Computational prediction of novel MAB phases

Adam Carlsson
Cover images: The evolution of predicted low-energy structures

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Abstract

The synthesis procedure of any materials system is often considered a challenging task if performed without any prior knowledge. Theoretical models may thus be used as an external input and guide experimental efforts toward novel exotic materials which are most likely to be synthesizable. The aim of this work is to apply theoretical models and develop frameworks for reliable predictions of thermodynamically stable materials. The material in focus herein is the family of atomic layered boride-based materials referred to as MAB phases.

The ground state energy of a material system may be obtained by applying first-principal calculations, such as density functional theory (DFT), which has thoroughly been used throughout this thesis. However, performing modern state-of-the-art quantum mechanical calculations, in general, relies on a pre-defined crystal structure which may be constructed based on an a priori known structure or obtained through the use of crystal structure prediction models. In this work, both approaches are explored. We herein perform a thermodynamical screening study to predict novel stable ternary boron-based materials by considering $M_2AB_2$, $M_3AB_3$, $M_4AB_4$, MAB and $M_6AB_6$ compositions in orthorhombic and hexagonal symmetries with inspiration from experimentally synthesized MAB phases. The considered atomic elements are $M = \text{Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co}$, $A = \text{Al, Ga, In}$, and $B$ is boron. Among the considered compounds, seven experimentally synthesized phases are verified as stable, and we predict the three hypothetical phases to be stable - Hf$_2$InB$_2$, Zr$_2$InB$_2$, and Mo$_4$AlB$_6$. Additionally, 23 phases of varying symmetries and compositions are predicted as close to stable or to be metastable.

However, the assumption of assigning initial crystal structures based on neighbouring compounds may drastically limit the outcome of a screening study. State-of-the-art techniques to generate low energy crystal structures within the considered material phase space is thus explored. More specifically, the Mo-Sc-Al-B system is studied along the ternary joints of $(\text{Mo}_{x}\text{Sc}_{1-x})_2\text{AlB}_2$ where $0 < x < 1$ by using the cluster expansion (CE) and the crystal structure prediction (CSP) codes, CLEASE and USPEX, in analogy. Previous attempts to study the Mo-Sc-Al-B system has been limited by only considering either hexagonal or orthorhombic symmetries. We challenge such approaches by covering larger portions of the phase space efficiently by combining CSP and CE frameworks. The $\text{Mo}_{4/3}\text{Sc}_{2/3}\text{AlB}_2$ ($R3m$) phase, previously referred to as $i$-MAB, is verified stable in addition to $\text{Mo}_{2/3}\text{Sc}_{4/3}\text{AlB}_2$ ($R3$).

The suggested approach of combining CE and CSP frameworks for investigating multi-component systems consists of initially performing CSP searches on the systems of smaller order constituting the system in focus. In the pseudo-ternary $(\text{Mo},\text{Sc}(1-x))_2\text{AlB}_2$ system, this refers to performing CSP searches on the ternary $\text{Mo}_2\text{AlB}_2$ and $\text{Sc}_2\text{AlB}_2$ systems. In addition, we also consider the structures of experimentally known phases.
with similar compositions. The complete set of structures obtained either from CSP or public databases, was later used to design CE models where mixing tendencies in addition to stability determined which model to further study. The predicted low-energy structures of the CE model were relaxed and used as seed structures within a complete CSP search covering the (Mo$_x$Sc$_{1-x}$)$_2$AlB$_2$ system for \(0 < x < 1\). We demonstrate that the use of seed structures, obtained from CE models, efficiently improved the search for low-energy structures within a multi-component system. The suggested approach is yet to be tested on any other system but is applicable to any alternative multi-component system.
Populärvetenskaplig sammanfattning

Material i olika former har länge använts för att förbättra samt underlätta vår tillvaro. Fynd från arkeologiska utgrävningar har hittat miljontals, rättare sagt närmare 3 100 000 år, gamla redskap skapade för att underlätta dåtidens situationer. I brist på vassa tänder så antas nu föregångare till Homo-sapiens Homo ha använt sig utav slipade redskap för bättre tillgång till näring i form utav protein. I dagens samhälle tar vi förivet att redskap som knivar ska vara vassa samt hållbara, men det är sällan vi frågar oss själva hur dessa egenskaper egentligen fungerar samt var de härstammar ifrån.

Begreppet material är definierat som en mängd substanser vilket tillsammans formar ett objekt. Dessa substanser utgörs i form av dramatiskt små byggstenar, atomer, som interagerar med varandra i form av olika krafter. Många utav dagens material är framtagna för att optimera dessa interaktioner vilket i sin tur ger upphov till olika egenskaper. Egenskaper som bland annat hårdhet, magnetism, ledningsförmåga av el och värme samtidigt som materialen blir allt mindre och mindre. Kraven på att ständigt söka förbättringsförmågor i våra liv har lett till att materialfysik är ett område som fröds det senaste seklet och dess betydelse kommer bli än viktigare i framtiden.

Det här arbetet grundar sig i teoretiska material-studier för att utforska nya potentiella material som är atomärt lagrade samt möjligheten att framställa de experimentellt. Inflytandet av atomärt lagrade material har dramatiskt ökat det senaste decenniet bland annat på grund av möjligheten till exfoliering från 3D-material till 2D-material vilket har haft ett stort inflytande hos den teknologiska utvecklingen inom områden som solceller, bränsleceller, alternativt energilagringsförmågan i batterier. Den egenskap som rent generellt har störst inflytande inom energilagring är materialets tillgängliga area, dvs den yta som är tillgänglig för reaktioner. Ett 2D-material är därmed optimalt eftersom arean per volym är betydligt större än i 3D-material. Mer specifikt så undersöks i detta arbete bor-baserade material på grund utav elementet bors exotiska egenskaper, som dess extrema mekaniska kvaliteter, samt en strukturell komplexitet beroende på externa omständigheter som temperatur och tryck. Bor-baserade material är några utav de hårdaste materialen, nästan lika hårt som diamant, och har en extremt hög småtpunkt. Dessa egenskaper har gjort att intresset för att blandna in atomlaget bor i materialsammanhangar har ökat drastiskt den senaste tiden.

MAB-faser är en grupp av material som är atomärt lagrade, bor-baserade (B) och dessutom består utav åtminstone en metall (M) samt ett A element (A). Därav namnet MAB. Fram tills idag finns dock endast ett fåtal experimentellt framtagna MAB-faser av olika atomära sammansättningar. Att leta efter nya MAB-faser, eller vilket material som helst, genom endast experimentella tillvägagångssätt är en otroligt svår uppgift
eftersom antalet möjligheter att kombinera alla olika atomslag är i princip oändligt. Teoretiska modelleringar motiveras därav för att underlätta och vägleda experimentella försök i jakten på nya exotiska material för nästa generations teknologier.

I den här studien används täthetsfunktionals-teori, DFT, ett populärt teoretiskt verktyg inom materialvetenskap, för att beräkna MAB-fasers energier vilket i sin tur används för att uppskatta stabilheten, dvs om ett material har potential att kunna framställas eller inte. Den absolut viktigaste indata som krävs för att utföra en täthetsfunktionals-teori-beräkning är en uppskattning av atomernas initiala positioner, en s.k. kristallstruktur. Genom att manuellt konstruera kristallstrukturer inspirerat av tidigare kända material så förutspår vi att tre MAB-faser, Zr$_2$InB$_2$, Hf$_2$InB$_2$ och Mo$_4$AlB$_6$, är stabila och därmed har en möjlighet att kunna framställas i labbet. Dessutom föreslås även en metod för att förutspå låg-energi kristallstrukturer genom att kombinera en maskininlärnings-baserad metodik med ett tillvägagångssätt baserat på evolutionära algoritmer vilket förutspår kristallstrukturer utan någon initial ansättning. Det kombinerade tillvägagångssättet lyckas effektivt att verifiera tidigare framtagna MAB-faser samt förutspår två nya låg-energi kristallstrukturer för Mo$_2$AlB$_2$ och Sc$_2$AlB$_2$. Målsättningen är att denna framtagna metodik ska användas för att hitta nya material utav högre ordnings materialsammansättning.
List of papers

Paper I

Theoretical predictions of phase stability for orthorhombic and hexagonal ternary MAB phases
Adam Carlsson, Johanna Rosen, Martin Dahlqvist.
Accepted in Physical Chemistry Chemical Physics.

Paper II

Finding stable multi-component materials by combining cluster expansion and crystal structure predictions
Adam Carlsson, Johanna Rosen, Martin Dahlqvist
In manuscript
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Material science has influenced humanity for millions of years. Some materials have played such a significant role that eras are now titled after them \cite{1, 2}. Two such examples are the Bronze and Iron ages named after the discovery of tools made of bronze and iron, designed to face challenges of that time, such as digging and cutting. The era which we currently are living in is referred to as the Silicon age due to the high impact of silicon-based materials since the middle of the 20th century. Today, silicon is found within almost any type of electrical component as transistors, which has led to the rapid development of computational power which is nowadays well integrated within modern society. The field of modern material science still seeks to further improve daily tasks, but also to tackle global challenges. Challenges as such are addressed within the Sustainable Development agenda of 2030 \cite{3}, where some materials are crucial in the development and deployment of low-carbon and green technologies, which may eventually leads to the decoupling of CO$_2$ emissions and energy usage. More specifically, new technological solutions are essential if the climate and energy targets are to be met \cite{4}. Possible technological advances which may assist reaching today’s and future energy demands while simultaneously reducing the footprint of greenhouse gases are carbon capture and storage, nuclear power, and renewable energy sources \cite{5}. While energy efficient solutions are a necessity, the sustainability of these newly developed technologies is a feature which must be considered.

The sustainability of a material is commonly reflected in the lifetime of a material and how its produced. The lifetime of an object, influenced by external forces and harsh conditions, may be significantly prolonged by applying an extra layer of a thin material, known as coating or thin film. Depositing a film is commonly in order to improve the mechanical properties, such as the hardness, of a substrate. The mechanical properties are, of course, vastly improved when coated with a material which have already demonstrated promising mechanical characteristics. One such group of materials are the boron-based materials.

