Linköping Studies in Science and Technology
Dissertation No. 2171

Theoretical Studies of the Coupling Between Electronic, Vibrational, Configurational and Structural Effects in Metal Borides

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Linköping 2021

Cover images: Phonon dispersion of MgB_2 at ambient conditions. The colourful broadening represents the strength of the electron-phonon coupling. Taken from Figure 4 in **Paper III**.

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ISBN 978-91-7929-024-5

ISSN 0345-7524

Printed by LiU-Tryck 2021

Abstract

This thesis addresses theoretical studies of the coupling between electronic, vibrational, configurational and structural degrees of freedom in metal borides. The effect of external conditions of temperature, pressure and composition on the interplay between internal degrees of freedom is investigated. The importance of excitations and disorder of the above types is well-established and known to dictate key materials science concepts such as phase stability, mechanical and electronic properties. Their mutual coupling composes the next level in complexity in understanding what parameters are to be necessarily included in the theoretical modelling of the system. The main tool used for making such predictions herein is density functional theory. It allows us to capture said excitations and disorder, and give accurate results with reasonable computational efficiency.

Metal borides are chosen because of technologically interesting combination of both ceramic and metallic properties, like high hardness, melting point, fracture toughness and electrical conductivity, as well as previous reports of interesting fundamental physical phenomena, like the conventional superconductivity of MgB_2 and the apparent off-stoichiometry of AlB_2 . The theoretical approach is chosen because of its ability to controllably couple and decouple different degrees of freedom to study their combined or isolated effect on the desired materials property. The level of theoretical modeling can be adjusted to fit what is reasonable in terms of efficiency, and still well be used for predictions with quantitative or semi-quantitative accuracy.

The configurational aspect of phase stability of binary boron compounds has been believed to be trivial to understand as they most often can be constructed by stacking alternating layers of metal and boron atoms. However, a closer inspection of AlB_2 , the very name-giver of one of the most usual crystal structures within metal borides, shows a surprising existence of ambiguity regarding both its stable composition and the configuration of metal-site vacancies. Here theoretical

approaches are used to reveal the configurational thermodynamics of these vacancies, the origin of their stability and coupling to the electronic structure of the compound. Furthermore, we answer the question why ideal stoichiometric AlB_2 is unfavourable, why the vacancy stability window is so narrow, and how different arrangements of vacancies couple with the vibrational degree of freedom, including thermal expansion.

If a second metal species is introduced the configurational problem becomes more complex. The arrangement of atoms on the metal sublattice is dependent on the bonding chemistry between the metal atoms and temperature driven thermodynamic effects, like entropy and lattice dynamics. The presented work on $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ is an example of this, where mixing and clustering thermodynamics is considered to further investigate the potential for age-hardening of this ternary diboride. In it, the effect of lattice dynamics and configurational clustering on phase stability is discussed.

The discovery of MgB_2 being a superconductor in 2001 sparked many fruitful experimental and theoretical studies on the topic. It is generally agreed that MgB_2 is a two-gap superconductor which originate in the σ (2D character boron p_x and p_y) and π (3D character boron p_z) bands, respectively. Superconductivity in itself arises mainly from strong coupling between the E_{2g} phonon mode, corresponding to in-plane bond-stretching vibrations of boron atoms, and electrons on the sigma bands. In the work presented, we use the coupling to the global structural parameters and external pressure to compare different theoretical models, with and without explicit treatment of electron-phonon coupling, and their ability to predict the superconducting transition temperature T_c of distorted MgB_2 . Moreover, a way to experimentally realize such lattice distorted MgB_2 through clever nanostructure design is theoretically explored. Epitaxially growing an alternating out-of-plane ordered Mg/M diboride, with M atoms that naturally have clustering tendencies with respect to Mg, is proposed to being able to provide the necessary lattice distortions of both a - and c -parameters that can lead to an increase in T_c .

All of the beforementioned covered compounds (TiB_2 , AlB_2 , $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ and MgB_2) crystallize in the AlB_2 -type structure with alternating hexagonal and metal 2D layers, that is most common in the diboride family. However, metal borides can also crystallize with puckered boron layers, while preserving the flat hexagonal metal layers, as in the case for ReB_2 . It is known for its exceptionally high Vickers hardness that varies from 30.1 ± 1.30 to 48.0 ± 5.6 GPa depending on indentation load. While boron-rich transition metal borides often are considered as potential candidates for hard and incompressible materials, rhenium borides with boron content higher than ReB_2 have not been experimentally realized. Theoretical work has proposed that ReB_4 adopts the same crystal structure as superhard WB_4 . In the presented papers, we report the successful synthesis of two novel ReB_3 and ReB_4 phases at high pressure that remain stable when decompressed down to ambient conditions. First-principles calculations are employed to characterize the electronic, dynamic and thermodynamic stability properties of these phases. Fur-

thermore, novel complex modular Re_2B_5 and Re_3B_7 structures are synthesized and characterized by hexagonal boron networks interconnected by short B_2 dumbbells.

The aim of the in-depth investigations contained in this thesis, using state-of-the-art simulation techniques in collaborations with experimental work, is to further the understanding of how the coupling between electrons, vibrations, atomic configuration, disorder and external conditions influences the properties of materials and to share the results with the scientific community.

Populärvetenskaplig sammanfattning

Människan strävar ständigt mot att få en bättre tillvaro i samhället med färre bekymmer och problem. Ett steg i rätt riktning kan vara förbättringen av en befintlig produkt, eller upptäckten av ett naturligt fenomen som kan anpassas till ny användbar teknologi. Oavsett vilket sätt människan stegar framåt är det värdefullt att ha ett systematiskt ramverk att förlita sig på när ny kunskap inhämtas och kartläggs - den vetenskapliga metoden. På det sättet kan forskare strukturera och förmedla nya upptäckter kvalitativt och, tillsammans med matematik som gemensamt språk, även kvantitativt. Med matematiska modeller och den numeriska beräkningskapaciteten vi besitter i dagsläget, tack vare superdatorer, kan vi ta oss an ambitiösa frågeställningar som tidigare betraktats som omöjliga.

Inom materialvetenskap arbetar forskare med, som namnet antyder, att förstå sig på egenskaper i material. Det kan handla om hårdhet, smälttemperatur, termisk och elektrisk ledningsförmåga, magnetism o.s.v. Forskningsinsatserna är vanligtvis antingen experimentella eller teoretiska, men slås ofta ihop där expertis från båda hållen arbetar kollaborativt. Detta ömsesidiga samspel är vad som lägger grunden för utveckling, oavsett forskningsområde.

I denna avhandling återspeglas båda ovannämnda typer av tillvägagångssätt i de inkluderade manuskripten. Täthetsfunktionalteori används här som primärt beräkningsverktyg. Det tillåter oss att, för varje externa randvillkor såsom tryck, temperatur och kemisk komposition, ta fram systemets grundtillstånd. Med detta menas det mest fördelaktiga sättet att arrangera atomerna på, med optimala avstånd till grannatomer, så att systemet är så stabilt som möjligt.

För materialsystemet $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$, där x anger beståndsandelen av aluminium, använder vi olika metoder inom täthetsfunktionalteoriens ramar för att undersöka huruvida atomiska vibrationer och olika sätt att arrangera titan och aluminium påverkar fasstabiliteten. I detta material sitter atomerna i en hexagonal kristallin

struktur, i ett arrangemang som ofta kallas för AlB_2 -typen, som namngetts efter just aluminiumdiborid.

Det intressanta med AlB_2 är att materialet själv inte har exakt samma struktur och stökiometri som den strukturklass av material det själv namnger. Många studier har nämligen kommit fram till att AlB_2 har intrinsiska metallvakanser. Däremot har det inte retts ut huruvida vakanserna är stabila inom ett visst koncentrationsintervall och inte heller om de föredrar att sitta på ett ordnat eller oordnat sätt.

Det upptäcktes att MgB_2 , som också är av AlB_2 -typen, övergår från ett vanligt ledande tillstånd till att bli supraledande vid temperaturer under 39 K, alltså ungefär -234°C . Supraledande tillståndet drivs till stor del av att elektroner kopplar till atomiska vibrationer inom lagren av bor i MgB_2 . I vår studie undersöker vi om det går att höja övergångstemperaturen, så att MgB_2 blir supraledande över 39 K, genom att trycka och dra i hela den kristallina strukturen.

ReB_2 är känt för att vara ett väldigt inkompressibelt material med en hårdhet som mätts upp till över 40 GPa på Vickersskalan, och klassas därmed till och med som superhårt. Däremot har ingen lyckats växa rheniumborider med mer bor än i ReB_2 . Teoretiska studier har förutspått att ReB_4 bör anta samma kristallina struktur som superhårda WB_4 . I vår studie visar vi hur man kan lyckas växa nya ReB_3 och ReB_4 vid höga tryck, och som bibehåller dynamisk stabilitet även vid atmosfäriskt tryck. Vi hittar också nya modulära Re_2B_5 och Re_3B_7 faser som kan beskrivas utifrån hexagonala nätverk av bor som kopplas samman med hjälp av par av bor, B_2 , vars utseende liknar hantlar.

Preface

This thesis is the result of my doctoral studies that started in the Thin Film Physics Division in Dec 2016, and that ends in the Theoretical Physics Division, at the Department of Physics, Chemistry, and Biology at Linköping University in Oct 2021.

The research was made possible by financial support from the Knut and Alice Wallenberg (KAW) Foundation, through Project grant number KAW 2015.0043, the Swedish Research Council (VR) through International Career Grant No. 2014-6336 and Grant No. 2019-05403, from Marie Skłodowska Curie Actions, Cofund, Project INCA 600398, and from the Knut and Alice Wallenberg Foundation (Wallenberg Scholar Grant No. KAW-2018.0194), as well as support from the Swedish Foundation for Strategic Research through the Future Research Leaders 6 program, FFL 15-0290. Support from the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFOMatLiU No. 2009 00971) is also greatly acknowledged.

All calculations were performed using supercomputer resources provided by the Swedish National Infrastructure for Computing (SNIC) at the National Supercomputer Centre (NSC).

Acknowledgements

I want to start off by thanking my main supervisor, Björn Alling, for trusting in me and giving me the opportunity to chase my life-long dream of becoming a scientist. These five years felt oh-so short, but you managed to teach me a lot about physics and materials science, enough so that I realize just how little I know. Your guidance, encouragement and feedback has been invaluable. I couldn't have done this without you. I'm in your debt.

To my co-supervisor Johanna Rosen, thank you for sharing your expertise and enthusiasm, and for being my link to the experimental world.

To Annop Ektarawong, I'm not sure if I should apologise or thank you for all the countless times you allowed me to interrupt you in your work to discuss and ask for advice. You have remained a constant throughout my studies.

Thank you Magnus Johansson for sparking my interest in theoretical physics, it was a pleasure to do my bachelor's diploma project under your wing.

Thank you Irina Yakimenko, I'm glad I was fortunate enough to attend all of your courses as both undergraduate and graduate student. I hope that you one day manage to put yourself in a superposition between the office and the lecture hall, as I want to remember you once wished for. A shared thanks goes to you and Karl-Fredrik Berggren (may he rest in peace) for an interesting master's diploma project.

To Elena Bykova and Leonid Dubrovinsky, thank you for introducing me to the exciting world of high-pressure physics and for such fruitful projects.

Thank you, in no special order, Davide, Marian, Florian, Boburjon, Ferenc, Amanda

and Luis for being part of fantastic research unit. To all in the theoretical physics division, thank you for your input and feedback throughout the years. My respect goes to Igor Abrikosov, I don't know how you manage to keep the division so tightly-knit and productive.

To the most important people in my life, my family, thank you for always believing in me, always supporting me in any and all ways, and just for being an eternal safe haven. The world is filled with many physical constants, but my only true constant in life is you, my family. Special thanks goes to Ruben for being the best bonkis, and to Blue for being a cuddly princess.

Finally, the deepest thanks and love goes to Linh, my sunshine, my only sunshine. Thank you for being the biggest supporter and cheering me on in everything I do.

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CHAPTER 1

Introduction

This thesis is the result of theoretical efforts in investigating coupling between internal degrees of freedom in materials and external conditions. Coupling on the atomistic level can have effects on properties observable to experimental techniques. The results presented in here include examples of purely theoretical predictions, and also collaborations with experiments where the combined efforts manage to bring forward new understanding of fundamental material properties. In order to predict properties tangible to the naked eye, on the macroscopic level, one must understand what is going on quantum-mechanically on the sub-microscopic level. The great task is, however, to find suitable approximations for obtaining numerical solutions to the fundamental equations, like the Schrödinger equation. Even for small systems with a handful number of electrons, the nature of many-body interactions makes it impossible to solve the equations by pen-and-paper. Analytical solutions are only possible in the most idealised cases, like single-electron hydrogen-like systems.

1.1 First-principles calculations

The calculations carried out in this thesis are based on a methodological framework that is parameter-free, and offers quantitative predictions of atomic scale properties. There are no assumptions made about the system of interest and no prior knowledge is needed. Everything is calculated *ab initio*, from first-principles. The modelling is a bottom up approach, where materials are constructed step-by-step. The focus here is on condensed matter, or more specifically, periodic crystalline solid solutions and compounds. The crystal lattice is constructed from a set of discrete points in space and is occupied by individual atoms. In principle, the knowledge of the exact present elements is not needed, but only their atomic

number Z and the number of electrons n , which fuels the system with electrostatic and quantum mechanical interactions. With the introduction of *density functional theory*, the workhorse of this thesis, the focus is shifted from the problematic many-body wavefunction to the electron density instead. It offers great accuracy at a relatively low computational cost. The electrostatic interactions are exact and all quantum effects are treated in the approximative so-called exchange-correlation functional. As such, the performance of this theory is governed by the accuracy of this functional, for which development of better approximations is an ongoing research field of its own. The study of material properties is not restricted to the case of atoms being static in their ideal positions. Indeed, there are a plethora of degrees of freedom that may couple between themselves and to external conditions.

1.2 Coupling between degrees of freedom

In this thesis, coupling between electronic, vibrational, configurational and structural degrees of freedom is addressed within the framework of density functional theory. How these respond to varying external conditions of temperature, pressure and composition is investigated. For each considered material system, it is not known *a priori* what degrees of freedom are important and less so if there is a mutual coupling between them. Generally speaking, on the timescale of physical processes on the atomic level, the kinetics of electrons can often for sake of computational efficiency be separable from that of the nuclei. It is on the nuclear timescale that thermodynamic processes happen, such as vibrations, diffusion-driven phase transitions, heat transport, and so on. For some systems, the approximation of separating these internal degrees of freedom loses its validity. Superconductors are good examples of this, as for them electron-phonon interactions are crucial for the description of the materials properties [1]. Although magnetism is not covered in this thesis, the importance of vibrations for its proper description at elevated temperature is known [2]. Thus, it is highly motivated to critically test the separability of the internal degrees of freedom.

In detail, **Paper I** investigates the phase stability of $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ and its coupling to vibrational and configurational degrees of freedom as function of temperature and composition. **Paper II** is on the electronic properties, phase stability and thermal expansion in metal deficient $\text{Al}_{1-\delta}\text{B}_2$, and how they depend on the temperature- and composition-dependent configuration of metal vacancies. **Paper III** investigates electron-phonon-structural coupling in MgB_2 , i.e. how hydrostatic pressure and anisotropic stress and strain couples to electron-phonon interactions and its critical transition temperature from regular conductor to superconductor. The calculations performed in **Papers IV** and **V** are on the novel rhenium boride phases ReB_3 and ReB_4 (**Paper IV**), and Re_3B_7 and Re_2B_5 (**Paper V**). Common to both papers is the characterization of electronic, mechanical and structural properties, and how thermodynamic stability differs as function of composition and pressure.

1.3 Metal Borides

The boride family of materials is compositionally and structurally diverse, and they have been synthesized in both bulk and thin film forms. Boron is a metalloid element whose atoms preferably bond with less electronegative elements. This thesis focuses on boron-rich metal borides, where the metal atoms donate electrons to the boron. In these compounds there are strong covalent and ionic M-B, covalent B-B and metallic M-M bonds. One structure type commonly adopted by metal borides is the AlB_2 -type, as seen in Fig. 1.1. It is a hexagonal crystal structure belonging to space group $P6/mmm$ where metal M atoms and B atoms occupy different sublattices, and are arranged in alternating and flat hexagonal layers. Due to the electron donation from M to B , the boron layers can become isoelectronic to graphene. Related structure types are seen in ReB_2 , where instead of being flat, the boron layers are puckered in a "chair" configuration [3, 4], and in RuB_2 and OsB_2 , where boron layers are puckered in a "boat" configuration [4].

Figure 1.1: AlB_2 -type (space group $P6/mmm$, No. 191) metal diboride MB_2 , consisting of alternating and flat metal and boron hexagonal layers. Visualization made in VESTA [5].

The advent of thin film synthesis by physical vapour deposition (PVD) [6] techniques, allowed for deposition at lower temperatures than in chemical vapour deposition (CVD) [7] techniques. The lower deposition temperature in PVD allows for synthesis in conditions that are far from thermodynamic equilibrium, with diffusion-driven decomposition being hindered, meaning that growth of metastable compounds and alloys like $Ti_{1-x}Al_xB_2$ in **Paper I** is made possible [8–11]. Thermodynamics of this system dictates that Ti and Al do not want to sit next to each other, and that they rather would form clusters with atoms of the same kind [10, 11]. Due to the low deposition temperature and the stochastic nature of the deposition technique, disordered solid solutions of metastable $Ti_{1-x}Al_xB_2$ can be realized. This calls for detailed yet effective and broad theoretical studies able to scan for boride alloys with desired properties and known thermodynamic driving forces, e.g. for possible age-hardening.

Metal borides as a family is known to possess technologically interesting combination of both ceramic and metallic properties. These properties include high hardness, melting point, fracture toughness and electrical conductivity. Notable examples include the prospect of using metastable $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ as candidate for hard protective coatings on cutting tools [10, 11] (studied in **Paper I**) and MgB_2 having the highest transition temperature ($T_c = 39$ K [12, 13]) among all binary superconductors (studied in **Paper III**). It was predicted that combining boron with some transition metals (Re, Os, and Ir) would form superhard materials [14]. It was then confirmed that ReB_2 has exceptionally high Vickers hardness [3], although its claim of superhardness was first met with criticism [15]. The structures and hardness of related compounds ReB_X ($X = 2-7$) is studied in **Paper IV**, and Re_3B_7 and Re_2B_5 in **Paper V**. Other notable examples are the high melting points of binary HfB_2 (3650 K), ZrB_2 (3520 K), TiB_2 (3470 K), TaB_2 (3370 K) and NbB_2 (3270 K) [16]. As a last example of remarkable properties exhibited by metal borides is the permanent magnetism in $\text{Nd}_2\text{Fe}_{14}\text{B}$ [17], where the boron content is low but still critical to realize a tetragonal crystal structure from which the excellent magnetic properties are derived [18].

Moreover, the metal borides are interesting candidates for topical studies on lattice dynamics, as they offer an interesting mix of heavy metal and light boron atoms, where ^{10}B vs ^{11}B can be used to study isotope effects. Boron atoms tend to assume spectator role in the mixing of metals in ternary $\text{M}^1_{1-x}\text{M}^2_x\text{B}_2$ alloys, effectively making them pseudobinary. This means studying configurational effects, like mixing and clustering, and capturing short-range order effects, is less cumbersome from a modelling point of view, yet allowing for possible configurational-vibrational effects to appear.

1.4 Objectives

The objective of this thesis is to map out, for a selected group of metal borides, the importance of electronic, vibrational, configurational and structural degrees of freedom, their disorder and coupling thereof, and how their interplay is affected by external conditions of temperature, pressure and composition. The step-wise plan is to:

For each system, find a theoretical model that accurately describes phase stability and material properties of interest.

For each theoretical model, investigate what internal degrees of freedom need to be included, if they favour disorder, and if there exist any distinct coupling between them.

For all essential internal degrees of freedom, understand how the ground state and excitations are affected by external conditions and their importance to the predictions of phase stability, mechanical and electronic properties.

1.5 Outline

The layout of this thesis is as follows. First, a rigorous description of all computational models are given. It begins with the introduction to electronic structure theory, before moving into the details and practicalities of density functional theory. Then, a discussion of modelling of disorder and order in alloys is given. After that, the theory of lattice dynamics is laid out with different methods for obtaining force constant matrices, for noninteracting phonons and in the picture of electron-phonon interactions. The modelling chapter is finished with discussions on thermodynamic stability and elastic properties. Thereafter, a chapter on the summary of the results is given. The thesis ends with conclusions, an outlook on future work, and the list of included publications.

CHAPTER 2

Computational Methods

This chapter introduces the theoretical background to and the model approach itself, density functional theory, with the hopes of giving the Reader some insight into its conceptual basis. It will be assumed that the Reader has some familiarity with quantum mechanics. My intention is to write it in deep enough detail, to provide a broad overview, but not in a lecturing manner. For further reading I recommend the book of Martin on electronic structure, basic theory and practical methods [19]. The presentation of the fundamental theory and its equation to come follows the book. Density functional theory is based on *ab initio* or *from first principles* calculations. This means there is no empirical modelling that includes fitting to experimental data, and as few assumptions as possible are made. The theory is exclusively based on the constituents of the elements, their electrostatic interactions, and the fundamental laws of quantum mechanics. I will introduce how density functional theory can be applied to derive physical properties like phonon dispersions, mixing and clustering thermodynamics, high-pressure phase stability and superconducting transition temperatures.

2.1 Background to electronic structure theory

The quest to unlock a deeper understanding of condensed matter and its properties, be it electrical, magnetic, mechanical or optical, inevitably brings you to exploring the electronic structure. As physicists, we tackle complicated problems and even more intriguing questions. In order to appreciate the beauty of the big picture, it is often instructive to divide it into smaller and more manageable pieces that, upon being individually understood and then put back together, do not contort what the sum of all pieces were originally meant to represent. What is "it" here? As a matter of fact, letting "it" be the *matter*, can later on lead to a lot of fact

about matter. A big cornerstone of this thesis is the dissection of the fundamental constituents of matter, electrons and nuclei. Performing quantitative calculations that give insight into fundamental properties of condensed matter means, for all practical purposes, solving fundamental equations for electrons and nuclei, and de facto exploring the electronic structure.

To begin, we need an operator that governs the fundamental equations that describe our system of n electrons and N nuclei. Thus, a natural starting point is the Hamiltonian,

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2 - \sum_{I=1}^N \frac{\hbar^2}{2M_I} \nabla_I^2 \\ &+ \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} - \frac{1}{4\pi\epsilon_0} \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} \\ &= \hat{T}_{\mathbf{r}} + \hat{T}_{\mathbf{R}} + \hat{V}_{\mathbf{r}} + \hat{V}_{\mathbf{R}} + \hat{V}_{\mathbf{r},\mathbf{R}},\end{aligned}\tag{2.1}$$

where electrons (charge $-e$ and mass m_e) are denoted by lower-case characters and nuclei (charge $+Z_I e$ and mass M_I at site I) denoted by upper-case characters. The first two terms represents the kinetic energy operator of the electrons and nuclei, respectively. The last three are potential energy terms arising from Coulomb interaction between charged particles, being electron-electron, nucleus-nucleus and mixed electron-nucleus, respectively. The factor $\frac{1}{2}$ in terms three and four takes care of double-counting. All interactions herein are solely electrostatic in their nature.

