giving a formula of ZrH_2). This is structurally similar to the ε hydride, except that the c/a ratio is 1. A new cell is generated from this starting point, by giving each H atom a random chance to be removed of 0.155 (or $1 - \frac{1.6}{2}$) This is repeated to generate a large number of cells, with the only caveat that new cells must be unique from previously generated cells (including symmetry). These cells then undergo geometry optimisation via the DFT package to provide energies for each configuration. No constraints are placed upon the number of H atoms in any given cell, meaning some cells will have more H than the 1.66 ratio, and some will have less. However, as the number of simulated cells increases, more will have a ratio close to 1.66 than will not. Providing the number of cells is large enough, the formulae of the different cells will follow a normal distribution with a mean of 1.66. This is analogous to tossing a fair coin, as over a large enough number of tosses, the expected probability of getting a head will approximate 0.5. Just as important, the set will have a number of different possible configurations, which allows us to examine how configurationally sensitive the energy of the hydride is. Taken together, an arbitrarily large set of these these cells provide a more complete description of the δ -hydride than any single periodic calculation.

In order to compare this method with established techniques, the random set is compared with SQS generated cells. The SQS technique, as detailed in reference [141], works on the assumption that in any random arrangement of atoms on a pre-defined set of atomic sites, some clusters of atoms will be more common than others. The more common clusters are defined by

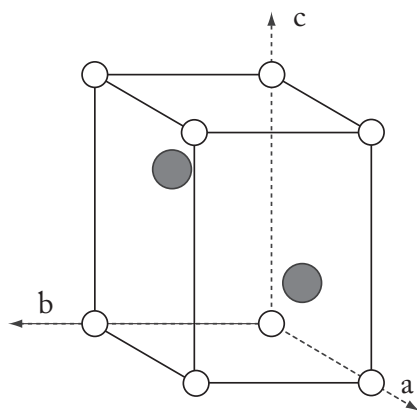
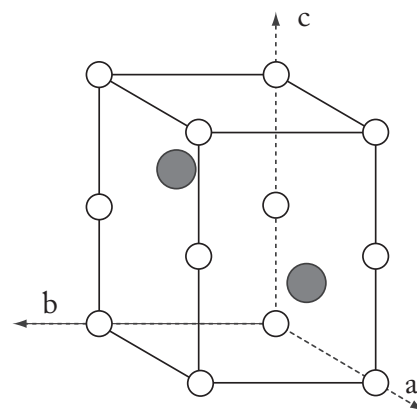
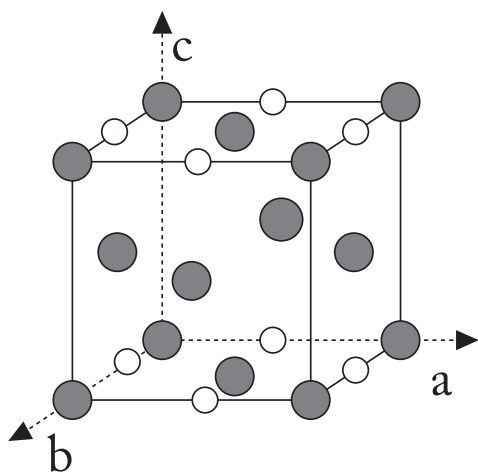
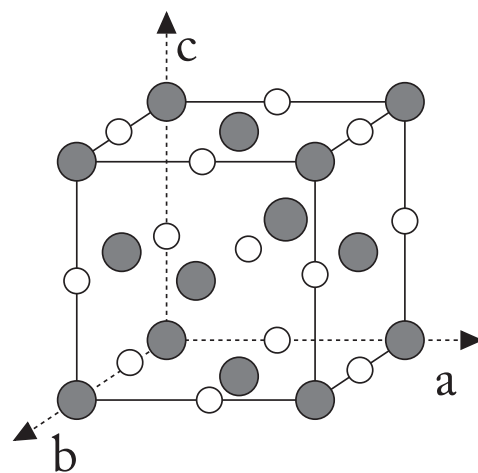
(a) HCP Zr_2H .(b) HCP ZrH .(c) FCC Zr_2H .(d) FCC ZrH .

Figure 5.3: Speculative Hydrides with H arranged on the octahedral sites. The H is shown in white, and the zirconium in grey.

the structure and stoichiometry of the simulated crystal. Thus, a number of "special" cells can be constructed that comprise the more common configurations, and less common configurations can be discounted. In this study, 3 different SQS cells are simulated containing 48, 52 and 56 H atoms, along with 32 Zr atoms. The SQS method has been recently applied to this system in order to model bulk parameters in reference [142]. The 3 most representative SQS cells in that paper are used again here.

However, some phases exhibit more order than the δ phase, such as the γ and ζ phases. Generally, these phases are simulated as ordered phases with a defined structure and no disorder. However, any real hydride will likely have a degree of disorder, particularly when a disordered phase can transform to an ordered phase, and vice versa. Thus, a method has been devised to introduce disorder into these structures, whilst biasing the results towards the known configurations. In this "Skew-Random" method, the starting point is a cell of the ordered structure. For each occupied H site, a small chance for removal of the H atom is introduced. Likewise, for each unoccupied site, a small chance is created to have a H atom added. In both of these cases the chance of 0.05 was used, as it created a reasonable spread of random structures, whilst still maintaining close to the stoichiometric ordered form of the ZrH hydride. As before, a large number of these cells are generated and only unique cells are simulated, to ensure that the full ensemble of simulations is relevant to a disordered hydride. A smaller number of random cells was also generated with no structure biasing, and a chance for H removal of 0.5. This is used purely as a comparison with the Skew-random cell.

All of these techniques present different ways of achieving the same end. Ultimately, all possible arrangements of the H on interstitial sites in Zr exist as points in the configuration space for this system. Each of these different methods presents a different sampling of that configuration space, aiming to ensure that valid points are modelled while unlikely configurations are discounted. Such sampling methods are required, as a single point is not sufficient to model all the important aspects of this system, while a full census of the configuration space carries a computationally prohibitive cost.

5.3 Results

5.3.1 Elements

In order to ensure the validity of the simulations performed, it is important to confirm that the results here can reproduce experimental data. As much of the more useful thermodynamic data makes use of single element reference states, it is also important to ensure that the modelled reference states are as accurate as possible. In Table 5.2, properties of reference states are shown compared with established literature values. Excellent agreement is achieved on all accounts, to within a maximum disagreement of 1.65%. The FCC structure possesses a positive phase stability with respect to the HCP structure, which confirms it is not favourable under energy minimised conditions. Of particular importance are the values for H. As most of the thermodynamic values in these studies are contingent on the presence and position of H atoms in a Zr cell, the values obtained for H are of critical importance. Small differences in the energy associated with H atoms can lead to large differences in enthalpies of solution or precipitation. For this reason, great care has been taken to ensure that the simulation parameters can accurately produce the properties of the H_2 gas reference state. These values are used as reference calculations throughout the next three chapters.

	Property	Modelled Value	Experimental	Literature DFT
Zr (HCP)	a (Å)	3.22	3.23 [34]	3.23 [44]
	c (Å)	5.20	5.145 [34]	5.18 [44]
	$E_{\text{vaporisation}}$ (eV/atom)	6.20	6.24 [132]	-
Zr (FCC)	a (Å)	6.41	-	-
	$E_{FCC}^f - E_{HCP}^f$ (eV/atom)	0.04	-	0.04 [45]
H (Gas)	Bond Length (Å)	0.75	0.74 [132]	0.76 [44]
	$E_{\text{dissasociation}}$ (eV/atom)	4.53	4.52 [132]	4.27 [44]
	Vibrational Frequency (cm^{-1})	4328.42	4401.21 [143]	4483.10 [44]

Table 5.2: Crystallographic and thermodynamic properties of Zr and H.

5.3.2 Solid Solutions

In the case of a dilute solid solution, the most useful metric to determine if dissolution is thermodynamically favourable is the solution energy. This is calculated via the following equation:

$$\Delta E^S = E(Zr_xH) - \left(E(Zr_x) + y \frac{1}{2} E(H_2) \right) \quad (5.1)$$

Where $E(Zr_xH)$ is the total energy of the dilute solution containing x Zr atoms, $E(Zr_x)$ is the total energy of a single element Zr cell containing x atoms, and $E(H_2)$ is the energy of a diatomic H gas molecule. In Fig. 5.4, the solution energies and defect strains are plotted for a series of cells of different sizes. The data is shown for both octahedral and tetrahedral configurations.

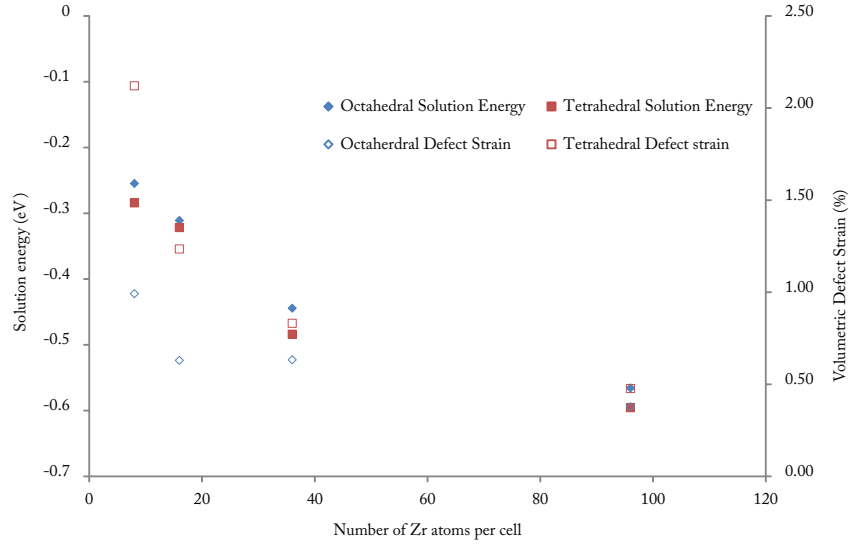


Figure 5.4: The solution energy and defect strains of dissolving H in cells containing different numbers of Zr atoms.

This work is often repeated in the literature, as is a necessary first step for many subsequent calculations. In particular, solution energies have recently been calculated by Domain et. al.[44], Udagawa et. al.[45], an Electric Power Research Institute report [81], and experimental results have been calculated via neutron diffractometry by [80]. The tetrahedral results for these are:

- Domain et. al.: -0.604 eV
- Udagawa et. al.: -0.52 eV

- EPRI Report: -0.435 eV
- Fukai et. al. (experimental): -0.67 eV

when using the most dilute concentration value (if multiple concentrations are used). This value has presumably also been calculated by Zhu et. al. [144], as a necessary value for some the results presented in that paper, however it is not reported. The tetrahedral site value for the most dilute solution (114 wt PPM) in this report is found to be -0.60 eV. This is fully congruent with the other results reported so far.

The octahedral results given in the literature are:

- Domain et. al.: -0.532 eV
- Udagawa et. al.: -0.44 eV
- EPRI Report: -0.373 eV

while this report predicts -0.57 eV. Firstly, it is important to note that all values are sufficiently close together that there appears to be a consensus on the order of magnitude of H atom solution energy, of around -0.5 ± 0.1 eV. There are potential sources of deviation between this report and the others. These include the quality of the H diatomic modelling, the relaxation of the cells, the fact that different DFT codes use different pseudopotentials, and the fact that the experimental study will include temperature effects, which are neglected by these simulations. Despite these differences, the results are similar enough to suggest a reasonably credible value. This study finds the difference between octahedral and tetrahedral sites to be slightly smaller than the other studies (by about 0.03 eV instead of around 0.06 eV). This is likely a consequence of the differences already mentioned. In particular, the other studies either state that the cells are not allowed to relax in terms of their volumes and lattice parameters, or no relaxation regime description is given. This study allows cells to fully relax in all directions.

The volumetric strain cause by H solution is also given in Fig. 5.4. As would be expected, the addition of extra atoms to the cell causes the cell to expand, in this case by between 0.5% and 2%, depending upon H concentration and site occupancy. The strain induced by H absorption is more significant for the higher H concentrations, and is always greater in the case of tetrahedral

site occupation, than when the H atom is on an octahedral site. As the concentration decreases, both the solution energy and the volumetric defect strain seem to converge towards constant values. In essence, although the solution energies and defect strain decrease as cell sizes increase, there are diminishing returns for the effect. This implies that the influence between proximal H atoms decreases quickly as the distance between them increases, implying that H-H interactions in a Zr lattice are fairly local.

5.3.3 Ordered Hydrides

The lattice parameters of various different hydrides are shown in Table 5.3. This also includes the speculative hydrides with octahedral site occupancy. With regards to the δ -hydride, this model neither attempts to simulate disorder or examine a broad range of stoichiometries, thus the approximate $\text{ZrH}_{1.5}$ structure is used. A conventional unit cell of FCC Zr offers 8 sites for H occupancy, 6 of which must be filled with the other two vacant. If the system is cubic, then symmetry reduces the number of configurations to three different arrangements. These arrangements consist of one where both vacancies are oriented along the [100], [110] and [111] directions. Of these, only the [111] type remains cubic after full relaxation, with the rest becoming tetragonal by a small, but noticeable, margin. Some simulators use this final [111] type configuration as an ansatz for modelling the true δ -hydride [144, 145], while others are not specific about how this phase is modelled [44, 45].

The octahedral hydrides are also shown in this Table. In all cases, the largest variance in lattice parameters generated by H addition is in the C-axis. Curiously, the FCC octahedral hydride with a greater H content is cubic, while the one with less H atoms is stretched along the c-axis. It is interesting that this is paralleled in the conventional tetrahedral FCC hydrides, in that more H atoms causes a contraction in the c-axis.

Structure	at% H	Property	Predicted Value
ζ Hydride	33	a (Å)	3.25
		c (Å)	10.78
γ Hydride	50	a (Å)	4.57
		c (Å)	5.01
δ Hydride ([100] orientation)	60	a (Å)	4.75
		c (Å)	4.83
δ Hydride ([110] orientation)	60	a (Å)	4.69
		c (Å)	4.94
δ Hydride ([111] orientation)	60	a (Å)	4.77
ε Hydride	66	a (Å)	5.00
		c (Å)	4.42
Octahedral HCP Hydride 1	33	a (Å)	3.23
		c (Å)	5.30
Octahedral HCP Hydride 2	50	a (Å)	3.24
		c (Å)	5.41
Octahedral FCC Hydride 1	33	a (Å)	4.43
		c (Å)	4.83
Octahedral FCC Hydride 2	50	a (Å)	4.59

Table 5.3: Lattice parameters of different ordered hydride structures.

As a point of comparison, enthalpies of formation of different ordered crystals are also shown. The formation energies were calculated via the equation:

$$\Delta E^F = \frac{1}{x+y} \left[E(Zr_xH_y) - \left(xE(Zr) + y\frac{1}{2}E(H_2) \right) \right] \quad (5.2)$$

where $E(Zr_xH_y)$ represents the energy of the hydride and the other terms refer to the pure elements. As the number of atoms in each simulation differs, the formation energy must be normalised with respect to the number of atoms, in order to not bias the formation energies towards the larger cells. This is presented in Fig. 5.5.

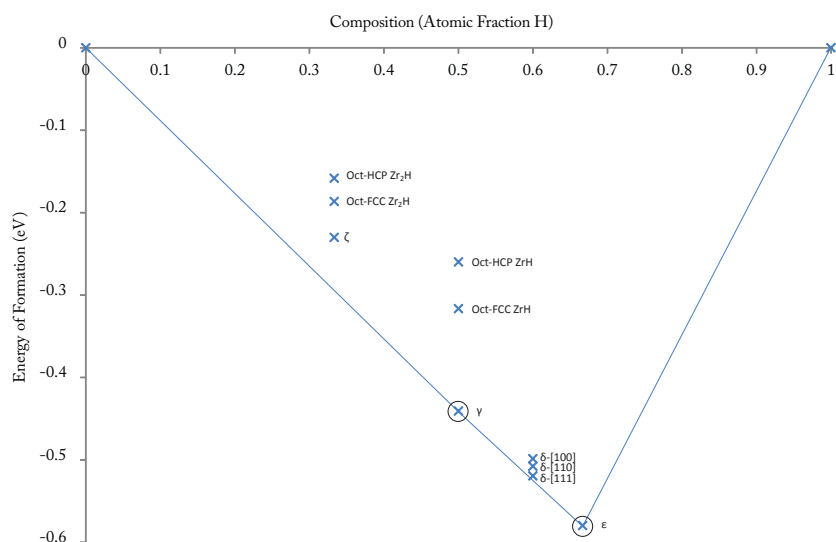


Figure 5.5: The energy of formation from single elements for ordered hydrides. Speculative hydrides with octahedral site occupancy are prefaced with "Oct" and the structure of their Zr sub-lattice.

There is a straight forward trend of increasing H content giving more negative formation enthalpies. As has been discussed previously, a convex hull can be drawn on this plot to help determine relative phase stability. In doing this, it can be seen that only the γ and ϵ -phase hydrides lie on the hull. Other phases, such as the δ -hydride, appear to be less stable. All of the octahedral hydrides have negative formation enthalpies, however they lie far above the convex hull when compared to the conventional hydrides. It is unlikely that they would be observed as other hydrides, or mixtures of other hydrides would appear more preferable. This supplies reasonable evidence that the octahedral site is less important than the tetrahedral site, and that models of hydrides are not likely to be significantly degraded by discounting the octahedral site as a location for H sequestration.

Interestingly, the δ hydride does not lie on the convex hull, despite the fact that it is the phase most commonly discussed in experimental literature. However, It does lie very close to the convex hull. As has been discussed previously, the delta hydride is very similar to the γ and ϵ -phase hydrides, as it has a c/a ratio, and stoichiometry between these two points. A similar

result was found by Domain et. al. in that γ and ε -phase hydrides are stable [44]. Although a convex hull was not drawn on the plot in question, it is not difficult to construct one from the data provided by Domain, which shows the same phenomenon of the δ -hydride remaining above the convex hull[44]. Zhu et. al. also provide a similar plot, however they find the δ -hydride to be substantially more stable than other hydrides, by multiple eV [144]. Given this study and Domain's, the claim of Zhu et. al. seems somewhat difficult to accept. Particularly given the magnitude of formation enthalpy claimed, and the fact that they do not seem to understand the concept of a convex hull, as that the presented "hull" does not obey the convex principle. This provides a reasonable theoretical supposition that the δ -hydride is not stable in and of itself, meaning it must be stabilised by other factors.

5.3.4 Disordered Hydrides

In order to ensure that the simulations are representative of the disordered system it is important that a large enough sampling of the configuration space is achieved. With this in mind, the statistical parameters generated in the sets used are shown in Table 5.4. The δ and solid solution series rely on a random distribution about the selected stoichiometry, while the ζ and γ phases use the skew-random method. A large enough sample will have been carried out when the sample forms a normal distribution centred on the target stoichiometry. A simple convention for determining normality is a plot of the cumulative distribution probabilities of the data against theoretical cumulative distribution probabilities generated by a standard normal distribution [146]. To generate the cumulative distribution function from the data, the stoichiometry range is divided up into a number of bins. The number of cells with a stoichiometry falling in each bin is counted, to produce a frequency distribution. It is possible to plot the frequency distribution against the theoretical normal distribution:

$$Normal(\sigma, \bar{x}) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\bar{x})^2}{2\sigma^2}} \quad (5.3)$$

Where x is the stoichiometry for the theoretical frequency, μ is the mean and σ is the standard deviation of the data-set in question (values which are given in Table 5.4). However, this can skew the resulting normality plot, depending upon the number and size of the bins. As the

parameters of the bins should not be a variable which determines how normal the data is, instead the cumulative distribution function is plotted, which is produced by adding up the total number of cells below the current bin size. Likewise, a similar transformation is applied to the theoretical values, where a given stoichiometry is used to produce a theoretical value which represents the probability of randomly selecting a stoichiometry below the current value. These two sets, the actual and the theoretical, are divided into percentile ranges, and plotted against each other. Should the data be normal, then it will give a linear fit with the theoretical data.