Boron in general is an interesting material with a range of characteristics, like chemical complexity, structural versatility, and great mechanical properties, which stems from the three localized valence electrons that favours the insulating state rather than metallic. This subtle transformation between a metallic and insulating state can thus easily be altered upon change of pressure, temperature and impurities \cite{6}. The polymorphic structure of $\gamma$-$B_{28}$ has reported to possess the highest hardness of the boron family, ~50 GPa \cite{7}, making it a member of the superhard materials. However, $\gamma$-$B_{28}$ is not
stable at ambient conditions. The best known commercially available superhard materials are diamond and the cubic boron nitride (cBN) with hardness’s ranging from 60-120 [8] and 30-45 [9] GPa, respectively. Boron-based materials have extensively been studied, mainly due to the excellent mechanical properties. Due to these properties, the interest for boride-based materials have dramatically increased within both academia and industry where binary [10], ternary [11, 12] and quaternary [13] compounds have all been thoroughly investigated. Boride-based materials may hold a solution to the development of sustainable wear resistant materials necessary to tackle the stringent environmental legislations.

An additional renowned group of materials which as of late have gained a significant increase of interest are the nanolaminated materials comprised of atomic-thin layers stacked on each other in repeated sequences, such as MAX phases [14] and van der Waals bound layered materials as graphite [15]. The bonds between the different atomic layers give rise to a diversity of desired properties, such as exfoliation towards 2D materials and mechanical properties prominent for tools used under extreme conditions such as elevated temperatures and/or pressure. Thus, a nanolaminated boron-based material may possess properties of even greater significance.

1.1 MAB phases

MAB phases are boron-based nanolaminated materials which were discovered in the 1957s with the synthesis of Mo₅SiB₂ by Nowotny et al [16] followed by the discovery of Fe₅SiB₂ [17] a few years later. Additional MAB compounds were discovered during the 1960s, such as Mn₂AlB₂ [18], MoAlB [19] and Fe₂AlB₂ [20]. These discoveries were followed by the finding of Cr₂AlB₂ during the 70s by Chaban et al. [21]. The notation “MAB” stems from the atomic elements which comprises these materials, where M represents a transition metal, A typically a Group 13 to 15 element and B is boron. In general, MAB phases are arranged in alternating stacks of M – B layers interleaved by layers of A with compositions \( M_{n+1}A_{2n} \) (n = 1, 2, 3), \( MAB \) and \( M₄AlB₄ \). The latter two are comprised of double-layered A (\( MAB \)) or M (\( M₄AlB₄ \)) atoms, as shown in Figure 1.
Figure 1. The crystal structures of the experimentally verified MAB phases considered within Paper I. (a) The general orthorhombic compositions, from left to right, are $M_2AB_2$ ($Cmmm$), $M_3AB_4$ ($Pmmm$), $M_4AB_6$ ($Cmmm$). Double-layered compositions $MAB$ ($Cmcm$) and $M_4AB_4$ ($Immm$) with double layers of A-layers and metals, respectively. (b) The hexagonal $M_2AB_2$ ($P6\overline{3}m2$). The unit cells are denoted in black.

As of this date, Cr$_2$AlB$_2$, Mn$_2$AlB$_2$, Fe$_2$AlB$_2$ ($Cmmm$), Cr$_3$AlB$_4$ ($Pmmm$), Cr$_4$AlB$_6$ ($Cmmm$) [22], and, Ti$_2$InB$_2$ ($P6\overline{3}m2$) [23] are MAB phases which have been experimentally synthesized and which fit the general formulation $M_{n+1}AB_{2n}$ where $n = 1, 2, 3$. Additional studied MAB phases which do not fit the general formulation are the double layered MAB compounds, MoAlB and WAlB ($Cmcm$) with double A layer [22], and the double metal layered $M_4AB_4$ compound, Cr$_4$AlB$_4$ ($Immm$) [24]. Similar to MAX phases, 2D materials have been formed by selectively etching the A-layer of MAB phases. This realization to exfoliate MAB phases into two-dimensional (2D) materials was recently achieved by Zhou et al. in 2021 by forming the 2D counterpart, coined boridene, by etching Al from the in-plane ordered ($i$-MAB) phases (Mo$_{2/3}$Y$_{1/3}$)$_2$AlB$_2$ and (Mo$_{2/3}$Sc$_{1/3}$)$_2$AlB$_2$ [25]. In addition to the possibility of exfoliation into 2D materials, the mechanical properties of boride based materials have previously demonstrated promising characteristics for unary [6, 7], binary [26, 27], ternary [28] and quaternary [13] boride-based systems.
The limiting number of experimentally synthesized MAB phases, in addition to a possible pathway towards new 2D materials as well as materials with promising mechanical characteristics, encourages theoretical studies to identify new and potentially synthesizable MAB phase candidates. In Paper I, the stability of 420 MAB phases comprised by the experimentally verified compositions, illustrated in Figure 1, in addition to manually constructed hexagonal crystal structures of equal composition is explored. The $M_{n+1}AB_{2n}$ and $MAB$ compositions tend to form, or favour, hexagonal symmetries for $M = Ti, V, Zr, Nb, Hf, Ta$ combined with $A = Ga, In$, whereas $M_4AB_4$ compositions were found to favorize the orthorhombic structure in terms of energy. Moreover, three new phases were predicted stable, seven synthesized phases were verified as stable and an additional 23 are close to stable.

The results of Paper I is limited by the assumption that the global energy minimum of all considered phases is found for either the considered orthorhombic or hexagonal symmetries. In Paper II, we challenge this approach by developing a framework to search for global energy minima structures within multi-component systems, i.e., ternary, quaternary, or quintenary systems. The framework relies upon applying crystal structure prediction (CSP) searches in addition to designing cluster expansion (CE) models to search the energy landscape thoroughly and efficiently for global energy minimum crystal structures. This approach is applied to the well-studied $(Mo_xSc_{1-x})_2AlB_2$ system in which we verify the recently discovered $Mo_{4/3}Sc_{2/3}AlB_2$ $i$-MAB phase.
Chapter 2

Methods

Before industry, or anyone else for that matter, can make use of any new material within a real application or product the material must, of course, be synthesized and demonstrated useful. Synthesizing a new material without any external input, e.g., in terms of theoretical guidance or from known information, is a challenging task performed in an Edisonian approach\(^1\) which is a costly and time demanding procedure. The combinatorial problem of alloying any number of components and compositions spanning the complete periodic table consists of an infinite number of combinations. Villars et al., \([29]\) estimated the proportion of studied chemical systems in 2013 which is illustrated in Figure 2 below.

\[\begin{array}{l}
\text{unary} & 100 \% \\
\text{binary} & 72 \% \\
\text{ternary} & 16 \% \\
\text{quaternary} & 0.6 \% \\
\text{quintenary} & 0.03 \%
\end{array}\]

Figure 2. Data collected from Villars [29] which shows the percentage of studied material systems.

According to the data collected by Villars, unary and binary systems are either close to or completely studied. For ternary systems, only 16 percent of the theoretically possible materials have been reported whereas, for even higher-ordered systems, quaternary and quintenary, practically nothing has been reported in contrast to the vast number of possible combinations. Figure 2 thus illustrates the challenges of tackling the search of all materials within an infinite phase space through experimental efforts only. Theoretical simulations may thus serve as a valuable tool when screening and identifying potentially

\(^1\) The Edisonian approach stems from the famous inventor Thomas Edison who (according to Nicola Tesla) was said to practice extremely inefficient methods as an immense ground had to be covered to obtain any result unless luck was involved. Tesla is said to have believe the guidance of theoretical input could have saved 90 percent of the labour.
stable materials which are most likely to be synthesizable. Before we find out if a material is synthesizable or not, one has to first define what stability is. A stable material, influenced by a set of conditions, is achieved when the energy of a certain compound is lower than the energy of all other possible rearrangements or combinations of the atoms within the considered system. A crucial part of materials nature is the drive of any system to reach the lowest possible energy. If the material is stable the system is within a global minimum. However, if it is not stable, lowering of energy within a system may arise from e.g. (i) decomposing into competing materials or (ii) through phase transition into an alternative polymorphic structure. The set of external conditions at which stability may be considered is temperature, pressure, chemical potentials, etc.

The use of various theoretical tools further allows for the identification and/or tailoring of materials with certain traits. Calculating material properties was in the beginning a very demanding task which builds upon a series of well-thought-out ideas and approximations which all started in the late 19th century with J. J. Thompson’s discovery of the electron. The development of theoretical simulations has since rapidly expanded and in the last decades, major improvements in computational power have enabled more complex simulations to be performed to push barriers even further. Modern technological solutions, such as high-performance computer clusters, allow scientists to find approximate solutions to many-body problems in the span of a few minutes to days. However, simulating atomistic properties for systems with increased complexity, such as including magnetism, may still be considered a daunting task even for modern supercomputers.

