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**A theoretical investigation of
 $\text{Ti}_{n+1}\text{AlC}_n$ and Mn_2GaC MAX phases:
phase stability and materials properties**

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Abstract

This thesis presents theoretical research on MAX phases (M =transition metal, A =A-group element, X =carbon and/or nitrogen), with focus on predictions of phase stability as well as of physical properties.

The first part is an investigation of the phase stability of the MAX phases Ti_2AlC , Ti_3AlC_2 , and Ti_4AlC_3 at elevated temperatures, where the former two phases have been obtained experimentally. Phase stability calculations of MAX phases usually do not take temperature dependent effects such as electronic excitations and lattice vibrations into consideration due to significantly increased computational cost. The results have nevertheless so far been quite accurate, with good agreement between theory and experiments. Still, the question whether the inclusion of temperature into the calculations could significantly alter the results as compared to previous 0 K calculations needs to be investigated, since this has bearing on the reliability of future predictions of the stability of not yet known MAX phases. However, it is shown that for $Ti_{n+1}AlC_n$, the different temperature dependent effects largely cancel each other. The results therefore suggest that to go beyond 0 K calculations for phase stability predictions of MAX phases is motivated only for borderline cases.

The second part investigates the Mn_2GaC MAX phase, which was recently predicted from theoretical phase stability calculations and subsequently synthesized. As a new member of the MAX phase family as well as being one of the first known MAX phases to exhibit magnetism, it is of interest to explore its physical properties. Here, we have used first-principles calculations to determine the electronic, vibrational and elastic properties. Analysis of the electronic band structure indicates anisotropy in transport properties, while the electronic and phonon density of states shows that the relative orientation of the Mn magnetic moments over the Ga layers affects the distribution of the electronic and vibrational states for both Mn and Ga.

The Voigt bulk, Voigt shear, and Young's modulus is also investigated, together with the Poisson's ratio, the elastic anisotropy, and the machinability via two machinability indices. In relation to experimental results of the moduli of other M_2AC phases, the Voigt bulk and shear moduli are concluded to be fairly low, 157 and 93 GPa, respectively, while the magnitude of the Young's modulus at 233 GPa is intermediate. The Poisson's ratio, which is 0.25, on the other hand, is comparatively high. The phase is shown to be elastically quite isotropic, and, just as other M_2GaC phases, also machinable. As all here investigated properties are affected by the choice of magnetic spin configuration, the results show the importance of identifying the correct magnetic ground state in future theoretical work on magnetic MAX phases.

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Preface

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Included papers

Paper I: Temperature dependent phase stability of nanolaminated ternaries from first-principles calculations

A. Thore, M. Dahlqvist, B. Alling, and J. Rosen

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Paper II: First-principles calculations of the electronic, vibrational, and elastic properties of the magnetic laminate Mn_2GaC

A. Thore, M. Dahlqvist, B. Alling, and J. Rosen

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1 Introduction

Throughout history, the search for and synthesis of new materials has mostly been a matter of experimental trial and error, with serendipity occasionally playing the leading role, as in the case of the discovery of, e.g., polytetrafluoroethylene (better known under the brand name Teflon). Since many existing technologies could benefit from materials with improved properties such as lighter weight, higher strength, and higher electrical conductivity, and since the creation of new technologies in some cases may even require these improvements, a faster, more systematic way of scanning through materials space is therefore highly desirable. Although experimental methods are being continuously refined, the greatest promise for a speedup of materials research comes from high-throughput computational screening, which has now become feasible thanks to the rapid advances in computer hardware as well as improvements in the efficiency and accuracy of software. This means that we have at our disposal a tool not only to help us screen for compounds, or *phases*, with interesting properties, but also to predict – unless they are already known to exist – whether these phases can be synthesized, or if they are likely to be outcompeted by the formation of some of the other phases within their respective materials systems. These predictions can then be used to guide experiment, potentially leading to drastic cuts in the time spent on synthesizing phases with few or no technologically useful properties, or on fruitless attempts to synthesize phases that calculations would have shown to be unstable with respect to competing phases.

While it seems like a certain bet that high-throughput computational screening will make up a significant part of materials research in the foreseeable future, this approach has, of course, yet to be perfected. One of the main problems is that the various software used to carry out the calculations are implementations of theoretical frameworks that are not exact. Also, calculating the behavior even of small atomic clusters is currently practically possible only using modern supercomputers, as smaller computers still have ways to go before they are powerful enough to solve the underlying equations within acceptable timeframes.

In order to lessen the demand for computational resources, the calculations are often simplified by approximating the conditions to which the phases under investigation are subjected. One particularly common approximation is that the temperature at phase formation is at absolute zero. While this speeds up the calculations significantly, it does not reflect experimental conditions very well, since synthesis usually occurs well above room temperature. Nevertheless, for at least one class of materials the results of phase stability calculations under this approximation have so far proven remarkably accurate: the class of so-called MAX phases, which are layered materials with a hexagonal lattice occupied by M , A , and X atoms (transition metals, A -group elements, and carbon and/or nitrogen, respectively). Paper I in this thesis is a first attempt at providing an explanation for this accuracy, using computational methods. The chosen materials system is the theoretically and experimentally well-explored Ti-Al-C ternary system, and the phases for which stability is investigated are the three MAX phases Ti_2GaC , Ti_3GaC_2 , and Ti_4GaC_3 , where the first two are known to exist and for which 0 K calculations correctly indicate phase stability.

In paper II we use computational methods to characterize the recently discovered MAX phase Mn_2GaC , which is one of the first magnetic MAX phases to be synthesized, thus making it especially exciting. The phase is characterized in terms of its electronic, vibrational, and elastic properties, all of which can be shown to be more or less affected by its magnetic configuration.

The outline of this thesis is as follows. Chapter 2 gives an introduction to MAX phases in general, as well as to the particular MAX phases investigated in paper I and II. In chapter 3, density functional theory, which is the theoretical framework at the heart of all calculations carried out in this thesis, is presented. Thermodynamic phase stability is the subject of chapter 4, which discusses the conditions for stability, and the effects of temperature. Chapter 5 contains a short discussion of elastic properties, and finally in chapter 6, a brief summary of the two papers included in the thesis is given.