Fig. 5.6 and Fig. 5.7 show normality tests for each set of data, generated from both the formula distribution and the formation enthalpy distribution. In both cases, all series display a good linear fit. For sample sizes of 50 cells per set, all datasets showed high coefficients of linear regression with the lowest R^2 being 0.96. The average formula value for each set is extremely close to the formula value considered representative for that hydride structure. This gives credence to the hypothesis that this set of randomly generated structures approximates a disordered material when taken as a whole.

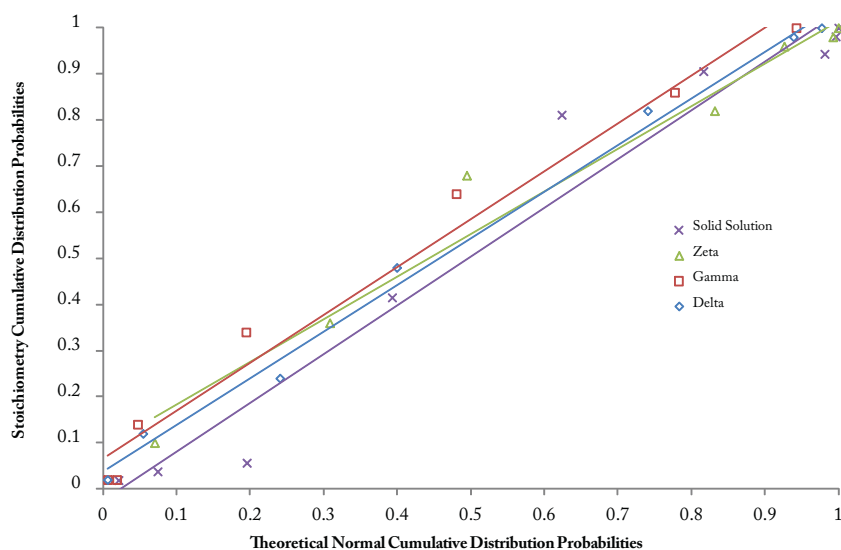


Figure 5.6: Normality test plot for the structures generated in this study. The results are generated from a frequency distribution analysis of values for x in the sample of ZrH_x structures.

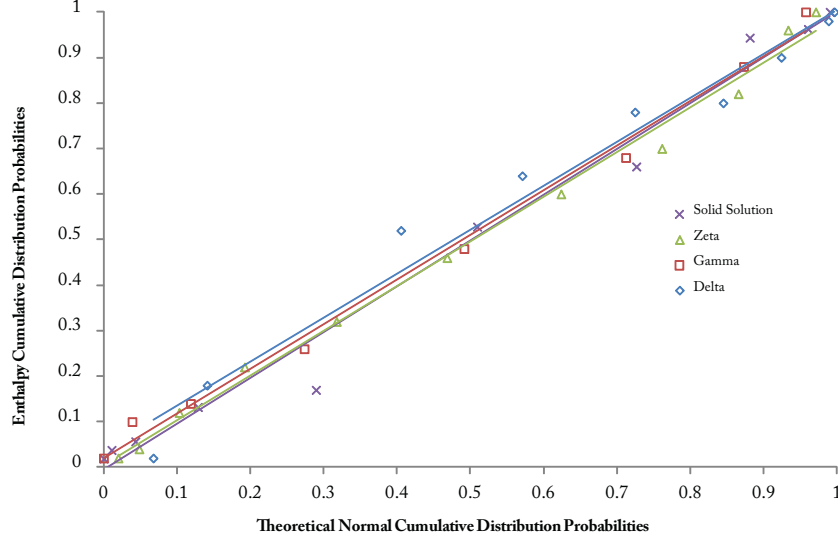


Figure 5.7: Normality test plot for the structures generated in this study. The results are generated from a frequency distribution analysis of formation enthalpy values in the sample of structures.

	N	$\sum H$	R_l	R_u	$\bar{x}_{stoich}$	σ_{stoich}
Solid Solution	50	800	0.13	0.50	0.19	0.08
Zeta Hydride	50	800	0.44	0.88	0.57	0.09
Randomised Gamma	15	480	0.63	1.25	1.00	0.16
Gamma Hydride	50	1600	0.75	1.38	1.03	0.18
Delta Hydride	50	1600	1.25	1.88	1.66	0.16
SQS Delta Hydrides	3	192	1.50	1.75	1.63	0.10

Table 5.4: Statistical values collected from the different data sets used in this work. N is the size of the set $\sum H$ is the total number of H sites, R_l and R_u are the lower and upper stoichiometric bounds, $\bar{x}_{stoich}$ is the arithmetic mean of the stoichiometry and σ_{stoich} is the standard deviation.

Given that there is now a degree of confidence that the data represents a large enough sample, the formation enthalpies can be investigated again.

In Fig. 5.8, all enthalpies are negative indicating that there is a thermodynamic driving force for formation. There is a general trend for increasing H content leading to more negative formation enthalpies. The configurations which lie on the convex hull are the 1% solid solution, the stoichiometric and ordered gamma hydride, and the epsilon phase with a c/a ratio of less

than 1. Within an individual set of data, and for a particular stoichiometry, there is often little difference between the different H arrangements, unless the stoichiometry is one known to have a favoured crystallographic structure (e.g. γ and ζ hydrides). The ζ and solid solution data sets lie relatively far above the convex hull, by energy on the order of 0.05 eV, suggesting a lack of preference for the HCP phases. This is reinforced by the notable discontinuity occurring at around 0.42 atomic fraction H, where the switch from HCP to FCC occurs.

Domain et. al. [44], provide a similar plot with no convex hull, however adding one demonstrates the same phases as stable and by similar magnitudes. This contrasts greatly with [144], who claimed that the δ -hydride is by far the most stable hydride by several eV. It is difficult to give credence to such results, particularly when the "Convex Hull" presented in that work was not actually convex.

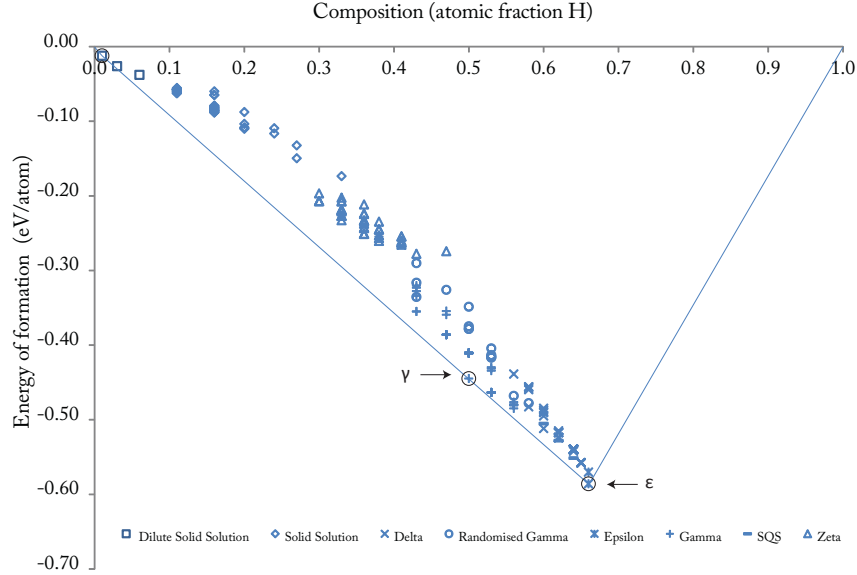


Figure 5.8: The energy of formation from pure elements for all structures studied in this work. The shape of the marker indicates which simulation series it belongs to. Structures which lie on the convex hull are circled.

Considering that a large number of hydride geometries have now been generated, it is also worth seeing if any trends can be seen in terms of how the H atoms are clustered, and if any particular arrangements are repeatedly found to be preferable. Cluster analysis is a well developed

field in computer-science and is often used in atomistic simulation to determine if particular configurations are favourable. However, as the cells in this study are comparatively small repeating units, it is difficult to employ such techniques. It is likely that conventional cluster analysis would be unable to distinguish the different cluster sizes and geometries, due to their small size, and subtle differences when modelled as a crystal. Instead, an extremely simple statistical technique has been developed, which merely aims to arrive at a number that notionally represents how sparsely or densely the H atoms are arranged.

The position of each H atom is defined by a three dimensional vector inside the simulation cell. If these vectors are summed, and divided by the number of H atoms, then an average vector is calculated. The average vector mathematically represents the center of the H distribution. Given an average, and a set of data, the standard deviation of that data set can be calculated. In a set of data with only one dimension (for example, the earlier discussion of the stoichiometry variation), the standard deviation is a measure of how much the data spreads. A large standard deviation means that the individual data points are broadly spaced from their mean, while a small value means the data points are close to the mean. If the standard deviation technique is applied to the H atom vectors, then what is effectively a three dimensional standard deviation is generated, which represents the spread of the cluster. The magnitude of this number represents the average distance of a H atom from the centre of the H cluster. The all vectors are calculated using Cartesian real-space vectors (not fractional), and then divided by the size of the cell in each direction to normalise it with respect to cell size. Otherwise, larger cells would always appear as more sparsely populated due to the H atoms always having a larger space to be placed in. This provides a simple measure of how densely the H atoms are distributed.

This is a relatively primitive technique, in that two separate clusters and one large cluster could both produce the same result. However, given the relatively small size of the cell, it is not reasonable to assume multiple clusters. The only information that can be gleaned from this is how sparsely or densely the cell is populated. The formation energy of the cell is plotted against this normalised standard deviation in Fig. 5.9.

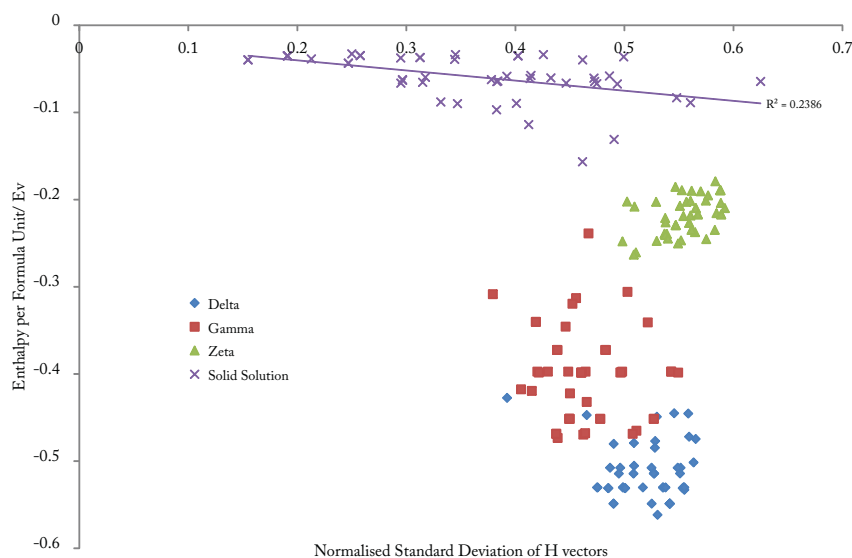


Figure 5.9: The energy of formation is plotted against the normalised standard deviation of H vectors. The standard deviation of H vectors represents a statistical analysis of how sparsely the H is dispersed in a cell, with a low standard deviation meaning a tightly clustered cell.

It is apparent that the data developed by this method is not well correlated, and fairly noisy. A line of best fit has been drawn for the solid solution data set, and its coefficient of linear regression fitting is displayed. This is the most likely candidate for a genuine trend, perhaps due to the fact that small numbers of H atoms are able to more closely approximate a cluster in a repeating cell, than forming an ordered hydride. This is evidenced by the fact that the solid solution data has a much broader range of nominal cluster size distributions. The other series showed extremely poor fitting coefficients, normally less than 0.1. The fitting coefficient for the solid solution series is not brilliant, indicating that only 24% of the data is accounted for in a linear regression fitting model. However, fitting coefficients are not necessarily the definitive description of the existence of a correlation. The R^2 value needed for a fit to be considered "good" is very dependent upon the field of inquiry and the method of data collection. As a simulation based study, this investigation would have no further sources of uncertainty than the already discussed limits of DFT and the convergence criteria. From this perspective, it is not unreasonable that this data constitutes possible evidence for more sparsely clustered cells to have

a lower energy of formation.

In light of the weak correlation of this data, it is entirely possible that the vector standard deviation approach is not suitable for this system. However a conventional cluster analysis based on nearest-neighbour searching may also not be appropriate, given the size of the cells simulated. It is entirely possible that present-day hardware limitations make DFT an unusable tool for analysing clusters in this system.

5.4 Discussion

5.4.1 H In Zirconium

In Fig. 5.4 it is important to note that the cells are allowed to fully relax geometrically, including cell dimensions and aspect ratios. This is important when considering the interference between two H atoms in detail. If a H atom is inserted into an interstitial site, then the Zr atoms surrounding it will move away from the H atom. This is a purely geometric effect, as the tetrahedral and octahedral sites in α -Zr have radii of 0.35 Å and 0.65 Å respectively [137], compared with a H atom radius of 0.529 Å (theoretical) [101] or 0.25 Å (empirical)[147]. However, the H atom's electronic configuration will have an impact on how large it is. Given that the H atom is thought to acquire an electron, shared from its nearest neighbours [44], the actual radius of the H atom may be larger still (the H^- ion can have a radius of up to 2.08 Å, although this is very dependant on how it is bonded [148]). Ultimately, it is reasonable to assume that the H atom does not fit into the lattice without positive lattice strain, as evidenced by the increased molar volume of hydrides with respect to Zr. Given this, allowing the cell to relax means that the cell may expand to accommodate this strain, and the stress introduced by the H atom will be effectively balanced. Introducing stress into a minimised crystallographic structure will always be considered energetically unfavourable, and so it is reasonable to assume that the cell would relax if at all possible. This means that the external stress state of the crystal will undoubtedly be an important influence in determining the behaviour of Zr-H solid solutions, and will be investigated later.

The tetrahedral site remains energetically favourable across all simulated concentrations,

compared with the octahedral. The difference between them is typically small, meaning it is possible that other effects, such as thermal influences or pressure, may drive H to occupy octahedral sites. However, it should be noted that H is well known for being *extremely* mobile in metals. H can diffuse through the entire thickness of the cladding in as little as 30 minutes at operating conditions [24]. This suggests that even small gains in energy may be enough to drive H migration, if the barrier to diffusion is low enough. This question is not one that could be answered from the data here, as this only provides information on the impetus for solution, not on the rate at which it may occur.

The fact that all energies of solution are negative shows a clear thermodynamic driving force for H atoms to become trapped in Zr metal. The magnitude of this driving force is not inconsequential, reaching as great as -0.5 eV for each atom of H in a dilute solution. To put this in perspective, this translates to approximately 48.2 kJ mol⁻¹, or approximately a quarter of energy released by forming liquid water from gaseous H₂ and O₂ at room temperature and pressure. This means that if H atoms can diffuse through the oxide barrier, and come in contact with Zr metal, there is a strong thermodynamic driving force for them to dissolve into the metal.

The volumetric defect strains shown in Fig. 5.4 decrease quickly as the cell size grows, as the strain is spread over a larger number of atoms. The solution energy also drops, as the strain is dissipated. This implies that H atoms have a tendency to cause the solution energy of other nearby H atoms to become more positive, as the higher concentration cells have a less negative solution energy. Thus, despite the fact that there is clearly an impetus for hydride formation (found in reality and in theory), there may be a barrier for H atoms to diffuse together. This conclusion is tentatively supported by the cluster analysis in Fig. 5.9, as the solid solution plot shows a weak trend for increasing formation energy with increasing H vector standard deviation. It is likely such a weak trend due to the small size of the cells, which mean there is little distinction between individual "clusters".

The defect strain imposed by the tetrahedral site is larger than the octahedral site, as would be expected from the tetrahedral site having a smaller volume. However, in spite of this, it always remains the most preferable site for H occupation. As an application of stress the Zr lattice will likely alter the energy of solution, the implication is that the H site preference is governed by factors beyond the purely geometric. The bonding regime between H and Zr must have either a

directional component, or a strong gain in energy for optimal bond length to such a degree that the H atoms still prefer tetrahedral sites in spite of the generated strain.

5.4.2 Zirconium Hydrides

Given that the magnitude of the thermodynamic driving force for solution is now confirmed (from an atomistic perspective), the behaviour of the H trapped in the metal can now be examined. Fig. 5.5, gives a simplified picture of which hydrides are expected to be stable. Initially the octahedral based hydrides are higher in energy than their tetrahedral counterparts. Given that H atoms prefer tetrahedral sites in solid solution, it is unsurprising that this behaviour continues into the hydride phases. What is perhaps more surprising is that the octahedral hydrides really are quite substantially unfavourable. The HCP ZrH octahedral hydride presents the greatest difference between a structure and the convex-hull in this plot. In solid solution, the difference between an octahedral H atom and a tetrahedral one is only 0.04 eV (for the most dilute solution). Yet in the hydride phase the difference between γ -ZrH and Oct-FCC ZrH (perhaps the two most comparable phases) is 0.12 eV, for an equivalent number of atoms. This suggests that octahedral hydrides experience some further structural effects whereby H becomes even more unlikely to enter octahedral sites, as evidenced by the greater than expected formation enthalpies.

The disordered series also show some interesting information. In Fig. 5.8, each set of data occupies its own distinct area, with some overlap with neighbouring series. It is curious that the general trend of this plot is that the solid solution and ζ series seem to have energies significantly more positive than the convex hull, while there is a trend for the FCC based hydrides to start to regress towards the hull as H content increases. The discontinuity between HCP and FCC based structures is particularly noticeable, occurring at about $\text{ZrH}_{0.43}$. It is clarified by the fact that both ζ , γ and randomised γ series exist over the same range between about $\text{ZrH}_{0.43}$ and $\text{ZrH}_{0.48}$. It is seen here, that while the ζ -phase is actually starting to increase in formation energy as H content rises, the γ and randomised γ start at a much lower energy and start to decrease. As shown in Table 5.2, Zr in an FCC configuration is less stable than HCP Zr under energy minimised conditions. It is therefore interesting, although not necessarily unexpected that the FCC structure substantially out-competes the HCP structure as the H content increases. It is

logical to assume that H atoms stabilise FCC Zr in some capacity. In FCC Zr, the tetrahedral site is approximately 1.02 Å and the octahedral site is 1.87 Å in diameter, assuming a simple contacting spheres model, and the lattice parameter from Table 5.2. However, in the hydride phases, the lattice parameter decreases, and if the cubic delta phase is considered to be the representative hydride, the tetrahedral interstitial site diameter drops to about 0.76 Å. This suggests a little of how H site occupancy works. In α -Zr from the perspective of the H atom, the octahedral site is too large, and the tetrahedral site is too small. The H atoms will prefer to sit in the tetrahedral site, and induce a positive defect volume (and compressive lattice strain), in order to force the Zr lattice to locally accommodate the H atom. However, the interstitial sites in the FCC lattice are much larger. Hence the H atom will still take the smaller tetrahedral site, and will induce a contraction of the lattice in order to account for the larger site. This suggests that one of the reasons that the octahedral ordered hydrides are unfavourable, is they rely on the H having to sit in a larger site. Overall, this implies that the H atom prefers to be in close contact with neighbouring Zr atoms.