Letting this Hamiltonian operate on the state of our system, described by the wave function $\tilde{\Psi}$, allows us to set up the non-relativistic time-dependent Schrödinger equation [20]

$$i\hbar \frac{\partial}{\partial t} \tilde{\Psi} = \hat{H} \tilde{\Psi},\tag{2.2}$$

whose solution describes the evolution of the system. The wave function

$$\tilde{\Psi} = \tilde{\Psi}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, \sigma_1, \sigma_2, \dots, \sigma_n, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, t)\tag{2.3}$$

is dependent on the positions $\mathbf{r}_i$ and spin σ_i of the electrons, positions $\mathbf{R}_I$ of the nuclei (disregarding nuclear spins), and time. Note, to account for relativistic effects one has to turn to the Dirac equation [21] or an approximation to it. This is most important for solids containing atoms with large atomic number Z . Solving Eq. 2.2 at this stage is a complex many-body problem with coupled particles that involves solving a multi-dimensional partial differential equation, which is a challenging task not feasible for modern day computational power. Even by disregarding the electronic spins, the wave function has $3n \times 3N$ degrees of freedom. In what follows, the journey to alleviating the complexity of the many-body problem into something more manageable begins, a journey consisting of a chain

of approximations. When there is no explicit time-dependence in any of the terms in the Hamiltonian, Eq. 2.2 can readily be separated into temporal and spatial parts, with the latter forming the time-independent Schrödinger equation

$$\hat{H}\Psi = E\Psi. \quad (2.4)$$

In the light of the adiabatic or Born-Oppenheimer approximation [22], it is in many cases a legitimate approximation to decouple the movement of the electrons from the movement of the nuclei. The idea is based on the fact that, since nuclear mass is typically four orders of magnitude larger than that of electrons, the parameter $1/M_I$ in Eq. 2.1 can be considered small. It follows that the kinetics of electrons and nuclei adhere to different timescales, and from the point of view of the electrons the nuclei can be approximated to remain static in their positions. In this picture, the electronic states are dependent on the positions of the nuclei $\mathbf{R}_i$, but not their movement $d\mathbf{R}_i/dt$. Put conversely, in the adiabatic approximation, the motion of the nuclei is described by a purely nuclear equation for each electronic state. Thus, the total (spatial) wave function can most often, but not always, be decoupled into nuclear and electronic parts (assuming the spins σ_i are included in $\mathbf{r}_i$):

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) \\ = \phi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N). \end{aligned} \quad (2.5)$$

If we then focus on the electron wave function alone (that now depends only parametrically on the nuclear positions) and tidy up the Hamiltonian by adopting Hartree atomic units ($\hbar = m_e = e = 4\pi\epsilon_0 = 1$) it can be expressed as

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{int}} + E_{II}. \quad (2.6)$$

Here, $\hat{T}$ is the kinetic energy operator for the electrons

$$\hat{T} = \sum_i -\frac{1}{2} \nabla_i^2, \quad (2.7)$$

$\hat{V}_{\text{ext}}$ is the potential that the electrons feel in the presence of the nuclei,

$$\hat{V}_{\text{ext}} = \sum_{i,I} V_I(|\mathbf{r}_i - \mathbf{R}_I|) = - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}, \quad (2.8)$$

$\hat{V}_{\text{int}}$ is the electron-electron interaction,

$$\hat{V}_{\text{int}} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (2.9)$$

and E_{II} is the energy of interaction between nuclei. As implied by the adiabatic approximation, the effect of the nuclei is now included in the potential term said to act upon the electrons "externally". Note, $\hat{V}_{\text{ext}}$ is not exclusively reserved

for interactions from atomic cores, but can also include electric fields and magnetic fields entering as Zeeman terms. Therefore, the Hamiltonian in Eq. 2.6 is central to the electronic structure problem.

Furthermore, when dealing with condensed matter with long-range periodicity, like in crystals, the macroscopic lattice (system) can be fully characterized by its smallest building block, the unit cell, that together with the symmetry of the lattice contains the full structural information of the system. This reduces the spatial probing region immensely. To give some perspective, a quick calculations of the number of molecules in a drop of water (say, 1 milliliter) gives you a number comparable to the Avogadro number $\sim 6 \times 10^{23}$. Think then of the computational challenge of solving Eq. 2.4 for even a small sample of a bulk crystal. Meanwhile, the number of atoms in a unit cell is typically in the lower end of 1-100 (with electron count depending on constituting elements), and thus, taking advantage of periodicity is indeed a neat trick. Bloch's theorem [23] then states that the wave function, that in principle should span from $-\infty$ to $+\infty$ in all spatial degrees of freedom, can be replaced by one that is repeating periodically over distances in the order of one to a few nearest-neighbouring atomic distances, and can be expressed as

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}). \quad (2.10)$$

Here, n is a discrete number called the band index that separates non-degenerate wave functions with the same reciprocal vector $\mathbf{k}$. On the right hand side, the wave function is described by a plane wave part $e^{i\mathbf{k}\cdot\mathbf{r}}$ and the function $u_{n\mathbf{k}}(\mathbf{r})$ that shares periodicity with the crystal lattice. Each $\psi_{n\mathbf{k}}$ is unique up to a constant reciprocal lattice vector $\mathbf{K}$, and satisfies $\psi_{n\mathbf{k}} = \psi_{n\mathbf{k}+\mathbf{K}}$. As such, it is only necessary to sample the wave vector $\mathbf{k}$ -space inside the first Brillouin zone (BZ), or in fact, the further symmetry reduced *irreducible* BZ.

Even so, there is the problem of many-body interactions still present at this level of electronic structure theory. Consider a system of measly six electrons, and let's say that you have a $10 \times 10 \times 10$ cubic grid of sampling points. To even store the many-body wave function would demand 1 exabyte (10^{18} bytes) which, according to Wolfram Alpha, is roughly equivalent to the information content of all words ever spoken!

Let us shortly mention two, out of a plethora of available electronic structure methods, that can be used to approximate and render the Schrödinger equation more manageable for numerical calculations, by making assumptions of the n -electron wave function. Both are self-consistent methods, where numerical solutions are obtained iteratively. The first one is the Hartree method [24], which is based upon the following wave function ansatz

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \chi_1(\mathbf{r}_1)\chi_2(\mathbf{r}_2) \dots \chi_n(\mathbf{r}_n), \quad (2.11)$$

where it has been assumed that the electrons are independent from another, and

the electron-electron interaction is modelled as an interaction between single electrons and the mean-field Coloumb interaction arising from the $n-1$ other electrons. However, this fails to capture an essential feature demanded by a fermionic wave function - the Pauli exclusion principle, i. e. no two electrons are allowed to occupy the same state. That is, that the wave function has to be antisymmetric with respect to exchanging any two electron positions, i.e. $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \mathbf{r}_j, \dots, \mathbf{r}_n) = -\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_j, \mathbf{r}_i, \dots, \mathbf{r}_n)$. This requirement for the so-called *exchange* mechanism can be met by constructing the wave function out of, again, single-electron orbitals χ_i , but now by the help of a single Slater determinant

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_1(\mathbf{r}_1) & \chi_2(\mathbf{r}_1) & \cdots & \chi_n(\mathbf{r}_1) \\ \chi_1(\mathbf{r}_2) & \chi_2(\mathbf{r}_2) & \cdots & \chi_n(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{r}_n) & \chi_2(\mathbf{r}_n) & \cdots & \chi_n(\mathbf{r}_n) \end{vmatrix}. \quad (2.12)$$

This approach corresponds to the Hartree-Fock method [25, 26], where exchange is treated in an exact way. However, the caveat is that "real" electrons interact in a more complex way than what can be described by a mean-field approximation in combination with the Pauli principle, and as such Hartree-Fock misses out on important electron *correlation* - the influence that an electron has on all other present electrons.

In the nextcoming section, we will see a method, DFT, that takes a different approach than the Hartree and Hartree-Fock methods, by focusing on the electron density instead of the wave function. Formally as a theory DFT is exact and succeeds where Hartree-Fock fails, as it manages to capture both important exchange and correlation. The downside being that it requires knowledge of the so-called exchange-correlation functional, for which the correct expression is not known. Many investigative efforts are directed towards this dilemma, the building and improvement of such functionals. Therefore, the accuracy of DFT is directly dependent on the quality of the approximate density functionals employed.

2.2 Density functional theory

In this alternative approach we will see that it is valid to use the electron density as a basic variable, which can be derived from the spin-independent particle density operator $\hat{n}$ as follows

$$\begin{aligned} n(\mathbf{r}) &= \langle \psi | \hat{n} | \psi \rangle = \langle \psi | \sum_{i=1}^n \delta(\mathbf{r} - \mathbf{r}_i) | \psi \rangle \\ &= n \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_n |\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_n)|^2. \end{aligned} \quad (2.13)$$

Here, the density $n(\mathbf{r})$ is in fact a measure of the probability of finding any electron situated at $\mathbf{r}$, which may or may not be intuitively understood, at least classically, as the δ -function approaches infinity in $\mathbf{r}$ and dies out everywhere else.

The first attempts of using the electron density dates back to 1927 and the *independent* works of Llewellyn Thomas [27] and Enrico Fermi [28], and later with the extension of the theory incorporating electron exchange by Paul Dirac [29] in 1930. The so-called Thomas-Fermi model is a semi-classical approach, that combines the use of energy functionals (instead of quantum operators) with certain ideas from quantum mechanics like the electron density, that here is idealized as non-interacting electrons in a homogeneous gas. Numerical applications finds the modelling to be too approximative, especially for the kinetic energy (that is expressed as an explicit functional of the density), and the theory is deemed not practical for today's standard. Moreover, it neglects both exchange and correlation. Even with the addition of exchange in the Thomas-Fermi-Dirac model, the theory lacked in accuracy for most applications. However, Dirac's formulation of local approximation for exchange remains as a building block in today's development of approximative functionals.

Later on, in their 1964 paper, Pierre Hohenberg and Walter Kohn [30] legitimized the model of using electron density to derive properties of a system, as established by Thomas, Fermi and Dirac. This important work would become the heart of DFT, and can be neatly summarized by the two Hohenberg-Kohn theorems.

2.2.1 Hohenberg-Kohn theorems

Theorem 1: For any system of interacting particles in an external potential $\hat{V}_{\text{ext}}(\mathbf{r})$, the ground state particle density $n_0(\mathbf{r})$ uniquely determines $\hat{V}_{\text{ext}}(\mathbf{r})$ within an additive constant.

Corollary 1: Since the Hamiltonian is fully determined, within a constant shift of the energy, it follows that the many-body wavefunctions for all states are determined. Thus, all system properties are completely determined by $n_0(\mathbf{r})$ alone.

Theorem 2: Let $E[n]$ define a universal functional for the energy in terms of the density $n(\mathbf{r})$, valid for any external potential $\hat{V}_{\text{ext}}(\mathbf{r})$. For any particular $\hat{V}_{\text{ext}}(\mathbf{r})$, the exact ground state energy of the system is given by the global minimum of this functional, and the density $n(\mathbf{r})$ that minimizes the functional is the exact ground state density $n_0(\mathbf{r})$.

Corollary 2: The functional $E[n]$ alone is sufficient to determine the exact ground state energy and density.

The energy functional can be written as a sum of functionals, recalling the Hamiltonian Eq. 2.6

$$\begin{aligned} E_{HK}[n] &= T[n] + E_{\text{int}}[n] + \int n(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r} + E_{II} \\ &\equiv F[n] + \int n(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r} + E_{II}, \end{aligned} \tag{2.14}$$

where the right-hand-side has conveniently been divided into three parts. The first being $F[n]$, that combines the kinetic energy and the Coulomb interaction potential between the electrons, as well as the nucleus-nucleus interaction into a single functional. The second part being the Coulomb interaction that connects the electron density $n(\mathbf{r})$ to the external potential V_{ext} . The third part being the nucleus-nucleus interaction term E_{II} that, by virtue of the Born-Oppenheimer approximation, becomes an additive constant. As $F[n]$ does not contain V_{ext} , it is said to be a universal functional, i.e. system independent. Similar to the case of Thomas-Fermi-Dirac, its exact form is not known for a system of n interacting electrons. If $F[n]$ was known, one could readily minimize the total energy functional in Eq. 2.14 with respect to variations in the density $n(\mathbf{r})$, and obtain the exact ground state energy and density. However, the two Hohenberg-Kohn theorems do not give any guidance on *how* to actually calculate the ground state density $n_0(\mathbf{r})$. Therefore, this formalism on its own has little practical use.

2.2.2 Kohn-Sham equations

In the 1965 paper by Walter Kohn and Lu Jeu Sham [31], an important breakthrough for DFT was made. It would become instrumental for implementing the DFT into a practical computational method, as it prescribes a convenient calculation recipe. Their work shows that it is possible, without any loss of generality, to map the fully interacting system of n electrons onto a fictitious auxiliary system of n non-interacting *quasiparticles*, or Kohn-Sham particles, in an effective potential. Strictly speaking, these are not electrons, but "non-interacting electrons", i.e. fermions with the charge and mass of electrons but with no interactions among themselves. It is this type of particles that enter the Kohn-Sham equations that we will see below.

For the system of independent "non-interacting electrons", each described by the single-particle wave function ψ_i , moving in an effective potential $V_s(\mathbf{r})$ (s denoting single-particle), the Schrödinger-like *Kohn-Sham equation* simply is

$$\hat{H}_{KS}\psi_i(\mathbf{r}) = \left(-\frac{1}{2}\nabla_i^2 + V_s(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (2.15)$$

in Hartree atomic units. This equation is more convenient to solve, in contrast to that of the many-body problem. The Kohn-Sham particle density $n(\mathbf{r})$ of this system with non-interacting particles can be obtained from

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2. \quad (2.16)$$

The genius of Kohn and Sham was to demand from energy minimization of this auxiliary non-interacting system to lead to the same ground state energy and density as in the fully interacting system, i.e. $n_s(\mathbf{r}) \equiv n(\mathbf{r})$. Arriving in the same solution is ensured by defining the effective potential to be

$$\begin{aligned}
V_s(\mathbf{r}) &\equiv V_{int}(\mathbf{r}) + V_{ext}(\mathbf{r}) + E_{II} \\
&\equiv V_{Hartree}(\mathbf{r}) + V_{xc}(\mathbf{r}) + V_{ext}(\mathbf{r}) + E_{II},
\end{aligned} \tag{2.17}$$

where the complex electron-electron interaction potential has conveniently been divided into 1) the classical Hartree potential $V_{Hartree}(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$ describing the self-interacting potential of the density $n(\mathbf{r})$ treated as a classical charge density, and 2) the exchange-correlation potential that accounts for all quantum mechanical and complex many-body effects. The latter term is calculated from the exchange-correlation energy functional via $V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$, and is the only term that is "problematic". As lightly mentioned in the previous section 2.1, the correct expression for this functional is generally not known, making it the only term in the Kohn-Sham approach that needs to be approximated, and will be touched upon later.

The Kohn-Sham total energy functional is then given by

$$E_{KS}[n] = T_s[n] + E_{Hartree}[n] + E_{xc}[n] + \int n(\mathbf{r})V_{ext}(\mathbf{r})d\mathbf{r} + E_{II}, \tag{2.18}$$

where $T_s[n]$ is the kinetic energy functional of the N non-interacting particles, calculated from the single-particle wave function solutions

$$T_s[n] = -\frac{1}{2} \sum_{i=1}^N \langle \psi_i | \nabla_i^2 | \psi_i \rangle \tag{2.19}$$

and the Hartree energy functional is given by

$$E_{Hartree}[n] = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \tag{2.20}$$

and E_{II} is the energy from the interaction between all nuclei. It is only $T_s[n]$ that is explicitly expressed as a functional of the wave functions ψ_i , while all other terms are functionals of the density. The ground state energy E_0 is obtained from the value of the functional E_{KS} minimized over all possible ground state electronic densities, that by the virtue of the Kohn-Sham scheme is identical to the expectation value of the Hamiltonian $\hat{H}$ minimized over all many-body wave functions Ψ in the many-body picture, i.e.

$$E_0 = \min_n E_{KS}[n(\mathbf{r})] = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle \tag{2.21}$$

The advantage of Kohn-Sham DFT is the formally exact treatment of the kinetic energy of the non-interacting fermionic particles by the functional T_s , which includes almost all of the kinetic energy of the real system, and differ by less than 2% [32]. On the other hand, older density functional methods, like the Thomas-Fermi-Dirac models [27–29], offer more approximative expressions for the kinetic

energy, that underestimates the kinetic energy of atoms and molecules by the order of 10%.

It can be enlightening to compare the energy functional of Hohenberg-Kohn (Eq. 2.14) and Kohn-Sham (Eq. 2.18) in the following way

$$\begin{aligned}
 E_{HK}[n] &= E_{KS}[n] \\
 &\iff \\
 E_{xc}[n] &= (T[n] - T_s[n]) + (E_{\text{int}}[n] - E_{\text{Hartree}}[n]), \tag{2.22}
 \end{aligned}$$

where indeed $E_{xc}[n]$ must be a functional of the density, as all of the terms on the right-hand side are functionals. This tells us that the mysterious exchange-correlation is given by the difference in kinetic energy between the fully interacting electrons and the non-interacting Kohn-Sham particles and the extra "quantum stuff" from the difference in the Coulombic repulsion energy between the electrons treated quantum mechanically and classically. Of course, this insight does not aid in computational effort as there is no exact numerical expression for it.

2.2.3 Exchange-correlation functionals

In this section we will see different approaches for dealing with the problematic exchange-correlation energy functional $E_{xc}[n]$, the only unknown piece in the Kohn-Sham puzzle. Kohn and Sham reasoned that, since the Hartree term takes care of long-range effects, and the fact that solids often can be considered as close to the limit of the homogeneous electron gas, the remaining effects exchange and correlation effects can be reasonably approximated local, or at least nearly local, in character. To facilitate the understanding of how the exchange-correlation functional E_{xc} typically is approximated we can first express it in the form

$$E_{xc}[n] = \int n(\mathbf{r}) \epsilon_{xc}([n]; \mathbf{r}) d\mathbf{r}, \tag{2.23}$$

where $\epsilon_{xc}([n]; \mathbf{r})$ is the exchange-correlation energy per particle, at point $\mathbf{r}$ that depends only upon the density $n(\mathbf{r})$ at or in some neighbourhood of point $\mathbf{r}$. Expressing the functional in terms of ϵ_{xc} is formally no different from E_{xc} , but if the above expression is considered as the functional definition, the choice of ϵ_{xc} is not uniquely defined. For instance, you can pick any set of ϵ_{xc} that differ only by an additive function that integrates to zero when multiplied with the density, and they would all be "correct" as they all integrate to E_{xc} . Development of E_{xc} functionals often takes advantage of this fact and expands ϵ_{xc} in power series of the density's spatial variation, for example. There are many approximations to E_{xc} available, out of which two widely used will be briefly outlined below.

Local Density Approximation (LDA)

This is arguably the simplest, but yet effective form of approximation and was outlined already in the seminal paper of Kohn and Sham [31]. This functional

is based on the assumption that ϵ_{xc} is a *local* functional of the electron density, i.e. $\epsilon_{xc}[n; \mathbf{r}] = \epsilon_{xc}(n(\mathbf{r}))$. For a homogeneous electron gas, the symmetry of the system dictates a constant electron density $n(\mathbf{r}) = n^{\text{hom}}$. It then follows that the exchange-correlation energy per particle is constant in space and is readily expressed as $\epsilon_{xc}^{\text{hom}}(n^{\text{hom}})$. LDA is therefore constructed by, for each space-point $\mathbf{r}$, taking the local $n(\mathbf{r})$ of the real system and assuming that each other point in space has the exact same density and inserts it into the homogeneous exchange-correlation per particle function. As such, the exchange-correlation energy functional in this approximation is the following integral over all space

$$E_{xc}^{\text{LDA}}[n] = \int n(\mathbf{r}) \epsilon_{xc}^{\text{hom}}(n(\mathbf{r})) d\mathbf{r}. \quad (2.24)$$

The success of LDA for solids was not always given, but at once efficient computational power and code implementations were at hand, it was solidified by the first convincing DFT calculations by Moruzzi in late 1970's [33] and Yin in early 1980's [34]. LDA does well in predicting the lattice constant of many solids, albeit systematically underestimating them. As errors in exchange and correlation usually cancel to a large degree, and with the calculations coming at the cost of a Hartree calculation, LDA is still a respectable functional to this day.

Generalized Gradient Approximations (GGA)

This flavour of approximations takes the step beyond the local approximation, and incorporates functional dependence of the magnitude of the density gradient $|\nabla n|$, as well as the value n at each point. By involving also the semi-local character in the density, the idea is to improve the accuracy over LDA. The general idea of such gradient expansion approximation (GEA) was suggested in the original Kohn and Sham paper [31], but the initial formalism breaks down for the case of large gradients in real materials. When electron densities are not slowly varying GEA does not, in contrast to LDA, fulfill the electron hole sum rule $\int \hat{n}_{xc}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = -1$ and the non-positivity constraint for exchange $\hat{n}_x(\mathbf{r}, \mathbf{r}') \leq 0$. Loosely stated, an electron in the density has to induce an "electron hole" $\hat{n}_{xc}(\mathbf{r}, \mathbf{r}')$ that correctly repels other electrons. GGAs are constructed in a manner that corrects the problems of GEA. For instance, GEA can be modified to fulfill these constraints by introducing cutoff functions that remove the problematic hole properties, resulting in the GGA of Perdew, Burke and Wang [35].

In general, the improved GGA functionals take on the form

$$E_{xc}^{\text{GGA}}[n] = \int n(\mathbf{r}) \epsilon_{xc}^{\text{GGA}}(n(\mathbf{r}), \nabla n(\mathbf{r})) d\mathbf{r} \quad (2.25)$$

with dependence on the local density and its squared gradient $s^2 = |\nabla n(\mathbf{r})|^2$. Different forms of GGAs explore a multiplicative refinement factor $F(n, s)$ and its density gradient series expansion. Three widely used forms are Becke (B88) [36], Perdew and Wang (PW91) [37], and Perdew, Burke and Enzerhof (PBE96) [38]. The latter is used extensively throughout this thesis as the exchange-correlation functional of choice.

2.2.4 Pseudopotentials and basis sets

The electronic states of a solid can mainly be divided into tightly bound localized core states and non-localized valence states. Core states can be further divided into inner core and external core, or semi-core, states. In most cases related to chemical reactions, bonding and many properties, the core electrons assume spectator roles and be described in the frozen core approximation, where they are precalculated in an isolated atomic environment and are kept frozen. In some cases, high-lying semi-core states may interact with valence states and need to be explicitly included in the calculations. For the proper description of the bonding physics in solids, it is most important that the valence states that reach between atoms are correctly considered. Note, to decide whether or not to include semi-core states, it is best to compare results of calculations with and without semi-core states in the valence, as this varies from system to system. Furthermore, the strong interactions, due to a diverging potential, close to the core cause the wave function of core electrons to rapidly oscillate with many nodes close to the nuclei. Regardless of basis set chosen to represent the Kohn-Sham wave functions ψ_i , this feature is hard to accurately capture and typically would require you to include far more terms in the basis set expansion series, coming with greater computational cost, compared to if the wave function was smoother close to the core, at least for delocalized valence states.

Figure 2.1: Schematic illustration of the principles behind pseudopotentials.

One way to circumvent this problem is the use of pseudopotentials (PPs). As it is concluded that the valence states predominantly dictate the bonding physics between atoms in solids, the basic principle of the PP approach is to replace the cumulative effect of the nucleus and core states by a smooth PP. The idea of the PP is to still preserve the scattering properties of the valence electrons from the nucleus outside a certain cut-off radius, which was arguably first proposed by Hellmann [39] already in 1935. A schematic illustration of the augmentation principle behind PPs is presented in Fig. 2.1. The real potential denoted by V is shown by the blue dashed line, and the corresponding all-electron wave function (AEWF) is marked by ψ and shown by the rapidly oscillating black dashed line. The vertical dashed orange line represents the cut-off radius r_c . It is inside this *augmentation*

sphere that the smooth PP $\tilde{V}$, in blue, gives rise to the more computationally manageable pseudo wave function (PWF) $\tilde{\psi}$. Outside of the augmentation sphere, the behaviour of the PP and PWF must be the same as the real potentials and wave functions.