2 MAX phases

The $M_{n+1}AX_n$ (MAX) phases, where $n=1-3$, together constitute a class of materials that to date contains more than 70 phases. They are characterized by a hexagonal crystal lattice with a vertical lattice parameter c typically 4-8 times longer than the basal plane lattice parameter a , and with individual atomic layers stacked on top of each other, as shown in Fig. 2.1.

Figure 2.1 The unit cell of a 211, 312, and 413 MAX phase. Image reproduced with permission from Martin Dahlqvist.

All MAX phases are made up of M , A , and X elements, which are found in the highlighted regions of the periodic table in Fig. 2.2. The M elements consist of transition metals, whereas the A elements are A -group elements¹. The X elements are either carbon or nitrogen, or both. However, although any given MAX phase must contain both M , A , as well as X elements, it does not necessarily have to be a ternary phase; for instance, several quaternary MAX phases with a solid solution on either one of the three different lattice sites have been synthesized, e.g., $(Cr,Mn)_2AlC$ [1], $Ti_3(Sn,Al)C_2$ [2], and $Ti_2Al(C,N)$ [3].

¹ This naming convention is now discouraged in favor of just using the group numbers, but it is still widely used in the MAX phase literature, which is why it is also used here.

2.2 Properties and applications

What makes MAX phases so promising is the fact that they exhibit a mix of metallic and ceramic properties. This mix can be attributed partly to the layered structure, and partly to the *M-A* and *M-X* bonds. The former bonds are predominately metallic in character and relatively weak, and the latter are predominately covalent and relatively strong. The metallic aspects of the MAX phases are reflected in, e.g., an often high electrical and thermal conductivity, high fracture toughness, a resistance to thermal shock, and high machinability, i.e., they can easily be cut, drilled, polished etc. Common electrical and thermal conductivities of MAX phases are $\sim 1.4\text{-}5\ \mu\Omega\cdot\text{m}$ (at room temperature) and $12\text{-}60\ \text{W/K}\cdot\text{m}$, respectively, which are numbers comparable to those for pure titanium [11]. However, unlike metals, but like ceramic materials, MAX phases are, in general, quite stiff and resistant to wear, oxidation and creep. They also retain much of their strength even at high temperatures ($>1000\ ^\circ\text{C}$).

The excellent high temperature properties paired with the fracture toughness of some MAX phases (as opposed to ceramic materials, which are resistant to heat but brittle) means that they could possibly be used in the construction of internal combustion engines (Fig. (2.3 (a)) that can operate at higher temperatures than is currently possible, thus making them more efficient. Examples of other potential applications for MAX phases are as coatings for electrical contacts (requires, e.g., heat and oxidation resistance, as well as good conductivity), rapidly spinning objects such as turbine blades (resistance to creep) (Fig. 2.3 (b)), and cutting tools (wear resistance) (Fig. 2.3 (c)). However, just as for other exciting materials such as, for instance, graphene, there are still challenges to be overcome with respect to industrial-scale production of MAX phases, whether it is in bulk or thin film form. Nevertheless, a few commercial MAX phase products already exist. Sandvik Heating Technology AB markets both Ti_2AlC and Ti_3SiC_2 in powder form and in the form of solid targets for use in the production of thin films (Fig. 2.3 (d)); however, the coatings themselves are nanocomposites, and thus not exclusively composed of MAX phases.

Figure 2.3 (a)-(c) Potential applications of MAX phases. Images taken from Refs. [12-14]. (d) Solid targets and powder of Maxthal 211 and 312 (Ti_2AlC and Ti_3SiC_2) manufactured by Sandvik Heating Technology AB.

2.3 MAX phases investigated in this work

In paper I we investigate the MAX phases within the Ti-Al-C system, and in paper II we investigate Mn_2GaC .

2.3.1 Ti_2AlC , Ti_3AlC_2 , and Ti_4AlC_3

Due in large part to the availability of the three different elements, the Ti-Al-C ternary system is both theoretically and experimentally very well-explored. On top of the single element phases, it contains several Ti-C and Ti-Al binaries, and one Al-C binary (Al_4C_3). Ternary phases are the perovskite³ Ti_3AlC and the two MAX phases Ti_2AlC and Ti_3AlC_2 , all three for which phase stability calculations and experiment are in agreement.

As previously stated, Ti_2AlC was among the first MAX phases to be synthesized, as well as one of the first MAX phases to be available for commercial use; the first reports on Ti_3AlC_2 , on the other hand, did not show up until the 1990's. A very interesting property of both Ti_2AlC and Ti_3AlC_2 from an applications perspective is that when they are heated, a layer of Al_2O_3 forms on the surface as Al reacts with – if present – O atoms. This layer strongly adheres to the underlying MAX phase and protects against further oxidation even after repeated thermal cycling, thus making Ti_2AlC and Ti_3AlC_2 suitable as protective coatings of high-temperature applications in oxidizing environments. However, for reasons that include an increased probability of Al_2O_3 formation in Ti_2AlC as compared to Ti_3AlC_2 , explained by the higher concentration of Al in the former phase, Ti_2AlC would likely be preferred over Ti_3AlC_2 for such applications [11, 15, 16].

³ A class of cubic ternary compounds that shows lots of promise for photovoltaic applications.

While the theoretical results for Ti_4AlC_3 in paper I do not clearly indicate either stability or instability, the fact that no reports on the synthesis of this phase exist and that there is a lack of reports on synthesized M_4AX_3 phases in general, renders likely the conclusion that it is indeed not possible to synthesize this phase.

2.3.2 Mn_2GaC

In the Mn-Ga-C system it is possible to find quite a few Mn-C and Mn-Ga binaries, but no gallium carbides. The only ternary phase that has so far been synthesized is the MAX phase Mn_2GaC , which, due to the nonzero magnetic moments of the Mn atoms, is one of few known magnetic MAX phases. Since this phase is such a recent contribution to the MAX phase family, the understanding of its physical properties is still limited. The theoretical investigation in paper II is one of the first attempts at changing this, and it also provides a reference for future experimental work.