There is some benefit to ordering the H positions. In the case of the ζ and γ series, the most favourable phases are those with the ordering as shown in Fig. 5.1. This contrasts with the δ phase where the relative difference between different configurations with the same stoichiometry is generally smaller. Determining the underlying mechanism for this would be challenging, and would require a much deeper understanding of the fundamental physics of the H-Zr bond, which is currently beyond this report. It is believed from the work of Domain et. al. [44] that the Zr-H bond has a significant d-electron character, which would impose directionality on this bond from the Zr side, if not necessarily from the H side of the interaction. This work does not aim to elucidate this physics further, but it does confirm that ordering is important in some phases, but not in others.

5.5 Conclusions

This investigation has lead to the following conclusions.

- The tetrahedral site is the most preferable site for H occupancy, in both FCC and HCP Zr

- A possible explanation of this can be developed from the relative size of the interstitial site.
- As a result, hydrides operating on an octahedral ordering configuration are less stable than tetrahedrally ordered hydrides.
- The ordering of H atoms does appear important in some hydrides, but not in others.
- The γ , ε and the most dilute solid solution phases remain the most relatively stable phases.
- Concentrated solid solutions and the ζ phase appear to be less stable than the other phases.
- There is a tenuous evidence for clustered H atoms to be more stable when sparsely positioned.

This forms a foundation of hydride modelling which can now be developed upon towards more physically relevant systems. It is important to note that all of the energies shown so far only represent the energy of forming hydrides from single elements. It does not put this reaction in the context of forming a hydride from a solid solution of H in Zr. The next sections of this thesis will explore precipitation of hydrides from this perspective, and will examine if the imposition of temperature or pressure effects this system.

Chapter 6

Zirconium Hydride

Thermodynamics

6.1 Overview

Up to this point, only energy minimised configurations of atoms have been considered. Effectively, the minimised state represents a system in which all of the available kinetic energy has been extracted from the system, leaving it in its ground state. This represents a lower bound for the energy of the system and any other configuration would be an increase in energy. Notionally, this corresponds to a simulation occurring at 0K, although there are some caveats to this, as will be described later.

However, this is not representative of the conditions that would be present in any real material. Pressurised water reactors operate at around 600 K. Thus, it is important to gain an understanding of how temperature influences the precipitation reaction. This is not an easy task when using static calculations. One possible option is to use dynamic calculations to evaluate temperature effects. When using DFT, this is known as quantum molecular dynamics, or QMD. In this kind of simulation, instead of a series of iterations which minimises the total energy of the system, the energy is kept constant or coupled to homoeostatic energy sink/source. Each iteration represents a step in time, whereby the atoms are moved according to an integration of

Newton's second law, with the forces output by the DFT simulation. However, in order to be representative of a genuine system, which is capable of disorder, a reasonably sized cell would be required. This raises the computational cost significantly, particularly as a large number of time steps would be needed for the system to equilibrate. For the size of systems necessary, the computational costs of a QMD approach are too substantial to be used in any meaningful manner. To summarise, QMD is not a feasible method of examining this system, although advances in computer technology may render it so in the future.

Static calculations remain the primary tool of this investigation. Thankfully, models have been developed which allow some examination of the temperature effects of this system from a static viewpoint. Ultimately, all temperature effects are due to the vibration of atoms. The greater the amplitude and frequency of atomic vibrations, the more energy is stored in the material and the greater the temperature of the crystal. The relationship between temperature and the energy stored in vibrating atoms is known as the heat capacity of the material. The possible directions that a particle can vibrate in are determined by the derivative of the forces experienced by the atom with respect to its displacement from its ideal lattice site. Such a displacement in a real lattice would move through the lattice dependent upon the strength of the atomic bonds. This represents a mobile collective excitation of the lattice and can be thought of as a quasi-particle, known as a phonon [149]. Thus, if the dispersion and amplitude of these phonons can be calculated, a description of the heat capacity of the material and how it alters with temperature can be developed. Furthermore, as the direction and motion of the phonons is a source of disorder, which is responsible for vibrational entropy, a description of the lattice phonons also allows us to calculate entropic terms and thus understand its impact on this system.

Discussion of hydrides has so far been limited to the energy of forming a Zr-H configuration from a mixture of elements. However, this is not appropriate if the goal is to understand the precipitation and stability of the hydrides with respect to temperature. Thus the reaction equation must be reformed in terms of the energy required to precipitate a quantity of hydride from solid solution. This study will then go on to introduce thermodynamic terms and explore the relationship of this reaction with temperature.

The work presented in this chapter is currently being edited for submission to the peer reviewed journal *Physical Review B*.

6.2 Methodology

The results in this chapter have been based upon the initial work done in the previous chapter. Thus, simulation parameters are identical to the ones described there. The same simulation cells are used, with the exception of the hydrides formed by filling octahedral sites, as these were deemed too unlikely to form to be worth considering.

6.2.1 Thermodynamic Considerations

In all static calculations, the main consideration is the energy change from one set of reactants to a different set of products. Relating the calculated energy changes to a real system is often a difficult task, as there are numerous different components which make up the total energy change and many factors present in a real system that are neglected or not present in a simulation. These different components and factors are often poorly communicated between experimentalists and simulators, leading to inappropriate assumptions about what people are discussing when using terms such as energy, enthalpy and entropy. To ensure a complete understanding of the different aspects of this (and other) systems, a breakdown of the calculated values is discussed.

As mentioned in chapter 3, the fundamental measure of the driving force behind a reaction is the minimisation of the Gibbs free energy. The change in Gibbs free energy is given by:

$$\Delta G = \Delta H - T\Delta S \quad (6.1)$$

where ΔH represents the total enthalpy change of the system and ΔS the change in entropy (while T is the temperature). Up to this point, the temperature has been neglected as a matter of convenience. Thus if T is set to 0 K, then terms of enthalpy and the free energy can be used quite interchangeably, as has been done to this point. This is a common convention amongst simulators. However, this approach is now expanded upon by using phonon calculations to investigate temperature effects, meaning this approximation is no longer made.

Experimentally, the total enthalpy change of the system is measured as the combination of the change in internal energy of the system, the amount of heat lost or gained by the system and the mechanical work done on or by the system. As the work done by the system is defined by

changes in the product of pressure and volume, systems where work is done are rarely modelled. The other two components are represented by the *Latent enthalpy* and the *Sensible enthalpy*.

The total entropy also has a number of different sources which add disorder to the system. These consist of the *Vibrational Entropy* and the *Configurational entropy*. The latter of these terms also has two contributing effects, which are the entropy caused by an inherently disordered lattice (if applicable) and the entropy caused by thermally generated intrinsic defects. As any disordered aspect of the system will produce an entropic term, there are also other sources, such as the arrangement of electron energy levels in the conduction band of a metal. However these are generally too small to have much effect outside of specific circumstances. Thus, the final change in free energy is given as:

$$\Delta G = (\Delta H_l + H_s(T)) - T(\Delta S_v(T) + \Delta S_{cl} + \Delta S_{cd}) \quad (6.2)$$

Where:

- ΔH_l is the latent enthalpy associated with the reaction in question. It is due simply to the formation or destruction of bonds and is independent of external conditions such as pressure or temperature. This is because it corresponds to the energy of a phase change, where temperature and pressure are fixed. When quoting results from DFT simulations, this is the most commonly given quantity and has what has been presented so far as the energy, for the sake of convenience.
- $\Delta H_s(T)$ is the sensible enthalpy and is related to the heat capacities of the different species involved in the reaction. It is defined as *The enthalpy change in a substance which is solely responsible for changes in the materials temperature* [98]. The sensible enthalpy change undergone by a material during a change in temperature is normally described by the standard equation:

$$H_s = mc\Delta T \quad (6.3)$$

where m is the mass of the substance and c is the heat capacity of the material. The heat capacity of the material is not a constant value and so must be calculated over a range

of temperatures. This is achieved by calculating the phonon dispersion of the materials in question and integrating the different acoustic and optical modes in a quasi-harmonic approximation.

- $\Delta S_v(T)$ is the vibrational entropy and is caused by the number of discrete vibrational energy levels which exist amongst the different acoustic modes of the system. This is determined by the application of the Boltzmann entropy equation to system of phonon configurations[150].
- ΔS_{cl} is the lattice component of the configurational entropy. This only applies to solids with a disordered lattice, which in this system consists of the H sub-lattice. An approximation of this to the system here is given in section 6.3.3.
- ΔS_{cd} is the configurational entropy generated by the presence of intrinsic defects. As the temperature of a solid increases, an increase in concentration of vacancies and self-interstitial defects would be observed. Although it is possible to estimate this concentration via the Arrhenius equation, to do so would require knowledge of the activation energy for vacancy formation and how it alters with defect concentration. Comprehensive study of these defects would require a significant number of simulations and is beyond the scope of this work.

In a precipitation event, there would also be stress related effects, as well as contributions arising from the creation of a hydride-Zr interface. This study cannot comment on such effects, as they are significantly larger than the scale it is practical to use DFT to investigate. However, the numbers produced in this work represent a large part of the overall driving forces for precipitation and can be used to estimate the scale of other effects.

6.2.2 Phonon Calculations

It is clear that the distribution of phonons must be calculated, in order to determine some of the thermodynamic terms. In the present study, this was achieved by means of the finite displacement method, in the (direct) supercell approach. In this method, the starting point is a geometry optimised cell. A supercell is necessary as it allows calculation of phonons at K-points

other than Γ . An atom in the cell is displaced by a small value in the direction of one of the cell axes (in this case 0.1 Å). The code then runs a single SCF calculation in order to determine the forces between atoms. This is repeated for each atom in each of the three orthogonal directions. From this, the distribution and frequency of the phonons crystal can be determined. From this, two things of interest may be calculated. The first is that a plot which shows which of the phonon modes are dominant in which directions may be generated. This is known as a phonon dispersion plot. Secondly, the fraction of how many different phonons exist at a given frequency, as a proportion of the total number of states may be ascertained. This produces a Density of States (DOS) plot.

The information that is actually desired is how this gives rise to thermodynamic values such as enthalpy and entropy. Effectively, the key calculation is the energy that may be stored in the oscillations of the atoms. It follows from fundamental wave mechanics that a higher frequency oscillation will store more energy than a lower one for a given amplitude and mass of oscillator (related via the Planck constant)[151]. Thus, the energy stored in the crystal due to vibrational effects is determined by integrating the vibrational frequencies over the range of the density of states [150]. If it is assumed that the atomic vibrations have a Bose-Einstein distribution of energy, then the energy stored in the atomic vibrations of a crystal is given by:

$$H_s(T) = \frac{1}{2} \int F(\omega) \hbar \omega d\omega + kT \int F(\omega) \ln \left[1 - e^{-\frac{\hbar \omega}{kT}} \right] d\omega \quad (6.4)$$

where ω represents the frequency, $F(\omega)$ represents the DOS at that frequency, k represents Boltzmann's constant and T is the temperature. This equation has two components, where the first is simply the latter with the temperature components omitted. This is because quantum systems must have a lowest energy state, which results in a zero point energy. The entropy introduced by multiple discrete vibrational modes is calculated in a similar manner:

$$S_v(T) = K \left\{ \int \frac{\frac{\hbar \omega}{kT}}{e^{-\frac{\hbar \omega}{kT}} - 1} F(\omega) d\omega - \int F(\omega) \left[1 - e^{-\frac{\hbar \omega}{kT}} \right] d\omega \right\} \quad (6.5)$$

using the same terms as before. These equations and their usage are described in greater detail in reference [150]. This gives us a grasp of the thermodynamic parameters, calculated from the outputs of a set of static DFT calculations.

6.3 Results

6.3.1 Phonon dispersion

In a phonon dispersion plot, the frequency of each of the different vibrational modes is plotted over the course of a high symmetry path through the cell. In a DOS plot, the DOS of the phonon spectra is plotted against the frequency. These plots are shown for α -Zr in Fig. 6.1. The α -Zr cell has two symmetrically different atoms, meaning that there are 6 total different acoustic modes in the three orthogonal directions.

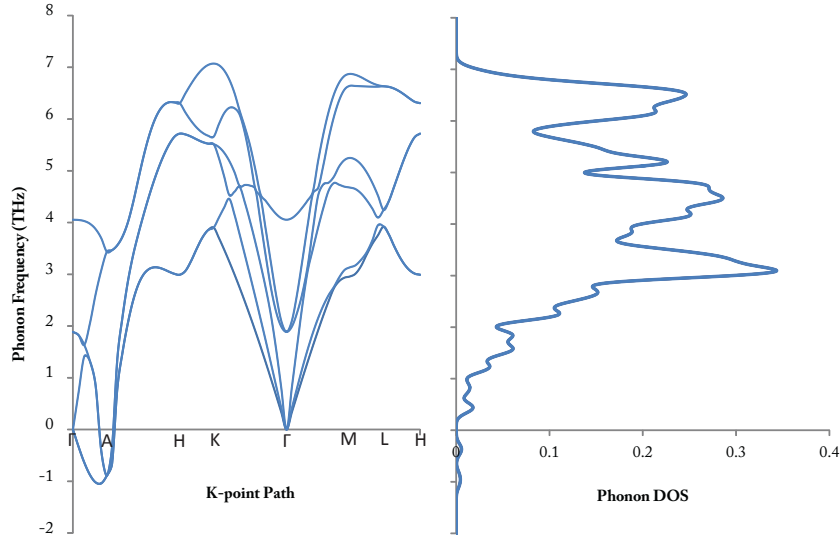


Figure 6.1: The dispersion (left) and DOS (right) of phonons in α -Zr. Both plots are scaled to the same vertical axis.

The leftmost plot shows the phonon dispersion and the rightmost plot shows DOS. These plots are useful, as they can highlight any issues with the phonon calculations, which may potentially show cause for concern. The dispersion plot calculates the frequency of phonons in directions which are found on a high-symmetry path through the Zr crystal. The points used and their K-space vectors are Γ $[0,0,0]$, **A** $[0,0,\frac{1}{2}]$, **H** $[-\frac{1}{3},\frac{2}{3},\frac{1}{2}]$, **K** $[-\frac{1}{3},\frac{2}{3},0]$, **M** $[0,\frac{1}{2},0]$ and **L** $[0,\frac{1}{2},\frac{1}{2}]$.

A potential issue of this plot is that some of the phonon frequencies become negative, on the Γ -**A** segment of the high symmetry path. Negative phonons are nonsensical in a real crystal and

imply imaginary frequencies. The reason for this is that the phonon frequencies are calculated via measuring the forces on each atom, as it is displaced away from its geometry optimised site. The expectation is that any displacement from the site will result in a greater force on the atom than found in its ideal location. However, if the force *decreases* as displacement increases, then the calculated angular velocity term of the oscillating atoms will be negative. Thus an imaginary frequency is produced. Therefore, the presence of negative phonon frequencies is indicative that the structure simulated is not in its ground-state and should be theoretically unstable.

This appears to be a serious concern for these situations, however closer inspection reveals it is not entirely unanticipated. Phonon calculations are extremely sensitive to the forces on atoms, meaning the relaxed geometry may simply need to be relaxed again with more stringent convergence criteria. A further potential source of error was discussed in Chapter 4, in that DFT based upon pseudo-potentials is sometimes known to anomalously predict the simple-hexagonal ω -phase as more stable than the observed α -phase. This is most likely due to limitations in the simulation of core electrons. If DFT predicts a different phase to be stable, then it is not-unexpected that the α -phase displays negative phonons. The reason that the DFT code did not converge on the ω -phase is that the number of atoms and enforced symmetry operations was not conducive to modelling the $\alpha \rightarrow \omega$ phase transition.

A similar result has been found by Souvatzis et. al. in the β phase, which is also known to be thermodynamically unstable at lower temperatures (both in DFT and in reality) [152]. In the referenced case, as the energy difference between the stable and unstable phases is greater than the difference in this work, the area contained by the negative area of the dispersion plot is also much greater. Looking at the DOS plot in Fig. 6.1, it can be seen that the area of the plot in the un-physical negative portion of the graph is very small compared to that in the physical positive portion. To put this in perspective, if a basic numerical integration of the DOS plot is performed (via Simpson's rule [153], with 1391 segments), the total interval is 1, the positive component is 0.997 and the negative component is 0.003. Given that a reason for this error is known and that the value of the error contributed by the negative phonons can be no greater than 3 parts in 1000, then these results can still be considered to form a reasonable basis on which to build further conclusions. Never-the-less, it is important to ensure that results dependent upon these phonon calculations are physically sensible. Thermodynamic values developed from these results

are compared with experimental values and observations throughout the rest of this chapter.

Beyond this issue, no more useful results are directly read off these plots. These are treated as purely intermediary stages in the development of more useful thermodynamic data. For this reason, the dispersion and DOS plots of the other phases are not shown, instead moving directly onto the thermodynamic data itself.

6.3.2 Enthalpies

Previously, the energy (or more accurately, the latent enthalpy) of forming hydride structures from their pure elements has been calculated. Ultimately, this is not the most useful metric of hydride formation. Hydrides are created from the precipitation of H which is already present in solid solution in the Zr matrix. The reaction of real interest is therefore given by the expression:

$$\Delta E^P = [E(Zr_xH_y) + (y)E(Zr_R)] - [yE(Zr_RH) + xE(Zr)] \quad (6.6)$$

This equation forms the basis of calculating the change in different thermodynamic parameters such as the latent enthalpy of precipitation. The term R is the number of Zr atoms in the solid solution reference cell. Precipitation enthalpies have been calculated using reference solutions containing 96, 36 or 16 atoms of Zr to one atom of H. This equation is balanced with free Zr on both sides because it ensures that the reaction maintains reversibility in situations where the concentration is different. As with the formation enthalpies, these precipitation enthalpies must be normalised to ensure that larger simulations are not shown as having larger enthalpies purely based on their size and not on changes in composition and thermodynamic behaviour. To this end, all simulations are divided by the total number of H atoms present in the hydride phase and then converted into kJ mol^{-1} . Thus, the enthalpies presented hence forth are in units of kJ molH^{-1} , representing the enthalpy change required for one mole of H atoms to precipitate from a solid solution.