There is a wide array of available methods based on the PP principles that have been developed to solve the Kohn-Sham equations more efficiently. In chemistry, where it is more common to study molecular complexes, it is often convenient to choose basis sets that are constructed from atom-centered functions, usually expressed as linear combinations of products between spherical harmonics and Laguerre polynomials. However, as hinted earlier, this thesis deals with periodic potentials and crystal lattices in solids, subject to Bloch's theorem (Eq. 2.10), for which the natural choice is a plane wave basis. Thus, the Kohn-Sham wave functions can be expanded as

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega_{\text{BZ}}} \sum_{\mathbf{K}} c_{n\mathbf{k}}(\mathbf{K}) e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}, \quad (2.26)$$

where $c_{n\mathbf{k}}(\mathbf{K})$ is the plane wave expansion coefficient and Ω_{BZ} is the volume of the BZ. The plane waves that appear in the expansion can be represented, for periodic systems, as a discrete grid in $\mathbf{k}$ -space. In principle, an infinite number of plane waves are needed to probe the whole space. In practice, this sum must be truncated by an energy cut-off

$$\frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{K}|^2 < E_{\text{cut}}, \quad (2.27)$$

i.e. all plane waves with kinetic energy smaller than E_{cut} are included in the basis set. The explicit dependence on $\mathbf{k}$ implies that the basis set is different for each $\mathbf{k}$ -point, which in practice leads to fast convergence for e.g. energy-volume calculations. Due to the smoothness of the augmented PWF, a smaller number of plane waves are needed and thus the demand for high E_{cut} is greatly reduced.

For plane wave basis sets, there are many suggested PP methods. Two such popular ones are the norm-conserving pseudopotentials (NCPPs) and ultrasoft pseudopotentials (USPPs). NCPPs were designed by Hamann, Schlüter and Chiang [40] in 1979 and were further developed by Kleinman and Bylander [41] in 1982. See also Refs [42–44]. For this approach, other than the criteria that the PWF has to be identical to the AEF outside the augmentation sphere and the preservation of scattering behaviour, the norm of each PWF inside r_c has to be identical to the corresponding AEF. It is known that this method requires a large number of plane waves for transition metals. USPPs, proposed by Vanderbilt [45] in 1990, aid in overcoming this problem. They are constructed to be as soft as possible in the core regions so that their plane wave expansion converges rapidly. It is achieved by replacing the part around each core, with rapidly varying density, with a smooth and auxiliary function. This comes at the price of giving up both the norm conservation and orthonormality constraint of atomic orbitals.

However, the orthonormality is recovered by introducing a generalized overlap operator that depends on the ionic positions.

Throughout this thesis, I have mostly used a generalization of the PP approach, the so-called projector augmented-wave (PAW) method as proposed by Blöchl in 1994 [46]. It seeks a linear transformation $\hat{\mathcal{T}}$ that takes us from the PWF $\tilde{\psi}$ to the all-electron Kohn-Sham single particle wave function ψ

$$|\psi\rangle = \hat{\mathcal{T}} |\tilde{\psi}\rangle, \quad (2.28)$$

where the operator can be expressed as

$$\hat{\mathcal{T}} = 1 + \sum_a \sum_i (|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle) \langle \tilde{p}_i^a|. \quad (2.29)$$

Here, a is an atom index, and i indexes the partial waves used to expand both the all-electron and pseudo wave functions *inside* the atom-specific augmentation spheres, and $|\tilde{\phi}_i^a\rangle$ denotes the projector functions. These are precomputed and therefore makes for great transferability, such that you can have a library of pre-computed PPs for each element, to use in a variety of chemical environments. $|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle$ is the difference between partial all-electron (ϕ_i) and pseudo ($\tilde{\phi}$) wave functions. As mentioned above, the behaviour of both these wave functions must be the same outside the augmentation spheres, by design, and therefore these difference are zero there.

The strength of this operator, and PAW as a whole, is that the method allows for the reconstruction of the real AEFW at the end of the calculation, in contrast to the preceding PP methods. As such, the accuracy of PAW calculations are comparable to those more computationally heavy all-electron and full potential Kohn-Sham approaches.

2.2.5 Brillouin zone sampling

The most compact way of representing the full symmetry of the crystal lattice in reciprocal space is by the Wigner-Seitz cell of the reciprocal lattice, the (first) BZ. It is defined by the planes that are the perpendicular bisectors of the vectors from the origin to the reciprocal lattice points, such that it becomes the zone that contains all points closer to the origin than to any other reciprocal lattice point. By virtue of the periodicity imposed by the factor $e^{i\mathbf{k}\cdot\mathbf{r}}$ in Bloch's theorem in Eq. 2.10, $\mathbf{k}$ -points outside the BZ do not provide any new information. Many properties (e.g. density, total energy) are averaged over the volume of the BZ, meaning calculations often involve integration in $\mathbf{k}$ -space over the BZ. If the unit cell has point symmetries, they can be imposed and further reduce the number of $\mathbf{k}$ -points that need to be sampled, saving computational cost. This leads to the *irreducible* BZ (that can be unfolded to recover the full BZ). In practice, in the averaging of some lattice-periodic property $F(\mathbf{k})$, integration is replaced by summation

$$\frac{1}{\Omega_{\text{BZ}}} \int_{\text{BZ}} d\mathbf{k} F(\mathbf{k}) \rightarrow \frac{1}{N_k} \sum_{\mathbf{k}_i} w_i F(\mathbf{k}_i) \quad (2.30)$$

over a discrete set, or mesh, of N_k $\mathbf{k}$ -points with some weight w_i ($\sum_i w_i = 1$). There are different techniques for the BZ sampling, of which the Monkhorst-Pack scheme [47] probably is the most commonly used. It offers economic sampling choices with automatic grid generation. One should always test convergence w.r.t. $\mathbf{k}$ -points sampling for each system.

2.2.6 Self-consistent loop of Kohn-Sham equations

The method of finding the ground state density that minimizes the Kohn-Sham total energy functional E_{KS} , as in Eq. 2.21, is a numerical self-consistent process and is outlined in Fig. 2.2. It starts with an initial guess of the electron density $n_0(\mathbf{r})$, from which the effective potential $V_s(\mathbf{r})$ (Eq. 2.17) can be constructed. Then the Kohn-Sham equations (Eq. 2.15) are solved and from the occupied single-particle wave functions ψ_i a new electron density $\tilde{n}_{k+1}(\mathbf{r})$ is constructed. If the new and the old densities ($k = 0$ in the first iteration) are not within a tolerance δ of each other, the density has to be updated as a linear combination of the two. The mixing schemes of Broyden [48] and Pulay [49] are efficient. The updated density $n_{k+1}(\mathbf{r})$ is then used to construct a new effective potential $V_s(\mathbf{r})$, and the loop repeats itself until the electron density converges within the set tolerance. At this point self-consistency is reached and the ground state density is used to calculate the total energy E_0 and so on. There are many computational packages available that has this implemented. In this thesis, the vast majority of all calculations were performed using the efficient iterative schemes as implemented in the Vienna Ab initio Simulation Package (VASP) [50, 51].

Figure 2.2: Flowchart of the self-consistent loop for solving Kohn-Sham equations.

2.3 Modelling of substitutionally disordered alloys

This chapter will touch on different methodologies used to describe chemical environments and bonding physics of alloys in solid solutions. Condensed matter can broadly be divided into either pure elements, substitutional alloys, interstitial alloys, or a combination of the two alloy types. Substitutional alloys are those where some of the composing elements are exchanged for another atomic type of similar size, like in bronze (Cu-Sn), brass (Cu-Zn) and <24K gold (Au-Ag/Cu). The presence of a secondary element may or may not lead to changes in the structure. They can form ordered patterns often called compounds, or disordered alloys. Furthermore, the mixture can be homogeneous or heterogeneous. Interstitial alloys are formed typically with smaller nonmetal atoms e.g. H, B, C and N, sitting inbetween positions of the host lattice, like the carbon and nitrogen atoms in some steels (Fe-N-C). Compounds are often formed when small non-metals are reacting with metals, like the *binary* borides covered here. For *ternary* borides where more than one atomic type share the metal sublattice, they are better referred to as alloys instead of compounds. Due to combined metallic and ceramic properties of metal borides, i.e. high hardness, melting point, wear resistance etc., these types of alloys are often called ceramic alloys.

The focus here will be on *substitutional* alloys on the metal-sites of metal-boron compounds. When studying alloys one typically begins by considering an ideally mixed disordered solid solution at a given global composition. Imagine a periodic array of lattice sites, and that we occupy each site with one of two kinds of atom, say A and B . They are randomly distributed over the lattice sites in the sense that the probability to find an A atom, at any site, is equal to the concentration of A atoms in the alloy C_A , and thus the probability of finding a B atom is $C_B = 1 - C_A$. This structure is called a random alloy. However, in a real life situation, a binary alloy usually has some degree of short range order, but not the long range order seen in ordered intermetallic compounds. The probability of finding an A atom on a given site depends on the surrounding local environment. To add to the complexity, the underlying lattice sites may be locally distorted due to strain effects arising from having A and B atoms of different sizes and different A - A , A - B , B - B bond-strengths, adding positional disorder to the picture. Disorder destroys the spatial periodicity of atomic potentials in the crystal, meaning the Bloch's theorem in Eq. 2.10 in principle loses its validity. However, even with atomic displacements from the ideal lattice positions, relative to the underlying lattice due to local atomic relaxations and the stochastic decoration of the positions, the translational symmetry is still preserved *on average*. A supercell large enough to *self-average* extensive properties (e.g. molar total energy, enthalpy, heat capacity, etc.) can thus be used for modelling and reproduce the statistical properties of the real alloy. Below we will see some of the different available methods developed for calculating the electronic states in a random alloy. There are two general types of approaches - direct calculations on supercells and methods that average over disorder. The latter is treated first.

2.3.1 Coherent potential approximation

The formulation of the coherent potential approximation (CPA) was introduced by Soven in 1967 [52] for the electronic structure problem of substitutional disordered alloys and by Taylor [53] for phonons in random alloys, and was expressed in terms of multiple-scattering theory by Györffy [54]. See also the work of Abrikosov and Johansson [55]. The methodology treats the motion of an electron, that necessarily is aware that it is in an alloy as it propagates between scattering events. The general idea is to find the best effective (or coherent) potential $w(\epsilon, \mathbf{r})$ that can be placed on each and every site of the alloy lattice, such that the resulting periodic model will mimic the electronic properties of the actual alloy. The effective potential $w(\epsilon, \mathbf{r})$ is placed on every site except for the central site. The real potential function for the A component of the alloy, $v_A(\mathbf{r})$, is placed on that site. In the surrounding environment, an electron will adapt itself to the constructed periodic effective potential

$$V_{\text{CPA}}(\epsilon, \mathbf{r}) = \sum_n w(\epsilon, \mathbf{r} - \mathbf{R}_n), \quad (2.31)$$

and propagate freely through the system until it encounters the potential $v_A(\mathbf{r})$ at which time it will be scattered. Here, the sum is over all translational lattice vectors $\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$ with $\mathbf{a}_i$ and n_i denoting the basis vectors and any integer number, respectively. As such the problem is formally identical to the scattering of a single impurity in an otherwise perfect crystal. The averaging over sites in the CPA, in an effective average environment, must equate to the weighted average over sites A and B with respective concentrations C_A and C_B , each in the same average environment. Therefore, the complex nature of the CPA potential can favourably be treated in terms of Green's functions. A Green's function G describes propagation of a particle from one event to another [56, 57], e. g. $G(\epsilon, \mathbf{r}, \mathbf{r}')$ describes propagation of an independent particle from point $\mathbf{r}$ to $\mathbf{r}'$ at energy ϵ . In CPA, the Green's function for this model is constructed as $G^{\text{CPA}} = C_A G_A + (1 - C_A) G_B$, where G_A (G_B) is the Green's function of A (B) sitting in the effective medium. Although not used in this thesis, it is worthy to mention this method as one of the alternative approaches in modelling of random alloys.

2.3.2 Special quasirandom structure method

In an effort to go beyond the nonstructural and single-site approximation of averaging methods like CPA and the virtual crystal approximation (VCA) [58] (not discussed here), Zunger introduced a method for designing special quasirandom structures (SQS's) in 1990 [59]. With this approach, the important information associated with the local atomic configuration surrounding a site is preserved. This sets up the possibility for direct supercell calculations that incorporate structural relaxations and local environment effects accounted for.

With the realization that interactions between distant neighbours generally contribute less to the total energy than close neighbours, the SQS method constructs

supercells that closely reproduce the perfectly random alloy for the first few coordination shells around a given site. Letting $\xi^{(n)}$ denote the n -site correlation function ($n = 2$ being pairs, $n = 3$ triplets, and so on), the binary case of A and B atoms forming an alloy $A_{C_A}B_{1-C_A}$, gives the many-body correlations $\langle \xi^{(n)} \rangle = (C_A - C_B)^n = (2C_A - 1)^n$ for a perfectly random configuration. Thus, at $C_A = \frac{1}{2}$ the SQS method has as guiding principle to place A and B atoms in such a way that as many coordination shells as possible of $\xi^{(n)}$ vanish. If any of them deviate from zero, it reflects errors relative to the idealized case of an infinite perfectly random alloy.

Due to finite size limitations of the resulting supercell, it is difficult to ensure that more than the first few coordination shells will vanish. Therefore, in practice, it is important to check the convergence with respect the SQS size, such that this type of error is minimal. Zunger showed that, in comparison to other structural-based techniques at the time, the SQS's converges rapidly with respect to supercell size. No technique can perfectly model random alloys, but with the SQS method it is possible to come arbitrarily close, and as such it provides a solid starting point. If one desires, the scheme can be altered to deliberately include some short-range order, depending on the size of the supercell. The SQS approach is applied to create disordered solid solutions in **Papers I and II**.

2.3.3 Cluster expansion

The CPA and SQS methods describe the configurational energy of random alloys, and are applied to system-specific problems. There is a need for a mathematical foundation that holds true for any system and that can give quantitative predictions in any alloy problem. In real systems, where order and disorder isn't simply black and white, with varying local atomic environments, a theory that can treat any arbitrary atomic configuration is required. In 1984, Sanchez, Ducastelle and Gratias [60] had developed a general formalism for the description of configurational cluster functions in multicomponent systems. The mathematical framework describes the configurational part of the total energy for a given multicomponent alloy (consisting of atomic species $A, B, C, \dots$) in any arbitrary configuration. The description of key concepts will follow the review by Ruban and Abrikosov [61].

The starting point is to construct a statistical representation that describes atomic configuration on the crystal lattice. The general Sanchez-Ducastelle-Gratias formalism is for an N -component alloy, but for brevity we will consider here the binary $A_{C_A}B_{1-C_A}$ that is easier to follow. For this case, it is convenient to adopt the language of the Ising model and assign spin-like variables σ_i to enumerate the occupation of lattice site i , such that $\sigma_{i,A,B} = \pm 1$ depending on whether atom type A or B sits on it. If we now let N be the number of lattice sites, instead of denoting the number of alloy components, the total alloy configuration is uniquely defined by the set of N spin variables $\{\sigma_i\}$ that composes the N -dimensional occupation vector $\boldsymbol{\sigma} = \{\sigma_1, \sigma_2, \dots, \sigma_N\}$. The total configuration can be subdivided into clusters α , each containing n sites, that can be used to define basis functions $\Phi_\alpha^{(n)}(\boldsymbol{\sigma})$ that are unique to each cluster. These are constructed by taking the spin

product running over all sites i contained inside clusters α , i.e.

$$\Phi_{\alpha}^{(n)}(\boldsymbol{\sigma}) = \prod_{i \in \alpha} \sigma_i. \quad (2.32)$$

The basis functions form a complete and orthonormal set. Letting α and β be two different clusters within the same configuration $\boldsymbol{\sigma}$, one can define the inner product between the two corresponding basis functions as

$$\langle \Phi_{\alpha}^{(n)}(\boldsymbol{\sigma}), \Phi_{\beta}^{(n)}(\boldsymbol{\sigma}) \rangle = \frac{1}{2^N} \sum_{\boldsymbol{\sigma}} \Phi_{\alpha}^{(n)}(\boldsymbol{\sigma}) \Phi_{\beta}^{(n)}(\boldsymbol{\sigma}) = \delta_{\alpha, \beta}, \quad (2.33)$$

where the summation is over all configurations $\boldsymbol{\sigma}$, and the Kronecker delta function $\delta_{\alpha, \beta}$ neatly encapsulates orthonormality. If α and β specifies the same cluster, the inner product equals 1, but if they differ in just one lattice site, it equals 0. Due to these properties of the basis set, it is possible to expand any physical function $F(\boldsymbol{\sigma})$ that depends on the configuration $\boldsymbol{\sigma}$ as

$$F(\boldsymbol{\sigma}) = \sum_{\alpha} F_{\alpha}^{(n)} \Phi_{\alpha}^{(n)}(\boldsymbol{\sigma}), \quad (2.34)$$

where the summation is over all symmetrically inequivalent clusters in the crystal, and the expansion coefficients are given by the inner product

$$F_{\alpha}^{(n)} = \langle F(\boldsymbol{\sigma}), \Phi_{\alpha}^{(n)}(\boldsymbol{\sigma}) \rangle. \quad (2.35)$$

In the application of the cluster expansion (CE) method in this thesis, the quantity that is expanded is the configuration-dependent total energy of the alloy, for which the expansion coefficients are the so-called n -site effective cluster interactions (ECIs),

$$V_{\alpha}^{(n)} = \langle E_{\text{conf}}(\boldsymbol{\sigma}), \Phi_{\alpha}^{(n)}(\boldsymbol{\sigma}) \rangle. \quad (2.36)$$

Deriving the ECIs is not a simple task, and is a central objective in alloy theory. Given that these are known, the strength of this methodology is that then one can readily calculate the total energy of an alloy with *any* arbitrary configuration $\boldsymbol{\sigma}$, which is given by

$$E_{\text{conf}}(\boldsymbol{\sigma}) = \sum_{\alpha} V_{\alpha}^{(n)} m_{\alpha}^{(n)} \xi_{\alpha}^{(n)}(\boldsymbol{\sigma}), \quad (2.37)$$

where $\xi_{\alpha}^{(n)}(\boldsymbol{\sigma})$ is the n -site correlation function for the cluster α , determined as the average of the corresponding characteristic basis function $\xi_{\alpha}^{(n)}(\boldsymbol{\sigma}) = \langle \Phi_{\alpha}^{(n)}(\boldsymbol{\sigma}) \rangle$. Due to symmetry reasons, the clusters and their effective interactions can be degenerate with some multiplicity $m_{\alpha}^{(n)}$ and are accounted for by that factor. Looking at Eq. 2.37 it becomes apparent that only clusters with $V_{\alpha}^{(n)} \neq 0$ can contribute to the configurational energy of the alloy, and only the correlation functions of those clusters are important. The interpretation of $V_{\alpha}^{(n)}$ is not always trivial, but in general the pair ECIs are usually the strongest and their corresponding correlation

functions for a given sample can be measured in diffuse scattering experiments and given via the so-called Warren-Cowley short-range order parameters [61, 62].

Let us for a moment consider, for instance, a two-dimensional square lattice with equiatomic concentration of A and B atoms. Then the $n = 2$ (pair) correlation functions of the first coordination shell, or nearest neighbours, can be trivially worked out for any configuration. Imagine that all A and B atoms are arranged like a chessboard, with each A -atom being surrounded by B -atoms, and vice versa. Then the nearest neighbour pair correlation function, now for the sake of argument given by coordinates (x, y) , becomes $\sigma_{(x,y)} \times (\sigma_{(x+1,y)} + \sigma_{(x,y+1)} + \sigma_{(x-1,y)} + \sigma_{(x,y-1)})/4 = -1$. If we instead segregate the A and B atoms of system with one half of pure A and one half of pure B , the same correlation function takes on the value approaching 1 as each atom is surrounded by its own kind, except for a small fraction of interface atoms. If the border between the A and B regions forms a straight line along either $\hat{x}$ or $\hat{y}$, the value for the interface atoms is 0.5. This is just a mental exercise, but it gives some general pointers. $\xi_\alpha^{(n)}(\sigma)$ of any binary alloy with coherent lattice will, on average, lean towards -1 if the two atomic types tend to mix, and lean towards 1 if they segregate and form clusters. In the case of the random alloy that lacks correlation in the atomic ordering, $\xi_\alpha^{(n)}(\sigma)$ will be zero.

The ECIs can be used to construct a configurational Hamiltonian that can govern the configurational energetics of a binary alloy for statistical mechanics simulations, like in the case of Monte Carlo (MC) simulations. The so-called generalized Ising-Hamiltonian is defined as

$$\begin{aligned} \hat{H}_{\text{conf}} = & V_0 + \frac{1}{2} \sum_p V_p^{(2)} \sum_{i,j \in p} \sigma_i \sigma_j \\ & + \frac{1}{3} \sum_t V_t^{(3)} \sum_{i,j,k \in t} \sigma_i \sigma_j \sigma_k \\ & + \frac{1}{4} \sum_q V_q^{(4)} \sum_{i,j,k,l \in q} \sigma_i \sigma_j \sigma_k \sigma_l + \dots, \end{aligned} \quad (2.38)$$

where V_0 is the ECI an empty cluster dependent on the volume and concentration alone, and the consecutive terms are summations over all pairs p , triplets t , quadruplets q , and so on. The formalism is complete in the limit that *all* n -site clusters are included in the expansion of the total energy, or any other property. It means that one would need to include even a cluster that contains all N atoms of the entire crystal. For practical reasons, it is not feasible to include such large clusters, and the sum has to be truncated after some $V_\alpha^{(n')}$. Although it comes out of necessity, it in fact turns out to be appropriate, as $V_\alpha^{(n')}$ tends to decrease as function of the number of sites n and as function of the longest pair-distance in the clusters. Moreover, the problem of obtaining the unknown ECIs remains. One widely used method for determining them is presented below.