Mn_3GaC_2 , Mn_4GaC_3 , and Mn_3GaC have all been shown through first-principles calculations to be outcompeted by other phases in the system, and it is therefore unlikely that any of these ternaries will be synthesized in the future.

3 Density functional theory

The theoretical framework underlying all calculations in this thesis is density functional theory (DFT), which provides a practical, first-principles based approach to the simulation of large systems of interacting particles. The use of DFT has increased rather dramatically over the past two decades, and today it is the premier tool for theoretical solid state physics research.

3.1 The electronic energy

Although a system of particles such as a crystal consists of both electrons and atomic nuclei, calculating the total energy of this system is mainly a problem of calculating the total electronic energy, due to the complicated dynamics of the electron-electron interactions. We may thus limit the discussion to a consideration of the Hamiltonian representing the total energy of a collection of electrons moving in the external electric potential $v_{ext}(\mathbf{r})$ generated by a set of static⁴, positively charged ions:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i v_{ext}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (3.1)$$

In this expression, the first term is the total kinetic energy, while the second and third terms are the total potential energy due to the electron-ion and the electron-electron interactions, respectively. Since the ions are static, $v_{ext}(\mathbf{r})$ must be static as well, and the challenge of calculating the electron-ion interaction energy is therefore significantly reduced. The electron-electron interaction energy, on the other hand, poses a considerable computational challenge, since the motion of each electron is affected by the simultaneous motion of every other electron in the system.

DFT was developed in order to circumvent this so-called quantum mechanical many-body problem, which arises for systems larger than $N \sim 10$ atoms. Even at such modest system sizes, the electronic many-body wave function Ψ_e required to correctly describe the motion of the surrounding electrons is, with its multiple degrees of freedom, complex enough that solving the Schrödinger equation becomes prohibitively expensive in terms of computational resources.

In contrast, DFT relies in principle (although not yet in practice, as will be discussed below) only on the electron density $n(\mathbf{r})$, which has three spatial degrees of freedom, and the required storage space and computational time thus scale much slower, the latter approximately as N^3 . Currently this allows for calculations of systems comprised of up to about 1000 atoms; however, further development of DFT may improve this scaling, which would allow for computational treatment of even larger atomic systems.

⁴ This is the so-called Born-Oppenheimer approximation, according to which the surrounding electrons, due to their much smaller masses, will reach their equilibrium states almost instantly upon small changes in the positions of the ions. This entails that the wave function describing the entire system can be written as the product of an electronic and an ionic part, and that the ionic part can be treated as a constant while calculating the electronic energy.

3.2 The Hohenberg-Kohn Theorems

At the root of DFT are the two so-called Hohenberg-Kohn theorems, named after their originators, Pierre Hohenberg and Nobel laureate Walter Kohn [17]. The first H-K theorem states that the external potential $v_{ext}(\mathbf{r})$ of a system of interacting electrons is uniquely determined by its ground state density $n(\mathbf{r})$, up to an additive constant. In other words, for a given ground state electron density, there is only one possible external potential. Since $v_{ext}(\mathbf{r})$ in turn uniquely determines the Hamiltonian of the system and thus the many-body wave function, it follows from the first H-K theorem that $n(\mathbf{r})$ therefore completely determines the system's ground state properties, including the ground state energy, which is the quantity of primary interest in this thesis.

From this follows the second Hohenberg-Kohn theorem, which states that for any given external potential $v_{ext}(\mathbf{r})$, one can define a functional – i.e., a function whose input argument is another function, and whose output is a number – of the density,

$$E_v[n] = F_{HK}[n] + V[v_{ext}, n], \quad (3.2)$$

where the Hohenberg-Kohn functional $F_{HK}[n]$ accounts for the electronic kinetic energy and for all electron-electron interactions (the $\mathbf{r}$ dependence of n and v_{ext} has been suppressed for the sake of readability). The theorem further states that for a particular $v_{ext}(\mathbf{r})$, the functional defined in Eq. (3.2) is minimized by the ground state density $n(\mathbf{r})$ associated with this potential. This variational principle can be formulated mathematically as

$$E_v[n] = F_{HK}[n] + V[v_{ext}, n] < F_{HK}[n'] + V[v_{ext}, n'], \quad (3.3)$$

where $n'(\mathbf{r})$ is any density separate from $n(\mathbf{r})$.

However, while the two H-K theorems prove that the electron density can in principle be used as the basic variable, they do not immediately lead to a practical recipe for calculating the ground state properties, since they do not give the exact form of the H-K functional $F_{HK}[n]$. To date, this form is still unknown. Even so, the realization that the energy of a system of interacting particles can be expressed as a functional of the density has proven very fruitful, as it has led to a reformulation of the intractable many-body problem into the significantly less demanding problem of calculating the energy of a system of non-interacting particles.

3.3 The Kohn-Sham approach to DFT

Today, DFT is more or less synonymous with the approach developed by Kohn and Lu Jeu Sham [18]. This approach rests on the assumption that for any system of interacting particles, it is possible to construct an auxiliary, fictitious system of non-interacting particles whose energy is minimized by the same density as the ground state density of the real system. While there is no general proof for this assumption, the fact that it has so far held up remarkably well makes the Kohn-Sham approach an invaluable tool for materials scientists.

The starting point of the Kohn-Sham approach is to write the H-K functional as the sum of the non-interacting part of the kinetic energy, $T_s[n]$, the classical potential energy due to electron-

electron Coulomb repulsion $J[n]$ (also called the *Hartree energy*), and $E_{xc}[n]$, the *exchange-correlation energy*, which contains the quantum mechanical parts⁵ of the kinetic and potential energy. Equation (3.2) thus becomes

$$E_v[n] = T_s[n] + J[n] + E_{xc}[n] + V[v_{ext}, n]. \quad (3.4)$$

The second step is to write an expression for the energy functional of the non-interacting system:

$$E_s[n] = T_s[n] + V[v_{eff}, n]. \quad (3.5)$$

In this system, the effective potential $v_{eff}(\mathbf{r})$ serves as the external potential for the non-interacting particles.