2.1 First-principles calculations

Nowadays, density functional theory (DFT) is a commonly used computational tool in physics, chemistry, and biology for calculating a wide variety of things such as searching for novel materials, determining chemical reactions, and identifying active sites within proteins. The DFT framework is applied to a quantum system, a system described by atomic interactions, namely the synergy between nuclei and electrons. These interactions, in turn, govern both physical and electronic material properties. Before introducing the concepts of DFT, a brief introduction to the electron structure theory is thus necessary. An arbitrary quantum system consisting of \( N \) nuclei and \( n \) electrons may be expressed in the form of a wavefunction \( \Psi \),

\[
\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n, \sigma_1, \sigma_2, \ldots, \sigma_n, \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N, t) = \Psi(\mathbf{r}, \sigma, \mathbf{R}, t),
\]

which is assumed to encompass all information necessary to portray a physical state of the system at a given time, denoted \( t \), and to describe the evolution of the system. \( \mathbf{r}_i \) and \( \mathbf{R}_i \) represents the electron and nuclei position, respectively, and \( \sigma_i \) the spin of the
2.1 FIRST-PRINCIPLES CALCULATIONS

electrons. The spin of the nuclei is disregarded. The wavefunction is thus the solution to the time-dependent Schrödinger equation,

\[ \hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi. \quad (2) \]

The Schrödinger equation is designed by letting the Hamiltonian \( \hat{H} \) operate on the state of the considered system, represented by the wavefunction \( \Psi \). The Hamiltonian for a system of interacting electrons and nuclei is written as

\[ \hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \nabla_i^2 - \sum_{i=1}^{N} \frac{\hbar^2}{2M_i} \nabla_i^2 + \sum_{i<j}^{n} \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i<j}^{N} \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 |\mathbf{R}_i - \mathbf{R}_j|} - \frac{1}{4\pi\varepsilon_0} \sum_{i<j}^{n} \frac{Z_i e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (3) \]

in which the two initial terms represent the kinetic energy of the electrons and nuclei. The latter three terms originate from the Coulomb interactions between electron – electron, nuclei – nuclei and electron – nuclei, respectively. This designated many-body problem is not solvable with today’s computational power unless a handful of crude approximations are applied. Initially, one usually assumes the mass of an electron to be much smaller than a nucleus which in most cases allows for the decoupling of the wave function into separate electron and nuclei segments. This approximation is known as the adiabatic, also referred to as the Born-Oppenheimer approximation, where the nuclei are assumed static in contrast to the electrons [30]. The static interpretation of the nuclei allows for the electrons to be treated as particles within an external field caused by the electron-nuclei interaction. Thus, a wavefunction governing this interpretation may be formulated as,

\[ \Psi_e = \Psi_e(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n, \sigma_1, \sigma_2, ..., \sigma_n, t). \quad (4) \]

Furthermore, the Bloch theorem is generally applied in order to further reduce the degrees of freedom when simulating bulk materials, as in the case of this thesis. Instead of considering every single atom within a macroscopic crystal, one may instead only focus on the unit cell due to the general periodic arrangement of atoms [31]. The periodic wavefunction under the influence of the Bloch theorem may be written as

\[ \psi_{nk}(\mathbf{r}) = e^{ik\cdot\mathbf{r}} u_{nk}(\mathbf{r}), \quad (5) \]

where the band index is represented by \( n \) which purpose is to distinguish wave vectors of the same reciprocal vector \( \mathbf{k} \). The reciprocal vector \( \mathbf{k} \) is principally within the first Brillouin zone. The right-hand side of Eq. 5 represents a plane wave \( e^{ik\cdot\mathbf{r}} \) in addition to the periodic function \( u_{nk}(\mathbf{r}) \) which has the same periodicity as the crystal lattice and may be formulated as
\[ u_{nk}(r) = u_{nk}(r + R). \]  

(6)

The Bloch theorem significantly reduces the number of variables. Instead of considering a complete macroscopic crystal with Avogadro’s number of atoms \( N_A \approx 6 \times 10^{23} \) the number of atoms is reduced to 1-100. Still, solving Eq. 2 is a formidable task for systems containing not more than a few particles even after applying both the Born-Oppenheimer approximation and the Bloch theorem. Hence, additional ways to solve Eq. 2 are thus needed. These additional frameworks which are to be introduced rely on the electron density as the main variable.

**Density functional theory**

The foundation of the density functional theory (DFT) evolves around the electron density distribution \( n(r) \), which may be interpreted as the probability of finding an electron located at position \( r \), rather than solving for the many-electron wavefunction \( \Psi_e \). The initial attempts to use the electron density as a basic variable to calculate atomistic properties yielded unreliable results and were carried out in 1927 independently by both Thomas [32] and Fermi [33]. In 1964, Hohenberg and Kohn established a framework that formulated an exact variational principle for the ground state energy using the electron density as the variational function [34]. The DFT model is encapsulated by the two Hohenberg-Kohn theorems which are stated as:

**Theorem 1**: Any system of interacting particles within an external potential \( V_{\text{ext}}(r) \), such as the static Coulomb interaction caused by the nuclei, can be determined uniquely (except for a constant) by the ground state electron density \( n_0(r) \).

**Theorem 2**: A universal energy functional \( E[n] \) of the electron density \( n(r) \), valid for any external potential \( V_{\text{ext}}(r) \), may be designed for a system of interest. Additionally, the ground state energy of the system is the global minimum of the energy functional, and the particle density which minimizes the energy functional is precisely the ground state electron density \( n_0(r) \).

Based on these theorems, the many-body wavefunction \( \Psi \) can be determined in analogy with the Hamiltonian \( \hat{H} \). Additionally, all properties of the states represented by \( \Psi \) may in analogy be determined by the ground state electron density \( n_0(r) \). For simplifications, I will designate the kinetic energy operator of the electrons as \( \hat{T} \), \( \hat{V}_{\text{ext}} \) as the potential energy sensed by the electrons from the static nuclei, \( \hat{V}_{\text{int}} \) as the electron-electron interaction energy and \( E_{\text{ll}} \) as the nuclei-nuclei energy interaction. Hence, the energy functional may in general be written as

\[ E[n] = T[n] + E_{\text{int}}[n] + \int n(r) V_{\text{ext}}(r) dr + E_{\text{ll}}, \]  

(7)

\[ u_{nk}(r) = u_{nk}(r + R). \]  

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\[ E[n] = T[n] + E_{\text{int}}[n] + \int n(r) V_{\text{ext}}(r) dr + E_{\text{ll}}, \]  

(7)
where the integral \( \int n(r) V_{\text{ext}}(r) \, dr \), which extends over all space, designates the electrons influenced by the external potential of the nuclei. The Hohenberg-Kohn theorems do not give any practical solution on how to obtain the ground state density \( n_0(r) \) which limits the use of the framework unless additional formulations are added.

### The Kohn-Sham equations

The work of Kohn and Sham in 1965 suggested a framework based on an auxiliary system of independent non-interacting particles of the same electron density which requires the replacement of the external potential with an effective single-particle potential \[ V_{KS}(r) \]. This approach allows the single-particle interaction with the effective potential to be described by the single-particle wavefunction \( \psi_i \). These assumptions allow for the consideration of the one-electron Schrödinger-like equation, which is significantly easier to solve than the many-body problem. However, the crucial detail is that the obtained density when solving the non-interacting Kohn-Sham system yields the same ground state density \( n_0(r) \) as the more challenging approach. The particle density \( n(r) \) of a system within the Kohn-Sham DFT consisting of \( N \) particles is given by

\[
n(r) = \sum_{i=1}^{N} |\psi_i(r)|^2
\]  

and the Schrödinger-like Kohn-Sham equation is written as

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

For simplification, Eq. 9 is written in Hartree units\(^2\). The energy eigenvalues of the non-interacting particles are denoted as \( \epsilon_i \) and effective potential \( V_{KS}(r) \) given by

\[
V_{KS}(r) = V_{\text{ext}}(r) + \int \frac{n(r')}{|r-r'|} \, dr' + V_{\text{xc}}(r) + E_{\text{II}},
\]

where \( V_{\text{ext}}(r) \) denotes the external potential of the nuclei and any other external fields, the classical Hartree potential \( V_{\text{Hart}}(r) = \int \frac{n(r')}{|r-r'|} \, dr' \) describes the potential of the electron density distribution and \( E_{\text{II}} \) the nuclei interactions. The exchange-correlation potential \( V_{\text{xc}}(r) \) is expressed as

\[^2\text{Within the frameworks of Hartree atomic units, the four physical constants known as the reduced Planck constant} (\hbar), \text{elementary charge} (e), \text{Bohr radius} (a_0) \text{ and the electron mass} (m_e) \text{ are defined to be unity. Namely} \hbar = e = a_0 = m_e = 1\]
\[ V_{\text{xc}}(r) = \frac{\delta E_{\text{xc}}[n(r)]}{\delta n(r)}, \]  

(11)

where the exchange-correlation energy functional \( E_{\text{xc}}[n(r)] \) is the troublesome term within the Kohn-sham approach due to the unknown solution of the functional. The expression of the complete Kohn-Sham energy functional is thus

\[ E_{\text{KS}}[n] = T_{\text{KS}}[n] + E_{\text{Har}}[n] + E_{\text{xc}}[n] + \int n(r) V_{\text{ext}}(r) dr + E_{\text{ll}}, \]  

(12)

in which \( T_{\text{KS}}[n] \) is the kinetic energy functional and \( E_{\text{Har}}[n] \) denoted as the Hartree energy functional representing the classical Coulomb interaction energy of the electron density, or rather the charge density interaction, with itself. The kinetic energy functional may be obtained through the \( N \) non-interacting single-particle wavefunctions

\[ T_{\text{KS}}[n] = -\frac{1}{2} \sum_{i=1}^{N} \langle \psi_i | \nabla^2 | \psi_i \rangle, \]  

(13)

and the Hartree energy function is expressed as

\[ E_{\text{Har}}[n] = \frac{1}{2} \int \frac{n(r')}{|r - r'|} dr'dr'. \]  

(14)

The sought-after ground sate energy \( E_0 \) may henceforth be obtained within the Kohn-Sham approach as the value of the Kohn-Sham energy functional \( E_{\text{KS}}[n] \) when minimized over all possible ground state densities \( n_0(r) \). However, the exchange-correlation interactions within the exchange-correlation energy functional \( E_{\text{xc}}[n] \) is still unknown which poses a problem. On the other hand, the remaining terms of Eq. 12 may be determined with little to no errors and makes up the major contribution of the ground state energy \( E_0 \). The exchange-correlation functional may be constructed by approximate solutions, such as the local density approximation (LDA) and the generalized gradient approximation (GGA) which will be further discussed in the sections to come.