2.3.4 Connolly-Williams method

As the $V_\alpha^{(n)}$ are not known *a priori*, there is a need for a method that can aid in this. The Connolly-Williams or the structure inversion method [63] is based on the assumption that Eq. 2.37 can be inverted. If a large set of predefined ordered structures (or configurations) $\{\sigma\}$ is generated, the total energies can be determined by DFT calculations. Working out the average correlation functions of all clusters α is a geometrical problem and they are well-defined for each σ . Then, the ECIs $V_\alpha^{(n)}$ can be determined either by direct solution or via least-squares fitting of an overdetermined system of linear equations

$$\mathbf{E}^{\{\sigma\}} = \Xi^{\{\sigma\}} \mathbf{V}. \quad (2.39)$$

$\mathbf{E}^{\{\sigma\}}$ is the column vector containing the total energies of the predefined ordered structures $\{\sigma\}$. $\Xi^{\{\sigma\}}$ is the matrix of correlation functions with elements $m_\alpha^{(n)} \xi_\alpha^{(n)}(\sigma)$, and $\mathbf{V}$ is the column vector containing $V_\alpha^{(n)}$. There are different codes under ongoing development available that implement this structure inversion method, one of which is the Alloy Theoretic Automated Toolkit (ATAT) by van de Walle and co-workers [64]. A weakness of this method is that the choice of basis functions, or n -site clusters, included in the expansion is not uniquely determined. The total number of included symmetrically inequivalent pair, triplet, quadruplet clusters, and so on, should not exceed the number of predefined structures $N_{\{\sigma\}}$ in order to preserve the *overdetermined* system of equations. Even with this upper limit, it is not known how many clusters or ECIs are needed. It means that several different sets of $V_\alpha^{(n)}$ in principle can reproduce the total energies of $\{\sigma\}$ equally well. As with any data fitting it is convenient to have a figure of merit to assess the prediction accuracy of the model. For instance, implemented in ATAT is a leave-one-out scheme with the cross-validation score defined as

$$CV = \left(\frac{1}{N_{\{\sigma\}}} \sum_{i=1}^{N_{\{\sigma\}}} \left(E_i^{\text{DFT}} - E_{(i)}^{\text{CE}} \right)^2 \right)^{1/2} \quad (2.40)$$

which is related to the root mean square error, but is specifically designed to estimate the error made in predicting the energy of the structures not included in the least-squares fit. The summation is over all structures included in the fit, and E_i^{DFT} is the 'true' calculated energy of structure i , while $E_{(i)}^{\text{CE}}$ is the predicted value of the one structure i that is left out from a least-squares fit to the $(N_{\{\sigma\}} - 1)$ other energies. A satisfactory CE is then one that contains a set of $V_\alpha^{(n)}$ that minimizes the CV score.

One can also choose to partition the total number of predefined structures into one subset that is used to train and fit the expansion, and one subset of structures excluded from the expansion used to validate the predictive power, i.e. $N_{\{\sigma\}} = N_{\text{fit}} + N_{\text{val}}$. The sub-sampling can either be done manually by conscious decision-making intended to bias the CE towards satisfactory performance for of a certain type of ordered $\{\sigma\}$, or by repeated random sub-sampling with the

results then being averaged over the number of partition splits.

This problem of finding a basis set and corresponding ECIs, as addressed in alloy theory since the 1983 [60, 63], is fundamentally related to all machine learning and artificial intelligence problems now included in every area of science and technology.

The CE method, as implemented in ATAT, is used in **Papers I** and **II** in this thesis.

2.4 Lattice dynamics

Many properties of materials, be it mechanical, electrostatic, thermal, etc., are determined by the variations of the total energy around the equilibrium configuration of atomic nuclei. A wealth of information about materials can be gathered from studies of vibrational spectra, both theoretically and experimentally. They can be measured using infrared absorptions, light scattering, elastic and inelastic neutron scattering, and other techniques. The vibrational spectra are key to many temperature dependent properties of solids, including free energies, heat capacity, thermal expansion and conductivity, phase stability and transitions, and so on. The framework introduced in section 2.1 belongs to the Born-Oppenheimer regime where the total energy is parametrically dependent on the positions of the nuclei $E(\{\mathbf{R}_I\})$ and independent of the nuclear velocities. This is an excellent approximation for lattice vibrations in most cases. Lattice vibrations too is a part of the electronic structure, as displacements of the nuclei induces a response in the electrons that in turn changes the total energy. The lowest thermal approximation is the static lattice, the absence of lattice vibrations, where it is assumed that the nuclei sit still at their lattice sites, their equilibrium positions. However, even at absolute zero, the nuclei are not exactly static due to zero-point motion. The next approximation is that the nuclei vibrate in the close vicinity of their equilibrium positions, and that the vibrational modes are independent. Below we will see different ways how to treat lattice vibrations in solids.

2.4.1 Introduction

A description of lattice dynamics [65] is given below. Assume that the material is a crystalline solid consisting of a unit cell that repeats periodically in all spatial directions, and that the unit cell is spanned by three linearly independent lattice basis vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$, forming a parallelepiped. Then, the origin of the l :th unit cell in the crystal is defined by

$$\mathbf{r}_l = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3, \quad (2.41)$$

where l_1 , l_2 and l_3 are integer numbers. These unit cells l are in turn inhabited by atoms μ in their equilibrium positions $\mathbf{r}_\mu$ relative to the origin of the unit cell. The equilibrium position of atom μ in unit cell l is therefore $\mathbf{r}_l + \mathbf{r}_\mu$. When this atom is nudged by the displacement $\mathbf{u}_{l\mu}$ the resulting position is then given by

$$\mathbf{R}_{l\mu} = \mathbf{r}_l + \mathbf{r}_\mu + \mathbf{u}_{l\mu} \equiv \mathbf{r}_{l\mu} + \mathbf{u}_{l\mu}. \quad (2.42)$$

At finite temperature, below melting, the displacements $\mathbf{u}_{l\mu}$ are mere fractions of the interatomic distances and can safely be assumed small, yet appreciable enough to lead to increases in the potential energy U of the crystal, that then can be expressed as a Taylor-series expansion of the displacements

$$\begin{aligned}
U(\{\mathbf{u}\}) = U_0 &+ \sum_l \sum_\mu \sum_\alpha \Phi_{l\mu}^\alpha u_{l\mu}^\alpha + \frac{1}{2} \sum_{lm} \sum_{\mu\nu} \sum_{\alpha\beta} \Phi_{lm\mu\nu}^{\alpha\beta} u_{l\mu}^\alpha u_{m\nu}^\beta \\
&+ \frac{1}{3!} \sum_{lmn} \sum_{\mu\nu\xi} \sum_{\alpha\beta\gamma} \Phi_{lmn\mu\nu\xi}^{\alpha\beta\gamma} u_{l\mu}^\alpha u_{m\nu}^\beta u_{n\xi}^\gamma + \dots
\end{aligned} \tag{2.43}$$

In the absence of displacements the above expression reduces to the equilibrium potential energy U_0 . The indices lmn , $\mu\nu\xi$ and $\alpha\beta\gamma$ denote unit cells, atoms in the unit cells and Cartesian x , y and z coordinates, respectively. The Taylor expansion coefficients

$$\Phi_{l\mu}^\alpha = \left. \frac{\partial U}{\partial u_{l\mu}^\alpha} \right|_{\{\mathbf{u}\}=0} \tag{2.44}$$

$$\Phi_{lm\mu\nu}^{\alpha\beta} = \left. \frac{\partial^2 U}{\partial u_{l\mu}^\alpha \partial u_{m\nu}^\beta} \right|_{\{\mathbf{u}\}=0} \tag{2.45}$$

$$\Phi_{lmn\mu\nu\xi}^{\alpha\beta\gamma} = \left. \frac{\partial^3 U}{\partial u_{l\mu}^\alpha \partial u_{m\nu}^\beta \partial u_{n\xi}^\gamma} \right|_{\{\mathbf{u}\}=0} \tag{2.46}$$

are the force constant matrices. As the partial derivatives are evaluated at the equilibrium positions $\{\mathbf{u}\} = 0$, the first-order force constants $\Phi_{l\mu}^\alpha$ in Eq. 2.44 describing the net force acting on atom $l\mu$ must be zero, with necessity. The second-order force constants $\Phi_{lm\mu\nu}^{\alpha\beta}$ in Eq. 2.45 give the force acting on atom μ in unit cell l when atom ν in unit cell m is displaced by $u_{m\nu}^\beta$ in the β -direction. In a similar fashion, the third-order force constants $\Phi_{lmn\mu\nu\xi}^{\alpha\beta\gamma}$ in Eq. 2.46 captures the response when taking into account of a third atom ξ in unit cell n that is moved in the γ -direction by $u_{n\xi}^\gamma$.

2.4.2 Harmonic Approximation

If the displacement amplitudes are sufficiently small, such that the quadratic terms will dominate $u_{l\mu}^\alpha u_{m\nu}^\beta u_{n\xi}^\gamma \ll u_{l\mu}^\alpha u_{m\nu}^\beta$, the Taylor-series expansion of $U(\{\mathbf{u}\})$ given in Eq. 2.43 can be truncated at the second-order terms and becoming

$$U(\{\mathbf{u}\}) = U_0 + \frac{1}{2} \sum_{lm} \sum_{\mu\nu} \sum_{\alpha\beta} \Phi_{lm\mu\nu}^{\alpha\beta} u_{l\mu}^\alpha u_{m\nu}^\beta, \tag{2.47}$$

which is the so-called *harmonic approximation* (HA). It works under the assumption that the static lattice equilibrium positions are true, or rather that they are the mean positions of the nuclei, thus fixing the volume, an approximation often adequate for low temperatures. The vibrational Hamiltonian in this approximation is

$$H_{\text{vib}} = U_0 + \frac{1}{2} \sum_{lm} \sum_{\mu\nu} \sum_{\alpha\beta} \Phi_{lm\mu\nu}^{\alpha\beta} u_{l\mu}^{\alpha} u_{m\nu}^{\beta} + \sum_l \sum_{\mu} \sum_{\alpha} \frac{(p_{l\mu}^{\alpha})^2}{2M_{l\mu}}, \quad (2.48)$$

where the third and last term is the kinetic energy of atoms due to the vibrations, with $p_{l\mu}^{\alpha}$ and $M_{l\mu}$ being the momentum component along α and mass of atom $l\mu$, respectively. Then from the Hamilton equations

$$\dot{p}_{l\mu}^{\alpha} = -\frac{\partial \hat{H}}{\partial u_{l\mu}^{\alpha}} \quad (2.49)$$

and

$$\dot{u}_{l\mu}^{\alpha} = \frac{\partial \hat{H}}{\partial p_{l\mu}^{\alpha}} \quad (2.50)$$

one can construct the equation of motion for the atom $l\mu$ as

$$M_{l\mu} \ddot{u}_{l\mu}^{\alpha} = - \sum_m \sum_{\nu} \sum_{\beta} \Phi_{lm\mu\nu}^{\alpha\beta} u_{m\nu}^{\beta}. \quad (2.51)$$

Although not explicitly written out in the equations above, the sums over the atom indices μ , ν and ξ are over all N atoms in the corresponding unit cell, meaning there are $3N$ equations of motion. As with the electronic states in $\mathbf{k}$ -space, the periodicity of the crystal lets one look for solutions on plane wave form

$$u_{l\mu}^{\alpha} = \frac{1}{\sqrt{M_{l\mu}}} \sum_{\mathbf{q}} \sum_s A_{\mathbf{q}} \epsilon_{l\mu}^{\alpha}(\mathbf{q}, s) e^{i(\mathbf{q} \cdot \mathbf{r}_{l\mu} - \omega_{\mathbf{q}s} t)}, \quad (2.52)$$

where the summations are over all vibrational wave vectors $\mathbf{q}$ in the first BZ, and over all band indices s . $A_{\mathbf{q}}$, $\epsilon_{l\mu}^{\alpha}$ and $\omega_{\mathbf{q}s}$ are defined as the amplitude at $\mathbf{q}$, the polarization vector describing the direction of the displacement, and the vibrational frequency of branch s at wave vector $\mathbf{q}$, respectively. In principle, the complex conjugate of the plane wave can be added to the ansatz above. The plane wave normal modes do not interact with each other and are thus independent. If the plane wave solution in Eq. 2.52 is substituted into the equation of motion in Eq. 2.51 one can construct the eigenvalue problem

$$D(\mathbf{q}) \epsilon(\mathbf{q}, s) = M \omega_{\mathbf{q}s}^2 \epsilon(\mathbf{q}, s) \quad (2.53)$$

where $\omega_{\mathbf{q}s}$ and $\epsilon(\mathbf{q}, s)$ are obtained as the eigenvalues and eigenvectors. There are three real eigenvectors that can be normalized so that $\langle \epsilon(\mathbf{q}, s), \epsilon(\mathbf{q}, s') \rangle = \delta_{ss'}$ ($s, s' = 1, 2, 3$). $D(\mathbf{q})$ is the so-called dynamical matrix, that is $3N \times 3N$ in size, with each element consisting of 3×3 submatrices $D_{lm\mu\nu}^{\alpha\beta}(\mathbf{q})$ that are Fourier transforms of the force constant matrices $\Phi_{lm\mu\nu}^{\alpha\beta}$, i.e.

$$D_{lm\mu\nu}^{\alpha\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_{l\mu} M_{m\nu}}} \sum_m \Phi_{lm\mu\nu}^{\alpha\beta} e^{i\mathbf{q} \cdot (\mathbf{r}_{m\nu} - \mathbf{r}_{l\mu})}. \quad (2.54)$$

Eq. 2.53 has a non-trivial solution if the determinant of the coefficients vanishes. Then the eigenvalues of the dynamical matrix give the allowed squares $\omega_{\mathbf{q}s}^2$ of frequencies for each $\mathbf{q}$. If the values $\omega_{\mathbf{q}s}^2$ are positive (and $\omega_{\mathbf{q}s}$ are real), it reflects that $D(\mathbf{q})$ is Hermitian, and the displacements from the equilibrium positions result in restoring forces. It then follows that the crystal is dynamically stable. In the contrasting case of $\omega_{\mathbf{q}s}^2$ being negative, the frequencies are imaginary, and thus the equilibrium positions in the crystal are dynamically unstable, and that the displacements induce non-restoring forces moving the atoms away to new positions. This happens when the second derivatives in Eq. 2.45 are negative.

Plotting the solution $\omega_{\mathbf{q}s}$ against $\mathbf{q}$ forms the so-called dispersion relation. Fig 2.3 presents the example of the phonon dispersion of the TiB_2 unit cell containing one Ti and two B atoms. The calculation is carried out at ambient conditions.

Figure 2.3: Phonon dispersion relation of the unit cell of TiB_2 containing one Ti and two B atoms at ambient conditions.

In general for n -atomic ($n > 1$) lattices, the vibrational modes can generally be divided into two types; acoustic and optical modes.

Acoustic modes are vibrations where the different atoms of the unit cell in the same direction, the atoms are in phase, and typically have low frequency. The resulting waves travel with the velocity of sound - hence the name *acoustic*. Near the center of the BZ, the dispersion relation is almost linear and it should converge

to zero at the origin if the system is dynamically stable, see regions around Γ in Fig. 2.3. When $\mathbf{q}$ lies along a high symmetry direction, the modes may be classified as either pure longitudinal (polarization $\epsilon(\mathbf{q}, s)$ parallel to direction of motion $\mathbf{q}$) or pure transverse (polarization $\epsilon(\mathbf{q}, s)$ perpendicular to direction of motion $\mathbf{q}$) modes. Each atom μ in the unit cell l has one longitudinal and two transverse modes. It is often the transverse modes that exhibit imaginary frequencies, that for instance can mark the phase transformation point of a solid. There are three acoustic modes with $\omega \rightarrow 0$ for $\mathbf{q} \rightarrow 0$ and the other $3s - 3$ modes are optical.

Optical modes are observed in crystals containing more than one atomic kind, and are characterized by out-of-phase displacements in the crystal, with adjacent atoms vibrating in opposite directions. Differences in electronegativity induce local charge transfers between the atoms, creating dipole moments that may couple to externally applied electromagnetic waves. They are non-zero at the BZ center, with typical frequencies higher than the acoustic modes, lying in the range of optical light - hence the name *optical*. In Fig. 2.3 the optical modes above 10 THz are mainly due to the vibrations of B atoms.

Up to this point the vibrations have been treated classically. In a quantum mechanical treatment, the collective vibrational modes of atoms in the crystal lattice are described by quantized excited states. In this picture it becomes convenient to introduce *phonons*, quasiparticles that are travelling quanta of vibrational energy. In the second quantization representation, the *bosonic* phonon ladder operators $\hat{a}_{\mathbf{q}s}$ and $\hat{a}_{\mathbf{q}s}^\dagger$, that read as the creation of a single phonon branch s and wave vector $\mathbf{q}$ and the annihilation of the same phonon, respectively, can be used to describe the plane wave solution and its momentum by the operators

$$\hat{u}_{l\mu}^\alpha = \sqrt{\frac{\hbar}{2NM_{l\mu}}} \sum_{\mathbf{q}} \sum_s \frac{\epsilon_{l\mu}^\alpha(\mathbf{q}, s)}{\sqrt{\omega_{\mathbf{q}s}}} e^{i\mathbf{q} \cdot \mathbf{r}_{l\mu}} (\hat{a}_{\mathbf{q}s} + \hat{a}_{(-\mathbf{q})s}^\dagger) \quad (2.55)$$

and

$$\hat{p}_{l\mu}^\alpha = -i\sqrt{\frac{\hbar M_{l\mu}}{2N}} \sum_{\mathbf{q}} \sum_s \sqrt{\omega_{\mathbf{q}s}} \epsilon_{l\mu}^\alpha(\mathbf{q}, s) e^{i\mathbf{q} \cdot \mathbf{r}_{l\mu}} (\hat{a}_{\mathbf{q}s} - \hat{a}_{(-\mathbf{q})s}^\dagger). \quad (2.56)$$

If these are substituted into the classically treated Hamiltonian H_{vib} in Eq. 2.48 one derives the corresponding Hamiltonian operator $\hat{H}_{\text{vib}}$ in the picture of quantum mechanics

$$\hat{H}_{\text{vib}} = \sum_{\mathbf{q}} \sum_s \hbar \omega_{\mathbf{q}s} \left(\hat{a}_{\mathbf{q}s}^\dagger \hat{a}_{\mathbf{q}s} + \frac{1}{2} \right), \quad (2.57)$$

where the number operator $\hat{N} = \hat{a}_{\mathbf{q}s}^\dagger \hat{a}_{\mathbf{q}s}$ is introduced. This number operator has eigenvalue $n_{\mathbf{q}s} = 0, 1, 2, \dots$ for the s :th vibrational mode at wave vector $\mathbf{q}$, such that the vibrational energy E_{vib} calculated from the expectation value of $\hat{H}_{\text{vib}}$ is

$$\hat{E}_{\text{vib}} = \sum_{\mathbf{q}} \sum_s \hbar \omega_{\mathbf{q}s} \left(n_{\mathbf{q}s} + \frac{1}{2} \right), \quad (2.58)$$

where $\sum_{\mathbf{q}} \sum_s \frac{\hbar \omega_{\mathbf{q}s}}{2}$ is the zero point energy. For this system of atoms collectively viewed as a set of independent harmonic oscillators one can define the vibrational partition function $\mathcal{Z}$ as

$$\mathcal{Z} = \prod_{\mathbf{q}} \prod_s \frac{\exp \left(-\frac{\hbar \omega_{\mathbf{q}s}}{2k_{\text{B}}T} \right)}{1 - \exp \left(-\frac{\hbar \omega_{\mathbf{q}s}}{k_{\text{B}}T} \right)}, \quad (2.59)$$

where k_{B} and T are Boltzmann constant and absolute temperature, respectively. The partition function above can be used to neatly derive the Helmholtz vibrational free energy F_{vib} in the following manner

$$\begin{aligned} F_{\text{vib}} &= -k_{\text{B}}T \ln \mathcal{Z} = \sum_{\mathbf{q}} \sum_s \frac{\hbar \omega_{\mathbf{q}s}}{2} + k_{\text{B}}T \sum_{\mathbf{q}} \sum_s \ln \left(1 - \exp \left(-\frac{\hbar \omega_{\mathbf{q}s}}{k_{\text{B}}T} \right) \right) \\ &= \int_0^{\infty} g(\omega) \left(\frac{\hbar \omega}{2} + k_{\text{B}}T \ln \left(1 - \exp \left(-\frac{\hbar \omega}{k_{\text{B}}T} \right) \right) \right) d\omega, \end{aligned} \quad (2.60)$$

In a large crystal, the set of discrete wave vectors $\mathbf{q}$ becomes dense, and so it becomes convenient to reduce the sum $\sum_{\mathbf{q}}$ by introducing the phonon density of states $g(\omega)$. It gives the total number of modes with frequencies in the infinitesimal range between ω and $\omega + d\omega$ per unit volume, and is given by

$$g(\omega) = \sum_s \int_{\text{BZ}} \frac{d\mathbf{q}}{(2\pi)^3} \delta(\omega - \omega_{\mathbf{q}s}) \quad (2.61)$$

A shortcoming of the HA introduced above, is that it results in a pressure that is dependent on volume, but not on temperature, since the vibrational frequencies do not depend on the amplitude of the oscillations at this level of theory. Harmonic phonons are uncoupled and have infinite lifetimes where they never scatter against other phonons, that leads to some implications, especially at high temperature when atomic displacements become large. The discarded higher order terms in Eq. 2.43 become increasingly important at high temperature as anharmonic contributions to the lattice dynamics can be attributed to them. The cubic term (first anharmonic term) represents the asymmetry of mutual atomic repulsion, giving phonon lifetimes, and the quartic term (second anharmonic term) represents the softening of vibrations at large amplitudes. Some anharmonic effects include thermal expansion, melting, symmetry changing/increasing phase transitions and a limited thermal conductivity.

As a more precise example, the HA predicts that thermal conductivity goes as $\kappa \propto T^3$, which is fine at low temperature, but fails at high temperature when the

actual phonon mean free path becomes smaller than the size of the crystal, inducing phonon-phonon scattering. This effectively saturates the thermal conductivity, making it decrease as $\kappa \propto 1/T^x$ ($0 < x < 1$) [66].

2.4.3 Quasiharmonic Approximation

The next step on the ladder of lattice dynamics complexity is the so-called *quasiharmonic* approximation (QHA) [67–69]. It is ‘quasi’ in the sense that the potential energy is still on the harmonic form (Eq. 2.47), but now with the introduction of implicit temperature dependence of the vibrational frequencies by volume modification. In the HA the vibrations are derived only at the equilibrium lattice positions at zero temperature, corresponding to the equilibrium volume V_0 for U_0 in Eq. 2.47. In contrast, the idea of the QHA is to derive harmonic vibrations for a set of fixed volumes $\{V\}$ containing V_0 , and fit the energy-volume curve of the combined effects of static lattice and vibrational free energies. The points can be fitted numerically using polynomials or on the form of third-order Birch-Murnaghan equation of state that is known to work well for the total energy [70, 71]. Assuming that we are interested in the equilibrium volume for each temperature, it is then possible to trace

$$V_0(T) = \underset{V}{\operatorname{argmin}} \left\{ U_0(V) + F_{\text{vib}}(V, T) \right\}, \quad (2.62)$$

i.e. the *thermal expansion*, and due to zero point energy from F_{vib} also capture zero point motion. It then follows in this notation that $V_0(T = 0) \neq V_0$. As a consequence the volume and temperature dependence of the frequencies in the real crystal $\omega_{qs}(V, T)$ is approximated by $\omega_{qs}(V_0(T))$. Naturally, the thermodynamic properties can also be derived under non-zero pressure conditions. The general expression for the Helmholtz vibrational free energy in the QHA is then

$$F_{\text{vib}}(V, T) = \sum_{\mathbf{q}} \sum_s \frac{\hbar \omega_{qs}(V(T))}{2} + k_B T \sum_{\mathbf{q}} \sum_s \ln \left(1 - \exp \left(- \frac{\hbar \omega_{qs}(V(T))}{k_B T} \right) \right). \quad (2.63)$$

Vibrational free energies derived at this level of theory are used in **Papers I and II** in this thesis. While the vibrational frequencies $\omega_{qs}(V(T))$ implicitly depend on temperature, the underlying potential U and force constant matrices Φ are evaluated at $T = 0$ K. One danger in this is that crystals that are indicated to be dynamically unstable might in reality be stabilized by anharmonic contributions. To go beyond harmonic and quasiharmonic approximation and explicitly treat phonon-phonon interactions and anharmonic contributions to the free energy is not easy and requires more computationally heavy methods, that can be based on *ab initio* molecular dynamics, such as the temperature-dependent effective potential (TDEP) method developed by Hellman [72–74].