Via Lagrange minimization of Eq. (3.4) and (3.5), it can be shown that the energy of both systems are minimized by the same density, if $v_{eff}(\mathbf{r})$ is defined as the functional derivative with respect to $n(\mathbf{r})$ of the sum of $J[n]$, $E_{xc}[n]$, and $V[v_{ext}, n]$ in Eq. (3.4), i.e., as

$$v_{eff}(\mathbf{r}) := \frac{\delta J[n]}{\delta n} + \frac{\delta E_{xc}[n]}{\delta n} + v_{ext}(\mathbf{r}), \quad (3.6)$$

where the first term is the Hartree potential $v_H(\mathbf{r})$, and the second term the exchange-correlation potential $v_{xc}(\mathbf{r})$.

Just as for the interacting system, the exact form of the energy functional of the non-interacting system is unknown. However, even without this knowledge, calculating the energy of the latter system is much easier: instead of solving the many-body Schrödinger equation, one solves a set of N Schrödinger-like so-called *Kohn-Sham equations*, given by

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_{eff}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (3.7)$$

where the ψ_i 's are the Kohn-Sham orbitals, which can be expressed as, e.g., plane waves. The total energy $E_s[n]$, which is the sum of the eigenenergies ϵ_i , is minimized when the density used to construct $v_{eff}(\mathbf{r})$ is reproduced by the sum of the squares of the K-S orbitals, i.e., when

$$n(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2. \quad (3.8)$$

⁵ Both the exchange and the correlation parts of E_{xc} can be explained physically by the Pauli exclusion principle, which says that two particles cannot be in the exact same quantum state.

In other words, equation (3.7) has to be solved self-consistently with respect to the density (for spin up/down), and the algorithm for this is described in Fig. 3.1.

Figure 3.1 The Kohn-Sham self-consistent cycle.

The self-consistency requirement follows from the H-K theorems, which also hold true for the non-interacting system. Hence, just as for the interacting system, the Hamiltonian and therefore the Kohn-Sham orbitals of the non-interacting system are uniquely determined by the electron density. This means that, if the Kohn-Sham orbitals do indeed generate a density that matches the guessed initial density, then the energy of both systems is necessarily minimized.

But even if the non-interacting and the interacting systems share a minimizing density, their ground state energies are not necessarily equal. However, a simple relation between the energy of the two systems exists. Together with the definition of the effective potential in Eq. (3.6), Eq. (3.5) can be rewritten as

$$T_s[n] = E_s[n] - 2J[n] - V[v_{xc}, n] - V[v_{ext}, n]. \quad (3.9)$$

If the right-hand side of this equation is substituted into in Eq. (3.4), the expression for the energy of the interacting system becomes

$$E_v[n] = E_s - J[n] + E_{xc}[n] - V[v_{xc}, n]. \quad (3.10)$$

Finally, the total ground state energy of the particle system is given by adding $E_v[n]$ to the potential energy of the atomic nuclei E_{II} , which is just the classical ion-ion Coulomb repulsion:

$$E_{tot} = E_v[n] + E_{II}. \quad (3.11)$$

3.4 Approximations of E_{xc}

The main theoretical obstacle in DFT is the exchange-correlation energy, whose exact form is currently unknown. This entails that the energy of the non-interacting system, which depends on the functional derivative of $E_{xc}[n]$ according to Eq. (3.5) and (3.6), cannot be calculated exactly, a problem that carries over to the interacting system. However, the development of $E_{xc}[n]$ functionals is an active field of research, and the outcome so far has been several different and often useful approximations.

One of the simplest exchange-correlation functionals, the so-called local density approximation (LDA), takes advantage of the fact that exchange and correlation in many solids are local in nature, i.e., they are short range effects. This means that the exchange-correlation energy density functional (energy per particle) $\epsilon_{xc}[n]$, which integrates to $E_{xc}[n]$ according to the equation

$$E_{xc}[n] = \int \epsilon_{xc}[n] n dr, \quad (3.12)$$

can be reasonably approximated at each point $\mathbf{r}$ in space by the exchange-correlation energy density *function* $\epsilon_{xc}^{LDA}(n)$ of a homogeneous electron gas (an electron gas with constant density). This is useful since approximate expressions for $\epsilon_{xc}^{LDA}(n)$ is easier to derive than the still elusive $\epsilon_{xc}[n]$.

$E_{xc}[n]$, and hence $\epsilon_{xc}^{LDA}(n)$, can be split into two separate parts with differing dependence on the density: one for exchange and one for correlation. For the exchange part there is a simple analytical expression, but the correlation part must generally be approximated, as exact expressions only exist in the limit of high density paired with weak correlation, and low density together with strong correlation. Since several different approximations for the correlation part exists, it is actually more correct to speak of local density approximations rather than a single LDA (although the latter is more convenient).

The LDA is exact for a homogenous electron gas and very accurate for spatially slowly varying densities [19], and compared to other $E_{xc}[n]$ approximations it is also fairly computationally inexpensive. However, one of the main drawbacks of the LDA is that it tends to overestimate $E_{xc}[n]$ for materials with strongly fluctuating densities, thus making the bonds between the atoms (and hence the lattice parameters in crystalline materials) too short. This may lead to erroneous predictions of a material's ground state structure and properties. An often cited example is Fe, where LDA calculations first yielded a nonmagnetic (or

antiferromagnetic – the two magnetic configurations were degenerate in energy) face centered cubic (fcc) ground state structure, and in a later study an antiferromagnetic hexagonal close-packed (hcp) ground state structure, whereas it was known from experiment to be ferromagnetic and body centered cubic (bcc) [20, 21]. Also, the LDA cannot treat Van der Waals interactions, as they are inherently nonlocal with respect to electron correlation [22]. This makes the LDA unsuitable for calculations on materials like, e.g., graphite, where it is Van der Waals interactions that make the graphene layers stick to each other. It should be noted, however, that in cases where the results from LDA calculations for individual phases are inaccurate only in a quantitative sense (e.g., the correct structure is found, but the lattice parameters are off by a significant amount), these results may still be used to accurately reflect *trends* in physical properties.