### 2.2 Exchange-correlation functionals

Kohn and Sham reasoned with the idea of approximating the exchange and correlation effects to be reasonably local. Their logic originates in the Hartree term governing the long-range effects and that solid systems may often be within the close limit of a homogeneous electron gas. Hence, the exchange correlation function may be generalized in
terms of the electron density $n(r)$ and $\epsilon_{xc}(n; r)$ which represents exchange-correlation energy per particle located at point $r$.

$$E_{xc}[n] = \int n(r) \epsilon_{xc}(n; r) dr.$$  \hfill (15)

**Local density approximation (LDA)**

One of the simpler approaches to approximate the exchange-correlation energy functional $E_{xc}[n]$ is the local density approximation (LDA) proposed by Kohn and Sham in their original paper [35]. LDA assumes that each point $r$ in space holds the same exchange-correlation energy density $\epsilon_{xc}(n(r))$ with the same form as a homogeneous electron gas $\epsilon_{xc}^{ho}(n(r))$. The energy functional of the LDA framework is given by

$$E_{xc}^{LDA}[n] = \int n(r) \epsilon_{xc}^{LDA}(n(r)) dr.$$  \hfill (16)

The LDA approach was suggested in the 1980s with the exchange-correlation energy obtained from Monte Carlo simulations of a homogeneous gas interacting with a uniform background potential [36]. The development of the LDA yielded successful simulations of material characteristics. However, a major weakness of the LDA framework is the risk of over-binding in systems which does not have a homogeneous electron density distribution as assumed within the framework. The electron density distribution of physical systems is often not homogeneous as it varies when considering positions far away from point $r$ in space [37].

**Generalized gradient approximation (GGA)**

To avoid the problems of handling regions of varying electron densities as within LDA, an improved exchange-correlation-functional known as the generalized gradient approximation (GGA) was developed. In contrast to LDA, GGA introduces the density gradient $\nabla n(r)$ as an additional ingredient to the framework. The energy functional within the GGA is given by

$$E_{xc}^{GGA}[n] = \int n(r) \epsilon_{xc}^{GGA}(n(r, \nabla n(r))) dr.$$  \hfill (17)

The GGA approach often yields more appropriate results than LDA and comes in many forms, such as Perdew and Wang (PW91) [38] and Perdew, Burke, and Ernzerhof (PBE) [39]. The latter is the exchange-correlation functional applied throughout this thesis. Beyond the use of LDA and GGA are functionals with improved features considering bandgaps and long-range interactions. Additional functionals are GW (solving the one-body Green’s function using the dynamically screened Coulomb interaction which is popular when calculating band structures), HSE (a hybrid density functional calculating
CHAPTER 2: METHODS

the exchange-correlation using the Hartree-Fock approach and was designed to ease the computational demands of simulating molecular properties) and vdW (a function designed for sparse systems influenced by long-range interactions, such as van der Waals forces). The wide variety of exchange-correlation functionals is, however, outside the scope of this work.

The vast selection of functionals is briefly discussed in Paper I regarding simulating phase stability. As an example, the thermodynamical stability varies with \( \pm 1 \text{ meV/atom} \) when comparing functionals AM05, PW91, PBE, PBEsol, and LDA for Mo\(_4\)AlB\(_4\). This is in accordance with Poulou et al. [40] reporting the contrast between functionals when calculating the stability of MAX phases to be \( \pm 10 \text{ meV/atom} \).

Pseudopotentials (PP) and the projector augmented wave method (PAW)

In order to actually apply the Kohn-Sham framework to material systems and to solve the Kohn-Sham wavefunctions numerically, the electron wavefunction has to be expanded in a basis set. Remembering the Bloch’s theorem introduced in Eq. 5, which motivates the formulism of the electron wavefunction to be considered as plane waves with the periodicity of the crystal lattice. Plane waves are therefore an exceptional choice for expanding the Kohn-Sham equation. For a periodic lattice it can be expressed as

\[
\psi_k(r) = \frac{1}{\Omega_G} \sum_G c_{kG} e^{i(k+\mathbf{G})\cdot r},
\]

where \( k \) a wave vector, \( \mathbf{G} \) is the reciprocal lattice vector and \( \Omega_G \) the volume of the first Brillouin zone. In practice, this selection of basis set must be truncated at a finite cutoff energy \( \frac{1}{2} |\mathbf{G} + k|^2 < E_{cutoff} \).

However, the nature of the electron wave functions turns out to be computationally demanding as the oscillation varies with the electron position. Electrons located close to the nuclei will generally oscillate rapidly (localized behaviour) yielding high kinetic energy regions where corresponding wave functions require a large number of plane waves with a large energy cutoff. This is in contrast to electrons located in outer shells, specifically the valence electrons, which tend to oscillate more slowly (delocalized behaviour) and thus require a smaller number of plane waves, as compared to the localized electrons, to represent the wavefunction. These problematics are typically approached by adding pseudopotentials (PP) which are to represent the nucleus as well as the inner core electrons tightly bound to the core. The pseudopotential may therefore be seen as the inner region of the atom acting on the outer region, namely the valence electrons. The implementation of the PP approach was suggested by Hellman in 1935 [41] which substitutes the Coulomb potential with a smooth effective potential designed to even the localized section of the wave function creating a more computationally manageable pseudo wave function (PWF). The frozen core approximation is commonly taken into consideration when using a PP approach in which the core electron shells are pre-
calculated and kept static during the calculation. In this thesis, the projector augmented wave (PAW) method is used extensively [42]. PAW, in contrast to the PP approach where a PWF is obtained, restores the complete electron wavefunction at the end of a calculation by seeking a linear transformation of precomputed pseudopotentials.

Self-consistent solution of the Kohn-Sham equations

The software used in Paper I and II for carrying out the DFT calculations and solving the Kohn-Sham equation of Eq. 9 is the Vienna ab initio simulation package (VASP) [43, 44]. The framework of VASP is a numerically self-consistent procedure aimed to minimize the Kohn-Sham energy functional $E_{KS}[n]$. The procedure is highlighted in Figure 3. The initial step of the procedure is to guess an initial ground state density $n_0(\mathbf{r})$ which is then used to calculate the effective potential $V_{KS}(\mathbf{r})$ in Eq. 10. The effective potential is thus used to solve the Kohn-Sham equations, Eq. 9. The single-particle wave functions of the Kohn-Sham equation can be obtained which is later used to construct a new electron density $\tilde{n}_{k+1}(\mathbf{r})$. The new and old ground state densities are regulated in contrast to a tolerance $\delta$. If the criteria of the tolerance $\delta$ are not met, a new effective potential is calculated with a linear combination of the densities, and the procedure is repeated until the set tolerances are met. The ground state energy, forces, and eigenvalues are thus calculated once the mixing of the ground state density has been met and convergence reached.

![Figure 3. The self-consistent loop for solving the Kohn-Sham equations in a DFT calculation.](image-url)
2.3 Simulating phase stability

The described frameworks for conducting a DFT calculation presented in section 2.1 and 2.2 may at best yield a ground state energy for a given composition under certain conditions, such as temperature and pressure. However, the ground state energy of a system does not provide any information about its stability which, in turn, can provide valuable information on whether it is likely to be formed or not. Instead, the obtained ground state energy needs to be put in context in order to evaluate the phase stability of the given material.

The simplest comparison of energies is known as the formation energy and was often used for representing the stability of a compound in elder studies [45-48]. The formation energy \( \Delta E_f \) represents the reaction energy when forming a compound from its constituent elements. For a general \( \text{M}_x\text{A}_y\text{B}_z \) phase, \( \Delta E_f \) is calculated as

\[
\Delta E_f(M_xA_yB_z) = E(M_xA_yB_z) - xE_M - yE_A - zE_B.
\]

\( E(M_xA_yB_z) \) represents the total energy of the \( M_xA_yB_z \) phase and \( E_i \) the ground state energy of elements \( i = \{ M, A, B \} \). However, \( \Delta E_f \) is not a particularly good indicator for a material’s stability, as illustrated in Figure 4 where \( \Delta E_f \) is negative (promoting stability) for all 42 considered \( M_2AB_2 \) phases while only two have been synthesized. Figure 4 also includes another descriptor for evaluating phase stability, the formation enthalpy denoted as \( \Delta H_{cp} \). Both descriptors are seen in Figure 4 for the \( M_2AB_2 \) compositions where \( M = \text{Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, and A = Al, Ga and In} \) in an attempt to enlighten the limited success of phase stability calculations of the \( \Delta E_f \) methodology in contrast to the more prominent \( \Delta H_{cp} \).
2.3 SIMULATING PHASE STABILITY

Figure 4. The formation enthalpy ($\Delta H_{cp}$) as a function of the formation energy ($\Delta E_f$) for the considered $M_2AB_2$ phases within Paper I. Stable phases ($\Delta H_{cp} < 0$) are denoted in blue and not stable ($\Delta H_{cp} > 0$) in red. Synthesized phases are marked with a black square and hypothetical phases with a circle.

All phases within Figure 4 are considered stable from the perspectives of the formation energy ($\Delta E_f < 0$), i.e., with respect to its constituent elements $M$, $A$ and $B$. The $\Delta E_f$ descriptor is thus rather an indication whether it is energetically favored for a compound to decompose into its elemental components ($\Delta E_f > 0$) or not ($\Delta E_f < 0$) and a crude approximation to phase stability. Only four phases, Cr$_2$AlB$_2$, Mn$_2$AlB$_2$, Fe$_2$AlB$_2$ and Ti$_2$InB$_2$, have been experimentally made among the herein considered $M_2AB_2$ phases and are all predicted stable according to their calculated formation enthalpy ($\Delta H_{cp} < 0$). The definition of $\Delta H_{cp}$ is presented in detail below. Additionally, two phases, Zr$_2$InB$_2$ and Hf$_2$InB$_2$, are predicted to be stable. It is apparent that the formation energy ($\Delta E_f$) may potentially indicate the stability of a phase while being far from stable when compared to all competing phases within the system ($\Delta H_{cp}$). Including higher-order materials such as binaries and ternaries will in most cases impact the theoretical stability. Bartel et al. compared the two stability methodologies $\Delta E_f$ and $\Delta H_{cp}$ by comparing the frameworks for ~85,000 phases where 55 percent was estimated stable according to the formation energy ($\Delta E_f < 0$) but unstable according to formation enthalpy ($\Delta H_{cp} > 0$) [49]. The formation enthalpy is thus the better descriptor when evaluating the phase stability of a material.

The formalism of the formation enthalpy $\Delta H_{cp}$ aims to compare energies of a compound with additional phases, which exist in a given material system, and includes not only elemental structures but also binaries, ternaries, and higher-order structures depending on the number of atomic species within the considered system. The phase stability is herein determined by comparing the ground state energy of a compound with the lowest energy given by a linear combination of a set of competing phases, or decomposition phases [50], which is further referred to as the formation enthalpy $\Delta H_{cp}$. The
framework mimics the experimental nature where in reality a set of phases are competing to be formed upon synthesis. The set of competing phases considered herein is obtained from public databases and previous published works. The used public databases were Materials project [51], Open Quantum materials database (OQMD) [52, 53], and Springer Materials [54].