As hinted in Eqs. 2.44–2.46, the key ingredient to lattice dynamics within DFT is, in essence, the calculation of derivatives of the energy with respect to perturbations, or rather, the changes in electronic charge density induced by the presense of

a phonon with wave vector $\mathbf{q}$. This is done by either direct methods or using perturbation theory and response functions. Brief outlines of commonly used methods to de-facto calculate force constant matrices and derive vibrational properties will be given below.

2.4.4 Direct methods

Two direct methods are the "frozen phonon" method [75] and "finite displacement" (FD) method [76]. The frozen phonon method relies on supercells with monochromatic (single ω) perturbations that are *frozen in* with finite amplitudes, representing snapshots of the phonon movement. Phonon energies are calculated as function of the displacement amplitude from finite difference in energies of distorted and ideal supercells. The supercells need to be sufficiently large to accommodate having $\mathbf{q}$ as reciprocal lattice vector and to ensure that the periodic boundary conditions are compatible with long-wavelength phonons. The finite displacement method also uses supercell calculations, and considers the forces arising from the displacements of the atoms. The Hellmann-Feynman theorem [77–79] is used to obtain the forces needed to construct the force constant matrix elements, as given in Ref [76]

$$\Phi_{lm\mu\nu}^{\alpha\beta} = -\frac{\partial F_{m\nu}^{\beta}}{\partial u_{l\mu}^{\alpha}} \approx -\frac{F_{m\nu}^{\beta}}{u_{l\mu}^{\alpha}}, \quad (2.64)$$

where $F_{m\nu}^{\beta}$ is the Hellmann-Feynman force in direction β on atom $m\nu$ due to the displacement $u_{l\mu}^{\alpha}$ of atom $l\mu$ in direction α . All information needed, for all phonons with a given $\hat{\mathbf{q}}$, can be derived by displacing each inequivalent plane of atoms and calculating the force of all the atoms. Each inequivalent plane of atoms and each inequivalent displacement requires a separate calculating. Therefore, this method becomes costly for low symmetry crystals, like in substitutionally disordered alloys where up to $6N$ individual displacement calculations. Then the dynamical matrix is obtained by a Fourier transform, giving the phonon frequencies upon diagonalization of this matrix. In the atomic displacement scheme of Parlinski-Li-Kawazoe [80], as implemented in the PHONOPY code [81], the finite displacements are typically in the range of 0.01 Å. The method usually considers all forces between atoms that are separated by less than a user-defined spatial cut-off distance. In order to obtain reliable results, the supercell size should therefore exceed the spatial range of the forces by at least two times. The finite displacement method is used in **Papers I-V**.

2.4.5 Linear response

In contrast to the direct supercell calculations, the advantage of the density functional perturbation theory (DFPT) [82–85] approach is that supercell construction is not required. This is because responses to perturbations of different wavelengths are decoupled, and phonon frequencies can be calculated at arbitrary wave vectors $\mathbf{q}$, resulting in a workload that is essentially independent of the phonon wavelength. The problem is reduced to finding the first-order variation or 'linear response' in

the charge density within the unit cell, induced by the presence of a phonon with a given wave vector $\mathbf{q}$. Assume that the energy functional can be expanded into power series of some perturbation parameter λ_i

$$E_{\lambda_i} \simeq E + \lambda_i \frac{\partial E}{\partial \lambda_i} + \frac{1}{2} \lambda_i^2 \frac{\partial^2 E}{\partial \lambda_i^2} + \dots \quad (2.65)$$

The first-order derivative $\partial E / \partial \lambda_i$ is just the Hellmann-Feynman force theorem which involves only the external potential and the unperturbed charge density $n(\mathbf{r})$

$$\frac{\partial E}{\partial \lambda_i} = \frac{\partial E_{II}}{\partial \lambda_i} \int n(\mathbf{r}) \frac{\partial V_{\text{ext}}(\mathbf{r})}{\partial \lambda_i} d\mathbf{r}. \quad (2.66)$$

The second-order derivative $\partial^2 E / \partial \lambda_i^2$ depends on the first-order derivative of the charge density $\partial n(\mathbf{r}) / \partial \lambda$ and can be generalized to (interchangeable) mixed derivatives

$$\frac{\partial^2 E}{\partial \lambda_i \partial \lambda_j} = \frac{\partial^2 E_{II}}{\partial \lambda_i \partial \lambda_j} + \int n(\mathbf{r}) \frac{\partial^2 V_{\text{ext}}(\mathbf{r})}{\partial \lambda_i \partial \lambda_j} d\mathbf{r} + \int \frac{\partial n(\mathbf{r})}{\partial \lambda_i} \frac{\partial V_{\text{ext}}(\mathbf{r})}{\partial \lambda_j} d\mathbf{r}. \quad (2.67)$$

For the purposes of this chapter on lattice dynamics, the perturbations λ_i are naturally atomic displacements. Within DFPT the key to force constant calculations is the knowledge of the linear response in the charge density $\partial n(\mathbf{r}) / \partial u_{l\mu}^\alpha$ in the presence of a phonon represented by the displacement $u_{l\mu}^\alpha$, such that the third term in Eq. 2.67 is known. Then, one can get the second-order expansion of the energy (left-hand-side) with respect to monochromatic perturbations $\partial^2 E / \partial u_{l\mu}^\alpha \partial u_{m\nu}^\beta$. From the force constants one can derive the dynamical matrix, along with phonon modes and frequencies. When applied to the same problem, the results of both approaches, DFPT and FD, must be the same except for errors that may be introduced by taking finite differences. DFPT is used to derive phonon dispersions from linear response in **Paper III**.

The strength of DFPT over FD is however that the theory holds beyond the adiabatic approximation. As such it is a tool to be used when studying materials where electrons are influenced by the movement of nuclei, with finite electron-phonon coupling, a phenomena playing a crucial role in the theory of transport and superconductivity in solids.

2.4.6 Electron-phonon coupling and superconductivity

The following introduction to electron-phonon coupling (EPC) and superconductivity is inspired by the review article of Giustino [1]. Since the development of the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity [86] it has been made clear that electron-phonon coupling may be important to describe physical properties of a system. Superconductivity is a quantum phenomenon at the macroscopic level of the electronic system. In the BCS theory its origin is attributed to the formation of correlated paired electrons (Cooper pairs), that were

shown in the seminal paper to be stabilized in the presence of an attractive interaction between the electrons, which is provided by the EPC. In conventional superconductors, ones described within BCS theory, the EPC is known to be the pairing mechanism. Such superconductors include the elemental and most compound superconductors, out of which the highest observed critical temperature is 39 K in MgB_2 [12, 13] which is treated in **Paper III**. The phonon-mediated superconductivity in BCS theory is valid for the weak coupling. Extensions to the theory, that bridge the gap into the strong coupling regime, were proposed in the Migdal-Éliashberg theory [87, 88] and allows for quantitative prediction of many properties of the superconducting state, related to the EPC.

A good starting point when discussing electron-phonon coupling effects in periodic solids is the Fröhlich Hamiltonian that is neatly expressed in the representation of second quantization

$$\hat{H} = \hat{H}_e + \hat{H}_p + \hat{H}_{ep}, \quad (2.68)$$

where the first term is the electron Hamiltonian (essentially Eq. 2.15)

$$\hat{H}_e = \sum_{n\mathbf{k}} \sum_{n'\mathbf{k}'} \langle n\mathbf{k} | \hat{H}_{KS} | n'\mathbf{k}' \rangle \hat{c}_{n\mathbf{k}}^\dagger \hat{c}_{n'\mathbf{k}'} = \sum_{n\mathbf{k}} \epsilon_{n\mathbf{k}} \hat{c}_{n\mathbf{k}}^\dagger \hat{c}_{n\mathbf{k}}. \quad (2.69)$$

Here $\epsilon_{n\mathbf{k}}$ is the Kohn-Sham eigenvalue of electronic band n at wave vector $\mathbf{k}$ and $\hat{c}_{n\mathbf{k}}^\dagger/\hat{c}_{n\mathbf{k}}$ are *fermionic* creation and annihilation operators. The second term in Eq. 2.68 is the harmonic Hamiltonian (Eq. 2.57)

$$\hat{H}_p = \sum_{\mathbf{q}s} \hbar\omega_{\mathbf{q}s} \left(\hat{a}_{\mathbf{q}s}^\dagger \hat{a}_{\mathbf{q}s} + \frac{1}{2} \right). \quad (2.70)$$

The third and last term in Eq. 2.68 is the electron-phonon Hamiltonian including atomic displacements to first or linear order

$$\hat{H}_{ep} = N_l^{-1/2} \sum_{nm\mathbf{k}} \sum_{\mathbf{q}s} g_{nm,s}(\mathbf{k}, \mathbf{q}) \hat{c}_{m\mathbf{k}+\mathbf{q}}^\dagger \hat{c}_{n\mathbf{k}} (\hat{a}_{\mathbf{q}s} + \hat{a}_{-\mathbf{q}s}^\dagger), \quad (2.71)$$

where N_l is the number of primitive cells and the electron-phonon matrix element is given by

$$g_{nm,s}(\mathbf{k}, \mathbf{q}) = \sqrt{\frac{1}{2M\omega_{\mathbf{q}s}}} \langle n\mathbf{k} | \delta_{\mathbf{q}\mu}^\alpha V | n'\mathbf{k} + \mathbf{q} \rangle_{\text{uc}}, \quad (2.72)$$

where M is the reduced mass and the prefactor $\sqrt{1/2M\omega_{\mathbf{q}s}}$ is the zero point phonon amplitude, and $\delta_{\mathbf{q}\mu}^\alpha V$ is the linear response of the potential felt by the electrons under a displacement of atom $l\mu$ in direction α with wave vector $\mathbf{q}$. The subscript "uc" indicates that the integral is carried out within one unit cell l of the crystal. Thus, the electron-phonon interaction can be interpreted in terms of the scattering of an electron with momentum $\mathbf{k}$ from band n to a state with momentum $\mathbf{k} + \mathbf{q}$ in band n' under the simultaneous absorption (emission) of a phonon with momentum $\mathbf{q}$ ($-\mathbf{q}$) and branch index s .

2.4.7 Anisotropic Migdal-Éliashberg theory

The central equations in the Migdal-Éliashberg theory are the two anisotropic coupled equations

$$Z_{n\mathbf{k}}(i\omega_j) = 1 + \frac{\pi k_B T}{N_F} \sum_{n'\mathbf{k}'j'} \frac{\omega_{j'}/\omega_j}{\sqrt{\hbar^2 \omega_{j'}^2 + \Delta_{n'\mathbf{k}'}^2(i\omega_{j'})}} \times \lambda_{n\mathbf{k},n'\mathbf{k}'}(i\omega_j - i\omega_{j'}) \delta(\epsilon_{n'\mathbf{k}'} - \epsilon_F), \quad (2.73)$$

$$Z_{n\mathbf{k}}(i\omega_j) \Delta_{n\mathbf{k}}(i\omega_j) = \frac{\pi k_B T}{N_F} \sum_{n'\mathbf{k}'j'} \frac{\Delta_{n'\mathbf{k}'}(i\omega_{j'})}{\sqrt{\hbar^2 \omega_{j'}^2 + \Delta_{n'\mathbf{k}'}^2(i\omega_{j'})}} \times [\lambda_{n\mathbf{k},n'\mathbf{k}'}(i\omega_j - i\omega_{j'}) - N_F V_{n\mathbf{k},n'\mathbf{k}'}] \times \delta(\epsilon_{n'\mathbf{k}'} - \epsilon_F), \quad (2.74)$$

where $\sum_{\mathbf{k}'}$ stands for integration of the BZ $\Omega_{\text{BZ}}^{-1} \int d\mathbf{k}'$. T is the absolute temperature, $Z_{n\mathbf{k}}$ is the quasiparticle renormalization function and $\Delta_{n\mathbf{k}}(i\omega_j)$ is the superconducting gap function. The functions $Z_{n\mathbf{k}}$ and $\Delta_{n\mathbf{k}}(i\omega_j)$ are determined along the imaginary frequency axis at the discrete set of fermion Matsubara frequencies $i\omega_j = i(2j+1)\pi k_B T/\hbar$ where j is an integer. $\lambda_{n\mathbf{k},n'\mathbf{k}'}(i\omega)$ is the anisotropic and frequency-dependent mass enhancement parameter

$$\lambda_{n\mathbf{k},n'\mathbf{k}'}(i\omega) = \frac{N_F}{\hbar} \sum_s \frac{2\omega_{\mathbf{q}s}}{\omega_{\mathbf{q}s}^2 + \omega^2} |g_{nn',s}(\mathbf{k}, \mathbf{q})|^2, \quad (2.75)$$

with $\mathbf{q} = \mathbf{k}' - \mathbf{k}$. The notion of mass enhancement is described shortly here. For a parabolic electronic band, near the Fermi surface, the noninteracting dispersions are given by $\epsilon_{n\mathbf{k}} = \hbar \mathbf{k}_F \cdot \hbar(\mathbf{k} - \mathbf{k}_F)/m^*$, where $\mathbf{k}_F$ is a wave vector on the Fermi surface, and the electron velocity is $\mathbf{v}_{n\mathbf{k}} = \hbar \mathbf{k}_F/m^*$. Due to the EPC, the velocity is renormalized to $\mathbf{V}_{n\mathbf{k}} = \mathbf{v}_{n\mathbf{k}}/(1 + \lambda_{n\mathbf{k}})$ while the Fermi momentum magnitude is preserved, such that the renormalization can be interpreted as an effective increase of the band mass from m^* to $m_{\text{ep}} = m^*(1 + \lambda_{n\mathbf{k}})$.

Equations 2.73 and 2.74 are solved in a self-consistent scheme for each temperature T . The superconducting critical temperature is obtained as the highest temperature for which a nontrivial solution is obtained, i.e. a solution with $\Delta_{n\mathbf{k}}(i\omega_j) \neq 0$. Solving the equations on the imaginary axis is more convenient, as only simple summations are required and no integrations with singularities. The disadvantage with the imaginary axis formulation is that it is less physical, it is the real axis frequency which corresponds to the quasiparticle energy. Marsiglio, Schossmann and Carbotte [89] showed in a general way how solutions to Green's function problems can be analytically continued to the real axis, with the Migdal-Éliashberg equations 2.73 and 2.74 being a specific case. It allows the superconducting gap at real frequencies to also be obtained, so that it is possible to compute various thermodynamic properties that can't be defined from the imaginary-axis formulation,

like transport properties. See also the work of Vidberg [90].

The spectral representation of the electron self-energy is expressed in terms of the so-called "Éliashberg spectral function", defined as

$$\alpha^2 F_{n\mathbf{k}}(\epsilon, \epsilon') = \sum_{m,s} \int \frac{d\mathbf{q}}{\Omega_{\text{BZ}}} |g_{nm,s}(\mathbf{k}, \mathbf{q})|^2 \times \delta(\epsilon - \epsilon_{\mathbf{k}+\mathbf{q}m}) \delta(\epsilon' - \hbar\omega_{\mathbf{q}s}). \quad (2.76)$$

This quantity encapsulates all material-specific parameters, is positive and temperature independent. It is proportional to the scattering rate of an electron $|n\mathbf{k}\rangle$ into any electronic state at the energy ϵ by emitting or absorbing any phonon of energy ϵ' .

2.4.8 Isotropic Migdal-Éliashberg theory

The equations above are computationally demanding to evaluate, and can be remedied by assuming that the material is *isotropic*. Then, the key quantities in the Migdal-Éliashberg formalism of superconductivity can, based on the collective effort of McMillan [91], Allen and Dynes [92, 93], Grimvall [94] and Allen and Mitrovic [95], be neatly expressed by the following four equations

$$\alpha^2 F(\omega) = \frac{1}{N_{\text{F}}} \int \frac{d\mathbf{k}d\mathbf{q}}{\Omega_{\text{BZ}}^2} \sum_{nms} |g_{nm,s}(\mathbf{k}, \mathbf{q})|^2 \delta(\epsilon_{n\mathbf{k}} - \epsilon_{\text{F}}) \times \delta(\epsilon_{m\mathbf{k}+\mathbf{q}} - \epsilon_{\text{F}}) \delta(\hbar\omega - \hbar\omega_{\mathbf{q}s}) \quad (2.77)$$

$$\lambda(\omega) = 2 \int_0^\omega \frac{\alpha^2 F(\omega')}{\omega'} d\omega' \quad (2.78)$$

$$\omega_{\text{log}} = \exp \left[\frac{2}{\lambda} \int_0^\infty d\omega \frac{\alpha^2 F(\omega)}{\omega} \log \omega \right] \quad (2.79)$$

$$T_c = \frac{\omega_{\text{log}}}{1.2} \exp \left[- \frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right]. \quad (2.80)$$

Eq. 2.77 is the isotropic version of the Migdal-Éliashberg function in Eq. 2.76, where N_{F} is the density of states at the Fermi level and the delta functions single out the states on the Fermi surface. Decomposed, $F(\omega)$ is the phonon density of states and α denotes an average over all phonons with energy $\hbar\omega$ in the BZ. Eq. 2.78 is the cumulative electron-phonon mass enhancement parameter that in the limit $\lambda(\omega \rightarrow \infty)$ becomes the total electro-phonon "coupling strength" λ . Eq. 2.79 is the logarithmically averaged phonon frequency. Eq. 2.80 is the McMillan-Allen-Dynes equation for estimating superconducting transition temperature, where μ^* is the Anderson-Morel Coulomb pseudopotential [96], which is difficult to calculate

from first-principles, and is treated as an adjustable parameter that typically is in the range $\mu^* = 0.1 - 0.2$. This introduces some uncertainty in the determination of T_c , especially at moderate coupling strengths. Nevertheless, the equation is found to be accurate for known materials with $\lambda < 1.5$ [91–93].

2.4.9 Wannier function interpolation

Calculating EPC-related properties from first-principles requires evaluating BZ integrals of matrix elements that exhibit strong fluctuations. This is especially true for the phonon and electron self-energies, whose denominators become large whenever the difference between two electronic eigenvalues approaches a phonon energy. These type of calculations quickly become a balancing act between numerical accuracy and efficiency. In DFT, the BZ is typically discretized $\mathbf{k}$ -meshes of the order of $10 \times 10 \times 10$ points in total energy calculations, while in EPC calculations much finer grids are desirable for eaching numerical convergence. Thus it is helpful to have efficient calculations schemes in order to calculate electron-phonon responses for such a large number of wave vectors. One such specialized numerical technique developed to make EPC calculations more affordable is implemented in the "Electron-Phonon coupling using Wannier functions" (EPW) computational package by Ponc, Margine, Verdi and Giustino [97].

The starting idea is similar to that of Bloch waves to describe electrons in a periodic solid, as in equations 2.10 and 2.26, but instead of plane waves an alternative approach views electrons as linear combinations of localized orbitals, Wannier functions [98]. The construction of a Wannier function starts by considering a Bloch state $\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$. Then the Wannier function is defined as

$$w_{m\mathbf{l}}(\mathbf{r}) = N_l^{-1} \sum_{n\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_l)} U_{nm\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r}), \quad (2.81)$$

where N_l is the number of primitive cells and $U_{nm\mathbf{k}}$ is a unitary matrix in the indices n and m denoting different electronic bands. It follows that the Wannier functions are normalized in the supercell $\langle w_{m\mathbf{l}} | w_{m'\mathbf{l}'} \rangle_{\text{sc}} = \delta_{m\mathbf{l}, m'\mathbf{l}'}$. Due to the periodicity of $u_{n\mathbf{k}}$ the function w associated with a different cell $\mathbf{r}_{l'}$ is the same function, except it is translated by $\mathbf{r}_{l'} - \mathbf{r}_l$, i.e. Wannier functions have the property $w_{m\mathbf{l}}(\mathbf{r}) = w_{m0}(\mathbf{r} - \mathbf{r}_l)$. Inverse transformation of Eq. 2.81 gives the Bloch eigenstate

$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{m\mathbf{l}} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_l)} U_{mn\mathbf{k}}^\dagger w_{m\mathbf{l}}(\mathbf{r}). \quad (2.82)$$

The unitary matrix $U_{nm\mathbf{k}}$ is completely arbitrary and not uniquely defined, and therefore there is a lot of freedom in the construction of Wannier functions. If one wants real valued Wannier functions, it is achieved by requiring that $U_{nm, -\mathbf{k}} = U_{nm\mathbf{k}}^*$. Marzari and Vanderbilt exploited this degree of freedom to construct maximally localized Wannier functions (MLWFs) [99, 100], that minimize the spatial extent of the functions, and that are used in the EPW computational

package. Wannier functions were first introduced to the study of EPC by Giustino, Louie and Cohen [101] and Giustino et al [102], where it was shown how they relate to the central electron-phonon matrix elements $g_{nm,s}(\mathbf{k}, \mathbf{q})$ via

$$g_{nm,s}(\mathbf{k}, \mathbf{q}) = \sum_{l'l'} e^{i(\mathbf{k} \cdot \mathbf{r}_l + \mathbf{q} \cdot \mathbf{r}_{l'})} \times \sum_{n'm'\mu\alpha} U_{mm'\mathbf{k}+\mathbf{q}} g_{n'm'\mu\alpha}(\mathbf{r}_l, \mathbf{r}_{l'}) U_{n'n\mathbf{k}}^\dagger u_{\mu,\mathbf{q}s}^\alpha, \quad (2.83)$$

with the inverse relation being

$$g_{nm\mu\alpha}(\mathbf{r}_l, \mathbf{r}_{l'}) = \frac{1}{N_l N_{l'}} \sum_{\mathbf{k}, \mathbf{q}} e^{-i(\mathbf{k} \cdot \mathbf{r}_l + \mathbf{q} \cdot \mathbf{r}_{l'})} \times \sum_{n'm's} (u_{\mu,\mathbf{q}s}^\alpha)^{-1} U_{mm'\mathbf{k}+\mathbf{q}}^\dagger g_{n'm's}(\mathbf{k}, \mathbf{q}) U_{n'n\mathbf{k}}. \quad (2.84)$$

These last two equations define a generalized Fourier transform of the electron-phonon matrix elements between reciprocal space and real space. If the quantity $g_{nm\mu\alpha}(\mathbf{r}_l, \mathbf{r}_{l'})$ decays rapidly as a function of $|\mathbf{r}_l|$ and $|\mathbf{r}_{l'}|$ then only a small number of matrix elements in the Wannier representation will be sufficient to generate $g_{nm,s}(\mathbf{k}, \mathbf{q})$ *anywhere* in the BZ by using Eq. 2.83. The interpolation strategy is as follows: one first determines matrix elements in the Bloch representation using DFPT on a *coarse* grid in the BZ. Then MLWFs are constructed using the procedures of Marzari and Vanderbilt [99] and Souza, Marzari and Vanderbilt [103]. This will give the rotation matrices $U_{nm\mathbf{k}}$ that will be plugged into Eq. 2.84. Then the Fourier transform that takes reciprocal space to real space, performed via Eq. 2.84, is performed. At this point, the matrix elements outside the Wigner-Seitz cell spanned by the coarse Brillouin-zone grid can be neglected, and Eq. 2.83 is used to obtain new matrix elements $g_{nm,s}(\mathbf{k}, \mathbf{q})$ on *very fine* grids. Note, the knowledge of rotation matrices $U_{nm\mathbf{k}}$ are required also on the fine grids, which are obtained from the Wannier interpolation of the band structures as described by Souza, Marzari and Vanderbilt [103]. The operation is computationally inexpensive and allows for the calculation of up to millions of electron-phonon matrix elements. This Wannier interpolation routine is implemented in the EPW simulation package.