Building on the LDA is the gradient expansion approximation (GEA) and the generalized gradient approximation (GGA). As their names imply, both approximations include the gradient of the density, but they differ in that the former is merely a Taylor expansion of the LDA with respect to the density, whereas the latter is deliberately constructed to reproduce properties of the real exchange correlation energy functional such as the sum rule⁶, something which the GEA does not. Because of these differences, the GGA is more frequently used than the GEA – the latter functional does in fact perform worse than the LDA in many cases. The GGA, on the other hand, is considered a general improvement upon the LDA. While the GGA tends to underestimate $E_{xc}[n]$ and make the atomic bonds too long, the magnitude of this error is usually smaller than the opposite error for the LDA. This and the fact that the GGA is comparable to the LDA with respect to the computational resources needed makes the GGA the better choice in most cases.

Just as for the LDA, various versions of the GGA exist; for MAX phase related first-principles calculations, the particular GGA developed by Perdew, Burke, and Ernzerhof (PBE, for short) [23] is probably the most popular one, and it is also the one used in this thesis. The PBE is a non-empirical (i.e., it does not use any parameter values derived from experiment) and thus transferable GGA that for MAX phases has proven to be relatively fast, and usually yields very accurate lattice parameters..

3.5 Practical considerations

In addition to the choice of exchange-correlation energy functional, the accuracy and speed of DFT calculations are affected by the size of the $\mathbf{k}$ -point grid (with respect to the Kohn-Sham orbitals), and the plane wave energy cutoff.

3.5.1 $\mathbf{k}$ -point convergence

A suitable basis set in which to express the Kohn-Sham orbitals in Eq. (3.7) has to be decided upon before running through the K-S self-consistent cycle. A basis set is any set of linearly independent functions that can be combined to represent every possible state of a particle or system of particles. A common choice of such functions when working with periodic

⁶ This rule says that a spatial integration over the so-called exchange-correlation hole, which is a local decrease in the density around an electron with respect to the average density, should be equal to -1 .

potentials, e.g., external potentials generated by the periodically arranged atomic nuclei in crystalline materials, is so-called *Bloch waves*. A Bloch wave consists of a plane wave part multiplied by a function which is of the same periodicity as the electron density (which in turn is of the same periodicity as the potential)⁷. It can be written as

$$\psi_{j,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{j,\mathbf{k}}(\mathbf{r}), \quad (3.13)$$

where j is the band index denoting the particular band in the first Brillouin zone to which the orbital belongs, and where $\mathbf{k}$ is the wave vector, or $\mathbf{k}$ -point, associated with this orbital.

Plugging the Bloch waves into Eq. (3.7) and (3.8) gives both the eigenenergies $\epsilon_j(\mathbf{k})$ of the Kohn-Sham orbitals and the electron density, the latter for which the expression becomes

$$n(\mathbf{r}) = \sum_j \int_{BZ} |\psi_{j,\mathbf{k}}(\mathbf{r})|^2 d^3k, \quad (3.14)$$

where the integral is taken over the first Brillouin zone, and the sum is taken over all occupied bands. Since the number of possible $\mathbf{k}$ -points is infinite, a finite sample of these points is chosen. This means that the integral in Eq. (3.14) is replaced by a discrete sum over $\mathbf{k}$, so that the density is instead calculated by interpolation between the terms in this sum. As shown in Fig. 3.2, a large enough sample of $\mathbf{k}$ -points has to be chosen in order to converge the ground state energy; a commonly used convergence criterion with respect to the $\mathbf{k}$ -point grid is that the calculated energy from the two largest grids should differ by no more than 0.1 meV/atom. How to choose this sample depends on the crystal structure and the length ratios between the lattice parameters. For a M_2AX phase unit cell, where the ratio between the basal plane lattice vectors $\mathbf{a}_{1,2}$ and the vertical lattice vector $\mathbf{a}_3$ is $\sim 1/4$, a grid with four times as many $\mathbf{k}$ -points along the $\mathbf{k}$ -space basal plane axes should be used as compared to the vertical axis, since the respective lengths of the basis vectors spanning $\mathbf{k}$ -space,

$$\begin{aligned} \mathbf{b}_1 &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} & \mathbf{b}_2 &= 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \\ \mathbf{b}_3 &= 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \end{aligned} \quad (3.15)$$

are related through $|\mathbf{b}_1| = |\mathbf{b}_2|$ and $|\mathbf{b}_3| = \frac{1}{4} |\mathbf{b}_{1,2}|$ when $|\mathbf{a}_1| = |\mathbf{a}_2|$. This yields the same $\mathbf{k}$ -point density along all three axes.

⁷ Note that a Bloch wave $\psi_{j,\mathbf{k}}$ does not itself have the same period as the potential, but is instead *quasiperiodic*, fulfilling the criterion that $\psi_{j,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = g(\mathbf{r}, \psi_{j,\mathbf{k}}(\mathbf{r}))$.

Figure 3.2. k -point convergence. For MAX phases convergence is reached when $\Delta E \leq 0.1$ meV.

Using only a small sample of $\mathbf{k}$ -points is possible for many materials since the magnitude of the Bloch waves is usually a slowly varying quantity; for metals, however, there are discontinuities in the integrand around the Fermi energy, which requires a larger $\mathbf{k}$ -point sample [24]. Another factor speeding up the calculations is that if the $\mathbf{k}$ -space associated with a particular crystal structure possesses several symmetries, as it is then enough to confine the calculations to only a part of the $\mathbf{k}$ -point grid.

3.5.2 Energy cutoff convergence and pseudopotentials

Since the function $u_{\mathbf{k}}(\mathbf{r})$ in Eq. (3.13) is periodic, it can be expanded in a Fourier series, thus yielding the expression

$$u_{\mathbf{k}}(\mathbf{r}) = \sum \mathbf{C}_{\mathbf{G}} e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (3.16)$$

Here, $\mathbf{G}$ is a reciprocal lattice vector given by

$$\mathbf{G} = \lambda_1 \mathbf{b}_1 + \lambda_2 \mathbf{b}_2 + \lambda_3 \mathbf{b}_3, \quad (3.17)$$

where $\lambda_{1,2,3}$ are positive integers. The Fourier coefficients $\mathbf{C}_{\mathbf{G}}$ in Eq. (3.16) become smaller and less important as $|\mathbf{G}|$ becomes larger, and it is therefore possible to exclude large values of $|\mathbf{G}|$ in order to further speed up the calculations. The energy defined by the largest reciprocal lattice vector included in the calculations, $|\mathbf{G}_{\max}|$, is the so-called *cutoff energy*,

$$\epsilon_{\text{cut}} = \frac{\hbar^2}{2m} |\mathbf{G}_{\max}|^2. \quad (3.18)$$