The minimum energy constructed by the linear combination of alternative phases within the composition space for an arbitrary $M_A^x A_B^y B_z^z$ phase of elemental constituent $b^x, b^y$ and $b^z$ is formulated as

$$\min E_{cp}(b^x, b^y, b^z) = \sum_{i=1}^{n} x_i E_i$$  \hspace{1cm} (20)

in which the amount and energy of compound $i$ is denoted by $x_i$ and $E_i$, respectively. The competing energy $E_{cp}$ is under the influence of the following constraints to represent a general composition

$$x_i \geq 0, \quad \sum_{i=1}^{n} x_i^x = b^x, \quad \sum_{i=1}^{n} x_i^y = b^y, \quad \sum_{i=1}^{n} x_i^z = b^z.$$  \hspace{1cm} (21)

The formation enthalpy is thus obtained by differentiating the energy of the considered $M_A^x A_B^y B_z^z$ phase in focus with the lowest obtained competing energy $\min E_{cp}(b^x, b^y, b^z)$ as given by

$$\Delta H_{cp}(M_A^x A_B^y B_z^z) = E(M_A^x A_B^y B_z^z) - \min E_{cp}(b^x, b^y, b^z).$$  \hspace{1cm} (22)

A negative formation enthalpy ($\Delta H_{cp} < 0$) represents a stable phase whereas a positive ($\Delta H_{cp} > 0$) indicates a phase being not stable or close to stable, where decomposition into its competing phases is more energetically favorable. Note that using a metastable region is convenient since several studies have demonstrated experimentally known phases with $\Delta H_{cp} > 0$ [55, 56]. An example is given in Paper I where the CrAlB$_6$ exhibits $\Delta H_{cp} = +16$ meV/atom and has been successfully synthesized. On the contrary, there are of course phases predicted thermodynamically stable according to the formation enthalpy which have not yet been synthesized [57, 58]. Bear in mind that phase stability calculations should rather be used as guidance.
2.3 SIMULATING PHASE STABILITY

The stability of a system is often displayed using the convex hull formalism which illustrates whether a compound is stable or if it will decompose into a linear combination of materials with the same average composition. The convex hull formalism builds on employing the simplex model which framework aims to find the optimal solution to an optimization problem of a linear programming model [59]. In the case of materials science, the most optimal (with respect to energy) compositions within a system constructs the simplex. Figure 5 below demonstrates a schematic view of a 2D simplex for a hypothetical binary A-B system.

![Figure 5. Schematic illustration of the simplex represented in a 2D view for a binary A-B system where the colours designate phases located on (green) or above (grey) the convex hull line.](image)

Figure 5 illustrates a schematic representation of the formation energy for the hypothetical A$_x$B$_{1-x}$ system. Stable phases within the binary system makes up the convex hull (green circles). However, within the convex hull formalism no information is given to what degree a phase is stable. Another descriptor which takes this into account is the formation enthalpy $\Delta H_{cp}$ which reveals the decomposition energy. In Figure 5 this is shown as the distance from a hypothetical convex hull without the considered phase. Here the AB$_2$ phase is used as an example. The dashed line between AB and AB$_3$ forms the hypothetical convex hull if AB$_2$ were not to be included in the convex hull construction (as it would otherwise be located on the convex hull). The hypothetical convex hull is thus the set of most competing phases, a.k.a. decomposition phases, which are used to design $\min E_{cp}(b^x, b^y, b^z)$ in Eq. 22. As AB$_2$ is located below the hypothetical convex hull it is considered stable. The AB$_3$ phase, however, is located above the convex hull and thus not stable.

The increased degrees of freedom for higher-order systems (ternary, quaternary, etc.) increase the difficulty of projecting the convex hull onto a 2D plane. The solution is commonly to colour the data points according to the distance to the convex hull. This descriptor is in general referred to as the $\Delta H_{hull}$. The main difference between the $\Delta H_{cp}$ and $\Delta H_{hull}$ is the inclusion of all competing phases within $\Delta H_{hull}$. The inclusion of all phases allows for comparisons with themselves. Stable phases which connect the hull, according to the $\Delta H_{hull}$ descriptor, thus takes the value zero ($\Delta H_{hull} = 0$). This is displayed for the hypothetical ternary A-B-C system in Figure 6.
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Figure 6. Schematic illustration of the simplex represented in a 2D view for the ternary A-B-C system. The colours represent the formation enthalpy ranging from stable phase on the hull (white) to those not stable above the hull (red).

The schematic ternary phase diagram illustrated in Figure 6 for the hypothetical ternary A-B-C system displays the colouring of the phases correlated to their distance from the convex hull, $\Delta H_{\text{hull}}$. The $AB_3$ phase is denoted red illustrating a phase far from the convex hull. Phases that construct the convex hull are denoted in white indicating a stable phase, such as the hypothetical ABC. The alternative descriptor, $\Delta H_{\text{cp}}$, would rather indicate how stable ABC is in contrast to decomposition into other phases. In the example given in Figure 6, $\Delta H_{\text{cp}}$ corresponds to comparing the energy of ABC with the linear combination $1/2 AB + 1/2 AC + 1/2 AB$. In practice, designating all decomposition phases of a certain phase is impractical as lines would cover the whole phase diagram.

In this work, I consider most ternary and pseudo-ternary phase diagrams. Figure 7 displays the result of a crystal structure prediction search applied to the Mo-Al-B system which includes the $\Delta H_{\text{hull}}$ for phases with $\Delta H_{\text{hull}} < 25$ meV/atom out of 18,700 phases.

Figure 7. Phase diagram of the ternary Mo-Al-B system with $\Delta H_{\text{hull}}$ as the descriptor. Phases which construct the convex hull and $\Delta H_{\text{hull}} < 25$ meV/atom are denoted as circles while phases above as crosses. Color ranging from white (located on the hull) to red (phases $\Delta H_{\text{hull}} = 25$ meV/atom above the hull).
The ternary phase diagram in Figure 7 demonstrates 17 phases located on the convex hull and an additional 63 metastable phases with ΔH_hull between 0 and 25 meV/atom, mostly along the Mo-Al axis. The phase located within the centre of the phase ternary diagram represents the experimentally known MoAlB [19] synthesized in 1966s. The complete set of considered phases in Figure 7 is ~18,700.

Figure 6 and 7 both illustrate one way of representing phase diagrams of ternary systems. However, illustrating systems with higher order, such as the quaternary system, is a greater challenge as humans, in general, have a tough time interpreting anything of higher dimensionality than three. With that said, Hedge et al., managed to construct a 100th-dimensional phase diagram by considering every inorganic element within the open quantum mechanical database OQMD [60]. The highest ordered system considered in this thesis is the pseudo-ternary system, which is covered in Paper II, (Mo₆Sc₅₋ₓ)₂AlB₂. The phase diagram of (Mo₆Sc₅₋ₓ)₂AlB₂ is easily projected onto a 2D plane as the mixing of Mo and Sc only covers phases between the ternary joints, Sc₂AlB₂ and Mo₂AlB₂. Figure 8 displays two phase diagrams of the (Mo₆Sc₅₋ₓ)₂AlB₂ system including 7,000 phases. Figure 8a displays the mixing tendencies with the isostuctural formation energy ΔH_iso whereas Figure 8b shows the stability represented by ΔH_sp.

The isostuctural formation enthalpy ΔH_iso displayed in Figure 8a is commonly used as the descriptor when exploring tendencies of mixing and not the phase stability. With ΔH_iso, the energy of a certain phase is compared with its end-structures (x = 0 and x = 1) rather than all competing phases. Here all compositions are composed of the same base structure hence the term isostuctural. A noteworthy observation is thus that all phases in Figure 8a are located below 0 and are deemed stable in contrast to a linear combination of its end structures. The convex characteristics of the convex hull do indicate strong mixing tendencies.
Figure 8b displays the stability of the \((\text{Mo}_x\text{Sc}_{1-x})_2\text{AlB}_2\) system with the formation enthalpy \(\Delta H_{cp}\) as the descriptor. In contrast to \(\Delta H_{iso}\), none of the phases demonstrates any characteristics of being stable as they are all located above zero. A noteworthy detail is the resemblance between the two descriptors. Both end-end structures make up the zero-point level governing the mixing tendencies when applying \(\Delta H_{iso}\), whereas the set of data determined by \(\Delta H_{cp}\) resembles the data of \(\Delta H_{iso}\) in Figure 8a but rotated to a certain degree. Furthermore, the path of determining \(\Delta H_{cp}\) for a whole phase space may be a challenging task as it requires not only the calculated energy of each individual phase but also evaluation of the linear combination of competing phases producing the lowest energy, \(\min E_{cp}(b^x, b^y, b^z)\), for every considered composition.

A number of attempts to find additional pathways to determine phase stability using different descriptors than ground state energies have thus been considered. Zhang et al. have suggested an approach where descriptors such as atomic size ratio and electron concentration are used for estimating stable MAX phases [61]. A similar approach was used by Shen et al. to identify stable magnetic MAB phases [62]. Additional attempts for determining material properties have also been conducted [63-65]. The use of such descriptors for stability evaluations is challenged in Paper I where it is demonstrated that no correlation between the size ratio, electron concentration, and electronegativity descriptors and the calculated phase stability nor with experimentally observed MAB phases can be made.