In **Paper III**, the Quantum Espresso (QE) [104–106] and EPW simulation packages are used to calculate $g_{mn,s}(\mathbf{k}, \mathbf{q})$ and related superconducting properties in MgB₂, in both anisotropic and isotropic approximations.

2.5 Thermodynamic stability

In a situation where a thin film has been grown and is subject to theoretical analysis, given that the global chemical composition can be considered constant, and if the surrounding environment can be viewed as both a temperature and pressure reservoir, Gibbs free energy is the most suitable thermodynamic potential and therefore is the quantity extensively used herein. Finding the equilibrium state of any system is equivalent to minimizing the given thermodynamic potential, which in this context means that equilibrium is found by the minimization of Gibbs free energy

$$G(x, T, p) = \min(E - TS + pV) = \min(H - TS) = \min(F + pV), \quad (2.85)$$

where E is total energy, T is absolute temperature, S is entropy, p is pressure and V is volume. The second and third equalities show different ways of expressing Gibbs free energy, using enthalpy $H = E + pV$ and Helmholtz free energy $F = E - TS$. The form of $G(x, T, p)$ indicates that minimization is achieved by a zero pressure situation and maximizing the entropy. For a system with configurational degrees of freedom, at high temperature with diffusion activated, maximizing entropy corresponds to obtaining a fully disordered configuration. In calculations of equilibrium properties of multicomponent phases, each constituent phase should be considered at its own equilibrium volume, where $p = 0$. Effects of temperature can be split up into separate electronic, configurational, vibrational, and magnetic contributions

$$G(x, T, p = 0) = E_0 + E_{el}(T) + E_{conf}(T) + E_{vib}(T) + E_{magn}(T) - T \left(S_{el}(T) + S_{conf}(T) + S_{vib}(T) + S_{magn}(T) \right). \quad (2.86)$$

Gibbs free energy extremas are the points that satisfy $dG = 0$. The most stable point is characterized by three criteria, $dG = 0$, $\partial^2 G / \partial X^2 > 0$, for some system descriptor X , and $G = G_{\min, \text{global}}$ as in the lowest global value. Metastable points satisfy the first two criteria, but with $G = G_{\min, \text{local}}$ being a local minimum. The third case is an unstable point, characterized by $\partial^2 G / \partial X^2 < 0$ such that any arbitrarily small perturbation destabilizes the system.

Studying the Gibbs free energy of one phase alone is not sufficient for investigating stability. The driving force is rather captured by *differences* in Gibbs free energy. For instance, comparing G of liquid and solid, or ordered and disordered, states of a phase can yield crucial information about transition temperatures. For multicomponent phases, comparing the Gibbs free energy of the compound itself to its constituent phases, at any given concentration, lets one derive information about the Gibbs free energy of *formation*. In the case of substitutional alloys that are constructed by mixing the constituents, it is commonly referred to as Gibbs *mixing* free energy. Regardless, it can be expressed on the general form

$$\Delta G(x, T, p) = \Delta H(x, T, p) - T\Delta S(x, T, V), \quad (2.87)$$

where at a given pressure (p) and temperature (T), the mixing enthalpy is defined as

$$\Delta H(x) = H(x) - \sum_i x_i H_i, \quad (2.88)$$

with $H(x)$ being the the enthalpy of the compound at composition x , and in the second term the summation is over all constituents i whose individual enthalpies are weighted by their atomic fraction x_i at the global composition x .

The sign of $\Delta G(x, T, p)$ gives hints about phase stability. In a compound, that does not necessarily have to be isostructural to its constituents, a negative sign $\Delta G(x, T, p) < 0$ means that it is preferable to form the compound, as it has lower free energy than the linear combination of its constituents at the given composition. It follows that it requires energy to dissociate the bonds. $\Delta G(x, T, p) > 0$ indicates that the structure is unstable with respect to the formation of free-standing constituents. For isostructural substitutional random alloys, $\Delta G(x, T, p) < 0$ indicates ordering tendency, that atoms prefer to mix and sit next to atoms of different kinds, in a solid solution. $\Delta G(x, T, p) > 0$ shows clustering tendency, where the atoms in the alloys prefer to sit next to atoms of the same kind, in segregated clusters. In the bordering case $\Delta G(x, T, p) = 0$ there is no correlation in the atomic configuration. There are many ways to form ordered and clustered configurations, in varying degrees. *How* the atoms order or cluster can be described in the picture of the CE method, and is determined from the effective cluster interactions and their respective average correlation functions.

In this thesis, the main focus is on configurational and vibrational contributions to Gibbs free energy in Eq. 2.86, and more importantly, how they affect phase stability. Magnetism and electronically excited states are not topical studies in the included articles. The methodological philosophy of how these contributions are captured is explained in steps below.

2.5.1 Alloy mixing thermodynamics

Let $A_{x_A}B_{x_B}$ be an isostructural binary alloy, in some arbitrary configuration σ . We consider 1 mole of atoms, $x_A + x_B = 1$, such that we can define $x_A = x$ and $x_B = 1 - x$. For a given composition x , temperature T , and pressure p we can express Gibbs mixing free energy of this system as

$$\begin{aligned} \Delta G^\sigma(x, T, p) &= \Delta G_{conf}^\sigma(x, T, p) + \Delta G_{vib}^\sigma(x, T, p) \\ &= \Delta H_{conf}^\sigma(x, T, p) + \Delta H_{vib}^\sigma(x, T, p) \\ &\quad - T\left(\Delta S_{conf}^\sigma(x, T, V) + \Delta S_{vib}^\sigma(x, T, V)\right). \end{aligned} \quad (2.89)$$

For all *ordered* configurations σ the configurational mixing entropy ΔS_{conf}^σ vanishes. For ideally disordered configurations, as in the random alloy, the configurational mixing entropy can in the mean field approximation be acquired analytically. If N is the number of lattice sites, occupied by n A atoms and $(N - n)$ B atoms, the number of possible ways to mix A and B is $g(N, n) = N!/(n!(N - n)!)$. Using the entropy relation $k_B \ln g$ and assign $x = n/N$ one can show using Stirling's approximation that

$$\Delta S_{conf}^{rand} = -k_B N \sum_i x_i \ln(x_i) = -k_B N [x \ln x + (1 - x) \ln(1 - x)]. \quad (2.90)$$

In this case, ΔS_{conf}^{rand} is temperature- and volume-independent because of the use of the mean-field approach, and mimics $T \rightarrow \infty$ lattice properties of an ideally random solid solution. The mixing enthalpy of the corresponding random alloy is modelled by sufficiently large SQS supercells, $\Delta H_{conf}^{rand}(x, T, p) = \Delta H_{conf}^{SQS}(x, T, p)$. If one desires to capture energetic short-range order effects, and let temperature dictate the configuration σ , one can cluster expand the total energy for a set of ordered configurations σ and map out the energetics of different local atomic environment, and construct a configurational Hamiltonian on the form in Eq. 2.38. This $\hat{H}_{conf}$ can then govern the energetics of canonical (NVT ensemble) MC simulations. Then it is possible to derive temperature dependent $\Delta H_{conf}^\sigma(x, T, p)$ and $\Delta S_{conf}^\sigma(x, T, V)$ from the MC configurational free energy.

Vibrational contributions $\Delta H_{vib}^\sigma(x, T, p)$ and $\Delta S_{vib}^\sigma(x, T, V)$ are in this thesis calculated in both harmonic and quasiharmonic approximations with the finite displacement method, for fixed ordered and disordered configurations. At the temperature-dependent equilibrium volume $V_0(T)$ in Eq. 2.62 these contributions are summarized, using Helmholtz free energy $F = E - TS$, to $\Delta F_{vib}^\sigma(x, T, V) = \Delta F_{vib}^{\sigma,(Q)HA}(x, T, V)$.

For binary alloys $A_x B_{1-x}$ it is customary to consider, other than the endpoints $x = 0, 1$, a discrete set of compositions where $\Delta G^\sigma(x, T, p)$ is calculated, where the voids are filled in with numerical interpolations to obtain a continuous function.

If $A_x B_{1-x}$ is an isostructural random alloy with clustering tendencies, there exists some global compositions x_{global} for which the two atomic species will want to form separate phases with widely differing compositions $x_{1,2}$ in order to minimize the free energy. These are usually found in the vicinity of local minima displayed in $\Delta G(x, T, p)$. The two new compositions that the random alloy wants to decompose into can be determined in at least two ways, using the common tangent construction or linear optimization. Phase decomposition is a diffusion process, driven by the chemical potential gradients. If diffusion is fully activated, an unstable alloy will decompose until two phases with equal chemical potential are obtained, terminating the driving force of diffusion. In the common tangent construction, one looks for the set of two compositions $x_{1,2}$ that have the same chemical potential

$$\mu_1 = \left. \frac{\partial \Delta G}{\partial x} \right|_{x=x_1} = \left. \frac{\partial \Delta G}{\partial x} \right|_{x=x_2} = \mu_2, \quad (2.91)$$

such that there is no driving force $\Delta\mu$ for further diffusion-driven decomposition. Furthermore they need to be connected by a straight line with the same slope

$$\frac{\Delta G(x_2) - \Delta G(x_1)}{x_2 - x_1} = \left. \frac{\partial \Delta G}{\partial x} \right|_{x=x_1}. \quad (2.92)$$

The linear optimization seeks to minimize the free energy by finding a new linear combination

$$\Delta G(x_{global}, T, p) = \min_{(f,x)} \left\{ f_1 \Delta G(x_1, T, p) + f_2 \Delta G(x_2, T, p) \right\} \quad (2.93)$$

under the constraints $f_1 x_1 + f_2 x_2 = x_{global}$, $f_1 \geq 0$ and $f_2 \geq 0$. The fractions $f_{1,2}$ of compositions $x_{1,2}$ are determined by the lever rule, and are given by $f_1 = (x_2 - x_{global})/(x_2 - x_1)$ and $f_2 = (x_{global} - x_1)/(x_2 - x_1)$. If not physically equivalent, the two methods are mathematically equivalent. They both find the equilibrium compositions for each temperature, corresponding to the *binodal lines* in $T - x$ phase diagrams. Additional information about phase stability can be obtained from also mapping out the *spinodal lines*, for which $(\partial^2 \Delta G / \partial x^2)_T = 0$. Doing so for a range of temperatures allows one to map and construct the phase diagram.

Decomposition will occur inside the binodal line in two different ways. In the region directly inside the binodal, but outside the spinodal, a clustering $A_x B_{1-x}$ alloy is subject to decomposition through the mechanism of nucleation and growth. Inside the spinodal region, characterized by a negative free energy curvature $(\partial^2 \Delta G / \partial x^2)_T < 0$, the alloy is unstable with respect to small composition fluctuations. There is no nucleation barrier and, as soon as atomic diffusion is active, spinodal decomposition occurs throughout the material. Outside the binodal region, the alloy is stable with respect to decomposition.

Fig. 2.4 shows an example of $A_x B_{1-x}$ with clustering tendencies. On the top is Gibbs mixing free energy for select temperatures ranging from 0 K to 2000 K in steps of 500 K. The red circles mark the equilibrium compositions $x_{1,2}$ that some phase of composition x_0 will be driven toward in the presence of atomic diffusion. Furthermore, dashed red lines highlight how $x_{1,2}$ are connected to the phase diagram, obtained by plotting $x_{1,2}$ at the corresponding temperature.

Figure 2.4: Example of how the binodal line is constructed, marking the border between where A_xB_{1-x} is stable as solid solution, and subject to decomposition. Red lines show the common tangent points $x_{1,2}$ at a temperature of 2000 K.

2.5.2 Thermodynamics at high pressure

From the point of view of materials properties, the difference between zero pressure and atmospheric pressure, or ambient conditions, is negligible. In high pressure situations far from equilibrium, where the pV term in Eq. 2.85 rivals the energy of chemical bonds, materials can undergo changes in their physical and chemical characteristics. The structural compression enhances electronic density and allows electrons, previously not involved in the bonding at low pressure, to become chemically active due to new overlapping of electronic orbitals. One such notable example is, for instance, the pressure-induced metallization of superconducting hydrides, such as sulfur hydride H_3S with $T_c = 203$ K at 155 GPa [107, 108] and lanthanum hydride LaH_{10} which has $T_c = 250\text{-}260$ K at 180-200 GPa [109, 110].

Experimentally, applying high static pressure on a sample requires specialized techniques using pressure cells, notably diamond anvil cells (DACs) [111]. These typically use two opposing diamond anvils to clamp samples in a chemically inert noble gas pressure-transmitting medium to achieve hydrostatic pressure. The reachable pressure range is related to the diamond culet size, that are on the micrometer level or below. It is possible to reach hundreds of gigapascals in a DAC (100 GPa is roughly one million times atmospheric pressure), mimicking even pressure-conditions of Earth's inner core. Diamond has the advantage of being transparent to many kinds of electromagnetic radiation, so by coupling spectroscopic techniques to DACs, like X-ray diffraction and Raman spectroscopy, one can probe structural and vibrational information of materials under extreme compression. Furthermore, laser-induced heating can be used to achieve sample temperatures of thousands of degrees, invoking atomic diffusion and permits elements in contact to chemically react and form compounds not attainable at ambient conditions.

In the framework of DFT the application of pressure is straightforward. One compresses the unit cell and locks the volume degree of freedom in the self-consistent loop. This is done for a set of volumes, for which typically a Birch-Murnaghan equation of state fitting is used, and the pressure at a certain volume falls out from the volume derivative of the calculated total energy.

In short, applying extreme conditions, such as high pressures and high temperatures and/or huge temperature gradients, opens up not only novel routes to metastable and kinetically hindered compounds, but also new frontiers in physical chemistry and developing new materials. **Papers IV and V** are prime examples of synergy between experimental and computational approaches in the discovery and characterization of novel structures that were realized by virtue of extreme conditions. The structures become thermodynamically stable at high pressure, and remain metastable once brought down to ambient conditions.

2.6 Elastic properties

This section follows the derivations from the book of Nye [112]. By studying elastic properties of materials one can gain the understanding of chemical bonds and cohesion of the system, probe anisotropy of compressibility and partial understanding of more complex mechanical properties such as hardness. In the elastic regime, where all deforming work is recoverable (thermodynamically reversible), materials exhibit a proportional relationship between the applied stress σ and the amount of strain ϵ it causes. In the case of small strains, the relation is linear and is given by Hooke's Law [112, 113]

$$\sigma_{ab} = \sum_c \sum_d C_{abcd} \epsilon_{cd}, \quad (2.94)$$

where σ_{ab} and ϵ_{cd} are stress and strain tensors, respectively, C_{abcd} is a fourth rank elastic stiffness constant tensor, and letters a, b, c and d denote Cartesian components. C_{abcd} contains $3^4 = 81$ independent coefficients and in full tensor notation Eq. 2.94 becomes the 9×9 array

$$\begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{31} \\ \sigma_{12} \\ \sigma_{32} \\ \sigma_{13} \\ \sigma_{21} \end{bmatrix} = \begin{bmatrix} C_{1111} & C_{1122} & C_{1133} & C_{1123} & C_{1131} & C_{1112} & C_{1132} & C_{1113} & C_{1121} \\ C_{2211} & C_{2222} & C_{2233} & C_{2223} & C_{2231} & C_{2212} & C_{2232} & C_{2213} & C_{2221} \\ C_{3311} & C_{3322} & C_{3333} & C_{3323} & C_{3331} & C_{3312} & C_{3332} & C_{3313} & C_{3321} \\ C_{2311} & C_{2322} & C_{2333} & C_{2323} & C_{2331} & C_{2312} & C_{2332} & C_{2313} & C_{2321} \\ C_{3111} & C_{3122} & C_{3133} & C_{3123} & C_{3131} & C_{3112} & C_{3132} & C_{3113} & C_{3121} \\ C_{1211} & C_{1222} & C_{1233} & C_{1223} & C_{1231} & C_{1212} & C_{1232} & C_{1213} & C_{1221} \\ C_{3211} & C_{3222} & C_{3233} & C_{3223} & C_{3231} & C_{3212} & C_{3232} & C_{3213} & C_{3221} \\ C_{1311} & C_{1322} & C_{1333} & C_{1323} & C_{1331} & C_{1312} & C_{1332} & C_{1313} & C_{1321} \\ C_{2111} & C_{2122} & C_{2133} & C_{2123} & C_{2131} & C_{2112} & C_{2132} & C_{2113} & C_{2121} \end{bmatrix} \begin{bmatrix} \epsilon_{11} \\ \epsilon_{22} \\ \epsilon_{33} \\ \epsilon_{23} \\ \epsilon_{31} \\ \epsilon_{12} \\ \epsilon_{32} \\ \epsilon_{13} \\ \epsilon_{21} \end{bmatrix}. \quad (2.95)$$

It is common to reduce the number of indices by introducing Voigt notation [114] that replaces pairs ab or cd by single digits i or j that are running indices from 1 to 6. The Voigt notation replaces $xx = 11 \rightarrow 1$, $yy = 22 \rightarrow 2$, $zz = 33 \rightarrow 3$, $yz = 23$ (and $zy = 32$) $\rightarrow 4$, $xz = 13$ (and $zx = 31$) $\rightarrow 5$ and $xy = 12$ (and $yx = 21$) $\rightarrow 6$. Numbers 1-3 are associated with *normal* stresses and strains, and numbers 4-6 are associated with *shear* stresses and strains. In Voigt notation, Hooke's law in Eq. 2.94 can be simplified to

$$\sigma_i = \sum_j C_{ij} \epsilon_j. \quad (2.96)$$

Doing so replaces the tensor C_{abcd} with the 6×6 matrix C_{ij} with $6^2 = 36$ independent coefficients. By also imposing symmetry relations $\sigma_{ab} = \sigma_{ba}$, $\epsilon_{cd} = \epsilon_{dc}$, $C_{abcd} = C_{bacd}$ and $C_{abcd} = C_{abdc}$, the number of independent coefficients are reduced to 21, and Eq. 2.95 becomes a symmetric 6×6 matrix

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{bmatrix} \begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{bmatrix}. \quad (2.97)$$

The number of independent coefficients in C_{ij} can be further reduced by crystal family specific rotational, mirror and inversion symmetries, making some constants have equal values and some equate to zero. For the hexagonal crystal structure family covered in this thesis, the number of independent elastic constants is five [112, 114], i.e. C_{11} , C_{12} , C_{13} , C_{33} and C_{44} , and the final matrix form is

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}(C_{11} - C_{12}) \end{bmatrix} \begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{bmatrix}. \quad (2.98)$$

Elastic stability is verified if the elastic constants C_{ij} satisfy the Born criteria [65] for hexagonal structures

$$\begin{aligned} C_{33} &> 0, C_{44} > 0, C_{12} > 0, \\ C_{11} &> |C_{12}|, \\ (C_{11} + C_{12})C_{33} - 2C_{13}^2 &> 0. \end{aligned} \quad (2.99)$$

Let $E_0(0)$ and V_0 be the equilibrium total energy and volume, respectively, of a stress-free reference state of the system. The Taylor expansion of the total energy expressed in power series of strains ϵ can then be expressed as [115]

$$E_0(\epsilon_1, \dots, \epsilon_6) = E_0(0) + \frac{1}{2} V_0 \sum_i \sum_j C_{ij} \epsilon_i \epsilon_j, \quad (2.100)$$

where the first-order term has been eliminated due to the stress-free reference state, and third-order and above terms are here neglected in the limit of sufficiently small strains. By distorting the lattice the total energy is increased by the elastic energy contribution given by the second term. The set of necessary distortions δ to probe the five independent elastic constants can be expressed in terms of the strain vector $\epsilon = \{\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4, \epsilon_5, \epsilon_6\}$. They are

$$\{\delta, \delta, 0, 0, 0, 0\} \rightarrow E_0(0) + V_0(C_{11} - C_{12})\delta^2, \quad (2.101)$$

$$\{0, 0, 0, 0, 0, \delta\} \rightarrow E_0(0) + \frac{1}{4}V_0(C_{11} - C_{12})\delta^2, \quad (2.102)$$

$$\{\delta, \delta, -2\delta, 0, 0, 0\} \rightarrow E_0(0) + V_0(C_{11} + C_{12} - 4C_{13} + 2C_{33})\delta^2, \quad (2.103)$$

$$\{0, 0, \delta, 0, 0, 0\} \rightarrow E_0(0) + \frac{1}{2}V_0C_{33}\delta^2, \quad (2.104)$$

$$\{0, 0, 0, \delta, \delta, 0\} \rightarrow E_0(0) + V_0C_{44}\delta^2. \quad (2.105)$$

In **Papers IV** and **V**, elastic constants are calculated by performing sets of $\pm 1\%$ and $\pm 2\%$ distortions δ without volume conservation, finding polynomial fits of energy as function of distortions δ , and evaluating second-order derivatives at zero strain [116]

$$C_{ij} = \frac{1}{V_0} \left. \frac{\partial E_0(\epsilon_1, \dots, \epsilon_6)}{\partial \epsilon_i \partial \epsilon_j} \right|_{\delta=0}. \quad (2.106)$$

From the elastic constants C_{ij} one can derive polycrystalline elastic moduli based on the Voigt-Reuss-Hill approximation [117]. For instance in the Voigt (V) model, bulk (B) and shear (G) moduli are expressed as [114, 117]

$$B_V = \frac{(C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{23} + C_{31})}{9} \quad (2.107)$$

$$, G_V = \frac{(C_{11} + C_{22} + C_{33}) - (C_{12} + C_{23} + C_{31}) + 3(C_{44} + C_{55} + C_{66})}{15}, \quad (2.108)$$

From elastic constants, there are several attempts with empirical models to predict hardness. However, hardness is a measure of resistance to *plastic* deformation where several other aspects of all materials enter, like dislocation dynamics, microstructure and alloying effects. Nevertheless, we have used the empirical model of Chen [118] to estimate Vicker's hardness values according to

$$H_V = 2(k^2 G)^{0.585} - 3, \quad (2.109)$$

where $k = G/B$ is Pugh's ratio [119]. The ratio B/G is used to measure the ductility/brittleness of a material, with value 1.75 is often set to distinguish between the two types, i.e. ductile materials have $B/G > 1.75$ and brittle ones have $B/G < 1.75$.

Although not treated in the works herein, it is worth to mention the case of random alloys. In the calculations of tensorial materials properties from SQS models, the point group symmetry of the underlying lattice is broken. The general triclinic lattice of SQS models and varying microscopic local environments means individual elastic constants may not obey symmetry relations, but on average the symmetry can be preserved. Tasnádi et al. pointed out that the convergence of

the elastic tensor with respect to SQS size is slow, and instead proposed a scheme that searches for SQSs resulting in point symmetry group averaged projections closest to the true elastic tensors [116].

This chapter aims to showcase the application of the computational methods previously presented. For full reports and details, I refer the Reader to the attached publications. Below I have handpicked *some* of the most illuminating examples of my calculations where the methods have been applied.

3.1 Paper I - Theoretical investigation of mixing and clustering thermodynamics of $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ alloys with potential for age-hardening

Metastable ternary ceramic alloys with clustering tendencies are candidates for hard coating applications. In this work, mixing thermodynamics and structural parameters of ceramic $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ alloys are investigated with theoretical first-principles based techniques. Lattice dynamics and temperature dependent phase stability is explored. The isostructural phase diagram is derived using both cluster expansion-based Monte-Carlo simulations and a mean-field approach. As-deposited states of $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ alloys at compositions $x = 0.125, 0.25, 0.375, 0.50, 0.625, 0.75$ and 0.875 are modelled by disordered supercells from the SQS approach. Lattice dynamics are treated in static lattice, harmonic and quasiharmonic approximations. Fig. 3.1 shows the composition and temperature dependence of the Gibbs mixing free energy ΔG_{mix} of $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ in the mean field approximation, for the three levels of lattice approximations.