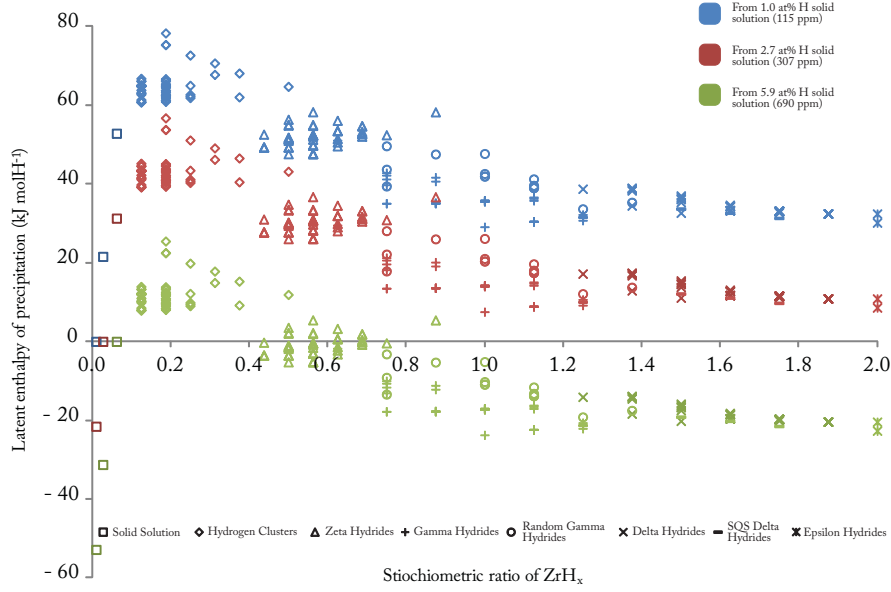


Figure 6.2: The Latent enthalpy of precipitation for all structures studied in this work. The shape of the marker indicates which simulation series it belongs to and the colour indicates the H concentration of the initial solid solution. These numbers are normalised with respect to the number of atoms in the reaction and the amount of H precipitated.

The latent enthalpy of precipitation is presented in Fig. 6.2. This contains all the different data series in this study as precipitated from solid solutions of three different concentrations. The conventions used in equation 6.6 mean that a positive value indicates a preference to remain in solution, while a negative value indicates a preference to form a precipitate. As before, a general trend is visible that precipitating H-rich hydrides is more preferable than H-poor hydrides. On the H poor side of the graph, all solid solution results suggest that a transition to a less concentrated solid solution is preferable. Increasing in stoichiometry of product, there is then a peak of unfavourable H clusters around $\text{ZrH}_{0.2}$, followed by a steady return to more the more preferable hydride phases. In particular, the γ -phase exhibits the strongest preference for precipitation, with the most preferable configuration being the structure typically modelled in other simulation based works and shown in Fig. 5.1. There is a notable discontinuity in all series at $\approx \text{ZrH}_{0.75}$, corresponding to the point where the series switched from modelling HCP hydrides to FCC hydrides. The series where precipitation occurs from more concentrated

initial solutions have a greater preference for precipitation. Overall, this suggests that H has a bimodal distribution in Zr, preferring to exist either as a sparsely distributed solid solution, or as a concentrated hydride. A middle-ground between these two modes appears unfavourable.

However, this only describes the latent enthalpy with no regards for the effects of temperature. The sensible enthalpy of precipitation is related to the heat capacities of the products and reactants of the precipitation reaction. Heat capacities calculated for 298 K are $23.00 \text{ kJ mol}^{-1}\text{K}^{-1}$ for α -Zr and $28.64 \text{ kJ mol}^{-1}\text{K}^{-1}$ for ε ZrH_2 , compared with the available experimental values of $25.45 \text{ kJ mol}^{-1}\text{K}^{-1}$ and $31.08 \text{ kJ mol}^{-1}\text{K}^{-1}$ [132]. This is an acceptable degree of accuracy in the phonon calculations. Fig. 6.3 gives the absolute sensible enthalpies for reference simulations, as they vary with temperature. The values for the three δ -phase stoichiometries are calculated using the SQS generated cells. There is a general trend for increasing sensible enthalpy with increasing H content. The ζ -phase has a substantially lower sensible enthalpy than the other hydride phases. As temperature increases, the variation in sensible enthalpies decreases. The enthalpy given at 0 K represents the zero point energy contribution to the enthalpy of this system.

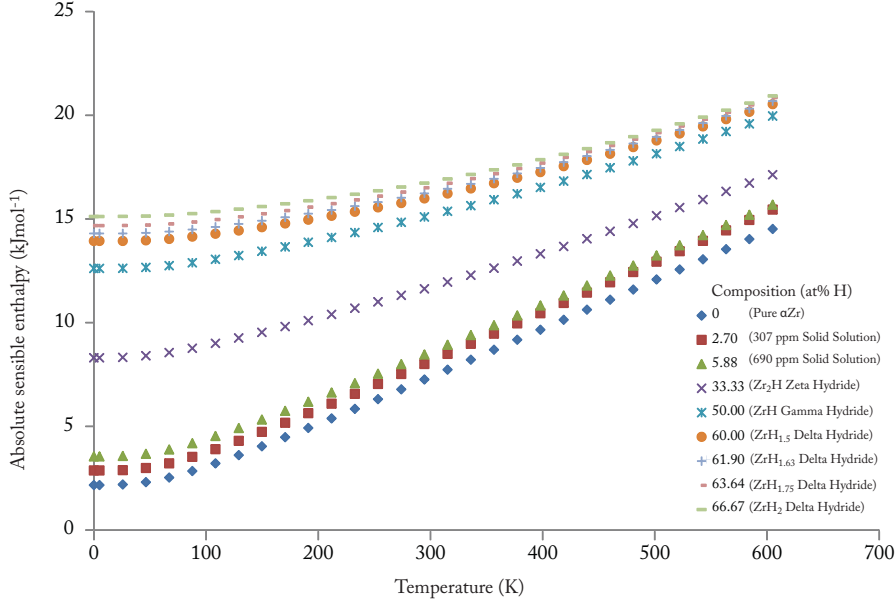


Figure 6.3: The absolute sensible enthalpy plotted against temperature for a variety of reference simulations. The temperature-composition-enthalpy surface resultant from this data is used to interpolate sensible enthalpies for further calculations.

However, the absolute sensible enthalpy is of less interest than the enthalpy change which occurs during precipitation. Using Fig. 6.3, a three dimensional surface is created to show the relationship between composition, temperature and sensible enthalpy. Using this surface, values are interpolated for sensible enthalpies for all the cells examined in this work. The enthalpy data points are sufficiently close together that a simple linear interpolation does not introduce unreasonable inaccuracies. Feeding this interpolation into equation 6.6, the sensible enthalpy change during precipitation for a variety of different stoichiometries and temperatures is generated and plotted in Fig. 6.4. This information is presented only for the precipitation from the 16 atom solid solution. Given that the sensible enthalpy is added to the latent enthalpy, a negative value represents a driving force for precipitation, while a positive value represents a driving force to remain (or re-dissolve) in solution. The addition of the sensible enthalpy appears to drive the system towards precipitation for all product stoichiometries of greater than $\approx \text{ZrH}_{0.08}$. As temperature increases, the driving force for precipitation also increases. There is a relative increase in this driving force for stoichiometries of $\approx \text{ZrH}_{0.4}$, which corresponds roughly with the stoichiometries found in the ζ -phase hydrides. The sensible enthalpy then rises for stoichiometries appropriate to gamma hydrides before dropping slightly for hydrides with even greater H content.

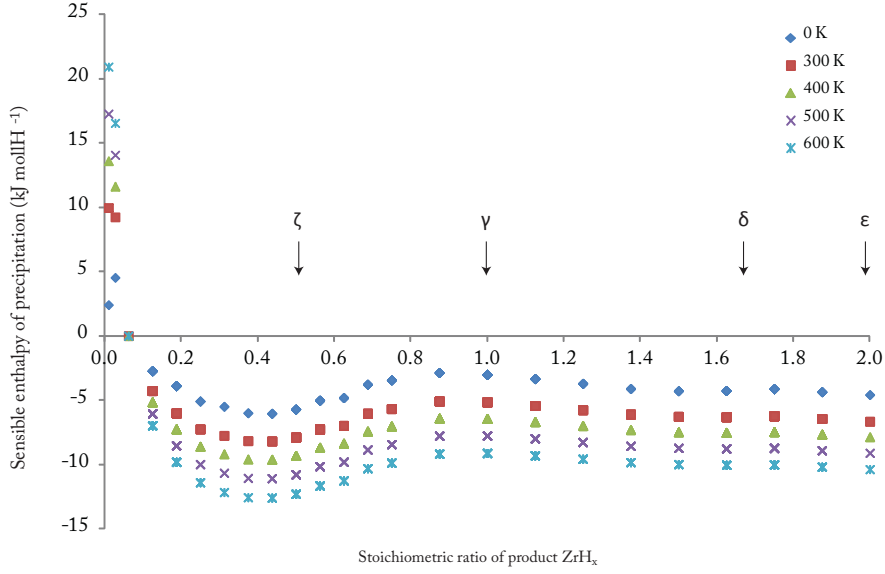


Figure 6.4: The sensible enthalpy change during precipitation as a function of stoichiometry. These numbers are normalised with respect to the number of atoms in the reaction and the amount of H precipitated.

6.3.3 Entropy

As described previously, computing the free energy of a reaction requires a description of the entropy as well as the enthalpy. In this study, two sources of entropy are examined - the vibrational and the configurational.

The basis of configurational entropy, stems from the disorder available when the structure of the compound may have multiple different forms. It is quantified by the Boltzmann entropy equation:

$$S_c = k \ln \Omega \quad (6.7)$$

Where Ω is defined as the number of different configurations or micro-states the system may be arranged in and k is Boltzmann's constant. There are multiple ways to describe Ω . In an atomistic context, the number of different structure configurations is given by adapting the standard permutations expression:

$$\Omega = (N_V + N_H)!/N_V!N_H! \quad (6.8)$$

Where N_V is the number of vacant sites that the H can occupy, while N_H is the number of H atoms. This assumes that H atoms are identical and that rearrangements of different H atoms on the *same* sites does not count as a meaningfully different configuration.

There is also a different way of calculating the configurational entropy. This system can be considered as a mixture of vacancies and H atoms on a total number of sites. With this in mind, the configurational entropy can be calculated via the entropy of mixing equation:

$$S_c = Kx \ln(x) + (1 - x) \ln(1 - x) \quad (6.9)$$

where x is the atomic fraction of filled sites. This is actually an expansion of equations 6.7 and 6.8, where the total number of available sites is assumed to be very large. Thus the relationship is expanded by sterling's approximation for $N!$, for a large number of atoms. This is relevant to calculations of continuous materials where the the number of atoms is large. Both of these two approximations are shown in Fig 6.5.

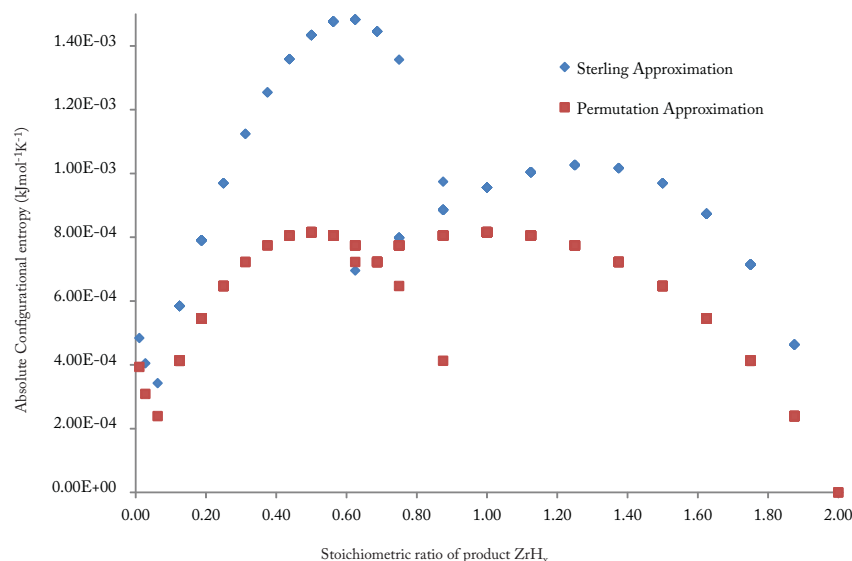


Figure 6.5: The configurational entropy of the different stoichiometries investigated in this work, as modelled by equation 6.8 and equation 6.9.

The Sterling approximation method represents a larger configurational entropy, although it is of a similar order of magnitude. Both show the entropy to undergo a discontinuity at the HCP-FCC transition stoichiometry, purely due to the different numbers of tetrahedral sites per Zr atom. The sterling method shows a greater entropy because it assumes a near continuously available distribution of H atoms on vacant sites. However, as the actual simulations have a discrete number of sites that the H may occupy, the system has less opportunity for disorder. This demonstrates that the systems modelled here are too small for the Sterling approximation. It was decided that the permutation method would be used to approximate the configurational entropy in this system, as it is closer to representing the actual simulations, rather than a theoretical ideal.

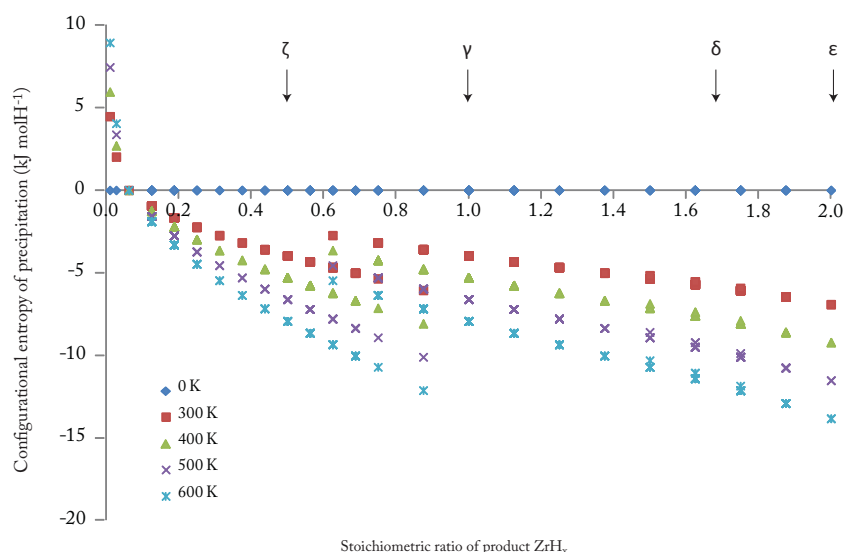


Figure 6.6: The configurational entropy change on precipitation of hydride from solid solution as a function of stoichiometry. These numbers are normalised with respect to the number of atoms in the reaction and the amount of H precipitated.

As before, the primary concern is not so much the absolute entropy, but change in entropy when precipitation occurs. Using the entropies calculated in equations 6.7 and 6.8, in the precipitation equation (with the H coming from the 16 atom Zr cell), the change in configurational entropy is produced across a range of stoichiometries and displayed in Fig. 6.6. These entropies are presented as a $T\Delta S$ product. As entropies are subtracted from enthalpies to generate a free energy (eq 6.1), a negative value here indicates a driving force to remain in solution while a positive value drives towards precipitation. For non-zero temperatures, the configurational entropy represents a driving force for solution, with increasing temperatures leading to more negative values. As before, there is a notable discontinuity when the simulated series shift to modelling FCC hydrides. This is because the FCC structure has more of the tetrahedral sites per Zr atom which are considered a possible sites for H occupancy. The shift from HCP to FCC is favoured by the configurational entropy and this driving force increases with temperature.

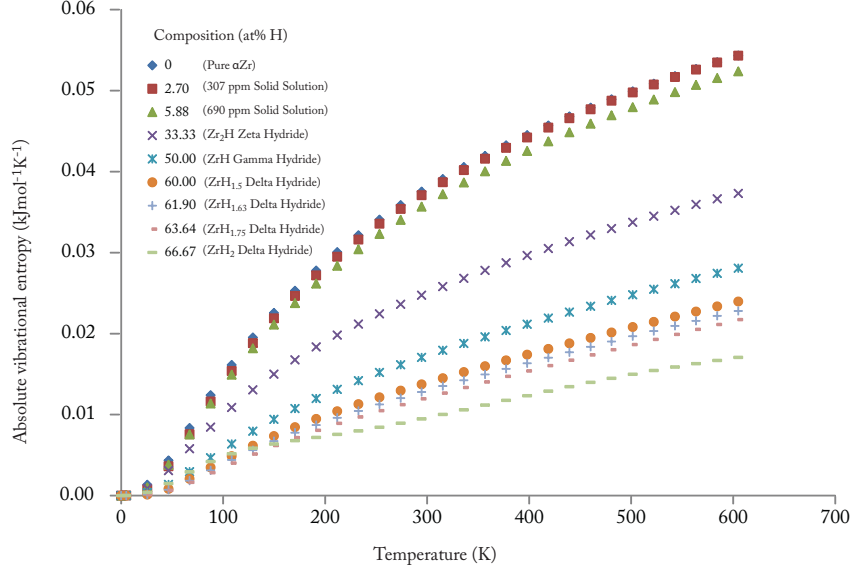


Figure 6.7: The absolute vibrational entropy plotted against temperature for a variety of reference simulations. The temperature-composition-entropy surface resultant from this data is used to interpolate vibrational entropies for further calculations.

The final contribution examined in this work is the vibrational entropy. Vibrational entropies are shown in Fig. 6.7 for the same reference cells as used in calculating the sensible enthalpies. Vibrational entropies at 298K are $37.52 \text{ kJ mol}^{-1} \text{ K}^{-1}$ for α -Zr and $31.387 \text{ kJ mol}^{-1} \text{ K}^{-1}$ for ϵ ZrH₂, compared with the available experimental values for the total entropies of $39.144 \text{ kJ mol}^{-1} \text{ K}^{-1}$ and $35.154 \text{ kJ mol}^{-1} \text{ K}^{-1}$ respectively [132]. Fig. 6.7 demonstrates a decreasing vibrational entropy with increasing H content. In a manner similar to the plotting of sensible enthalpies, this plot is used to interpolate values from a three dimensional temperature-composition-entropy surface. Applied across the range of compositions studied in this work, the vibrational entropy is given in Fig. 6.8 as a $T\Delta S$ product. This plot shows negative values for all compositions above $\approx \text{ZrH}_{0.08}$ and temperatures above 0 K. This suggests that the vibrational entropy drives the reaction towards solution, with the effect increasing with temperature. The vibrational entropy change during precipitation is positive for solid solutions, becomes negative for H clusters and becomes more negative as H content increases. There is a decrease in the magnitude of the entropy change for hydrides of around $\approx \text{ZrH}_{1.5}$, suggesting vibrational entropy may contribute

to stabilising the δ phase.

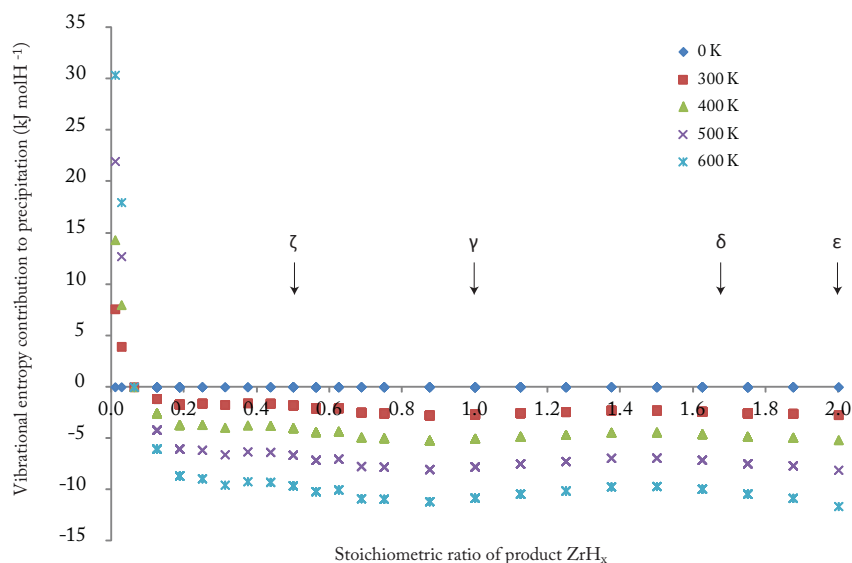


Figure 6.8: The vibrational entropy change during precipitation as a function of stoichiometry. These numbers are normalised with respect to the number of atoms in the reaction and the amount of H precipitated.