2.4 Theories for mixing atoms

Crystal structures are the state-of-the-art alternative when representing the arrangement of ionic, atomic, or molecular substances in crystallography. One would quickly realize the difficulties of manually designing crystal structures without any prior knowledge of where to place an atom as the phase space of any system consists of an infinite way of varying the variables defining the crystal structure, e.g., the atomic positions and their relative position to each other, atomic species, and lattice vectors. The challenge of predicting a crystal structure correlated to the global energy minima is thus referred to as a nondeterministic polynomial (NP) problem as the number of combinatorial combinations dramatically rises as the dimensionality of the system increases. Systems of interest are often high dimensional systems with many degrees of freedom making it impossible to find the global energy minimum crystal structure by trying all possible variants. Consider the simple case of a cubic crystal lattice with \(N\) identical atoms located within the fixed volume \(V\). Additionally, one may consider the positions of the atoms to only occupy discrete positions on the nodes of a grid with the resolution \(\delta\). The resolution variable \(\delta\) may be chosen to be a significant fraction of the characteristic bond length (e.g., \(\delta = 1 \text{ Å}\)). The number of combinations \(C\) of the atomic coordinates may then be expressed as
2.4 THEORIES FOR MIXING ATOMS

\[
C = \frac{1}{(V_{\text{tot}}/\delta^3)!} \left(\frac{V_{\text{tot}}}{\delta^3} \right)! \left(\frac{V_{\text{tot}}}{\delta^3} - N\right)! N!
\]  \hspace{1cm} (23)

Assuming the atomic volume to take the value of a typical atomic volume \(V_A \sim 10 \text{ Å}^3\), hence the total volume is \(V_{\text{tot}} = N V_A\), allows the number of combinations \(C\) to be estimated if using the Stirling’s formula large factorials \(n\),

\[
n! \approx \sqrt{2\pi n} \left(\frac{n}{e}\right)^n.
\]  \hspace{1cm} (24)

The number of combinations may be calculated for a different number of atoms \(N\), as shown in Table 1, in which the combinations are seen to increase exponentially as \(N\) is increased. The large set of combinations makes the search for the global energy minima structure impossible as the required computational time of a single elemental system consisting of 30 atoms would require \(10^{31}\) years.\(^3\)

<table>
<thead>
<tr>
<th>Element A</th>
<th>Compound AB</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N)</td>
<td>(C)</td>
</tr>
<tr>
<td>10</td>
<td>(10^{11})</td>
</tr>
<tr>
<td>20</td>
<td>(10^{25})</td>
</tr>
<tr>
<td>30</td>
<td>(10^{49})</td>
</tr>
</tbody>
</table>

Table 1. Demonstration of the exponential increase of the number of combinations \(C\) of structures within a single element A system and a compound AB system with number of atoms \(N\).

The influence of recent computational advances, such as machine learning and artificial intelligence, has introduced a paradigm shift within the field of computational materials science considering combinatorial problems as such. The implementation of algorithms that further improves the accuracy and reduces the resources are found within codes such as crystal structure prediction frameworks as CALYPSO [66] and USPEX [67], cluster expansion methods ATAT [68] and CLEASE [69] and general platforms for handling DFT calculations such as AFLOW [70] and Pymatgen [71]. These are just a handful of examples implementing either machine learning, high-throughput calculations, or artificial intelligence. Paper II aims to identify a framework suitable for identifying low-energy structures when mixing metals in a quaternary system. The modelled system, Mo-Sc-Al-B, is motivated by the recent discovery of the in-plane ordered MAB phase \((\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlB}_2\) with the chemical ordering of \(\text{Mo}_4\) and \(\text{Sc}\). Here we combine cluster expansion (CE) models using the CLEASE code with the evolutionary algorithms within the crystal structure prediction framework titled USPEX to find out how

\(^3\) With the assumption that the CPU time of a 1 atom system is equal to 1 second.

\(^4\) The mere coincident that number 42, the “answer to the ultimate questions of life, the universe and everything” according to Douglas Adams Hitchhiker’s Guide to the Galaxy, is the atomic number of Mo should suffice the reasoning why it is herein considered.
theory can be used to verify global energy minimum structures and pave the way for future discoveries.

2.5 Cluster expansion

Cluster expansion (CE) is one of numerous frameworks used for investigating thermodynamic properties from first-principles calculations and which utilizes the crystalline configuration of an underlying grid of atomic sites to map out the energy of a certain configuration. The methodology revolves around assigning a spin-like configuration variable $\sigma_i$ which takes certain values depending on if site $i$ within a crystal structure is occupied by a certain atom type. The structure may thus be decomposed into a set of clusters $\alpha$-defined by number of sites $n$. However, it is customary to only include clusters of a certain size and order as the nature of the CE model is greater influenced by the short-range interactions. For simplicity, we may consider an arbitrary binary system $A_xB_{1-x}$ in which $\sigma_i = \pm 1$ whether site $i$ occupied by atom specimen $A$ or $B$. In reality, the CE model may be extended to any arbitrary multicomponent systems consisting of $M$ atomic species ($A, B, C, ..., M$) in which $\sigma_i = \pm m, \pm (m - 1), ..., \pm 1$ (0) where $M = 2m$ (or $2m + 1$) if the number of species is even (uneven) [72]. If the considered crystal structure consists of $N$ lattice sites, the total number of alloy configurations is thus defined by a set of $N$ configuration variables constructing the configuration vector $\sigma = (\sigma_1, \sigma_2, ..., \sigma_N)$. The construction of unique basis functions $\Phi^{(n)}_{\alpha}(\sigma)$ forming a complete and orthogonal set for each cluster may thus be expressed by considering each cluster $\alpha$ of $n$ sites and applying the spin product over all sites $i$,

$$\Phi^{(n)}_{\alpha}(\sigma) = \prod_{i \in \alpha} \sigma_i.$$  \hspace{1cm} (25)

The complete and orthogonal set of unique basis functions allows for any physical quantity normalized with the number of atomic sites $N$ of configuration $\sigma$ to be designed. The physical quantity of interest in this study is the configuration-dependent total energy of an alloy, $E_{\text{conf}}(\sigma)$, given by

$$E_{\text{conf}}(\sigma) = \sum_{\alpha} m_{\alpha} J_{\alpha} \Phi_{\alpha}(\sigma),$$  \hspace{1cm} (26)

where $m_{\alpha}$ denotes the number of clusters $\alpha$ per atom, referred to as the cluster multiplicity which governs the degeneracy of the clusters and their effective interactions due to symmetry reasons. $J_{\alpha}$ is the effective cluster interactions (ECI) and $\Phi_{\alpha}$ is the n-site correlation function which is the average value of the cluster function in cluster $\alpha$ and is determined through $\Phi_{\alpha}(\sigma) = \langle \Phi^{(n)}_{\alpha}(\sigma) \rangle$. If considering the binary $A_xB_{1-x}$ system,
\( \phi_\alpha \) governs the tendencies of clusters between species \( A \) and \( B \). Considering a quadratic lattice with one half-filled with \( A \) and the other with \( B \), the value of \( \phi_\alpha \) would approach 1 as large tendencies of clustering takes place. Considering the case of species \( A \) only surrounded by species \( B \), then \( \phi_\alpha \) will take the value of -1 as the considered species tend to mix. Furthermore, the generalized Ising-Hamiltonian \( H_{conf} \) of a system is thus constructed by considering the ECIs of all 2-body, 3-body, 4-body, ..., \( n \)-body interactions

\[
\hat{H}_{conf} = J_0 + \frac{1}{2} \sum_p J_p^{(2)} \sum_{i,j \in p} \sigma_i \sigma_j + \frac{1}{3} \sum_t J_t^{(3)} \sum_{i,j,k \in t} \sigma_i \sigma_j \sigma_k + \frac{1}{4} \sum_\alpha J_\alpha^{(4)} \sum_{i,j,k,l \in t} \sigma_i \sigma_j \sigma_k \sigma_l + \cdots
\]  

(27)

where \( J_0 \) is the ECI of an empty lattice. The ECIs are still undetermined which may be unravelled by the structure inversion method suggested by Conolly and Williams [73]. A schematic representation of different 2-, 3- and 4-body interactions is displayed in Figure 9 for a two-dimensional square lattice.

Figure 9. A schematic illustration of the 2-, 3-, and 4-body interactions within a square lattice.

The Connolly-Williams method builds upon inverting Eq. 26 and truncating the cluster interactions according to predefined configurations which have been evaluated by performing DFT calculations. The accuracy of the model depends on how the truncation is made. Selecting too few interactions yields an underfitting, whereas too many results in overfitting. The values of the ECIs may be determined directly or by least-square fitting a training set of configurations which have been relaxed using DFT.

In general, the CE formalism relies upon a training set that has been calculated using DFT in which the total energies of each structure are stored within a total energy vector \( \mathbf{E} \). A pool of clusters may further be defined using the product \( m_\alpha \phi_\alpha \) and stored within matrix \( \mathbf{X} \). Similarly, vector \( \mathbf{J} \) is defined and includes all ECIs. Thus, the following matrix form may be formulated

\[
\mathbf{E} = \mathbf{XJ}.
\]  

(28)

However, the interactions coefficient \( \mathbf{J} \) still remains unknown and needs to be determined. In order to increase the precision of the CE model, one aims to find the
interaction coefficients which minimizes the energy between the training set and the predicted phases. Namely minimization of the ordinate least square

$$\min_J \|E_{\text{DFT}} - XJ\|_2^2.$$  \hfill (29)

A unique solution of the ECIs in Eq. 29 is found as $\hat{J} = (X^T X)^{-1} X^T E_{\text{DFT}}$. Generally, this regularization leads to possibilities of overfitting and usually requires a large set of clusters. Alternative regularization schemas are the $l_1$ and $l_2$ norms. Both norms implement a weight parameter, $\lambda$, which is to promote sparsity. However, the $l_1$ norm lacks an analytical solution and needs to be solved iteratively. The $l_1$ takes the following form

$$\hat{J} = \min_J \|E_{\text{DFT}} - XJ\|_2^2 + \lambda \|J\|_1.$$  \hfill (30)

The $l_2$ norm, in contrast to $l_1$, has an analytical solution which is expressed as

$$\hat{J} = \min_J \|E_{\text{DFT}} - XJ\|_2^2 + \|J\|_2^2 = (X^T X + \lambda I)^{-1} X^T E_{\text{DFT}}.$$  \hfill (31)

The minimization of the $l_2$ norm often leads to overfitting which in general limits the prediction power of unseen structures [74]. Alternative regularization techniques are based on Bayesian Compressive sensing [75] which implements the $l_1$ norm regularization instead of the $l_2$. Both $l_1$ and $l_2$ regularizations were considered in Paper II which did not improve nor significantly affect the quality of the model’s accuracy in prediction.