Thus, just as for the $\mathbf{k}$ -point grid, the ground state energy must be converged with respect to

ϵ_{cut} . The exact size of ϵ_{cut} needed to reach convergence depends on how the potential in the core regions, i.e., the regions near the atomic nuclei, is treated. Since chemical bonds between atoms, whose nature and strength determine, e.g., the electric and mechanical properties of a phase, involve mainly the valence electrons, changes in the chemical environment do not affect the core electrons to any significant degree. This means that the difference in the ground state energy between two different phases is primarily given by the difference in energy between their respective valence states. Thus, the potential that the valence electrons feel from the core electrons can be regarded as fixed, and can therefore be combined with the external potential generated by the nuclei to form an effective ionic potential – a *pseudopotential* – that is much weaker than the real (external) potential in the core regions, but identical to it outside some cutoff radius r_c . The partially reduced strength of this potential makes it possible to replace the real wave functions of the valence electrons with pseudo wave functions that are smooth in the core regions instead of rapidly oscillating⁸, thus requiring fewer Fourier components than the real wave functions. Consequently, a smaller ϵ_{cut} is possible.

Several methods that build on the concept of pseudopotentials exist. Currently the projector augmented wave (PAW) method developed by P.E. Blöchl [25] is one of the most frequently used for solid state physics calculations, as it generalizes the pseudopotential method by using all-electron wave functions. In both paper I and II, PAW is the method of choice.

⁸ The oscillations are a consequence of the fact that the valence wave functions have to be orthogonal to the core wave functions, which are rapidly oscillating as well.

4 Phase stability calculations from first principles

4.1 Thermodynamic stability and metastability

A central concept when discussing phase stability is the thermodynamic potential. In analogy with an electric potential, which is the energy required to bring a point charge from some reference point A to point B, the thermodynamic potential is a measure of the energy it takes to form a phase under constant temperature T and pressure p from a reference state which can be defined by, e.g., the free constituent atoms at T and p . In its most general form, this potential can be expressed as

$$G(p, T) = E_0(V) + F_{el}(T, V) + F_{vib}(T, V) + F_c(T) + pV. \quad (4.1)$$

This is the so-called *Gibbs free energy*, where the first term is the zero-temperature energy, the second and third term is the electronic and vibrational contribution, respectively, which account for thermal excitations of electrons and phonons, and where the fourth term is the configurational energy, which is nonzero only for configurationally disordered phases. The last term is the mechanical work the particle system has to perform against its surroundings to reach its final volume V .

Phase stability can be driven either by thermodynamics or by reaction kinetics. Thermodynamically driven phase stability is determined by calculating the Gibbs free energy of formation ΔG , defined by the difference between the Gibbs free energy of the investigated phase and the Gibbs free energy of any polymorph⁹ or set of other competing phases with chemical compositions that, when properly weighted, combine to the same composition as that of the investigated phase (for example, for an M_2AX phase, a set of competing phases might consist of the binaries MA and MX). The phase is thermodynamically stable if $\Delta G < 0$ with respect to all possible competing phases and combinations thereof, i.e., if the Gibbs free energy of the investigated phase is at the global minimum of the Gibbs free energy landscape, as illustrated in Fig. 4.1. If this is indeed the case, the phase will tend to form spontaneously. In other words, just as there is a natural tendency for a negatively charged particle to minimize its potential energy by moving towards the positive source charge of an electrostatic field, there is a natural tendency for a collection of atoms to combine into the phase, or set of phases, with the lowest value of G .

⁹ That is, a phase with the same chemical composition as another phase, but with a different crystal structure.

Figure 4.1. Hypothetical Gibbs free energy landscape for an M-A-X system. The M_2AX phase is at the global minimum, while the respective sets of competing phases $MA+MX$ and $M+A+X$ are found in local minima, i.e., they are metastable.

However, even if formation of the investigated phase is favored thermodynamically, it is still possible to end up with competing phases as very long-lived intermediate products – practically they may thus be seen as alternative end products. An important factor when it comes to phase stability is the activation energy, which is the energy needed to weaken or break the bonds between the constituent atoms of the initial phases in order to initiate the phase transition(s). In Fig. 4.1, there are two possible transition pathways with different activation energies (given by the height of the "bumps") and different end products. Although pathway A leads to an end product that is only *metastable*, i.e., at a *local* minimum of the Gibbs free energy landscape, it may still be favored over pathway B that leads to the global minimum of G , if the activation energy of pathway A is lower. Metastability is kinetically driven, which means that it depends on the rate of formation of the end products, a rate determined by the activation barrier together with external factors such as pressure and temperature. If this rate is higher for a metastable end product than for a competing, thermodynamically stable one, the former will be favored initially; however, over time the latter will form instead. At standard pressure and temperature, the carbon allotrope diamond is an example of a metastable phase that, on a time scale of billions of years, will transform into the thermodynamically stable allotrope graphite.

In this thesis, however, all focus is on thermodynamically driven phase stability; in other words, the phase stability calculations in paper I are calculations of the Gibbs free energy of formation, ΔG , of the investigated MAX phases.

4.2 Finding competing phases

The first step in an investigation of the stability of a particular phase is to identify all competing phases, a task that requires careful study of the experimentally derived phase diagram of the relevant materials system. If the system is not very well-explored, hypothetical phases other than the phase under investigation may have to be included. One way to decide which hypothetical phases to include is by looking at neighboring systems; if there are phases in these systems with crystal structures that cannot be found in the system of interest, it might be reasonable, as a first guess, to use these structures in the construction of hypothetical phases. However, if the neighboring systems are also not very well-explored, another approach for determining which hypothetical phases to include is to use evolutionary algorithms [26], although this has not been necessary in this work.

Previous phase stability studies focused on MAX phases often suffered from incomplete sets of competing phases, leading to results that did not necessarily reflect the experimental data [27-29]. However, following the recently developed, by Dahlqvist *et al*, linear optimization procedure to quickly determine the set of most competing phases, this has the potential to change [30]. This procedure is described and used in paper I to identify the set of most competing phases with respect to three $\text{Ti}_{n+1}\text{AlC}_n$ phases.