6.3.4 Free Energy

With the change in both the enthalpy and entropy calculated for the precipitation reaction, the free energy can be calculated by means of eq. 6.2. The sensible enthalpy, configurational entropy and vibrational entropy all have a similar order of magnitude. This suggests that none of these variables can be discounted as negligible and all have a part to play in determining phase stability. In figures 6.9 - 6.11, the lowest energy configuration from each data set is plotted as a free energy, with respect to the stoichiometry. Figs 6.9, 6.10 and 6.11 represent the free energy of precipitation from the 96, 26 and 16 atom cells respectively.

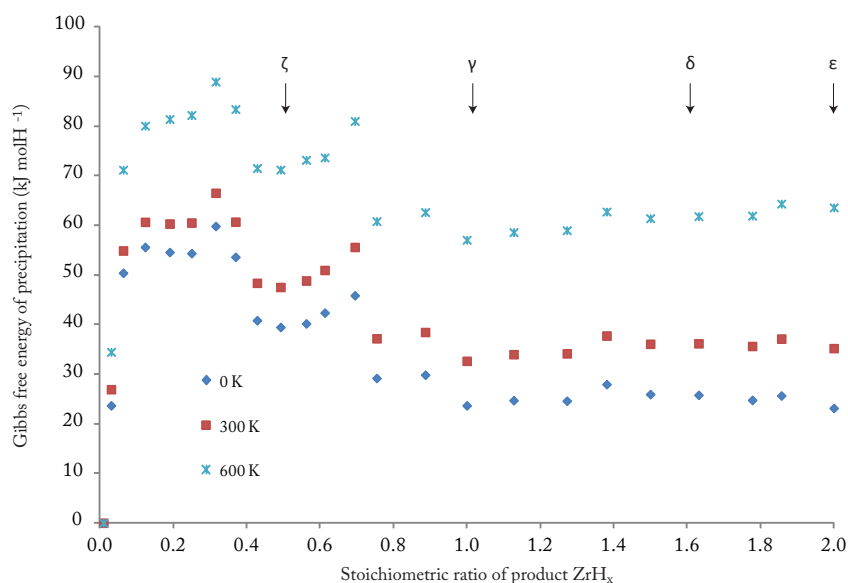


Figure 6.9: The final change in Gibbs free energy of the hydride precipitation (from a 1.0 at% H solid solution) reaction as a function of stoichiometry. These numbers are normalised with respect to the number of atoms in the reaction and the amount of H precipitated.

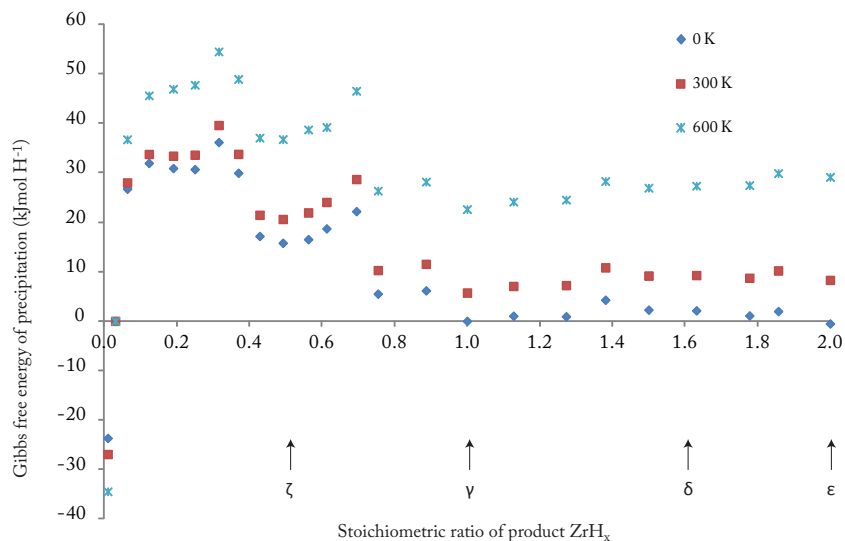


Figure 6.10: The final change in Gibbs free energy of the hydride precipitation (from a 2.7 at% H solid solution) reaction as a function of stoichiometry. These numbers are normalised with respect to the number of atoms in the reaction and the amount of H precipitated.

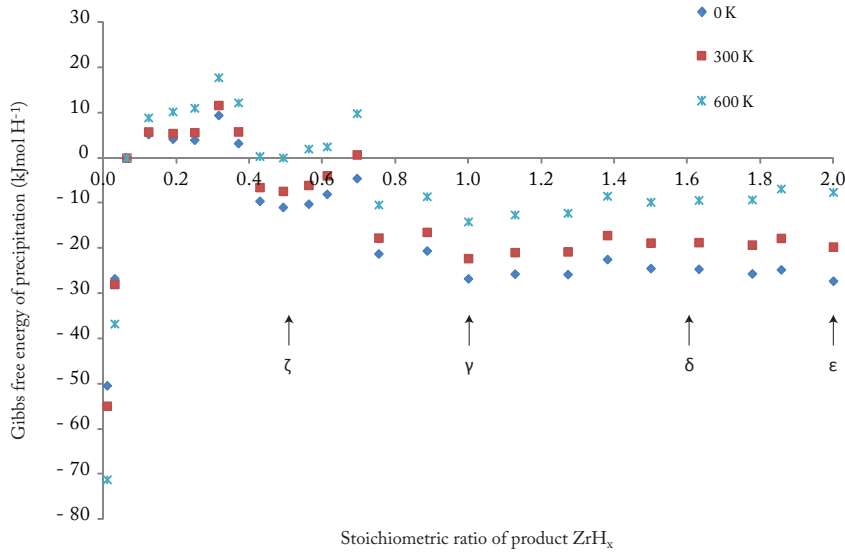


Figure 6.11: The final change in Gibbs free energy of the hydride precipitation (from a 5.9 at%H solid solution) reaction as a function of stoichiometry. These numbers are normalised with respect to the number of atoms in the reaction and the amount of H precipitated.

In the first of these plots, Fig. 6.9, the free energy remains positive across the entire stoichiometry range. Temperature increases the energy substantially compared with the 0 K values. As with all these plots, there appear to be five distinct regions, defined by stoichiometry. The first occurs at $\approx \text{ZrH}_{0-0.1}$. Here, increasing the stoichiometry drastically increases the free energy of precipitation, suggesting that concentrating the H in the lattice is energetically unfavourable. This reaches a relatively flat region 2, made up of clusters of H atoms. This is particularly unfavourable, suggesting that H prefers to remain sparsely distributed. There is then a significant decrease in free energy entering into a third region. The start of region three contains both H clusters and sub-stoichiometric ζ -hydrides as modelled by the skew-random technique. The ζ -Hydrides are more energetically favourable and have a minimum energy point at $\text{ZrH}_{0.5}$, for the expected structure of the ζ -hydrides. However, as H content continues to increase, the free energy rises again and is out-competed by the sub-stoichiometric γ -phase at the start of region 4. This phase remains competitive until region 5 is entered, where stoichiometries are closer to that of the δ phase than the γ . Beyond this energies remain relatively flat until the terminating

ε phase is reached. As temperatures increase, region 5 begins to show a slight upwards slope, signifying it is more preferable to precipitate larger quantities of H-poor hydrides, than smaller quantities of H-rich hydrides.

The results are similar with a initial concentration of 2.7 at% H in Fig. 6.10. Although the same region structure follows, the 1.0 at% H solid solution, γ and ε -phases are now negative, showing precipitation is now favourable at 0 K. At higher temperatures, the reaction is still driven towards solid solution. The free energies are lower overall and the difference brought about by increasing temperature is smaller.

Finally, the the free energies drop significantly when moving to an initial concentration of 5.9 at% H. Fig. 6.11, shows negative precipitation across the full range of stoichiometry and temperatures, with the exception of stoichiometries in the range of $\text{ZrH}_{0.1-0.4}$ (region 2). Below this, there is still a thermodynamic driving force for H dispersal and above this, there is impetus for hydride formation. As in all prior plots, increasing temperature cause free energies to become more positive and drives solution. At the higher temperatures, the ζ phase increases energy to the point where it is no longer thermodynamically favourable for it to form at all. The tendency for regions 4 and five to become upwards loping at higher temperatures is even greater when precipitation occurs form a more concentrated initial solution. The most favourable phases are γ and ε , although higher temperatures seem to favour γ -hydrides. Overall, this remains consistent with a bimodal H distribution, as described previously.

6.4 Discussion

6.4.1 Hydrogen In Zirconium

In figures 6.9 and 6.10, the lowest free-energy configuration is the 1.0at%H solid solution, suggesting that H will preferentially form a dilute solid solution if possible. Temperature effects drive this behaviour further, in that it either makes the 1.0at%H lower in energy, or the other solid solutions higher in energy. In order to produce this behaviour, there must be some sort of interaction between H atoms which raises the energy of the system. Given that electron interactions have been previously demonstrated to be extremely localised to H atoms in the H-Zr

system [44], it is unlikely that the chemistry of H is driving this response. This leaves geometrical factors and most notably stress. A speculation is that the stress fields created by the insertion of H atoms into interstitial positions in the Zr lattice are mutually repulsive.

6.4.2 Implications for hydride precipitation

If there is an initial impetus for H atoms to remain in solid solution, then given that hydrides have been noted to form experimentally, at some point conditions *must* change to favour hydride precipitation. As more and more H atoms are absorbed by the Zr, the barrier for H atoms to congregate must be overcome. In Fig. 6.11, a high starting concentration of 5.9at% H provides this condition. This suggests at some point between 307 wt ppm and 690 wt ppm, that H atoms will be so numerous that they will be pushed past their mutually repulsive behaviour and will start to form hydrides. These values are significantly higher than those seen in reality, implying Zr has a much higher global H carrying capacity than suggested experimentally [87]. If this is the case, in order for precipitation to occur, forces beyond those predicted in these DFT simulations must generate a driving force for concentration and hence precipitation. Given this case, it is possible that global stress states, such as those provided by micro-scale defects or cracks, could lessen this mutually repulsive force, allowing H atoms to diffuse together more easily. The idea that stress impacts diffusion is not new in this field and has been proposed as a key mechanism in the DFM model of DHC [86, 87]. It is reasonable to assume that the Zr lattice around an interstitial H atom is in a state of compression. Given this, a tensile stress field would provide a nullifying effect on the repulsive interaction. Coupled with areas that are not under stress, there would be an impetus for H atoms to move away from regions where H atoms are in close proximity and not under tension, towards areas where they can congregate more favourably. This argument is speculation based upon the existence of the aforementioned barrier to congregation, but provides an area which can be investigated in future studies.

Temperature also has the effect of driving the system towards solution, by raising the composition of the first point where hydriding may occur. In the room temperature series (300K), the first hydride with a negative free energy of precipitation has a composition of about $\text{ZrH}_{0.43}$, while in the operating temperature series, this is raised to over $\text{ZrH}_{0.7}$. The second of these two

hydrides would be more difficult to form as more H must diffuse together. The main reason for this increase is entropic, in that both the configurational and vibrational entropy drive the reaction towards solution.

Finally, these free energy curves may also have a part to play in determining the hysteresis effect observed with H resolution. It has been noted that if a hydrided sample of Zircaloy is re-heated above the point where precipitation initially occurred, less of the precipitate will re-dissolve than precipitated on initial cooling [86]. Consider Fig. 6.11 for the 600K series. At this temperature, there is little difference in the free energies of the hydrided phases and the dilute solid solutions. There is little driving force for any H to precipitate, or for it to remain precipitated once a hydride has formed. As the temperature is dropped, the precipitate phases become steadily more preferable and the reaction will favour their creation. H atoms will have to move past the energy barrier, but once they do, there is significant energy gain in forming a precipitate.

If the case of the temperature being raised from 300 K to 600 K is now considered, the driving force to return to solution at a depressed temperature will be positive. More importantly, the energy barrier that H atoms must climb is greater with the reaction moving in the opposite direction. This is brought about by the asymmetrical nature of the energy barrier at lower temperatures. Thus, in order to overcome this energy barrier, H atoms will require more energy, or a greater temperature would be required to shift the balance such that the energy barrier is less steep on the hydride side of the reaction. Either way, this requires an elevated temperature, suggesting that the hysteresis in the H solubility limits in Zr are at could potentially be explained by thermodynamic effects. However, the current explanation, based upon the influence of crystal plasticity on hydrogen solubility, performs reasonably well when predicting hydride resolution. In order to confidently suggest that thermodynamic effects were even partially responsible for solution hysteresis, the magnitude of energetic terms between the two models would need to be compared. This is complicated by the fact that there appears to be a difference between the globally measured solubility limit in experimental studies (on the order of 80 wt ppm[79]) and the local solubility limit suggested in this investigation (somewhere between 300 and 600 wt ppm). Without such a comparison, the results here cannot be taken as sufficient evidence for a thermodynamic basis for the solubility hysteresis

6.4.3 Zirconium Hydrides

The free energy curves produced in this study also have an impact on determining which hydride phase will precipitate, should precipitation occur. The recently found ζ phase is normally theorised to be a metastable phase [97]. These precipitation energies support this picture, as the free energy curve forms a local minima about the $\text{ZrH}_{0.5}$ composition. The sensible enthalpy plays a large part in the stabilisation of this phase over others. Interestingly, it is the only phase in Fig. 6.11 which shows a transition from negative to positive precipitation energy with increasing temperature. The results suggest the ζ phase should not be observed in high temperature samples.

At 0K, the most stable hydride in all free energy figures are either the γ or ε phases. The commonly found *delta*-phase rests somewhere between these two structures. It can be seen in 6.11 that as temperature increases, the stability of the γ -phase relative to the ε increases. The primary driver of this will be the configurational entropy. Thus, in reactor, the expectation purely based on these results is to see γ -phase hydrides, while at room temperature or lower, hydrides with a greater H content are favoured. Due to the difficulties present in observing hydrides at operating temperatures, the exact morphology of hydrides present in a reactor are unknown and are generally inferred from low temperature experiments. The fact that the γ -hydrides were first observed in quench cooled samples (where the high temperature phase has insufficient time to alter as the material cools) presents evidence to support this result[23].

However, it has also been noted that γ -phase hydrides can form in slowly cooled samples, suggesting that the γ -phase may be stable under equilibrium conditions in some cases [93]. Furthermore, there is experimental evidence suggesting that δ -hydride precipitates may reorder into γ -hydride precipitates when a tensile uni-axial stress is applied. It is also notable that there are other factors in the precipitation of hydrides that are difficult to investigate using DFT. For example, although the work here provides the thermodynamic driving force for precipitation of a quantity of hydride from a quantity of Zr-H solid solution, there is also the issue of forming a surface, which may or may not be coherent, resulting in an additional parameter. If such a parameter disproportionately increased the energy of the γ or ε phases, then the δ would be more preferable. Overall, it is reasonable to say that the thermodynamic forces present a subtle

influence on this system, which would need to be examined in the context of several other factors before sensible predictions can be made as to which hydride will precipitate.

6.5 Conclusions

This investigation has lead to the following conclusions.

- H favours a bimodal distribution within the Zr lattice. Initially it prefers to maintain a sparse concentration, with a high energetic barrier to hydride formation. As more H is absorbed by the Zr, this barrier is overcome and hydride precipitation become energetically favourable.
- The concentration of the H solutions required to initiate precipitation in this study is greater than observed experimentally, suggesting there may be mechanisms needed to enhance local H concentration to drive precipitation. Stress may play a part in this.
- The calculation of latent enthalpies alone are insufficient to fully describe this system, although they remain an important part.
- Sensible enthalpies drive the reaction towards precipitation and are particularly significant for the ζ hydride.
- Configurational entropy drive the system towards solution. They are particularly significant when contemplating the difference between HCP and FCC based hydrides.
- Vibrational entropy drives the system towards solution.
- Increasing Temperature drives the system towards solution.
- Generally, the γ phase is the most stable, suggesting other mechanisms, (such as precipitate interface lattice strain) may be responsible for the commonality of δ hydrides.

This has developed a more detailed understanding of the effect of temperature on this system. Perhaps the most interesting implication of these results is the suggestion of a barrier to H atom congregation, which must be overcome by increased concentration. It has also been suggested

that stress may play a role in this reaction. Hence, the next chapter of this work will examine the impact of pressure on this congregation barrier and upon the energy for precipitation.

Chapter 7

Zirconium Hydrides and Pressure

7.1 Overview

The interaction of hydrogen with stress fields in Zr metal is of critical importance in understanding the phenomenon of Delayed Hydride Cracking (DHC). The key observations of DHC are that hydrides will form at a crack tip (or other stress raiser) over a period of time, allowing the crack to move further into the material and more hydrides to grow. The literature currently describes two possible mechanisms which may explain this phenomena [89].

The diffusion first model (DFM) is the classical explanation originally proposed by Dutton and Puls in the 1970s [89]. It holds that H atoms have a lower chemical potential in a Zr lattice under tensile stress. This would result in a tendency for H atoms to diffuse towards any stress concentration feature such as a crack tip, raise the local concentration above the solubility limit and cause precipitation of a hydride [87].

The precipitation first model (PFM) is a more recent hypothesis. It suggests that the application of a tensile hydrostatic stress would cause the solubility of H in Zr to decrease the point of precipitation of extremely small hydrides at the crack tip. The lack of H atoms in solution local to the defect would then set up a concentration gradient between the crack tip and the bulk, which would drive further H diffusion towards the hydride, resulting in its growth [16].

From this point, both mechanisms suggest that the crack would propagate through the hydride

until it reached un-hydrated metal and the cycle would begin again. More detail on the evidence for these explanations is found in Section 2.5. The two mechanisms each provide a testable prediction, which can be examined with DFT. DFM suggests that a tensile stress would generate a more negative chemical potential for H atoms dissolved in sites under a tensile stress. PFM suggests a more negative precipitation energy for systems under a tensile hydrostatic stress. These two predictions are not necessarily mutually exclusive, meaning that both aspects must be evaluated. This can be investigated with DFT to a certain extent, as lattice parameters of simulated crystals can be altered, effectively imposing a strain on the material. Furthermore, CASTEP has functionality built in to apply an external pressure by means of creating a force on the cell boundaries [113].

This work was conducted as a simulation based counterpart to an experimental investigation carried out by D. Dye and H. Weekes. Analysis of the experimental component is not conducted in this work and will hopefully be presented along with the results of the simulations shown here, in a submission to *Physical review letters*.