Figure 3.1: Gibbs mixing free energy $\Delta G(x, T)$ of $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ as function of composition x for different temperatures, at zero pressure. The shaded blue region shows the temperature range of interest for cutting tool operation.

Solid lines represent the static lattice approximation, which only includes configurational contributions to the free energy. It is the DFT ground state energy of the SQS models for a random alloy where temperature is introduced together with configurational entropy. Dashed lines represent the HA, for which harmonic phonons are added to the static lattice free energy. The dotted lines represent the QHA, for which the harmonic phonons have quasi-harmonic corrections added to them in order to incorporate effects of zero point motion and thermal expansion to the total free energy. From the temperature dependence shown in Fig. 3.1 one can see in the range 0-1000 K that the three lattice approximations practically lie on top of each other. Hence, it is not until temperatures beyond 1000 K that the vibrational free energies contribute significantly, compared to the configurational part, to the total Gibbs mixing free energy. It is therefore made apparent that it is important to include the effect of lattice vibrations when investigating phase stability of $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ mainly at elevated temperature.

Fig. 3.2 shows the theoretical mean field phase diagram constructed by applying the common tangent method on the total Gibbs mixing free energy mean field curves. The binodal lines are shown in solid, indicating the boundary between the region where a $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ alloy has a thermodynamic driving force to mix into a single-phase solid solution (outside), and where it is favourable for it to phase separate (inside). The static lattice approximation is drawn in black, green for HA and red for QHA. The dashed lines are the chemical spinodal lines, marking the inflexion points of the total Gibbs mixing free energy curves. Isostructural decomposition will occur inside the binodal in two different ways. In the region directly inside the binodal, but outside the spinodal, a $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ alloy is sub-

ject to decomposition through the mechanism of nucleation and growth. Inside the spinodal region, characterized by a negative free energy curvature $\partial^2 \Delta G / \partial x^2 < 0$, the alloy is unstable with respect to small composition fluctuations. There is no nucleation barrier and, as soon as atomic diffusion is active, spinodal decomposition occurs throughout the material.

Figure 3.2: Phase diagram for disordered $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$. Solid lines show binodal lines and dashed lines are the spinodal lines. The shaded blue region shows the temperature range of interest for cutting tool operation.

The shaded blue region in Fig. 3.2 indicates the aforementioned temperature range (1000 to 1500 K) of relevance for hard coatings on tool edges during cutting operation. It shows how this system experiences a miscibility gap that closes only well beyond the temperature of prospect applications. By comparing the black and green curves one can see that inclusion of vibrations in the HA moves the closing of the miscibility gap to a higher temperature, as well as shifting its position towards the composition centre. The binodal line predicts that the Al-rich phase remains close to pure AlB_2 . On the Ti-rich side the maximum solubility of Al, at a given temperature, decreases when lattice vibrations are taken into account. This effect is more enhanced for the spinodal line, where even the Al-rich phase boundary is shifted. In other words, the miscibility gap is shifted towards more Ti-rich alloys, as compared to the static lattice approximation.

Vibrations in the QHA shifts the miscibility gap boundary towards even more Ti-rich composition in the Ti-rich region. However, in the Al-rich region the HA and QHA curves are very similar. Going far beyond the melting temperature of AlB_2 would make the QHA calculation unstable. Upon reaching temperatures close to 2000 K, the free energy-volume landscape starts to flatten out for AlB_2 . For those and even higher temperatures it would be essential to have full capture

of anharmonic effects.

In order to investigate how short-range configurational clustering affects phase stability, 1500 ordered $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ structures were generated and used to cluster expand the total energy and train a model using 66 pair, 116 triplet and 18 quadruplet clusters. The predictive power of the model is quantified by the CV scores CV^{fit} of 3.26 meV/f.u. and CV^{pred} of 3.30 meV/f.u. for fitted and predicted structures, respectively. This CE is used as a Hamiltonian for canonical MC simulations using the EMC2 subroutine of ATAT to derive the free energy as a function of temperature and concentration.

Figure 3.3: Gibbs mixing free energy, ΔG , for select temperatures: 0 K (black) to 6000 K (red) in steps of 1000 K, capturing the whole temperature range simulated in MC. Solid lines are those of CE+MC, and dashed are from the SQS+MF approach.

Fig 3.3 shows the zero pressure Gibbs mixing free energy as function of Al concentration for select temperatures, as derived from the CE+MC approach, as well as for SQS+MF. The simulations were carried out at fixed compositions between 0 and 1 in steps of 0.0625, and the composition range was then made continuous with spline interpolation. The MC simulation box starts in a disordered state at the initial temperature of 6000 K, and is then annealed down to 0 K in steps, with the atomic configuration being temperature-dependent such that at some critical temperature an order-disorder transition occurs and short-range ordering (clustering) effects are captured. At this point, thermodynamic integration is halted and therefore the curves are cut at low temperature. From our results, below 2300 K is when Ti and Al atoms want to start cluster next atoms of the own kind. Three examples of what the resulting MC simulation boxes can look like at the end of the annealing process are shown in Fig. 3.4. It should be noted that the configuration found is dependent on the size of the simulation box.

Figure 3.4: $16 \times 16 \times 13$ (9984 atoms) $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ MC simulation boxes at final step $T = 0$ K.

To see how short-range clustering affect phase stability, the phase diagram based on CE+MC calculations is derived, and is presented in Fig. 3.5.

Figure 3.5: Phase diagram in mean field approximation (black) and one based on cluster expansion and canonical MC simulations (red). No vibrations included.

The red curve shows the phase diagram as derived from the chosen CE. It is cut when crossing the order-disorder temperature from above, for any fixed composition, to avoid thermodynamic integration across heat capacity peaks. It predicts that the miscibility gap closes at 2420 K, in contrast to the mean field

approach in black (identical to the black curve in Fig. 3.2) that closes at 3120 K. Thus, the critical temperature for closing the miscibility gap is reduced by about 20%, due to the presence of short-range clustering, which is in line with what can be expected with respect to a mean-field approximation of the Ising-like alloy problem [120].

3.2 Paper II - Coupling of lattice dynamics and configurational disorder in metal deficient $\text{Al}_{1-\delta}\text{B}_2$ from first-principles

In this work we perform theoretical simulations, in particular alloy theory simulations and lattice dynamics simulations based on electronic structure theory to investigate the following outstanding questions for AlB_2 : which configurations of Al vacancies form stable structures with respect to the constituent elements, ideal stoichiometric AlB_2 , and each other? What is the stable composition range for the compound as a function of temperature? Why is it reported to be narrow? What is the effect of lattice dynamics on stability and what is the effect of configurational order and disorder on lattice dynamics and thermal expansion? To compare with the latter, we performed in-situ X-ray diffraction (XRD) measurements during heating of commercial AlB_2 powder to obtain the lattice constants of $\text{Al}_{1-\delta}\text{B}_2$ as a function of temperature (not presented here, see **Paper II**).

Figure 3.6: Formation energy of $\text{Al}_{1-\delta}\text{B}_2$ calculated with DFT, as function of aluminium composition, x in $\text{Al}_x\text{B}_{1-x}$. Black crosses correspond to ATAT-generated structures. The green shaded area shows where $\text{Al}_{1-\delta}\text{B}_2$ is stable with respect to its constituent elements, but only the darker shaded stripe is where $\text{Al}_{1-\delta}\text{B}_2$ is part of the convex hull.

The relevant concentrations and configurations of metal vacancies are analysed using CE and SQS methods combined with vibrational free energy calculations within the QHA for ordered and disordered phases. Fig. 3.6 displays the DFT derived formation energy, ΔE , with respect to elemental fcc-Al and α -B, for 1047 metal deficient $\text{Al}_x\text{B}_{1-x}$ structures generated with ATAT. Every black cross corresponds to a different structure, with a vacancy concentration of 0 – 25%. Each considered concentration has around 100 structures, each with a different vacancy configuration. The green shaded area shows the narrow com-

position range, $0.280 \leq x \leq 0.333$ ($0 \leq \delta \leq 0.222$), for which $\text{Al}_x\text{B}_{1-x}$ vacancy structures are stable with respect to pure fcc-Al and α -B, with $\Delta E(x) \leq 0$, and the darker green area the even more narrow region that constitutes the convex hull at 0 K, $0.310 \leq x \leq 0.315$ ($0.080 \leq \delta \leq 0.101$). From what our calculations predict, $\text{Al}_x\text{B}_{1-x}$ structures with 25% vacancies are all unstable. The blue curve is the 0 K convex hull.

From calculating the 1047 ordered structures using DFT, three vacancy structures are predicted to lie on the 0 K convex hull as ground states. They are denoted by the number of Al and B atoms in their primitive supercell, and are given the names Al_9B_{20} ($\Delta E = -55.22$ meV/atom, 10% vacancies), $\text{Al}_{11}\text{B}_{24}$ ($\Delta E = -55.53$ meV/atom, 8.33% vacancies) and $\text{Al}_{12}\text{B}_{26}$ ($\Delta E = -55.42$ meV/atom, 7.69% vacancies). Meanwhile, stoichiometric AlB_2 itself has a formation energy $\Delta E = -42.93$ meV/atom, and lies 11.07 meV/atom *above* the convex hull. This explains the experimental findings of off-stoichiometry in AlB_2 samples. Fig. 3.7 shows relevant structures in the modelling of vacancies, namely two SQSs with disordered vacancies in Fig. 3.7a, and different views of the three 0 K convex hull crystal structures are displayed in Fig. 3.7b.

These ordered structures have line vacancy formations that propagate throughout the metal sublayer. Looking from the side perspective, one can see that the vacancy lines are alternatively shifted, forming a zig-zag pattern between interplanar nearest-neighbouring (nn) vacancy lines. The in-plane distance between vacancies and their neighbouring vacancy lines vary with vacancy concentration. From top to bottom in FIG. 3.7b, Al_9B_{20} has a nn distance between two vacancies of 6.01 Å, and the distance between two adjacent in-plane vacancy lines is 13.11 Å. Similarly, $\text{Al}_{11}\text{B}_{24}$ has distances of 7.96 Å and 12.03 Å, while $\text{Al}_{12}\text{B}_{26}$ has 7.96 Å and 13.11 Å. In each structure a vacancy is surrounded by an aluminium hexagon. For Al_9B_{20} , the nn vacancies have overlapping of such aluminium hexagons that share vertices. Both $\text{Al}_{11}\text{B}_{24}$ and $\text{Al}_{12}\text{B}_{26}$, having the same vacancy nn distance of 7.96 Å, have their corresponding closest hexagon vertices separated by one lattice spacing.

Figure 3.7: Visualization of selected relevant structures. Purple, green and red spheres represent boron, aluminium and Al vacancies, respectively. **a)** Two considered SQSs with 10.0% (left) and 12.5% (right) disordered vacancies. **b)** Primitive supercell (left), top (middle) and side (right) view of the crystal structure of the three ordered defective AlB₂-type structures that lie on the 0 K convex hull. Black boxes in the top view correspond to the primitive supercells.

To gain an understanding why metal vacancies are intrinsic and energetically favourable in $\text{Al}_{1-\delta}\text{B}_2$, and not only induced by entropy at high temperature, the electronic density of states (DOS) is calculated. Fig 3.8 presents this, from bottom to top, for the stoichiometric AlB₂ unit cell, the three ground state primitive supercells, lying on the 0 K convex hull, and the two disordered vacancy structures.

Black curves are the total electronic DOS, while purple corresponds to boron, and green to aluminium. Dotted coloured lines show the summed up s -orbital contribution of the respective atomic species, and solid coloured lines show that of the p -orbitals. The red shaded area represents the rigid-band model prediction by Loa et al. [121] that lowering E_F by 0.9 eV should deplete anti-bonding Al- s states that destabilize stoichiometric AlB_2 . Boron has a Pauling electronegativity of 2.04 and aluminium 1.61, meaning boron will attract $3p$ and $3s$ electrons from aluminium. Consequently the aluminium atoms contribute weakly to the total electronic DOS.

Figure 3.8: Calculated electronic DOS, in arbitrary units, of AlB_2 , the three ordered defective AlB_2 -type structures on the 0 K convex hull, and two disordered SQSs. The energies are given with respect to the Fermi energy E_F of each structure, while the shift in E_F relative to AlB_2 is given in the legend. Black solid line is the total DOS, and the coloured solid lines are the p -orbital contribution from aluminium (green) and boron (purple). Dashed coloured lines are the s -orbital contributions to the DOS.

The main characteristic of the defective structures is that the Fermi energy E_F has been shifted to the bottom of the pseudogap, depleting partially filled

antibonding Al-*s* from the conduction band. This is most distinguishable for Al_9B_{20} , $\text{Al}_{11}\text{B}_{24}$ and the $\text{Al}_{0.90}\text{B}_2$ SQS. For disordered $\text{Al}_{0.875}\text{B}_2$, the Fermi level is slightly to the left of the pseudogap, indicating that vacancy concentrations higher than 12.5% will start depleting favourable bonding orbitals. This is in line with the quickly increasing ΔE of such structures in FIG. 3.6, regardless of configuration. The exact shift in the Fermi energy ΔE_F , relative to stoichiometric AlB_2 , is -0.83 eV for $\text{Al}_{12}\text{B}_{26}$, -0.91 eV for $\text{Al}_{11}\text{B}_{24}$, -1.11 eV for Al_9B_{20} , -1.14 eV for the $\text{Al}_{0.90}\text{B}_2$ SQS, and -1.42 eV for the $\text{Al}_{0.875}\text{B}_2$ SQS.

A CE model is trained on the 1047 ordered structures, with 100 pair-interactions, 100 3-site cluster interactions and 10 4-site cluster interactions, and is used to construct a Hamiltonian for canonical MC simulations. This extends the modelling beyond 0 K ordered configurations into finite temperatures with interplay between configurational order and disorder. In addition, we also go one step further by also including vibrational contributions to the total free energy in both HA and QHA. From free energy curves, the phase diagram is derived and presented in Fig. 3.9. The green shaded shows the narrow concentration range where metal vacancies are thermodynamically stable. At concentrations close to the 7-12% range, vacancies are predicted to undergo a transition from ordered to disordered at temperatures above 200 K.

Figure 3.9: Phase diagram of $\text{Al}_x\text{B}_{1-x}$ predicting a narrow stability region (green area spanned by CE+MC+QHA), outside which the compound faces decomposition. Level of approximation is given by the different symbols in the legend. The compositional dependent order-disorder transition temperature is given by the grey circles.

One can notice the close matching of HA (open squares) and QHA (solid circles) with static lattice approximation (open circles), derived directly from the

CE approach and MC simulations. This suggests that vibrational contributions to the configurational formation energy in both HA and QHA, are not likely to have distinct impact on overall phase stability. This can be understood from the view that the energetic contribution from the thermal expansion of the defective phases is balanced by those of the constituent elements (pure Al and B). In other words, phase stability is seemingly dictated by the atomic configuration on the metal sublattice in this system. However, configuration on the other hand does influence vibrations and thermal expansion, see **Paper II**.

3.3 Paper III - The effect of strain and pressure on the electron-phonon coupling and superconductivity in MgB₂

Different theoretical methodologies are employed to investigate the effect of hydrostatic pressure and anisotropic stress and strain on the superconducting transition temperature T_c of MgB₂. This Paper goes in depth into the analysis of the Kohn anomalies present on the E_{2g} optical branch of B-B bond-stretching vibrational modes [122–128], but is not discussed here for brevity. The focus of this summary will be on the explicit treatment of EPC in the Migdal-Éliashberg formalism implemented in QE and EPW computational codes. The zero pressure phonon band structure (left), with each branch broadened by the corresponding phonon linewidth, and electronic band structure (right) is shown in Fig. 3.10.

Figure 3.10: Band structure plots of MgB₂ at zero pressure. **a)** *Phonon* band structure with branches broadened by the phonon linewidth $\gamma_{\nu\mathbf{q}}$ showcasing the modes and directions that has strongest electron-phonon coupling. **b)** *Electronic* band structure. The two σ -bands marked in blue and green are essential to the superconducting properties of MgB₂ as they couple the strongest to the phonons. Those and the π -band in red make up the Fermi surface.

For the phonon band structure, this reveals that the anomalous E_{2g} band in the 60-80 meV range along $\Gamma - K$, $\Gamma - M$, $\Gamma - H$ and $\Gamma - L$, originating from B atoms, indeed have strong EPC and contribute to superconducting properties. Γ -A of the same band is also found to have strong coupling. The electronic band structure in fig. 3.10b reveals three important boron bands highlighted in colour; two σ -bands (blue and green) and one π -band (red). The two σ -bands with $p_{x,y}$ character straddle the Γ -A line with negligible dispersion near ϵ_F . Furthermore, they cross ϵ_F

parabolically along Γ - $\mathbf{q}$ ($\mathbf{q}=K, M, H, L$) providing the majority of the contribution to $N(\epsilon_F)$ and the EPC. The features seen in Fig. 3.10 are evidencing the presence of Cooper-Pairs, from the coupling of optical B - B bond-stretching vibrations in the 60-80 meV range (at ambient pressure) and the holes at the top of the σ -bands.

For pedagogical visualization purposes, the effect of hydrostatic pressure on the EPC in MgB_2 is best captured by the Éliashberg spectral function $\alpha^2 F(\omega)$, given in the isotropic approximation in Fig. 3.11. The cumulative electron-phonon mass enhancement parameter $\lambda(\omega)$ is also shown.

Figure 3.11: Electron-phonon properties of MgB_2 derived using QE. Solid lines show Éliashberg spectral function $\alpha^2 F(\omega)$ at different pressures, ranging from -20 to 25 GPa in steps of 5 GPa. Dashed lines correspond to the cumulative mass enhancement parameter $\lambda(\omega)$, that once becoming a straight flat line as the spectral function dies out reveals the total electron-phonon coupling value λ .

The most striking feature of the spectral function is that the position of its peak aligns with the location of the anomalous E_{2g} optical branch, dwarfing all contributions from other phonons - c.f. the light-blue $p = 0$ curve in Fig. 3.11 with Fig. 3.10a. From our calculations we find that the total EPC, λ , decreases with pressure. Using QE (EPW), at the lowest considered pressure of -20 GPa it goes from its maximum $\lambda = 1.498$ (1.259), to 0.649 (0.621) at ambient pressure, and down to 0.476 (0.459) at 25 GPa. How this relates to T_c is presented in Fig. 3.12, where the EPC is one of the inputs in the isotropic McMillan-Allen-Dynes formula. The T_c values using this formula, together with $\mu^* = 0.16$, for the QE and EPW codes are shown by coloured solid squares. Using $\mu^* = 0.16$ as a free parameter and setting it to 0.01, albeit outside the typical range of 0.1-0.2, gives good agreement with experiments (in black), here shown for the QE case by open blue squares. We also go beyond the isotropic approximation and calculate the closing of the distribution of the anisotropic superconducting gap $\Delta_{n\mathbf{k}}$ on the Fermi surface, obtained both from the real axis using Padé approximants and the imaginary axis

for comparison. In both cases the standard choice of $\mu^* = 0.16$ was employed. Our calculations show that both the real and imaginary axes approaches yield the same values. The red solid circles represents the results from calculations on the real axis.

Figure 3.12: Superconducting transition temperature T_c versus pressure for different methods. Blue (red) boxes show McMillan-Allen-Dynes T_c (Eq. 2.80) calculated using QE (EPW), with μ^* shown in legends. Red circles shows pressure dependent closing of the anisotropic superconducting gap $\Delta_{n\mathbf{k}}$ on the Fermi surface, obtained from the real axis using Padé approximants and using $\mu^* = 0.16$. Coloured stars correspond to direction-averaged T_δ values from finite displacements and linear response phonons (not described in this summary). Black symbols correspond to experimental values.

Superconducting T_c is also calculated, in the isotropic approximation using McMillan-Allen-Dynes formula, for anisotropically strained MgB₂ in order to capture the *absolute change* in T_c . This is shown on the right in Fig. 3.13 together with total EPC on the left.

Figure 3.13: Superconducting properties of anisotropically strained MgB_2 (a, c) grid points. **a)** Total electron-phonon coupling, λ , calculated using QE. Green point and transparent plane corresponds to the equilibrium value $\lambda = 0.643$. **b)** Absolute change in T_c relative to equilibrium MgB_2 , calculated with QE using the McMillan-Allen-Dynes formula with $\mu^* = 0.16$.

A green point and transparent plane is used to guide the eye to the value corresponding to unstrained MgB_2 . In both subfigures it is clear that compressing either a or c alone, or in a combination as in the case of hydrostatic pressure, the EPC strength and consequently T_c are suppressed. The most minute change to the lattice, captured by the grid, is achieved by stepping either $\pm 2\%$ along the a -direction. A 2% compression of a alone is here predicted to reduce T_c by 2.6 K, while on the contrary a 2% expansion increases it by 5.5 K. The grid with explicit treatment of EPC shows how individually stretching either a or c alone or in unison enhances the superconductivity in MgB_2 . Stretching a while compressing c is found to suppress superconductivity. For instance, stretching a by 2% while compressing c by 7% lowers T_c by 9.3 K. This is in contrast to the reverse case, whereby compressing a by 2% and stretching c by 7% increases T_c by 11.3 K. This degree of strain is hard to achieve experimentally by means of standard epitaxial growth-strain, on for instance SiC and AlN, as an increase in a or c tends to lead to a decrease in the other with a compensating effect on T_c . Instead, we propose clever nanostructure design together with other diboride candidates as ways to achieve these strains, see **Paper III**.

3.4 Paper IV - Novel class of rhenium borides based on hexagonal boron networks interconnected by short B_2 dumbbells

In this work, a new class of rhenium borides was identified by synchrotron single-crystal X-ray diffraction in experiments in laser heated DACs between 26 and 75 GPa. Structural, mechanical and electronic properties derived both theoretical and experimental methods are used to characterize the new class. Prior to this, rhenium borides with boron content higher than in ReB_2 have never been obtained experimentally. Rhenium triboride (ReB_3) and rhenium tetraboride (ReB_4) are identified as novel compounds. Crystal structures of all boron-rich rhenium borides, ReB_x ($x = 2 - 4$), share many similarities. They are composed of hexagonal layers of Re atoms interchanging with a network formed by covalently bonded boron atoms. In the simplest case of ReB_2 , the boron network is organized as a one-dimensional layer formed by condensed six-membered rings in a puckered chair-like configuration, slightly different from the AlB_2 -type structure considered in **Papers I-III**.

The structure of ReB_3 is obtained by giving half of all boron atoms of each network an additional boron atom, forming B_2 dumbbells oriented along the c -axis. The distances in the dumbbells are found to be the shortest ones in the structure, about 1.66 Å at ambient pressure. ReB_4 is obtained by giving all boron atoms in the ReB_2 -like boron networks an extra boron atom, such that all form vertical B_2 dumbbells, resembling double-layered chair-like sheets. The structure organization of ReB_3 and ReB_4 allows us to propose a new class of rhenium borides that can be stabilized by high pressure. In a similar way that ReB_3 and ReB_4 relates to ReB_2 , the structures of hypothetical ReB_5 , ReB_6 and ReB_7 were constructed by hand. The side views of ReB_x ($x = 2 - 7$) are presented in Fig. 3.14.

Figure 3.14: Generation of homologous ReB_x ($x > 2$) compounds by adding boron atoms with the short bonds oriented parallel to c -axis to boron chair-like hexagonal sheets. Big grey spheres show Re atoms, and smaller black spheres show B atoms.