4.3 Thermodynamical phase stability at 0 K

Most first-principles based phase stability calculations are carried out using the approximations that the pressure is 0 GPa and that the temperature is 0 K, which reduces the Gibbs free energy given by Eq. (4.1) to the first term only, i.e., to the zero-temperature energy E_0 . While these approximations describe a system quite different from real-world experimental conditions, the predictions of MAX phase stability have so far proven to be accurate, which is fortunate since the use of these approximations significantly cuts down the amount of required computational resources; for calculations on large supercells, for instance, they can lead to a decrease in computational time of several days.

4.3.1 Calculating E_0

Since the zero-temperature energy E_0 depends on the phase volume, the equilibrium volume, for which the calculations yield the global minimum value of E_0 , needs to be identified. The equilibrium volume V_{eq} is found when E_0 increases as one moves away from V_{eq} in both directions, as seen in Fig. 4.2, and convergence has been reached with respect to the $\mathbf{k}$ -point grid and the plane wave cutoff energy.

Figure 4.2. Gibbs free energy as a function of volume at 0 K. The equilibrium volume V_{eq} is found at the global minimum of the Gibbs free energy.

4.4 Thermodynamical phase stability at $T > 0$ K

The accurate results from the 0 K calculations notwithstanding, until now no attempts at providing an explanation for this accuracy have been made. Such an explanation, which should reduce the uncertainty with respect to the reliability of future predictions of MAX phase stability, is provided in paper I.

When considering to which degree temperature dependent effects influence phase stability predictions, there are at least two more contributions to the Gibbs free energy in addition to E_0 that should be included in the calculations, namely the free electronic and free vibrational energy, i.e., the second and third terms in Eq. (4.1). In case of a disordered phase, the fourth term, the free configurational energy, also contributes, and should then be included as well.

4.4.1 Electronic free energy

If the temperature is raised above 0 K, some of the electrons are excited into states with higher energy. While these excitations are associated with a positive contribution E_{el} to the Gibbs free energy, it is counteracted by the simultaneous increase in the number of available electronic states and hence the electronic configurational entropy S_{el} . In other words, the electronic contribution to the Gibbs free energy is given by the difference

$$F_{el}(V, T) = E_{el}(V, T) - TS_{el}(V, T). \quad (4.8)$$

The entropy term tends to dominate the expression even at very low temperatures, thus leading to a lowering in the Gibbs free energy; this is seen for the investigated phases in paper I.

4.4.2 Vibrational free energy

At 0 K the atoms in a crystal lattice are essentially motionless. At nonzero temperatures (up to a certain limit), however, they form quantized modes of harmonic collective oscillations. Due to their mix of wave- and particle like behavior (just like particles, they carry momentum), these vibrations are called *phonons*, in analogy with photons. Phonons contribute significantly to, e.g., the heat capacity of a solid, as well as to thermal conduction, and just as for thermally excited electrons, they give a nonzero contribution to the Gibbs free energy consisting of an energy term and an entropy term:

$$F_{vib}(V, T) = E_{vib}(V, T) - TS_{vib}(V, T). \quad (4.9)$$

Again there is a tendency for the entropy term to dominate the expression even at low temperatures, also seen paper I.

Equation (4.9) can also be written as

$$F_{vib}(V, T) = \frac{1}{2} \sum_{\mathbf{q}, \nu} \hbar \omega_{\mathbf{q}, \nu} + k_B T \sum_{\mathbf{q}, \nu} \ln[1 - \exp(-\hbar \omega_{\mathbf{q}, \nu} / k_B T)], \quad (4.10)$$

where $\mathbf{q}$ is the phonon wave vector, and ν is the band index. The allowed phonon frequencies $\omega_{\mathbf{q}, \nu}$ can be calculated using either a direct method or the linear response method, the latter which is also known as *density functional perturbation theory* (DFPT) [31, 32].

In this thesis, DFPT as implemented in the VASP (Vienna ab initio simulation package) code is the method of choice. DFPT uses the fact that the first derivative of the electron density with respect to a shift in the positions of the ions – i.e., a perturbation of the external potential – is directly related to the second derivative of the energy with respect to this shift, which yields the interatomic force constants (IFCs) that are then plugged into the dynamical matrices to obtain the phonon frequencies. The derivative of the density for a given perturbation can be found through a self-consistent calculation analogous to the Kohn-Sham cycle in DFT, with the first derivatives of the unperturbed (ground state) K-S orbitals as solutions to the resulting eigenequations. In order to determine the phonon dispersion, self-consistent calculations have to be performed for several different phonon perturbations, each with a specific wave vector $\mathbf{q}$. In regular DFPT, the calculations are confined to the unit cell; however, VASP DFPT only calculates the frequencies at the Γ point ($\mathbf{q} = 0$), which means that the free vibrational energy has to be converged with respect to supercell size. For the Ti-Al-C MAX phases in paper I, sufficient convergence was reached for $3 \times 3 \times 1$ supercells.

4.4.3 Configurational free energy

The configurational free energy comes into play for phases where one or more of the crystal sublattices are disordered because of, e.g., alloying or vacancies. Again there is an energetic cost associated with the excited, disordered state, and a counteracting term due to the increased entropy:

$$F_c(T) = E_c(T) - TS_c(T). \quad (4.11)$$

Generating a disordered phase can be done – and has been done in this thesis – using the special quasirandom structure (SQS) method developed by Zunger *et al* [33].

4.4.4 Thermal expansion

As indicated in Eq. (4.1), the Gibbs free energy depends on the volume of the phase. In the so-called *harmonic approximation* (HA) this dependence is neglected, which has the advantage that a significant amount of computational time is saved. However, as most materials expand with increasing temperature, the accuracy of the results may increase if the *quasi-harmonic approximation* (QHA) is applied instead.