7.2 Specific Methodology

The basic parameters of simulations are kept the same as in the previous two chapters, including plane wave cut-off energy, K-point density and geometrical convergence criteria. However, an external pressure is now specified and simulations have been re-run on a number of the already geometrically optimised cells. The pressure is applied hydro-statically, as exploring uni-axial, shear and other more complex stress states would vastly increase the number of simulations needed to be run. Furthermore, as Zr alloys are polycrystalline materials, it is not a trivial issue to determine how different stress states apply to real materials. Especially if precipitates and grain boundaries are present, which are difficult to account for in ab-initio techniques. Thus, it was decided that only hydrostatic stresses would be investigated. This remains a physically relevant calculation as the stress field around large scale imperfections such as a crack tip can be approximated as hydrostatic at a given point. Once the pressure is applied, the cell undergoes geometry optimisation at the new pressure. Data is extracted from these cells, which have been optimised at a variety of different pressures. The cells selected for pressurisation included α -Zr,

the 2.7 at% H solid solution (307 wtppm) and ordered γ , δ and ϵ hydrides.

The stresses chosen were in a range from -40 GPa to 8 GPa. The convention of negative pressures representing compression and positive representing tension will be adhered to throughout this report. At first glance, these numbers appear significantly greater than materials are thought to experience in a real scenario. However, it is important to note that forces applied to a small atomic lattice are not necessarily those that might be found in a macroscopic engineering component. There are issues which complicate the relationship between these two scales. For example, individual atoms can be moved significantly from their ideal lattice points, particularly in the presence of stress fields around atomic scale defects (dislocations, grain boundaries) and larger defects (crack tips, surface flaws, holes). As a result, the strain on the atomic scale may be significantly larger than the actual engineering strain witnessed in a macroscopic component. Another significant issue is that forces in DFT simulations can only examine elastic deformation. There is no mechanism in these simulations to account for dislocation motion or twinning, as described in section 2.2. As a result pressures will be significantly higher, as plastic deformation mechanisms are unavailable to relieve the build-up of inter-atomic forces, once the yield stress has been surpassed. A rough estimate of the maximum appropriate stress would be to calculate the theoretical yield stress of the material, assuming a perfect lattice with no dislocation motion. In this case, the theoretical yield stress of distorting the entire crystal at once is given by:

$$\tau = \frac{G}{2\pi} \frac{c}{a} \quad (7.1)$$

where G is the shear modulus of the lattice. Based upon the experimentally determined value of the shear modulus for Zr being 33 GPa [132] and the c/a ratio being 1.59, the theoretical yield stress can be calculated as approximately, 8.35 GPa. For this reason, the maximum tensile limit of this investigation has been scaled up and set at 8 GPa. In compression, the lower limit of -40 GPa was set to be congruent with the planned experimental collaboration, in which an X-ray Diffraction study is performed on Zircaloy in a diamond anvil cell. This experiment is significant because a common experimental methodology in determining a cause of a specific effect is to amplify the supposed cause in order to make the supposed effect easier to resolve from noise. The cause in this case is suspected to be tensile stress. However, there are limits in how far

the tensile stress can be increased, as the sample will yield and eventually break. However, this experiment instead seeks to take the opposite approach and put the sample under compressive stress. As there is less chance of sample failure, the stress can be significantly greater, meaning changes in hydride structure and solubility should be easier to measure. The possible upper limit of the diamond anvil cell was advertised at approximately 36 GPa, however when the actual experiments were attempted, about half of this was actually achieved.

It should be noted that in this chapter, temperature effects are no longer being considered. Thus the approximation that the latent enthalpy is equal to the free energy (for energy minimised systems) is once more in effect.

7.3 Results

7.3.1 Elastic Moduli

It is important to ensure that the elastic response of the system is congruent with other work on Zr. The elastic moduli are calculated via the standard method of deforming the cell in a series of directions, then observing the change in cell energy and atomic forces. These are presented in table 7.1

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	K
Present Work	140	55	67	155	24	39	88
PW91/UPP DFT	142	-	64	164	29	39	92
Experimental	155	67	65	173	36	44	97

Table 7.1: Elastic moduli of α -Zr as calculated in this study. Literature values were taken from [145]

Although not flawless, the numbers here are comparable with other results. A GGA based DFT method would be expected to slightly underestimate elastic constants while LDA would be expected to overestimate. Therefore, although error is present, it is an understood error in the context of DFT. In an ideal world, more stringent convergence criteria would be applied, which would be expected to improve these values.

When dealing with hydrostatic forces, the most appropriate measure of the elasticity of a material is its bulk modulus. This is generally defined as:

$$K = -V \frac{dP}{dV} \quad (7.2)$$

where V is the volume and P is the hydrostatic pressure. Given that the simulations performed present a variety of different pressures and the volume of the cells is an available output, it is not difficult to find the bulk modulus for the examined structures over the pressure range investigated. This is shown in Fig 7.1

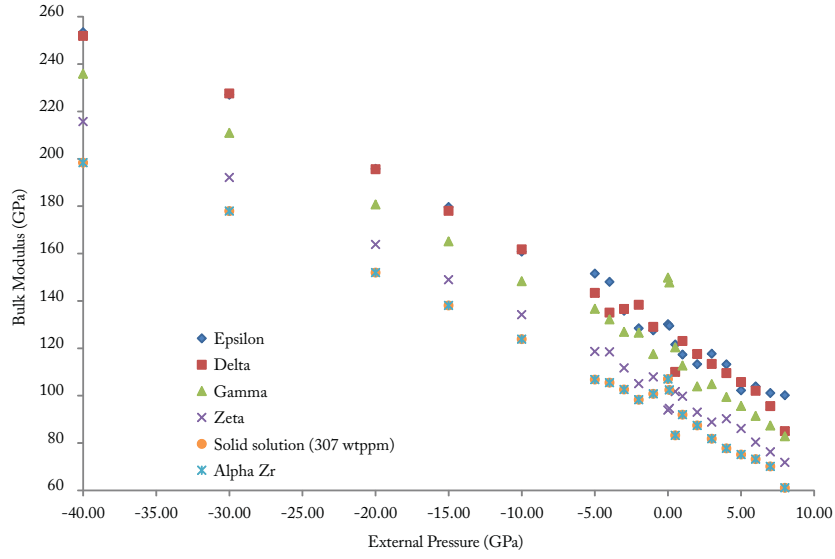


Figure 7.1: The relationship between bulk modulus and external pressure for a variety of hydrides and α Zr.

It should be noted here that the data around 0 GPa will be less reliable than the data at more extreme pressures. This is an artefact of the calculation method, as small fluctuations in cell volume extracted from the DFT results (as a consequence of convergence criteria), will be a greater proportion of the full cell volume change when the cell volume change is small. This is effectively an issue in the error of measuring small numbers and would ideally be rectified by more stringent simulation parameters.

There is a steady increase in bulk modulus with increasing H content. This is to be expected, as hydrides are known to be stiff, but brittle. Perhaps more interestingly is that the lines are

near parallel, with only a slight increase in the gradient as the H content increases. One of the important properties of elastic moduli are that they determine how much energy may be stored in a material for a given deformation. As has been demonstrated in the previous chapter, the absolute energy of phases does not give rise to much in the way of environmentally dependent behaviour. What matters is how the relative difference in energies alters with the environmental variable under consideration. Thus, the fact that the relative change is quite small suggests that differences in precipitation energy will have a relatively subtle relationship with pressure.

7.3.2 Hydrogen Solubility

The solubility of hydrogen with respect to pressure is one of the relative energy changes that may have an impact on hydride precipitation. Furthermore, understanding how the solution energy varies will grant insight into the variance of the H atom chemical potential within the lattice. Thus, the solution energy is determined as described previously in Eq. 5.1. The pressure of the pure Zr component and the solid solution are varied, although the H_2 gas is left unpressurised as a reference state. This is due to the convention in plane-wave DFT of modelling gasses as simply isolated atoms in a very large cell size, so as to ignore intermolecular forces and ascertain the value of removing one atom of hydrogen from the gaseous state. Adding a pressure to this cell would simply cause the model to collapse into a solid hydrogen crystal, of dubious physical significance in these circumstances. Also, it should be noted that the H atoms, in this reference state, are assumed as coming from outside the Zr metal, thus it is doubtful they will be in the same pressure state as the other species (although future work could correct this by altering the chemical potential of the H atoms). With this limitation in mind, the solution energy of a H atom into a Zr lattice for both octahedral and tetrahedral sites is given in Fig. 7.2.

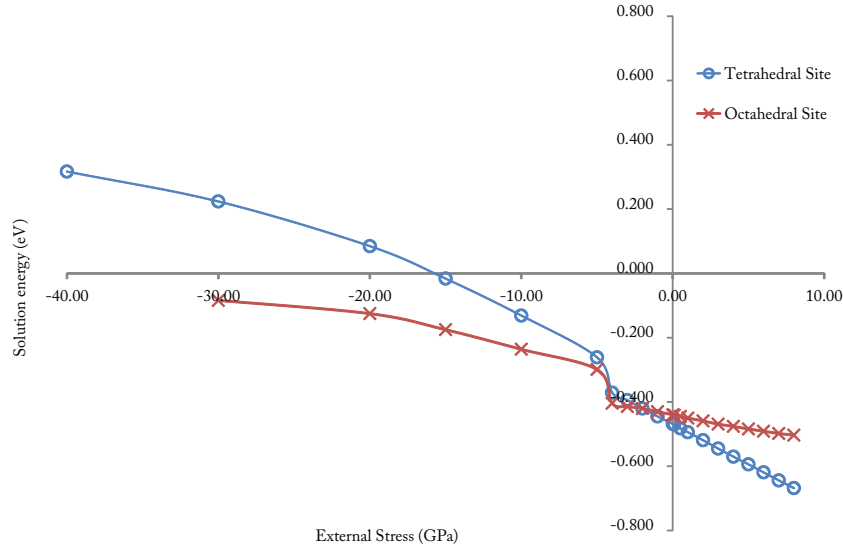


Figure 7.2: The energy of solution of a single hydrogen atom on different sites over a range of pressures. The difference between two points represents the chemical potential generated by an applied external pressure.

The datum point for the octahedral site at -40 GPa is omitted due to computational difficulties. There is a clear trend of a negative gradient linear relationship between -5 and 8 GPa for both sites. A tensile stress causes the solution energy to become more negative. The tetrahedral site is more favourable than the octahedral site under no external pressure (as described in chapter 5) and becomes more favourable as a tensile hydrostatic stress is applied.

Under compressive states of a magnitude greater than -3 GPa, the octahedral site becomes more favourable, followed by a sudden discontinuity at -5 GPa. The compressive stress forces the tetrahedral site to stop being a stable site for H solution at around -15 GPa. The switch from tetrahedral to octahedral site occupancy is not unexpected from a geometrical point of view, although it has yet to be observed experimentally. If the H atom is considered as having a preferred separation distance, then the octahedral site would be expected to stay closer to this preferred value as the lattice shrinks, by virtue of its larger volume. This can be investigated further by examining the volume occupied by the site as it alters with pressure. In order to do this, the coordinates of the H atom and its nearest neighbours were extracted from each cell (4

for the tetrahedral site and 6 for the octahedral). The average distance between the H atom and these nearest neighbours was then calculated and the radius of a Zr atom subtracted from it in order to create a radius of that site. The volume of that site can then be calculated (assuming a spherical interstice) and the percent change of that volume with pressure is plotted in Fig. 7.3. The average volume change in a Zr atom is also presented as a point of reference. This is calculated from the lattice parameters of the cell, to obtain a value representative over the entire cell.

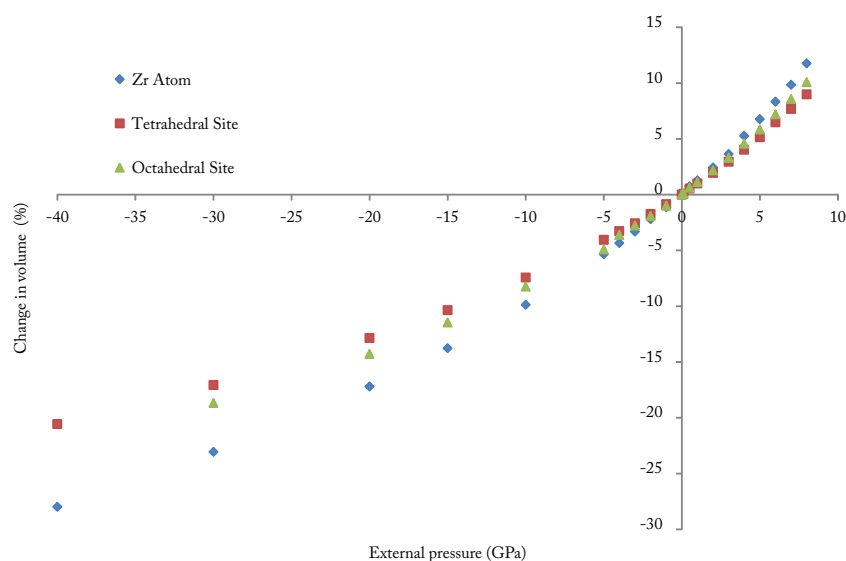


Figure 7.3: The size of an interstitial site, (assuming a contacting spheres model) and its variation with pressure.

Given that the octahedral site already has several times the volume of the tetrahedral site ($1.15 \text{ \AA}^3$ vs $0.18 \text{ \AA}^3$), the volume changes here do not represent enough for one site to overtake the other. Hence, geometric effects cannot be the only influence. Combine this with the fact that the sudden discontinuity from Fig. 7.2 shows no presence on this plot and it is clear that more mechanisms must be at work here. The most obvious suggestion is that there is a change in bonding regime of some description, which could potentially be investigated more in the future. A further investigation of this would be to examine the local density of states of the Zr atoms which are the nearest neighbours of the H interstitial. It is already believed that the Zr-H bonding

state involves d-electrons from the Zr atom [44], suggesting that a high degree of directionality in bonding preference is likely.

Further phenomena can still be seen in this plot. Both sites change in size less than the average size of a Zr atom. The only force responsible for this is the H atom resisting the inwards or outwards movement of the lattice. The tetrahedral site shrinks the least, suggesting that the H atom can be thought of as "stiffest" in the tetrahedral configuration. Overall, more of the cell's deformation is contributed by the shrinkage of Zr-Zr bonds than by the Zr-H bonds.

7.3.3 Lattice parameters

The most obvious response of a material to an applied stress is a change in the material's shape or size. In the case of a hydrostatic stress, a material will decrease or increase in volume, dependent upon whether the stress is compressive or tensile. However, Zr is well known as an anisotropic material. Thus, it is important to ensure that the response of a Zr lattice to pressure is reasonable. In Fig. 7.4, the lattice constants and c/a ratio are plotted against the external hydrostatic pressure. The c/a ratio is plotted on the secondary axis.

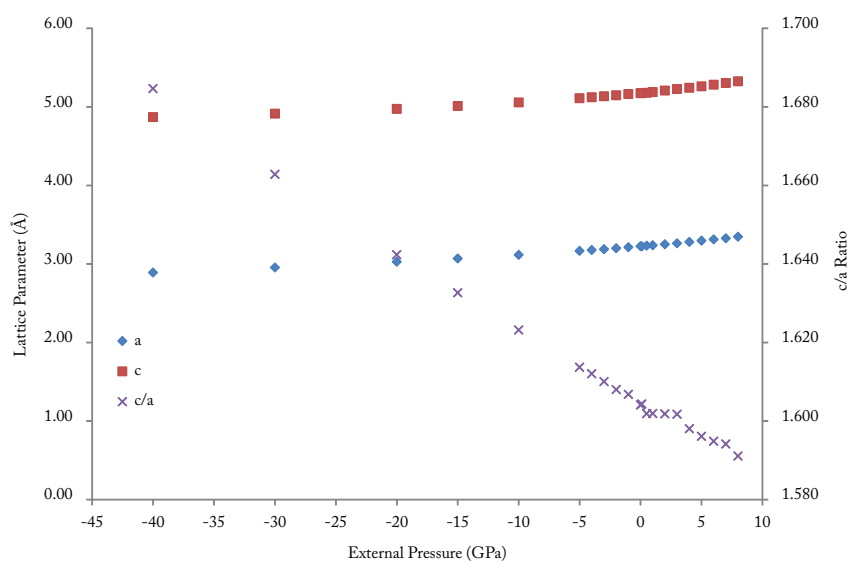


Figure 7.4: The lattice parameters and c/a ratio of α -Zr under a range of pressures

As the amount of compression increases, the c/a ratio is seen to increase as well. This means that the c -axis is shrinking more slowly than the a -axis, suggesting that α -Zr is more stiff in the c direction. The ideal c/a ratio for a hexagonal material is 1.633. This would be analogous to a c/a ratio of 1 in a cubic structure. α -Zr has an experimentally verified c/a ratio below the ideal ratio, with a value of 1.593 (calculated from table 5.2 in chapter 5), while the fully relaxed (and un-pressurised) structure calculated in this body of work gives 1.604. Given that the ideal ratio of 1.633 represents the most efficient way to pack spheres, it is common for non-ideal HCP structures to move towards this value as they are placed under a compressive hydrostatic load, in order to lower the energy penalty associated with packing inefficiency. However, this trend can continue past the point of the ideal ratio, as Zr atoms are not actually perfect spheres. Their "shape" is determined by complex interactions between different electron orbitals. The lattice response to pressure can also be examined for other structures in this system, such as the γ , δ and ε hydrides (Figs. 7.5, 7.6 and 7.7).

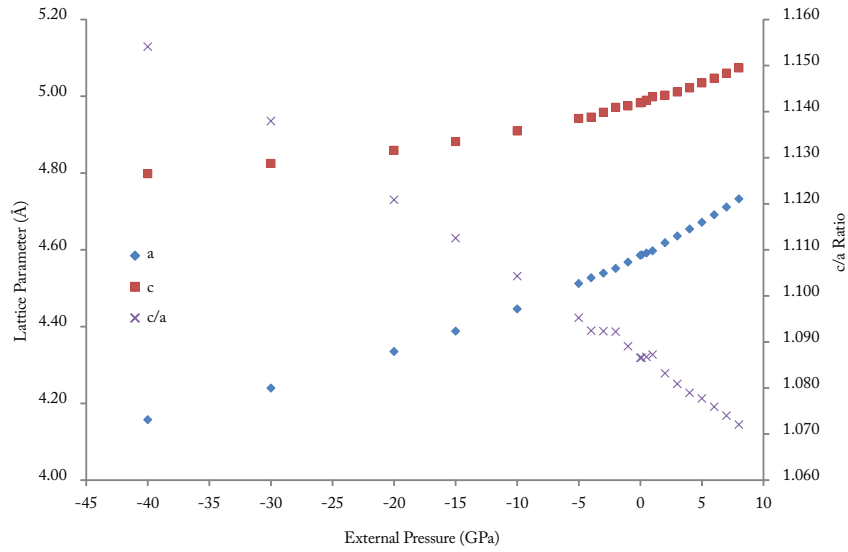


Figure 7.5: The lattice parameters and c/a ratio of ZrH γ -hydride under a range of pressures.