The accuracy of the predictive power of the CE model should be assessed regardless of the applied fitting schema. The cross-validation (CV) score is a technique commonly used for describing the accuracy and reliability with respect to the calculated training set of the model. The root mean square error technique known as the leave-one-out CV (LOOCV) score is generally used within CE frameworks and is defined as

$$CV = \left(\frac{1}{N_{\sigma}} \sum_{i=1}^{N_{\sigma}} (E_{i,\text{DFT}} - E_{i,\text{CE}})^2\right)^{\frac{1}{2}},$$  \hfill (32)

where $N_{\sigma}$ is the number of predefined training configurations, $E_{i,\text{DFT}}$ is the calculated energy and $E_{i,\text{CE}}$ the predicted energy of phase $i$. An alternative training procedure is the $k$-fold CV score which is popular within machine learning communities. The $k$-fold CV score splits the training set into $k$ subsets which are randomly distributed. Each subset is then used as the test data set whereas the remaining $k-1$ subgroups are used as training set. This means that every subset is thus given the opportunity to train the model. In

---

4 Compressive sensing stems from the field of signal and image processing which has lately been adopted to build physics models.
practice, the evaluation of the CE model should be converted until a sufficient CV-score is reached through multiple evaluation of considered CE models to find the best. The convergence of the CV-score for an arbitrary CE model considered in Paper II with respect to the number of included structures within the training set is displayed in Figure 10a. The CV score is converged for three different training sets, designated as d1, d2, and d3, and evaluated using the \( k \)-fold CV-score where \( k = 25, 10, 5 \) and the LOOCV score. The convergence of the CV score is further verified by varying the training set, hence the inclusion of three separate databases (d1, d2 and d3). In addition, Figure 10b displays the energy of the training set and CE predictions for the 25-fold evaluated database designated as d3.

Figure 10. (a) The convergence of the CV score for a CE model based on the \( P\bar{6}m2 \) symmetry within the \((\text{Mo}_{x}\text{Sc}_{1-x})_2\text{AlB}_2\) system for three different databases considering the validation techniques 25-, 10-, and 5-fold interactions and the LOOCV score. (b) Energy of the training set denoted as DFT and predicted CE energies for the 25-fold d3 dataset.

The CV score displayed in Figure 10a converged towards the energy minimum of 5 meV/atom when including roughly 300 structures within the training set. This feature is displayed for all considered databases (d1, d2, and d3), and all validation techniques (5-fold, 10-fold, 25-fold and the LOOCV score) Figure 10b displays the contrast between the DFT energies used in the training set and corresponding predicted energies for 300 phases using CE and for the 25-fold d3 dataset. As illustrated, some phases are very well fitted whereas a few phases differ with ~12 meV/atom which illustrates the selected validation technique to not be overfitting.

In this study, the CLEASE code [69] provides the framework of the used CE model by integrating CE with the open-source atomic simulation package (ASE) [76] in which both the \( l_1 \) and \( l_2 \) norms are implemented. The CLEASE is used in Paper II to identify promising low-energy crystal structures of hexagonal and orthorhombic symmetries within the \((\text{Mo}_{x}\text{Sc}_{1-x})_2\text{AlB}_2\) system.
2.6 Crystal structure prediction

A critical drawback of the CE model is its dependence on the predefined input structure needed to describe the n-body interactions. In Paper II, CE was used to explore the mixing of Mo and Sc within four different crystal structures, i.e., the hexagonal $P\bar{6}m2$, the orthorhombic $Cmmm$, and $Pnmm$ space group symmetries, and the tetragonal $P4/mbm$ symmetry. However, only considering hexagonal, orthorhombic, and tetragonal symmetries may limit the actual output as such may result in the identification of a local energy minima. The global minima would require the consideration of the complete energy landscape which considers all possible space group symmetries. The energy landscape of the $(\text{Mo}_{x}\text{Sc}_{1-x})_2\text{AlB}_2$ system is thus explored using a CE model in addition to the crystal structure prediction code USPEX. The USPEX code builds on implementing the use of evolutionary algorithms and has successfully predicted new stable materials in addition to exotic properties, such as hardness, the maximum bandgap, and magnetic configurations [64, 77-79].

The crystal structure prediction code USPEX, which stands for Universal Structure Predictor: Evolutionary Xtallography, is a framework developed by Oganov et al. [67, 80, 81]. Instead of looking through the set of all the different structure combinations needed to solve the NP problem, USPEX relies on the use of evolutionary algorithms which optimizes the search for a global energy minima structure by iteratively searching low energy regions within the energy landscape of the system. This procedure uses different variational operators which actively aim to design low-energy structures based on the fingerprints from previous generations of low-energy structures. The fitness of a generated structure generally reflects on the energy and its evolution. Recent advances in the USPEX code lets users specify additional properties to include within the fitness parameter which allows multiple parameters to be optimized simultaneously [82]. Examples of such parameters are volume, hardness, elasticity properties, bandgap, density, and structural order.

Initially, a large set of random structures are generated in order to span the energy landscape of the system. Once their energy has been calculated, a fraction of the most prominent structures are used as input for creating the next-generation offspring structures which are designed by using different variational operators. The worst structures, i.e., high-energy structures, of each generation are discarded. This procedure is iterated until a given convergence criteria are fulfilled and may continue for several hundreds of generations. If performed long enough, the global energy ground state crystal structure should be reached. A simplified schematic view of the energy landscape in addition to the evolution of an arbitrary system is illustrated in Figure 11.
2.6 CRYSTAL STRUCTURE PREDICTION

Figure 11. A schematic overview of the evolution of the CSP applied to the \((\text{Mo}_{x}\text{Sc}_{1-x})_2\text{AlB}_2\) system where \(x = 0.67\). (a) Illustration of a schematic energy landscape with designated local minima and the global minima after the initial (red), 25 (yellow) and final (blue) generation. (b) Energy evolution as function of generation for an USPEX calculation. The dotted line is the best individual whereas data points above the line demonstrate alternative individual structures.

The schematic overview of the energy landscape in Figure 11a portrays the evolution of the energy by the colour of the crosses illustrating the initial random sample (red), after 25 generations (yellow), and the final generation (blue). The initial sample is observed to populate all over the energy landscape. After 25 generations (yellow), structures are seen to populate more low-energy basins while still covering the energy landscape. The final generation (blue) makes up for the majority of low-energy basin structures which includes the global minimum of the landscape. This schematic may be a crude exaggeration but should give an idea of what the aim behind using crystal structure prediction is.

Figure 11b illustrates the evolution of the \((\text{Mo}_{x}\text{Sc}_{1-x})_2\text{AlB}_2\) system where \(x = 0.67\). The dotted black line indicates the lowest energy structure of each generation. The best individual structure is observed to converge after ~65 generations. Data points located above the best individual are the remaining generated structures within each generation. The number of low energy structures generated during later generations is observed to increase which depictures the search for low-energy basins using the employed variational operators.

To efficiently generate a structure for the next generation, information from previous generations is used as an input where those of low energy are deemed more valuable. These structures are further “fed” to typical variational operators like heredity, randomness, transmutation, and soft-mode mutations which are described in short below. In addition, Figure 12 illustrates the schematic procedures of the mentioned operators.
CHAPTER 2: METHODS

Heredity operator

The heredity operator, shown in Figure 12a, constructs an “offspring” structure by combining the slabs of two promising low-energy structures from the previous generation. This operator is used to combine the characteristics of multiple low-energy structures into a single descendant structure.

Mutation operations

The mutation operators are designed to generate an offspring structure based on the input of a previous structure but with permutations, i.e., conservative, or non-conservative changes to the ratios of the atomic specimens. These are shown in Figure 12b. The transmutation operator is given when conducting variational operator calculations in which a non-conservative change of atomic identity takes place (e.g., a Mo atom is replaced with a Sc atom). The permutation operator is similar to transmutation, however, it conserves the composition of the crystal and swaps the atomic species with one another.

Random operator

Another operation is to construct offspring structures randomly by either i) designing the structure based on a random selected space group symmetry and populating the sites with the specimens randomly or ii) constructing a randomly topological structure by taking an ideal net\(^6\) from a given database, in this case the ToposPro [83] database, which includes both observed and hypothetical structures. The selected net must contain basis nodes with the equivalent number of atoms as the number of atoms for each specific species within the parent structure. For example, Mg\(_4\)Al\(_8\)O\(_{16}\) may consist of four basis nodes, two which governs the 4 Mg atoms and two which governs the 8 and 16 Al and O atoms, respectively.

Soft-mode mutations

With operations like the soft-mode mutation illustrated in Figure 12d, atoms are moved along their eigenvectors, testing both positive and negative directions. A dynamical matrix is constructed from the bond hardness coefficients [84] which may then be considered as a fast approximative approach (since an ab-initio construction of the dynamical matrix would be too computationally expensive).

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\(^6\) An infinite periodic structure, or rather any atomic lattice with periodic boundary conditions, is commonly referred to as net within the topology crystal structure community.
2.7 COMBINING CRYSTAL STRUCTURE PREDICTION AND CLUSTER EXPANSION

An additional feature of USPEX is the possibility to use seed structures to govern the direction or rather speed up the optimization procedure. The feature of biasing the prediction schema of USPEX is considered a risky task as the outcome of a system with little a priori knowledge may be directed towards a local energy minimum rather than global. Similarly, an ‘antibias’ feature is present within USPEX used to avoid getting stuck within a local minimum. This feature penalizes structures that already appeared by storing two parameters, the width and the height of a Gaussian, which evolves with time and regulates the diversity of the population.

2.7 Combining crystal structure prediction and cluster expansion

While the CE model is heavily influenced and relies on input structures, the CSP search using USPEX allows one to potentially consider the entire energy landscape without
any prior knowledge. On the contrary, the computational resources required to construct the CE model is significantly smaller than the CSP search. Each CE model within Paper II, for all considered symmetries, was designed using 300 DFT training structures with the addition of roughly 100 phases further investigated in means of DFT calculations. An arbitrary CE model designed based on the specifics given in Paper II was thus built upon roughly 400 DFT calculations. This is in contrast to the CSP search where the initial random sample of the variable composition search covering the (Mo$_{x}$Sc$_{1-x}$)$_{2}$AlB$_{2}$ system consisted of 800 DFT computations, which were followed by at least 50 generations consisting of 100 DFT calculations each. In addition, the stochastic framework of the CSP search motivates several global energy minimum searches to be conducted in parallel which sums up to a large set of DFT calculations.