The electronic DOS of ReB_x ($x = 2 - 7$) is shown in Fig. 3.15. Our calculations suggest that all compounds have metallic behaviour, owing to the finite DOS

crossing at E_F . Beginning at ReB_2 , there is a significant overlap between Re-5d and B-2p states from deep within the valence band and surviving into the conduction band. The hybridization between these two orbitals is indicative of strong covalent bonding. As B is more electronegative than Re, there is a charge transfer from Re to B, characteristic of ionic bonding, making the boron sublattice isoelectronic to neutral C, at least in ReB_2 . The overlap between Re-5d and B-2p remains present in all ReB_x compounds. The overall shape of the DOS below E_F is the same for all boron concentrations, with the most noticeable difference being the deepest valence states, dominated by B-2s, getting shifted downwards upon further addition of boron. Moreover, as one could expect, it is apparent that Re contributes less to the total DOS as the boron concentration increases.

Figure 3.15: Calculated electronic DOS, in arbitrary units, of ReB_x ($x = 2 - 7$) at ambient pressure. Energies are presented with respect to the Fermi energy of each compound. Black solid lines are the total DOS, while red and purple are for Re and B, respectively. Explanations to the partial s -, p - and d -orbital contributions are given in the legends.

There is a peak in the DOS of ReB₂ at E_F , mainly consisting of Re-5d states. This type of peak is also seen in the related 3d metal diboride TiB₂. Symmetry projection of Ti *d*-states in TiB₂ revealed that this feature mainly comes from 3d_{z²} and 3d_{x²-y²} states, and it even survives in pure hexagonal Ti. If ReB₂ is understood within a rigid band model, with three additional electrons, it is therefore indicative that this peak in the DOS is due to Re 5d-5d hybridization in the *c*-direction. As more boron is added in between the hexagonal Re layers, this hybridization likely weakens. Nevertheless, from an electronic structure point of view, the general resemblance of the boron rich ReB_{*x*} phases is suggestive of them having mechanical properties comparable to ReB₂.

Experimentally measured and theoretically calculated structural parameters as function of pressure of studied rhenium borides is presented in Fig. 3.16. Powder XRD finds at ambient conditions the following cell parameters of; ReB₃ - $a_0 = 2.9172(3)$ Å, $c_0 = 4.5809(8)$ Å, $V_0 = 33.760(8)$ Å³; ReB₄ - $a_0 = 2.9305(2)$ Å, $c_0 = 10.8148(14)$ Å, $V_0 = 80.434(12)$ Å³. Theoretical calculations correspond well with experimentally obtained values.

Figure 3.16: Unit cell volume, relative unit cell parameters and c/a ratio of rhenium borides studied in the current work as function of pressure: ReB₂ (a); ReB₃ (b); ReB₄ (c). Solid filled symbols represent experimental data, dash lines correspond to the values computed by DFT.

Dynamical stability of ReB_{*x*} ($x = 2 - 7$) at ambient pressure is checked by

calculating phonon dispersions ω_{qs} using the finite displacement method. All phases are dynamically stable, except for ReB_7 that displays imaginary boron vibrational modes. These are attributed to boron atoms situated in the middle of the thick boron networks that sandwich the flat Re-layers, as seen to the right in Fig. 3.14.

Figure 3.17: Phonon dispersion curves and partial DOS at ambient pressure calculated in the harmonic approximation for ReB_x ($x = 2 - 7$). Solid red and purple lines are combined partial DOS of Re and B atoms, respectively, while dashed lines are partial DOS for individual atoms.

Thermodynamic stability of ReB_x ($x = 2 - 7$), with respect to hcp Re and most stable B allotrope, is investigated as function of pressure. In accordance to my calculations, α -B is used from 0-18 GPa, γ -B from 19-90 GPa, and ζ -(α -Ga type)B from 91 and onwards, for the considered pressures.

Figure 3.18: (Left) Distance to convex hull of ReB_x ($x = 2 - 7$) phases as function of pressure up to 200 GPa. Solid lines represent static lattice and dotted lines are vibrating lattice in the harmonic approximation at 1600 K for ReB₃ and 2600 K for ReB₄. (Right) Convex hull plots at pressures of 30, 100, and 150 GPa. Open circles are metastable phases and filled circles are stable phases sitting on the convex hull. As a guide to the eye, the most relevant ReB_x ($x = 2 - 7$) phases are given larger circles and are coloured in accordance with the left image. No vibrations included.

ReB₂ is thermodynamically stable and part of the convex hull at all pressures. Rhenium borides with higher boron content tend to become thermodynamically stable at higher pressures. Following the solid lines corresponding to static lattice approximation, in good agreement with experimental data, ReB₃ becomes stable at >25 GPa. For ReB₄, the lowest border of synthesis is 33 GPa, while theory

predicts, at 0 K, that it located just 25 meV/atom above the convex hull at 33 GPa. Further, it comes within 0.4 meV/atom at 90 GPa, but never quite enters the convex hull, due to the stabilization of ζ -B at 91 GPa.

Left in Fig. 3.18, vibrational energy contributions in the harmonic approximation let us capture the *qualitative* impact of temperature on the thermodynamic stabilization of novel ReB_3 and ReB_4 phases. In an attempt to mimic the temperature conditions of when the phases first were observed in the experiments, we add vibrational free energy of formation contributions at 1600 K to ReB_3 , and at 2600 K to ReB_4 . It is found that the effect of temperature on the stabilization pressure reduces it from 43 GPa to 30 GPa, and from non-existent to 38 GPa, for ReB_3 and ReB_4 , respectively. These temperature *trends* are in line with experimental values. Hypothetical ReB_5 , ReB_6 and ReB_7 are predicted to never become thermodynamically stable at 0 K. The kinks around 20 GPa are due to the formation of Re_2B_5 , to be discussed in Paper V.

Ambient pressure elastic constants C_{ij} were calculated by straining fully relaxed unit cells with $\pm 1\%$ and $\pm 2\%$ distortions, fixing the cell volume, and then fitting the total energy to a second-order Taylor expansion. For dynamically stable ReB_x ($x = 2 - 6$) phases, five independent elastic constants are calculated to complete the elastic tensor, namely C_{11} , C_{12} , C_{13} , C_{33} and C_{44} . They were used to estimate Vickers hardness via Chen's model $H_V = 2(G^3/B^2)^{0.585} - 3$, where B is the bulk modulus, and G is the shear modulus. This is presented in Fig. 3.19, where, according to my calculations the dynamical stability is further substantiated by the elastic constants satisfying the Born stability criteria. ReB_2 is predicted to be the hardest, with the more boron rich compounds having similar mechanical properties.

Figure 3.19: Mechanical properties of ReB_x as function of B composition **a)** Elastic constants C_{ij} **b)** Estimated Vickers hardness H_V .

3.5 Paper V - High-pressure high-temperature synthesis of Re_3B_7 and Re_2B_5 with complex modular structures

We report on high-pressure and high-temperature (HPHT) synthesis and crystal structure of two novel rhenium borides, Re_3B_7 and Re_2B_5 , found in synthesis at 33 GPa and 1700 °C. Trirhenium heptaboride Re_3B_7 crystallizes in sp.gr. P-6m2 ($a = 2.9106(3)$, $c = 12.0499(17)$ Å), while dirhenium pentaboride, Re_2B_5 , has sp.gr. P63/mmc ($a = 2.9159(4)$, $c = 16.642(3)$ Å). Both compounds consist of hexagonal layers formed by rhenium atoms that interchange with puckered networks of boron atoms. The structures feature with short B_2 dumbbells oriented along c -axis that contributes to a strong anisotropy in elastic properties similarly to what is observed in other anisotropic borides, ReB_3 and ReB_4 . The crystal structures of the previously known ReB_2 and the by us discovered boron-rich rhenium borides Re_3B_7 , Re_2B_5 , ReB_3 and ReB_4 can be rationalized as a series of homologous compounds where rhenium layers interchange with variously structured puckered boron networks. Re_3B_7 and Re_2B_5 are unique because they are the first examples of rhenium borides that combine boron networks of various kinds within one crystal structure.

Figure 3.20: Evolution of crystal structures of rhenium borides with increasing boron content. A primary element of all structures is a single-layer puckered hexagonal boron network (a, black spheres) that in a simplest case of ReB_2 (b) interchange with flat close packed layers built from rhenium atoms (grey spheres). When half of boron atoms in hexagonal network attach additional boron atoms and form short B-B distances oriented along to c -axis (orange bonds) we call the resulted network as "1.5-layer". In case when all boron atoms are arranged with dumbbell boron atoms, we call it 2-layer network. Crystal structures of Re_3B_7 (c) and Re_2B_5 (d) are built from 1- and 1.5-layer networks that vary in different order, while ReB_3 (e) has only 1.5-layer and ReB_4 (f) only 2-layer networks.

The theoretical characterization starts with calculating the electronic DOS of novel Re_3B_7 and Re_2B_5 , presented in Fig. 3.21, where ReB_2 is included for comparison. Both novel structures show metallic behaviour with finite DOS crossing at E_F . Similar to other boron rich rhenium borides, there is an overlap between Re-5*d* and B-2*p* states from deep within the valence band, indicating strong covalent Re-B bonding. The overall shape of the total DOS is the same in Re_3B_7 and Re_2B_5 , as in ReB_2 , with the exception of the Re-contribution being weaker at E_F . Structural and electronic similarities indicate that novel phases should have mechanical properties comparable to ReB_2 .

Figure 3.21: Calculated electronic DOS, in arbitrary units, of (a) ReB_2 , (b) Re_3B_7 and (c) Re_2B_5 at ambient pressure. Energies are presented with respect to the Fermi energy of each compound. Black solid lines are the total DOS, while red and purple are for Re and B, respectively. Explanations to the partial *s*-, *p*- and *d*-orbital contributions are given in the legends. Grey, orange and magenta lines correspond to total, Re and B DOS at the pressures at which Re_3B_7 (4 GPa) and Re_2B_5 (21 GPa) are predicted to become thermodynamically stable.

Calculations of phonon band structures at ambient conditions indicate that both novel structures are dynamically stable upon decompression, as is seen in Fig. 3.22.

Figure 3.22: Phonon dispersion curves and partial DOS at ambient pressure calculated in the harmonic approximation for (a) Re_3B_7 and (b) Re_2B_5 . Solid red and purple lines are combined partial DOS of Re and B atoms, respectively, while dashed lines are partial DOS of individual atoms.

Elastic constants of ReB_2 , Re_3B_7 and Re_2B_5 are presented in Table 3.1. They were used to derive mechanical properties such as isotropic bulk modulus (B),

shear modulus (G), Young's modulus (E), Vickers hardness (H_V), all in units of GPa, and Poisson's ratio (σ). Novel Re_3B_7 and Re_2B_5 phases show anisotropic compressibility and mechanical properties similar to ReB_2 .

Composition	Sp.gr.	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B	G	B/G	E	σ	H_V
ReB_2	$P6_3/mmc$	636	156	126	1010	259	240	344	276	1.24	654	0.18	38.5
Re_3B_7	$P-6m2$	624	132	142	970	245	246	339	267	1.27	635	0.19	36.8
Re_2B_5	$P6_3/mmc$	614	124	150	951	237	245	336	261	1.29	622	0.19	35.5

Table 3.1: Calculated mechanical properties of ReB_2 , Re_3B_7 and Re_2B_5 (all units in GPa).

The thermodynamic stability of Re_3B_7 and Re_2B_5 is assessed by calculating the vertical distance to the convex hull as function of pressure. Unstable and metastable phases become thermodynamically stable when this quantity goes to zero. It is predicted in Fig. 3.23 that Re_3B_7 stabilizes at 4 GPa and the more boron-rich Re_2B_5 at 21 GPa, in the static lattice approximation. Harmonic vibrational contributions to the formation enthalpies are added at 1970 K, chosen to mimic the synthesis temperature of 1700-1900 °C. For Re_3B_7 , this reduces the stabilization pressure down to 1 GPa, and to 7 GPa for Re_2B_5 . These latter values are only qualitative in that force constant matrices are evaluated at zero pressure and temperature. Experimental synthesis is carried out at 24 and 33 GPa, and thus my calculations are suggestive of milder pressures being sufficient.

Figure 3.23: Distance to convex hull of ReB_2 , Re_3B_7 and Re_2B_5 as function of pressure up to 25 GPa. Solid lines are static lattice and dotted lines are vibrational lattice in the harmonic approximation at 1970 K, mimicking the synthesis temperature condition.

CHAPTER 4

Conclusion

In this thesis I have studied the coupling between internal degrees of freedom of electronic, vibrational, structural and configurational origin in metal borides, and seen how external conditions, such as temperature, composition, and pressure interplay with the degrees of freedom. Wherever applicable, effects of order and disorder, and isotropy and anisotropy of internal excitations is investigated. State-of-the-art computational methods have been applied to simulate materials at a variety of conditions, be it absolute zero, finite temperature, or even extreme conditions, where both pressure and temperature is far above ambient conditions. Methodologically layered approaches, with increasing complexity, have been presented. Underlying theory from different aspects of condensed matter theory has been summarised. Purely theoretical considerations, but also collaborative efforts with leading experts in the fields of experimental physics and chemistry, have been fruitful and lead to advancements worthy of sharing with the scientific community.

In detail, configurational mixing free energies of disordered $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ special quasirandom structures have been calculated in the mean field approach, with additions of vibrational free energies in harmonic and quasiharmonic approximations. The mean field phase diagram of $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ shows the importance of including effects of vibrations *in general*. In the practically relevant temperature-range of cutting tools in operation, potentially coated with $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ it is concluded that vibrations in this system can be disregarded, and that configurational and electronic degrees of freedom predominantly dictate phase stability. By cluster expanding the total energy and constructing a configurational Hamiltonian to govern canonical Monte Carlo simulations, where the atomic configuration minimize the free energy, it is found that short-range clustering comes into effect below 2300 K. As compared to the mean field estimate, short-range clustering lowers the closing of the miscibility gap by about 20%.

In the study on the intrinsic metal vacancies in AlB_2 , a number of open questions were treated. My calculations revealed that out of a plethora of considered defects, only Al vacancies are stable. Stoichiometric ideal AlB_2 is not stable with respect to Al-vacancy formation and pure Al at any temperature. Electronic density of states calculations showed how vacancy formation is favourable in the system as it depletes antibonding states. Out of a considered 1047 ordered vacancy structures, I have indentified three structures that lie on the 0 K convex hull, all displaying vacancies ordered along in-plane lines. I have predicted that configurational disorder is favourable already at 200 K, marking the relevance of a disordered state in applications at and above room temperature. For all temperatures in the range 0-1200 K, with and without vibrational contributions, my phase stability calculations predict a very narrow stability range of $\sim 7.5\text{-}10\%$ metal vacancies, corresponding to a variability between $\text{Al}_{0.925}\text{B}_2$ and $\text{Al}_{0.9}\text{B}_2$. This reconciles the experimental Al-B phase diagrams that typically show a line compound of AlB_2 type with the known existence of the phase off stoichiometry, that in other systems often result in a broader composition range of stability. I find that thermal expansion is sensitive to the configuration of metal vacancies, and that disordered models match our experiments.

I benchmarked different methodologies capturing the effect of strain and pressure on electron-phonon coupling and superconductivity. The idea was to compare the models for not only just one given case, but as function of an external condition. Pressure in MgB_2 was identified as an excellent candidate for this topical study of high T_c , due to the straightforwardness in applying hydrostatic pressure and anisotropic strain, and the simplicity of the MgB_2 unit cell, just having one Mg atom and two B atoms and no magnetism involved. First-principles methods at different levels of complexity and computational costs are probed; one strictly focusing on the so-called Kohn anomalies present in the phonon dispersion, and two that explicitly treat electron-phonon coupling in isotropic and anisotropic approximations. I find that all considered methods are suitable candidates and manage to calculate T_c as function of pressure well. I pointed out how anisotropic tensile strain enhances T_c and suggested that co-deposition of MgB_2 with $(\text{Zr}/\text{Hf},\text{Y})\text{B}_2$ may form 3D intertwined coherent nanostructures supplying favourable strain in all directions.

In collaboration with leading experts from the high pressure chemistry community, I characterized and confirmed dynamical and thermodynamic stability of four novel rhenium borides; trirhenium heptaboride Re_3B_7 , dirhenium pentaboride Re_2B_5 , rhenium triboride ReB_3 and rhenium tetraboride ReB_4 . By calculating their electronic structure and structural parameters I found indications of them displaying similar mechanical properties to ReB_2 . The calculation of elastic constants, that then were used to estimate mechanical properties such as Vickers hardness, confirmed this hypothesis. I find that the boron to rhenium ratio 2:1 is ideal for hardness, and that introducing more boron tends to soften the structure. These boron-rich rhenium borides can be rationalized as a series of homologous

compounds where rhenium layers interchange with variously structured puckered boron networks. The absence of phonons in the modelling tends to overestimate the pressure needed for stabilization, but as qualitative calculations show this discrepancy is remedied by vibrational free energy contributions.

CHAPTER 5

Future work

I will use this space to bring forward a few aspects in my research that I find interesting and deserve to be further scrutinized, as if I were to be handed my publications as starting points and be asked where the next step would be.

In relation to the investigation of coupling between configurational and vibrational degrees of freedom in **Papers I-II**, I would like to see the unification of these effects into one model and its application to both the $(\text{Ti,Al})\text{B}_2$ and $(\text{Al,Vac})\text{B}_2$ pseudobinary systems. It is, of course, not a new thing to make cluster expansions of *free* energies. Dealing with such a large number of structures (>1000) begs to question if it is practical to calculate vibrational free energies in the quasiharmonic approximation on the individual level, even if they are ordered with high symmetry. Regardless, in this way one can derive effective cluster interactions that are temperature dependent. If computational cost is really not a concern, the even next step would be to also perform concentration dependent cluster expansions. The possibilities make for interesting methodological benchmarking. Further, for the calculation of mixing and formation energies, it would be illustrative to also consider intermediate phases as competing phases, and not only the compositional endpoints, TiB_2 and (stoichiometric!) AlB_2 in **Paper I** and fcc-Al and $\alpha\text{-B}$ in **Paper II**. The structurally complex aluminium dodecaboride AlB_{12} is one such candidate. Moreover, the now undeniable importance of metal vacancies in AlB_2 , and in the light of the work by Dahlqvist [129] who studied the influence of boron vacancies on phase stability, bonding and structure of other AlB_2 -type metal borides, opens up for future testing of boride alloys with high degree of configurational freedom.

The non-uniqueness in the basis set choice in the cluster expansion approach, and the high-dimensionality of the parameter space, makes the problem fit for machine

learning. It would be interesting to see if more sophisticated optimization algorithms would select a basis set and corresponding interactions much different from the ones I used in **Papers I** and **II**. I don't believe that qualitative predictions would differ, but nevertheless it makes for an interesting problem.

In the modelling of lattice dynamics at elevated temperature, close to melting as in **Papers I-II**, or in the extreme conditions of **Papers IV-V**, it becomes increasingly important to include phonon-phonon interactions to get the complete vibrational picture. Anharmonic effects are captured in part by the thermal expansion in the quasiharmonic approximation, but phonon lifetimes remain infinite. Inclusion of phonon-phonon interactions requires a self-consistent approach in solving finite-lived quasiparticle self-energy. Such approaches are often based on *ab-initio* molecular dynamics, as for instance implemented in the Temperature Dependent Effective Potential (TDEP) package by Hellman [72–74] or formally exact thermodynamic integration as in the works of Grabowski and co-authors [130–134]. These types of effects might be interesting to look into for the considered materials systems, although inexplicit treatment of anharmonic contributions to the free energy in **Paper II** were estimated to not significantly affect phase stability.

Isotope effects have not been treated in this thesis. Let $\tilde{m}$ be the average mass of some element, whose isotopes have mass m_i and abundance c_i . Then one can define a parameter $\gamma_i = c_i(m_i - \tilde{m})^2 / \tilde{m}^2$ that describes the mass fluctuation of the i :th isotope, such that the total mass-fluctuation of the element is captured by $\Gamma = \sum_i \gamma_i$. Applying this definition to the first hundred or so elements in the periodic table, the following plot is derived:

Figure 5.1: Mass-fluctuation of the first 103 elements in the periodic table.

It shows that isotope effects are substantial in boron, second only to lithium,

and also considerable in magnesium. Naturally, effects of both B and Mg isotopes on superconductivity in MgB_2 have been studied before, see e.g. Refs. [125, 135–137], but for the novel boron-rich Re-B phases it is a possible topical study for the near future.

In relation to the approach of estimating superconducting T_c from Kohn anomaly features in the phonon band structure, it would be interesting to see it applied to other materials systems, and study the pressure behaviour and benchmark against other methods and available experiments in the literature. Further, I would like to see experimental tests of our prediction of high T_c for MgB_2 strained by $(\text{Zr}/\text{Hf}, \text{Y})\text{B}_2$ nanostructures.

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List of included publications and my contributions

- (I) **Theoretical investigation of mixing and clustering thermodynamics of $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ alloys with potential for age-hardening**

Erik Johansson, Annop Ektarawong, Johanna Rosen, and Björn Alling

Journal of Applied Physics, **128**, 235101 (2020)

Author's contribution

Main author - responsible for and carried out all first-principles calculations. In charge of analysis of results, writing and iterating original draft with co-authors, and finalizing revised versions.

- (II) **Coupling of lattice dynamics and configurational disorder in metal deficient $\text{Al}_{1-\delta}\text{B}_2$ from first-principles**

Erik Johansson, Fredrik Eriksson, Annop Ektarawong, Johanna Rosen, and Björn Alling

Journal of Applied Physics, **130**, 015110 (2021)

Author's contribution

Main author - responsible for and carried out all first-principles calculations. In charge of analysis of results, writing and iterating original draft with co-authors, and finalizing revised versions.

- (III) **The effect of strain and pressure on the electron-phonon coupling and superconductivity in MgB_2 - Benchmark of Theoretical methodologies and nanostructure design**

Erik Johansson, Annop Ektarawong, Ferenc Tasnádi, Johanna Rosen, and Björn Alling

In manuscript (2021)

Author's contribution

Main author - identified the methodological ambiguity in previous works, responsible for and carried out all first-principles calculations and analyzing their results. In charge of writing and iterating original draft with co-authors, and finalizing revised versions.

(IV) Novel class of rhenium borides based on hexagonal boron networks interconnected by short B₂ dumbbells

Elena Bykova, **Erik Johansson**, Maxim Bykov, Stella Chariton, Jesse Smith, Hongzhan Fei, Sergey Ovsyannikov, Alena Aslandukova, Benoit Merle, Björn Alling, Igor A. Abrikosov, Vitali B. Prakapenka, Tomoo Katsura, Natalia Dubrovinskaia, Alexander F. Goncharov and Leonid Dubrovinsky

In manuscript (2021)

Author's contribution

Co-author - responsible for theoretical half of the study, performing all first-principles calculations, assisted in interpretation of results and writing theoretical parts for the manuscript and iterating the full manuscript.

(V) High-pressure high-temperature synthesis of Re₃B₇ and Re₂B₅ with complex modular structures

Elena Bykova, **Erik Johansson**, Maxim Bykov, Stella Chariton, Jesse Smith, Hongzhan Fei, Sergey Ovsyannikov, Alena Aslandukova, Benoit Merle, Annop Ektarawong, Björn Alling, Igor A. Abrikosov, Vitali B. Prakapenka, Tomoo Katsura, Natalia Dubrovinskaia, Alexander F. Goncharov and Leonid Dubrovinsky

In manuscript (2021)

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Papers

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FACULTY OF SCIENCE AND ENGINEERING

Linköping Studies in Science and Technology, Dissertation No. 2171, 2021
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