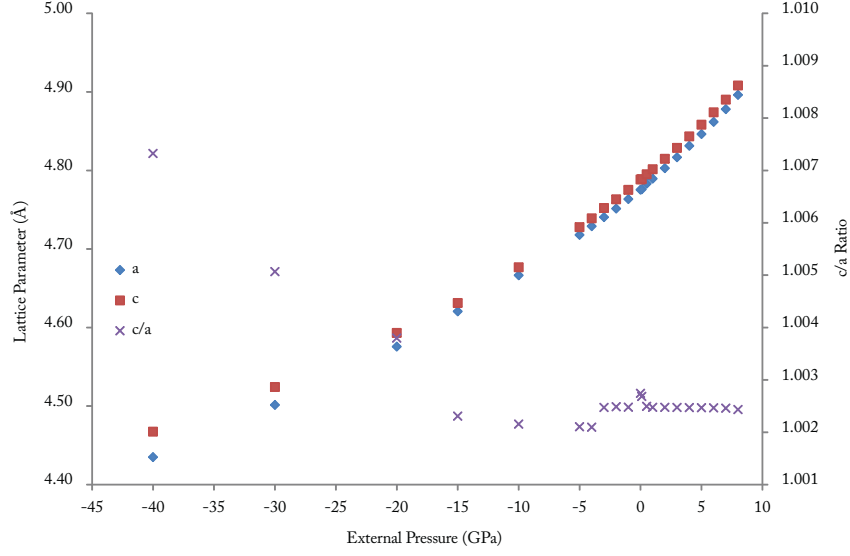


Figure 7.6: The lattice parameters and c/a ratio of δ -hydride under a range of pressures. The δ -hydride is modelled as the ordered $\text{ZrH}_{1.5}$ structure, as discussed in chapter 5.

Both the γ and δ results show a similar picture of increasing c/a ratio under compression and decreasing ratio under tension. However, it is important to note the scale of this change, particularly in the case of the δ -hydride. The change in c/a ratio is around 0.5% for the δ -phase, while the change for the γ -phase is at least an order of magnitude greater. Unlike the previous results, the change in c/a ratio for the δ -phase is not a roughly linear relationship, with very little difference observed when the crystal is in tension, even though the lattice parameters themselves are observed to respond. Considering that the γ phase is already tetragonal (with $c/a > 1$), this suggests that adding additional hydrogen acts to weaken the anisotropic response, effectively strengthening the material's lattice in the c -axis when in compression. In tension, the δ -phase c/a series is almost flat, suggesting that under tension, the material behaves isotropically.

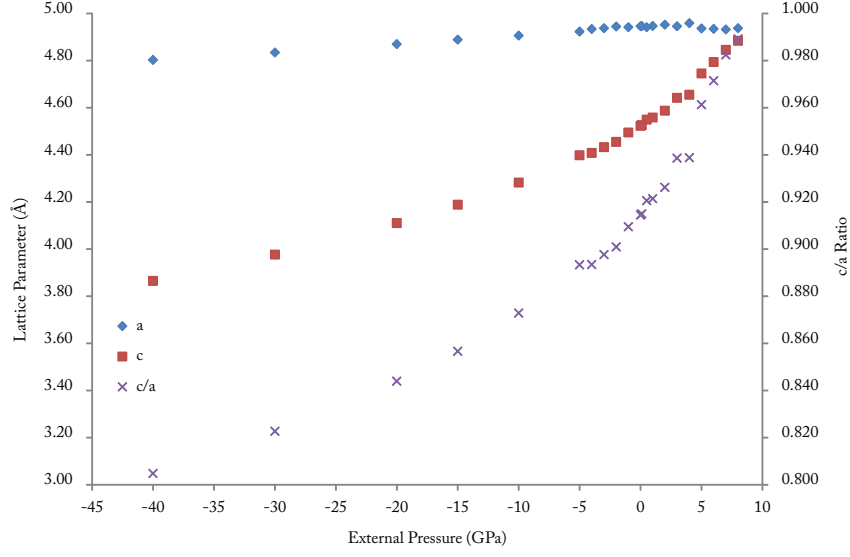


Figure 7.7: The lattice parameters and c/a ratio of ε -hydride (ZrH_2) under a range of pressures.

The ε phase has the opposite response as observed so far and the magnitude of c/a ratio change is greater than the other hydrides. As compression increases, the c/a ratio drops. Tension pushes the c/a ratio towards 1. Furthermore, while the response of pure Zr and γ -hydrides was roughly linear, the δ and ε phases clearly are not. Instead, there is a pattern of decreasing c/a ratio parameter and increasing stiffness of the c-axis, as more hydrogen is added. This could potentially be confirmed by performing simulations on an intermediary point between the $\text{ZrH}_{1.5}$ and the ZrH_2 stoichiometries. An additional hydride cell was selected from the randomly generated series described in chapter 5. This cell had the lowest energy configuration with the selected stoichiometry of $\text{ZrH}_{1.75}$. This was pressurised in the same manner as the other cells. If this pattern holds true, then the prediction is that it would behave somewhere between the δ and ε phases, as described so far. The lattice parameters for this cell are shown in Fig. 7.8. All of the c/a ratios are plotted on the same axes in Fig. 7.9.

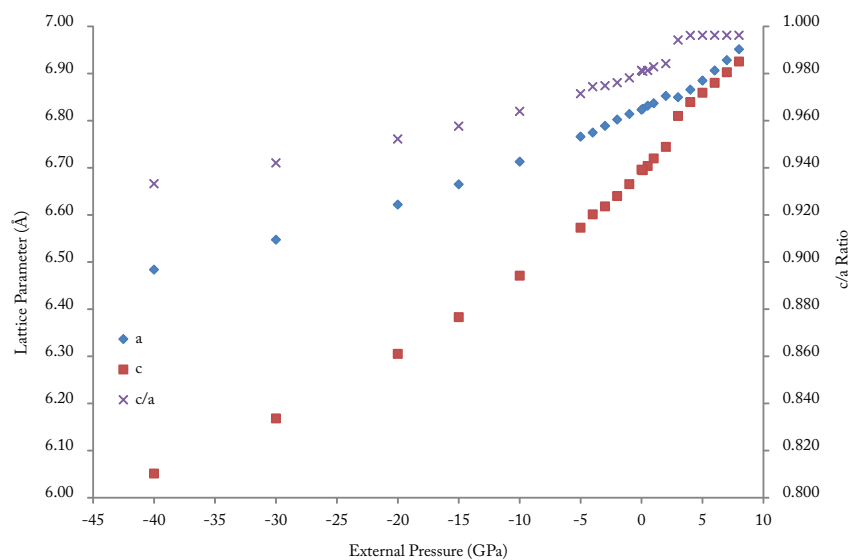


Figure 7.8: The lattice parameters and c/a ratio of a δ -hydride ($\text{ZrH}_{1.75}$) under a range of pressures.

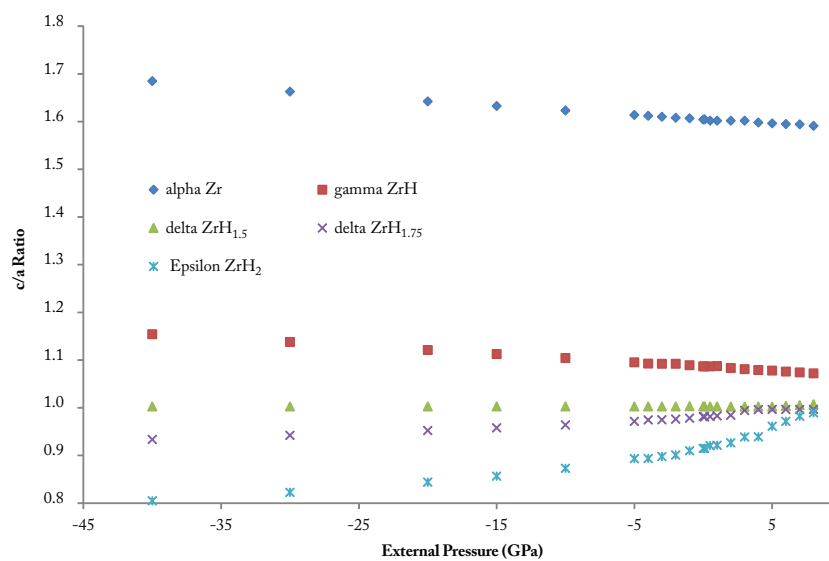


Figure 7.9: The c/a ratios of different hydrides are compared against each other under hydrostatic pressure.

Fig 7.9 shows that this additional simulation fits this pattern well. The c/a ratio shows a slight decrease as compression is increased, but decrease is not as pronounced as is seen in the ϵ -phase. Tension does not appear to alter the c/a ratio as significantly.

7.3.4 Precipitation and pressure

It is of interest to examine if the precipitation energy alters with the pressure state of the material. Although these simulations have created a description of the energy response of a crystal with respect to the hydrostatic pressure imposed on that pressure, a knowledge of what pressure state the different components of the precipitation reaction is in are required. To clarify, there is the pressure state in the initial solid solution and the pressure in the precipitated hydride, both of which must be known. If the energy of a crystal is considered as a function of the pressure imposed on the crystal, then the precipitation equation used so far becomes:

$$\Delta E^P = [E(Zr_xH_y, (P_{Hydride}) + (Ry)E(Zr, (P_{Zr}))] - [yE(Zr_RH, (P_{Zr})) + xE(Zr, (P_{Zr}))] \quad (7.3)$$

where P is the hydrostatic pressure. The previous thermodynamic calculations investigated concentrations where R was equal to 16, 36 or 96, however, for this series of simulations, only the case where $R = 36$ will be used, as the necessity of repeating simulations at different pressures made the addition of another dimension impractical. This concentration is low enough to maintain physical relevance, without imposing an unreasonable burden of having large numbers of atoms to simulate. The solid solution is taken to be the most favourable interstitial site occupancy, as determined by Fig. 7.2. This means that the tetrahedral site is used when the solid solution pressure state is above -4 GPa and octahedral is used below this value.

When one of these reaction equations is formulated, the case is being considered whereby both sides of the equation coexist and the energy of the equation states which side the reaction will be driven towards. Thus, both the reactants and the products must be thought of having pressure states that are linked to each-other. The simplest model of this would be to assume that both the hydride and the solid solution are both experiencing the same hydrostatic pressure. However, this is most likely an overly simplistic model, as Fig. 7.1 shows that hydrides and Zr

have different responses to pressure.

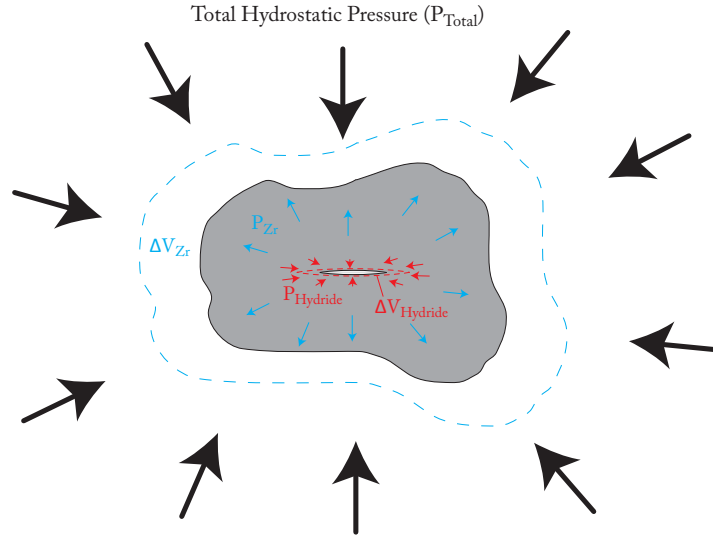


Figure 7.10: A simple diagram of a hydride embedded in a volume of Zr Metal.

In a real system, hydrides will form embedded in the metal. Their shape and orientation is such that they minimise the lattice strains. An example diagram is given in Fig. 7.10. In this case, the system can be thought of as a quantity of "hard" material surrounded by a volume of "soft" material. Intuitively, if this system is squeezed, the expectation is that the soft material would deform more than the harder material. The pressure states in each would be determined by the ratio of how stiff the materials are to each-other, assuming a perfectly bonded interface. Thus, an estimation can be made in which the stress in the Zr and the hydride is partitioned by the ratio of their bulk moduli:

$$\frac{K_{Hydride}}{K_{Zr}} = \frac{P_{Hydride}}{P_{Zr}}. \quad (7.4)$$

In this work, the values for K are taken from Fig. 7.1. Although this model is *slightly* more sophisticated, there are still further complications. The orientation of the hydride will alter its stiffness due to the needle-like shape of hydrides. More complex models would take into account the idea that the hydrides would appear stiffer down their long axis than down their short axis.

Also, if the pressure state in the Zr or the hydride increases beyond the yield point, then the elastic stress as used in this model will reach a maximum value and increase no further, as additional stress is relieved by plastic deformation, although the atomic scale stresses will still be larger than the macroscopic yielded stress as discussed previously. It is difficult to account for yielding with DFT, however experimental observations or finite elements models can assist in giving a sense of the magnitude of the pressures involved.

Experimental results cannot directly monitor the stress state in both the hydride and Zr phases. However, X-ray diffractometry is capable of measuring the change in the spacing of inter-atomic planes, via observing the shift in diffraction peaks as the sample is pressurised. Recent work by Allen et. al. [96], measured the strain in both hydrides and Zr around crack tips. They report maximum strains of 7.2×10^{-3} - 8×10^{-3} in the hydride and 4.10×10^{-3} - 5.10×10^{-3} in the metal. Much of the focus of their work involved a study of creep, however these values were extracted from their data on samples without creep, to avoid adding even more complexity. These provided a third ratio relationship between the stresses in hydrides and Zr metal.

These three models give three possible stress ratios which can reasonably be expected to have some bearing on the actual system. With the two variables of the system (pressure of hydride and pressure of Zr) and the output of the energy of precipitation, the parameter space of the system can be represented as a surface. This is presented in Fig. 7.11.

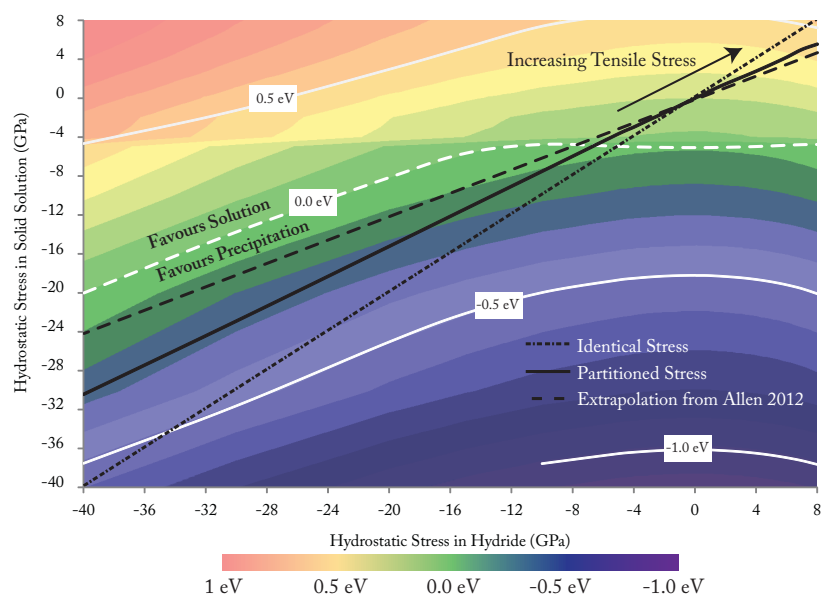


Figure 7.11: The energy of precipitation, as dependent upon the pressure states of the reactants and products. Three different models describing the relationship between pressure states are shown. The line "Allen 2012" is extrapolated from data found in reference [96].

The coloured contours represent the energy of precipitation of a δ -hydride from a solid solution of 307 wtppm. In this case, the energies are calculated for a hydride with a stoichiometry of 1.625, as this is the closest to the 1.666 ratio available with the cell sizes used. The configuration of H atoms was selected as the most favourable configuration for that stoichiometry, as found from the disordered series investigation in chapter 5. On this contour plot, the three different stress state models represent lines, which can be thought of as vertically orientated slices through this energy landscape.

Fig. 7.11 shows that the precipitation enthalpy has a tendency to become more negative as the solid solution stress becomes more compressive. The surface is less sensitive to increasing compression in the hydride phases. There is a small discontinuity around -4 GPa in solid solution pressure as the site occupancy changes from fully tetrahedral to fully octahedral. In reality, if this site occupancy preference is correct, it would be reasonable to expect that this change would be gradual, as more H atoms shift from one type of site to the other. All three of the models show an increase in precipitation energy with system tension and a decrease with system compression,

although the partitioned stress and the Allen extrapolation roughly follow the contours of the surface at pressures below -15 GPa in hydride stress. All models show that precipitation is initially unfavourable from this concentration (in agreement with the previous study), but it becomes more favourable with increasing hydrostatic compression, with a switch between -4 and -8 GPa. The data of the surface is interpolated along the three lines to generate Fig. 7.12.

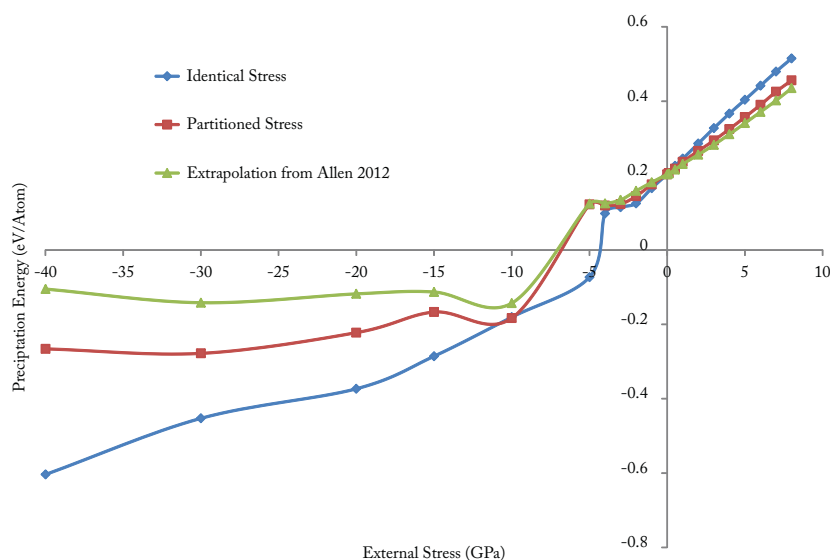


Figure 7.12: The energy of precipitation, as dependent upon the pressure state in the precipitated hydride. The lines effectively correspond to slices taken from Fig. 7.11 along the three different lines. Negative energies favour hydride precipitation.

This plot more clearly shows the expected behaviour as theorised from the suggested models. They are all consistent in a qualitative sense and the key features remain - a linear increase above -3 GPa, a sudden negative shift between -3 and -10 GPa, followed by the data remaining negative at pressures below this point. The partitioned model and the extrapolation from experimental data suggest that below -10 GPa, the precipitation energy stabilises and is no longer particularly sensitive to pressure. The sudden jump is related to the sudden discontinuity on the solution side of the reaction, as shown in Fig. 7.2. It should be noted that the magnitude of the pressures required to induce these changes is relatively high.