The CE model is, however, limited by the input lattice which may produce a disparity between predicted and calculated energies. This discrepancy is discussed within Paper II with a focus on the verified i-MAB phase (Mo$_{2/3}$Sc$_{1/3}$)$_{2}$AlB$_{2}$, and within Ref [85] regarding i-MAX phases. The limitations of the predictions within the CE model in contrast to the computationally demanding CSP method within USPEX motivate the search for a quicker methodology while still thoroughly covering the energy landscape. Paper II proposes the framework of a combined approach using CE in analogy with CSP. This combined framework is applied to the pseudo-ternary (Mo$_x$Sc$_{1-x}$)$_2$AlB$_2$ system which phase space is investigated and verified.

Figure 13 demonstrates a schematic illustration of the combined method for the specific (Mo$_{2/3}$Sc$_{1/3}$)$_{2}$AlB$_{2}$ configuration. All phases located below a 50 meV cutoff from a CE model based on the (Mo$_x$Sc$_{1-x}$)$_2$AlB$_2$ system with a focus on the $x = 0.67$ configurations are illustrated in Figure 13a. Figure 13b depicts the evolution of the CSP search for the same configuration, $x = 0.67$, with and without seed structures applied. The seed structures are the relaxed phases within the CE model for this specific configuration.

The suggested methodology of combining CE with CSP to efficiently cover the energy landscape is briefly illustrated in Figure 13. A total of six phases are used as seed
structures, denoted as blue in Figure 13a, including the recently discovered i-MAB (Mo_{2/3}Sc_{1/3})_2AlB_2 [86]. An energy minimum (ΔH_{cp} = −30 meV/atom) is found immediately after applying the low-energy structures from the CE model. This is in contrast to the CSP without seed structures which locates an unstable (ΔH_{cp} = 29 meV/atom) local energy minimum after 100 generations where each generation includes 40 newly generated structures. Furthermore, the number of low-energy phases generated is observed to increase as seed structures are applied. The individual phases are displayed as dots in Figure 13b.
Chapter 3

Summary of included work

3.1 Paper I

A large phase stability screening study covering experimentally known and hypothetical crystal structures with orthorhombic and hexagonal symmetries was carried out. The study included the $MAB$, $M_2AB_2$, $M_3AB_4$, $M_4AB_4$, $M_5AB_6$ compositions where $M = \text{Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co}$, $A = \text{Al, Ga, In}$, and $B = \text{boron}$ and verifies the thermodynamical stability of seven previously known phases in addition to three newly predicted. The selection of method regarding phase stability predictions of either formation energy or enthalpy is considered in which the formation enthalpy is the well-defined better framework. The formation enthalpies of the considered phases are demonstrated in Figure 14 where the notation of the metals illustrates the symmetry of the lowest energy, being either hexagonal or orthorhombic. The colour of each metal represents the stability of the considered compounds ranging between blue (stable) and red (metastable). Ten MAB phases are stable, out of which seven have been synthesized. An additional 23 MAB phases are close to stable with a maximum of $\Delta H_{\text{cp}} = 17$ meV/atom. This results in 16 MAB phases being stable or close to stable yet to be discovered through synthesis.

In addition, the symmetry preference was further investigated in Paper I in which the $A$-element interactions were suggested to be the predominant factor as of why Al-based MAB phases favoured orthorhombic symmetries. This is contrast to Ga-, and In-based MAB phases which demonstrated a prefers to hexagonal symmetries. This observation held true for all considered compositions except for the double-metal layered $M_4AB_4$. Furthermore, the use of alternative phase stability descriptors in attempts for effortless identification of novel materials was challenged in Paper I. Descriptors such as atomic size and electron concentrations showed no distinct relation to the calculated phase stability or experimental findings.
Figure 14. Calculated formation enthalpy for $M_AB$, $M_2AB_2$, $M_3AB_4$, $M_4AB_6$, compositions in which $M = Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co$, and $A = Al, Ga, In$. The lowest energy symmetry is denoted with hexagon or square representing either hexagonal or orthorhombic crystal structure. The color of each phase ranges from blue to red indicating stable or not stable phases, respectively. Experimentally verified phases are marked with a black square or hexagon.
3.2 Paper II

The search of low energy structures within higher-order multi-component systems, e.g., ternary, quaternary and quintenary systems, is challenging as the complexity dramatically increase with the increased number of considered atomic species. The investigation of the phase space for these multi-component systems often relies on theoretical state-of-the-art approaches such as crystal structure prediction (CSP) methodologies or cluster expansion (CE) models. CSP methodologies are often computationally demanding whereas CE models usually produce results biased to an input lattice.

In Paper II, we combine two approaches of CSP and CE to design an approach that efficiently covers the energy landscape. This is demonstrated for the pseudo-ternary \((\text{Mo}_{x}\text{Sc}_{1-x})_{2}\text{AlB}_2\) system. Initially, CSP search was applied to the ternary joints of \((\text{Mo}_{x}\text{Sc}_{1-x})_{2}\text{AlB}_2\) namely \(\text{Mo}_2\text{AlB}_2\) and \(\text{Sc}_2\text{AlB}_2\) resulting in the \(P4/mmb\) and \(Pmnm\) symmetries, respectively. In addition, low energy structures of experimentally verified phases of similar configurations were also considered, such as the two MAB phases \(\text{Cr}_2\text{AlB}_2\) \((Cmma)\) and \(\text{Ti}_2\text{InB}_2\) \((P63m2)\). Furthermore, CE models were designed based on the four collected crystal structures which were built on a set of 300 training structures and at least 5,000 additional generated phases whose energies were predicted using the CE model. Both stability, \(\Delta H_{\text{stabil}}\), and mixing tendencies, \(\Delta H_{\text{mix}}\), governed whether further investigations were to be conducted or not. The \(P63m2\) symmetry was further studied as the CE model demonstrated mixing tendencies and a total of 105 predicted phases were located beneath a cutoff region. The predicted phases located beneath the cutoff energy were relaxed using DFT calculations and later used as seed structures for the CSP using the USPEX code. This approach is further illustrated in Figure 15.

Figure 15. A schematic representation of the process combining cluster expansion with crystal structure prediction. Grey labels represent computational procedures whereas yellow label denote sections which require user input.
Two configurations of (Mo$_x$Sc$_{1-x}$)$_2$AlB$_2$ were determined stable, $x = 0.33$ and $x = 0.67$, with $\Delta H_{cp} = -18$ and $\Delta H_{cp} = -30$ meV/atom, respectively, which verifies previous studies. The predicted low energy structures of the ternary joints, Mo$_2$AlB$_2$ and Sc$_2$AlB$_2$, were close to the stable with $\Delta H_{cp} = 5$ and $\Delta H_{cp} = 16$ meV/atom. The obtained symmetry for the Mo$_2$AlB$_2$ configuration ($P4/mbm$) illustrates a unique structure in contrast to previously reported MAB phases which have only been reported within the binary metal alloy W$_2$CrB$_2$ while the $Pmmm$ symmetry obtained for the Sc$_2$AlB$_2$ configuration resembles previously reported orthogonal MAB phases. Both derived symmetries are motivated to be considered within future screening studies, similar to Paper I. Finally, the derived approach is motivated to be applied to alternative high-order systems to ease the search for low-energy symmetries.
Chapter 4

Conclusion and outlook

The screening of ternary MAB phases demonstrated in Paper I reveals that a handful (10) of phases are stable and likely to be synthesized even though only two, orthorhombic and hexagonal, crystal symmetries were considered. In addition, a large set (23) phases were considered metastable. The limited number of crystal symmetries considered within the screening study may actually not cover the global energy minima for each of the considered phases. The derived low energy structures of the Mo$_2$AlB$_2$ and Sc$_2$AlB$_2$ in Paper II signify this. One suggestion for future work is thus to at least consider the $Pmmm$ and $P4/mmb$ symmetries within a similar screening as in Paper I. Alternatively, CSP searches may thus be motivated to be performed on all remaining compositions, $M_3AB_4$, $M_4AB_6$, $MAB$, and $M_4AB_4$, which may increase the number of likely synthesizable phases. However, applying CSP searches to every individual composition included within Paper I would be a very computationally demanding task. Alternatively, CSP would be performed on a handful of selected compounds. The obtained low-energy symmetries of these searchers would further be screened.

The combined approach of CE and CSP suggested to be used when searching for low energy phases in quaternary systems should definitely be applied to other alternative systems. An initial idea is to apply the combined framework to similar compositions, such as $M_3AB_4$, in hopes of expanding the family of quaternary MAB phases. Any low energy structure is further motivated to be included within a large screening study by combining different metals for potential stable phases, similar to previous proposed strategies [87]. Alternative properties which would be interesting to consider within future projects are the effects of vacancies and the entropy effects within disordered systems. In addition, the suggested approach of combining CE and CSP should be applied to any alternative hexagonal symmetry in order to further verify the limitations of the CE model and structural transformations due to specific chemical ordering.

The possibilities of future projects motivated by the CSP search is endless. With that said, the true limitation in this retrospective is time. An already started project is the exploration within the ternary Mo-Al-B system using USPEX in hopes of verifying the low-energy $P4/mmb$ symmetry in addition to any alternative low-energy phases. The newly gained knowledge in Paper II should be further applied to this project. Previously known symmetries are strongly motivated to be used as seed structures while running several CSP searches in parallel to overcome the stochastic features of the CSP framework. Further suggestions would be to investigate the mechanical properties of the obtained low-energy phases. This is because the mechanical properties of MAB phases are
repeatedly considered to be of significant importance and is thus something I would eagerly like to apply within my work.
References

54. Springer Materials: The Landolt-Börnstein database.


Chapter 5

Results
Papers

The papers associated with this thesis have been removed for copyright reasons. For more details about these see:

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Computational prediction of novel MAB phases

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