7.4 Discussion

7.4.1 Cell Deformation

The ε phase is interesting, as it is believed to have two different stable structures, one with a $c/a < 1$ observed both experimentally and via ab-initio calculations and one with $c/a > 1$ which has only been predicted by DFT. These two forms have been hypothesised to play a role in DHC, as the shift from δ -Hydride to one of these forms may assist in relieving misfit strains [95]. In the work studied here, a cubic structure was taken as the starting point, then allowed the simulation to relax as necessary, which has so far always provided an ε phase with a $c/a < 1$ (see Fig 7.7). It would be intuitive to expect that a tensile stress state would stabilise the $c/a > 1$ phase and compression would stabilise the $c/a < 1$ phase. Despite this, the ε phase never shifts to the $c/a > 1$ phase, even with the additional tension. It is suggested by Ackland that the $c/a > 1$ phase is slightly more stable than the other, according to DFT calculations[95]. The results from the present study suggest that if the energy landscape of this system does have a minima for a $c/a > 1$ phase, then it is potentially a metastable state and the breadth of the "well" of this minima would be small, otherwise it is likely that these calculations would have found it.

There is an interesting trend with c/a variation under pressure across the range of hydride stoichiometries, most easily visible in Fig. 7.9. It appears that the slope of the compressive region of the starts negative and then becomes smaller as hydrogen is added. Somewhere between a stoichiometry of $\text{ZrH}_{1.5}$ and $\text{ZrH}_{1.75}$, the gradient is flat, whereupon the addition of more hydrogen will cause it to go positive. The point of having no gradient coincides with a c/a ratio of 1. This leads to a coherent picture of H atoms having a contracting and stiffening effect on the c-axis. It is reasonable to assume that a genuine disordered δ -hydride, with a stoichiometric ratio of 1.66 would lie somewhere between the $\text{ZrH}_{1.5}$ and $\text{ZrH}_{1.75}$ series. Given that the slightly sub-stoichiometric series has a (small) negative gradient and the super-stoichiometric series has a slightly positive gradient, the implication is that a cubic hydride will respond isotropically to stress. It has long been suggested that the δ -hydride exists at the point where the c/a ratio changes from < 1 to > 1 . These results also suggest that it exists on the cusp of having the ratio of stiffness in c and a directions to also be equal to 1. This is a sensible conclusion, as it is reasonable for isotropic structures to respond to stress isotropically. The change from

anisotropic to isotropic and back again (in the opposite direction) appears to be induced solely by the addition of more hydrogen in this lattice.

7.4.2 DHC Models

Firstly, the merits of the DFM hypothesis will be examined in the context of these results. The key data agreement sought is that tensile stress lowers the chemical potential of H atoms in a Zr lattice. This chemical potential can be computed from Fig. 7.2. The chemical potential of one of the sites would be found as the difference between the 0 pressure value and a given pressure. Thus, a tensile pressure of 8 GPa corresponds to an decrease of the H atom chemical potential by -0.20 eV, on tetrahedral sites. This suggests that if the H atoms are able to diffuse to a tensile region of the Zr lattice, then there is a thermodynamic driving force for the m to do so. This is in full agreement with the DFM postulation.

Furthermore, the agreement is not just qualitative, but quantitative. The DFM assumes that there is a linear relationship between chemical potential and applied hydrostatic stress. The change in H chemical potential with stress is given by:

$$\Delta\mu_H = -P1.7 \times 10^{-6} \quad (7.5)$$

where the constant is the partial H molar volume and has the units of $\text{m}^3 \text{molH}^{-1}$ [87]. It amounts to a constant of proportionality between the pressure and the chemical potential change. As energy (or more usually, work done) is the product of a pressure and a volume this unit can be re-written as $\text{J molH}^{-1} \text{Pa}^{-1}$. The tensile region of Fig. 7.2 has a gradient of $-0.02503 \text{ eV GPa}^{-1}$. Conversion of this value into $\text{J molH}^{-1} \text{Pa}^{-1}$ gives a value of $-2.42 \times 10^{-6} \text{ J molH}^{-1} \text{Pa}^{-1}$. Accounting for the sign convention change, the fact that the DFT investigation finds this constant is of a similar order of magnitude and size to the experimental value lends significant credence to both the DFM and the DFT investigation. The difference between these two figures is likely due to the DFT investigation being at 0K and the fact that it assumes that all H atoms are in tetrahedral sites, where in reality, a small proportion may occupy other sites.

However, this does not rule out the PFM in entirety. In order to support the PFM, the results here would need to show a decrease in the energy of precipitation as tensile stress increases.

However, this conclusion is not supported in Fig. 7.12, where a tensile pressure results in an increase in the precipitation energy. All the models agree on this particular issue, with only a small amount of variation. This makes sense from the context of the previous assertion about hydrogen solution. If the solid solution side of the reaction is becoming more preferable, then the Hydride side must become even lower in energy in order for the reaction to proceed in the forwards direction. This is unlikely to be the case as the deformation of the hydride crystal structure away from the ideal lattice will only raise its energy, not lower it. In fact, the energy of precipitation only starts to drop significantly under substantial compression. This result is something that can be commented on further when analysis of the experimental counterpart to this investigation is completed.

The originators of the PFM suggest that the accumulation of defects around a crack tip may provide some of the impetus for the suggested model [16]. This study is not able to comment on such a hypothesis, but in the context of a purely elastic lattice, no support is found for the PFM.

Depending upon the model, varying amounts of compressive stress are required to induce precipitation, with the primary driver of this being the fact that H atoms become significantly less energetically favourable in solid solution when the compression is applied. However, the pressure-path of the model through the energy landscape does suggest some differences under high compressive stresses. In the Allen model, the energy of precipitation holds steady at around -0.17 eV. This is due to the fact that the Allen model is roughly parallel with the contour plots of the system. This observation leads to an interesting concept. As hydride precipitation occurs, a small positive volume change is induced in the lattice, which leads to a compressive stress occurring around the hydride. This could in-turn have an impact on the energy of precipitation, possibly driving further hydride formation (as the plots above suggest compression favours precipitation), resulting in a feedback effect, limited only by the availability of H atoms. However, if the system behaves in a similar fashion to the Allen model, the change in precipitation energy levels off after a certain amount of stress has been generated. This possibly suggests that the issues of hydrides generating compressive stress and compressive stress favouring hydride precipitation may balance out at a certain stress. There is even a small increase in the energy of precipitation between 10 and 15 GPa, suggesting that at this point, the generation of more precipitate induced

stress would be unfavourable.

Of course, the magnitude of energy change here is very small, meaning it probably isn't significant. However, it would not take a large change in the stress relationship model to cause this change to become more important. It should be noted as well that a number of simplifications made in this model would also have an effect. Perhaps the two biggest would be the fact that a real sample would have both tetrahedral and octahedral occupancy (here, either/or is considered) and there would also be significant interface stresses between the hydride and the Zr, as evidenced by dislocation loops found surrounding hydrides [90]. Overall, the effects found here only examine one component of the full impact, although it is a large enough component to still be considered significant.

7.5 Conclusions

This investigation has lead to the following conclusions;

- Hydrides are stiffer than Zr metal in terms of their bulk modulus, however the increase in stiffness with pressure is similar for hydrides and Zr.
- H Atoms prefer tetrahedral sites under tension, but will switch to octahedral sites under compression.
- The increase in solution energy with tension agrees well with the diffusion first model.
- There is an un-explained discontinuity in solution energies under compression at around -4 GPa. This does not correlate with any sudden jumps in site volume and may be indicative of a change in bonding.
- H atoms act to contract the c-axis as more are sequestered in a Zr Lattice. They also act to stiffen the lattice in the same direction.
- The δ -Hydride with a 1.66 stoichiometry is suggested to show not only isotropy in its lattice parameters, but also in its response to pressure. No evidence is found for an epsilon hydride with $c/a > 1$.

- The precipitation energy increases with tension and decreases with compression. This does not lend support to the precipitation first model.

The end of this study concludes the results released in this thesis. Throughout this work, investigations have looked at the impact of alloying agents, hydride structure, H concentration, temperature, and pressure on the impact of hydriding in Zr alloys. The next chapter gives a brief summary of some of the key findings of this work, details some of the limitations or areas for improvement of this work and suggests areas that would be interesting to investigate with more time and resources.

Chapter 8

Conclusions and Future Work

The results displayed in this thesis help elucidate some of the atomic scale behaviour which occurs in Zr alloys. The main areas covered have been a description of how alloying agents behave in Zr, and how H precipitates into hydrides under different conditions, based on concentration, temperature and pressure. So far, this work has formed a starting point for other individuals to continue the investigation of this system.

A brief summary will be given of the key conclusions reached in each results chapter. Following that, some of the limitations of the approaches used in this work will be discussed, along with some suggestions of how this work could be developed and expanded with more time and resources.

8.1 Conclusions

8.1.1 Alloying Additions

The work done in this chapter showed good agreement with broad experimental observations and DFT predictions. The solution energies of pure elements and of intermetallic phases made sense in the context of the binary phase diagrams of the different elements. Although other DFT investigations have placed alloying additions in solid solution, few considered the possibility of interstitial sites to the same degree that this investigation did. This provided strong confidence in the conclusion that Fe, Cr, V and Ni are interstitial solid solutions. The formation energies

in particular seemed of interest when determining SPP stability. Perhaps the most interesting aspect of this was the evidence that the Ni and Fe SPPs stabilise each other in the Zr-Rich type structure, even though the laves phase is more preferable. The impact of introducing vacancies provided evidence for mechanisms which may help in understanding SPP dissolution under irradiation. Whatever phenomena are responsible for this, such as ballistic displacement of SPP atoms, the large incorporation energies present the possibility of a dissolution mechanism where vacancies assist in the dissolution of SPPs.

8.1.2 Basic Hydride Modelling

Being able to effectively model hydrides is a prerequisite for much of the work in this study. Chapter 5 demonstrated that DFT has no issue with modelling these structures. The tetrahedral site was found to be more preferable site than the octahedral for solid solution, in accordance with other studies. Extending this investigation into novel territory, it was found that the small difference between these sites was not reversed with the addition of more hydrogen and that hydrides based on these octahedral sites remained universally less stable than their tetrahedral counterparts. Coupled with a study on H disorder, it was found that the most stable hydrides were the γ and ε phases, despite the δ hydride being the most commonly observed in reality. There is also evidence of H clusters being more favourable when the H atoms are sparsely distributed.

8.1.3 Hydride Thermodynamics

Phonon calculations provide a method to examine the temperature response of a material, despite being modelled under energy minimised conditions. As could reasonably be expected, strong evidence was found for increasing temperature driving the system towards solution. The concentration of H atoms proved critical in providing a thermodynamic impetus for precipitation. Furthermore, this gave evidence for a hitherto un-discussed repulsive effect between H atoms. It appears that H atoms prefer not to congregate, unless the concentration is high enough to force precipitation. The fact that concentration of H atoms was higher than experimentally determined suggests that other forces must be at work in order to locally concentrate H atoms. The

different thermodynamic values were investigated and it was found that enthalpies drive towards precipitation with increasing temperature, while entropies drive towards solution.

8.1.4 Hydrides and Pressure

The final component of this work looked at the effect of pressure on hydride precipitation. It appears that H atoms stiffen the Zr matrix, particularly in the c direction. It would appear that the δ -hydride exists at a position of isotropy in terms of lattice parameters and elastic response. Perhaps the most important result was the prediction of increasing chemical potential with increasing hydrostatic tensile stress. This matches the prediction of the DFM hypothesis of hydride precipitation and even has a similar coefficient in terms of the relationship between stress and change in chemical potential. Various models of the relationship between the stress in the solid solution and in the precipitate were examined and compared with the overall precipitation energy landscape. It was found that there was a general trend for the precipitation energy to become more positive under tension and negative under compression. This does not support the observations expected if the PFM hypothesis is correct.

8.2 Further Work

8.2.1 Extending Existing Investigations

The investigations carried out here have given some useful information and have provided a novel perspective on some aspects of the Zr-H system. However, there were still limitations involved, for example the fact that the Zr ω phase appeared more stable under energy minimised conditions than the α phase. Ideally these discrepancies would be removed by the application of a more rigorous electronic model. For example, if more time and computational resources were available, then some of the simulations could have been performed by using all-electron models, or a more physically rigorous exchange correlation function.

Some of the techniques developed later in this work could also have been applied to other areas of study. The techniques used to model disordered hydrides would be well suited to modelling disorder in mixed intermetallic phases. For example, the $\text{Zr}(\text{Cr,Fe})_2$ intermetallic

often has around 60% of the the alloying addition sites occupied by Fe atoms and the rest occupied by Cr. This means that the randomised structures could be used to create a number of different configurations with alloying addition ratios around this experimental value. The effect on formation energies could then be examined. The phonon calculations could also be applied to these intermetallics in order to gain an understanding on how their stability varies with temperature.

The investigation into pressure was forced to omit the effect of temperature as a computational saving. With more time or resources, it would have been interesting to run phonon calculations on some of the pressurised cells. With this, it may be possible to extend these calculations over the full range of operating conditions and examine any interdependence between pressure and temperature effects.

It would also be possible to combine both the alloying elements investigation and the study of hydrides. Given that some work has been done on inserting hydrogen into intermetallic phases, a reasonable idea would be to examine if hydrogen atoms experience any binding energy with alloying agents dissolved in a Zr lattice. It is already known that the region around an SPP will become increasingly rich in dissolved alloying additions as in-reactor time increases. Examining if hydrogen has a preference for occupying sites near alloying addition elements would help elucidate its behaviour in this region.

One other direct expansion of this would be the investigation of the kinetics of H in Zr. DFT can be used to investigate transitional pathways for H atom diffusion, using methods such as the Nudged Elastic Band technique. Perhaps one of the most salient features of metal-hydrogen systems is that the hydrogen tends to be extremely mobile. Thus, understanding the barriers to H atom migration would provide insight into a number of different aspects of this system, including the possibility of proving quantitative data for use in larger scale models. It would also be interesting to compare the barrier to H atom migration in a defect free Zr lattice with one containing alloying addition impurities.

8.2.2 Electronic structure calculations

One of the major advantages of DFT has not been used to great effect in this study. This is the ability of DFT to produce information with regards to the electronic structure of the simulated materials. Such information could potentially go a step further into developing a full understanding of how these materials behave. For example, some early investigations with VASP were able to produce electronic density profiles for the material. Furthermore, there is functionality to limit the displayed energy density to a particular energy level in relation to the Fermi-energy. As the bonding state of Zr-H bonds is predicted to exist at approximately -6.5 eV below the Fermi level it is effectively possible to view the charge density that is only responsible for the Zr-H bond. Preliminary investigations with vasp were able to produce this kind of plot, which is shown in Fig. 8.1.

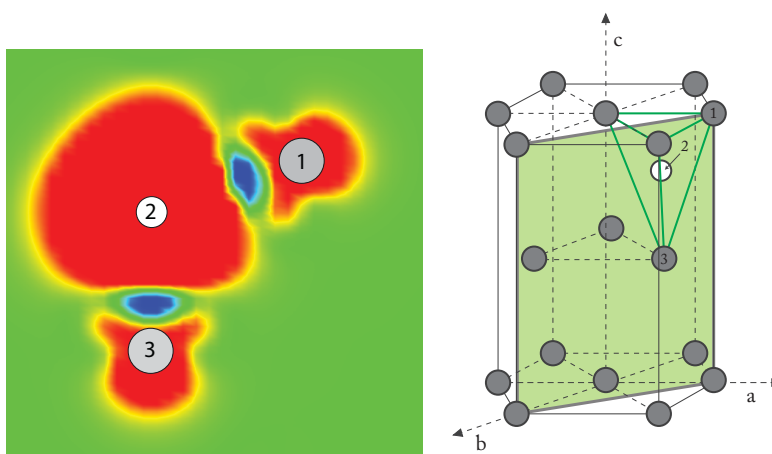


Figure 8.1: The electron density for the Zr-H bond is shown on the $(11\bar{2}0)$ plane. Red areas denote high electron density, green denotes the median density and blue denotes low.

However, it was ultimately difficult to extract quantitative data from such plots. It would have been preferable to investigate this avenue in more detail, however it was decided to stick with simulation techniques which had already yielded qualitatively reasonable results. It would have been particularly interesting to examine the electron density maps with respect to pressure,

as there is a possible change in bonding regime, as has been discussed in Chapter 8. This could also have been investigated with electronic density of states plots, particularly when they can be localised for individual atoms, or to show the DOS available in a particular s,p or d orbital. However, given the large amount of data already generated in these studies, it was decided to analyse the already acquired information, rather than try to run more simulations.

8.2.3 Potential Derivation

The investigations carried out so far have been limited by the chosen model of this system. Different models present different limitations, but also new opportunities for investigating different phenomena. One of the tools which could have been used to investigate this system is a set of empirical potentials describing H in Zr and hydrides. Some of these potentials do exist, for example the one detailed in reference [83] and more recently [81]. However the first of these displays notable inaccuracies and the provenance of the second is yet to be demonstrated. Both use the Embedded Atom Method style of potential

The Embedded Atom Method or EAM is a potential with some similarities to DFT methods. Specifically, an EAM potential adds a term that relates the energy of an atomic configuration to the electron density. Effectively an EAM potential decomposes the total potential energy of an atom into two terms - a pairwise term describing the repulsion of the atom from other atoms and a many body term describing the energy gained by embedding the atom in a given electron density. EAM potentials take the form:

$$E_{total} = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{i,j,i \neq j} V_{ij}(r_{ij}) \quad (8.1)$$

Where r_{ij} represents the distance between atoms i and j , V_{ij} represents the pairwise component of the function, F_i represents the “embedding” function and ρ_i is the electron density for atom i , given by the expression:

$$\rho_i = \sum_j \phi_{ij}(r_{ij}) \quad (8.2)$$

The form of this equation means that an EAM potential is composed of three different

functions: The embedding function(F_i), the pairwise function(V_{ij}) and the density function(ϕ_{ij}).

The pairwise function is simply a short range function to account for repulsion of the atoms at short distances. The embedding function is an attractive term that relates the energy of the atom to the electronic density. The premise of the embedding function is that for any given electron density, there is an energy associated with inserting an atom into it. Therefore, as long as there is an approximation of the electron density at distance r from an atom, the energy of inserting another atom at this distance can be approximated. In order for this to work accurately, the electron density must be summed for a large number of atoms in the system, meaning that the combination of the embedding function and the density function is effectively a many-bodied potential. However, as only a simple summation is required to compute the electron density and as the electron density can be specified in an easily read tabulated file, EAM potentials are computationally inexpensive. It is not uncommon to run EAM simulations containing many thousands of atoms with relatively modest computational resources. As a result, the generation of a EAM potential for the ZrH system would offer the opportunity to look at phenomena that have previously been difficult to examine.

Some work was initially carried out where a H potential was fitted to the MA07#3 potential [37]. However the preliminary results were not encouraging and presented situations which were considered to be extremely inaccurate (such as H atoms displacing Zr atoms off their lattice sites and becoming a substitutional solution). It was decided that although this method may possibly yield results in the long run, time would be more efficiently spend on perusing the existing DFT approach.

However, since this early attempt, fitting tools have been developed within the Atomistic Simulation Group which may be applicable to this system. Creating a new potential fitted to DFT parameters may be a more appropriate attempt than fitting a H potential to a pre-existing Zr potential. This could potentially be a long and difficult project, but a high quality Zr-H potential would offer an entirely new perspective on this system. Combined with DFT results this could present a more complete picture of the mechanisms present in this system.

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