In the QHA, the expansion is modeled in the following way: at a given temperature T , the volume of the phase (and hence the lattice parameters) is increased in a stepwise fashion, and at each volume the zero-temperature energy, the phonon dispersion (under the assumption that the HA is valid), and the electronic contribution is calculated. These contributions are then added together, and an fit between the resulting data points yields the minimum of the Gibbs free energy and the equilibrium volume at T . When this process is repeated for several different temperatures, the result is usually in line with that shown in Fig. 4.2: the equilibrium volume increases with temperature, while the Gibbs free energy decreases.

Figure 4.2. Gibbs free energy vs. volume with increasing temperature; each of the six curves represent the results at a given temperature, which increases strictly from 0 K to T_5 . The line crossing the curves indicates the minimum energy and equilibrium volume at each temperature.

5 Elastic properties

First principles calculations of elastic properties of MAX phases including the bulk modulus do not yet match experimental data as well as, e.g., calculations of the lattice parameters. They are, however, often valuable for analysis of trends, as shown in paper II in this thesis.

The elastic properties of a crystalline phase are obtained from its elastic constants, which can be determined by distorting the crystal structure and calculating its total energy.

5.1 Elastic constants

For phases with a hexagonal structure such as a MAX phase, there are five independent elastic constants: C_{11} , C_{12} , C_{13} , C_{33} , and C_{44} ¹⁰. To calculate these constants, five different strains need to be applied to the crystal structure, each of which is represented by a particular distortion matrix

$$\begin{pmatrix} 1 + \alpha_1 & \alpha_6 & \alpha_5 \\ \alpha_6 & 1 + \alpha_2 & \alpha_4 \\ \alpha_5 & \alpha_4 & 1 + \alpha_3 \end{pmatrix}, \quad (5.1)$$

where the off-diagonal strain parameters α_i are pairwise identical due to the symmetry of the structure [34]. The basis of the strained structure, given by the product of the matrix (5.1) and the 3×3 basis vector matrix of the unstrained structure, then serves as input for a DFT calculation of its total energy $E(V, \alpha)$. This energy is given by the equation

$$E(V, \alpha) = E(V_0, 0) + V_0 \left(\sum_i \tau_i \alpha_i \xi_i + \frac{1}{2} \sum_{i,j} C_{ij} \alpha_i \xi_i \alpha_j \xi_j \right). \quad (5.2)$$

where $E(V_0, 0)$ is the energy of the unstrained structure at the equilibrium volume V_0 , τ_i are stress tensor elements, and ξ_i are coefficients that equal 1 for $\alpha_{1,2,3}$ and, because of the pairwise symmetry, 2 otherwise. When all five strains have been applied, the result is five different equations derived from Eq. (5.2):

$$E(V, \alpha) - E(V_0, 0) = V_0 ((\tau_1 + \tau_2)\alpha + (C_{11} + C_{12})\alpha^2), \quad (5.3)$$

$$E(V, \alpha) - E(V_0, 0) = V_0 ((\tau_1 - \tau_2)\alpha + (C_{11} - C_{12})\alpha^2), \quad (5.4)$$

$$E(V, \alpha) - E(V_0, 0) = V_0 \left(\tau_3 \alpha + \frac{C_{33}}{2} \alpha^2 \right), \quad (5.5)$$

$$E(V, \alpha) - E(V_0, 0) = V_0 (\tau_4 \alpha + 2C_{44} \alpha^2), \quad (5.6)$$

¹⁰ In the literature this constant is sometimes labeled as C_{55} .

and

$$\begin{aligned}
 E(V, \alpha) - E(V_0, 0) &= V_0 \left((\tau_1 + \tau_2 + \tau_3) \alpha \right. \\
 &\quad \left. + \left(C_{11} + C_{12} + 2C_{13} + \frac{C_{33}}{2} \right) \alpha^2 \right). \tag{5.7}
 \end{aligned}$$

Since the right hand sides of Eqs. (5.3)-(5.7) are second degree polynomials with respect to α , a way to extract the factors containing the elastic constants is to plot $E(V, \alpha) - E(V_0, 0)$ as a function of α , as in Fig. (5.1), to perform a quadratic fit on the data, and then take the second derivatives of the fitted curves. If the curves are not symmetric around $\alpha = 0$, the chosen strains are either too large, or the structure is mechanically unstable; the latter case would indicate that the particular crystal structure is not the ground state structure.

Figure 5.1. Energy vs. strain parameter for the five different strains yielding the five elastic constants for a MAX phase.

Once the elastic constants have been obtained, it is straightforward to derive, e.g., the bulk and shear modulus of the phase, since the moduli depend solely on the elastic constants, as shown in paper II. However, it is important to note that, if the investigated phase is magnetic, a careful search for the magnetic ground state configuration should be performed before calculating the elastic constants, since the magnetic configuration may influence the values of the elastic properties, as seen in Ref. [35] and paper II.

6 Summary of included papers

6.1 Paper I: Temperature dependent phase stability of nanolaminated ternaries from first principles calculations

In this paper, we investigated the phase stability as a function of temperature of three MAX phases: Ti_2AlC , Ti_3AlC_2 , and Ti_4AlC_3 . The aim was to compare the results to previous predictions from 0 K calculations, in order to determine the importance of the inclusion of temperature dependent effects with respect to studies of MAX phase stability.

The Gibbs free energy of the three MAX phases as well as of 14 competing phases within the Ti-Al-C system was calculated using density functional theory and density functional perturbation theory, both as implemented in VASP. The temperature dependent effects included were the electronic free energy, the vibrational free energy, the configurational free energy, and thermal expansion; however, results from calculations both including and excluding thermal expansion were considered and compared.

The results showed that up to 2000 K the Gibbs free energy of formation for each MAX phase is essentially the same as obtained at 0 K, thus meaning that the phase stability is weakly dependent on temperature. The reason for this is twofold: first, each individual temperature dependent contribution to the Gibbs free energy for each MAX phase is to a large extent cancelled by the corresponding contribution for their respective sets of most competing phases. Second, the individual contributions to the Gibbs free energy of formation partially cancel each other.

Our results suggest that phase stability of MAX phases is mainly governed by the zero-temperature energy term, and that to go beyond such calculations for phase stability predictions is therefore not motivated, with the exception of borderline cases in zero-temperature investigations.

6.2 Paper II: First-principles calculations of the electronic, vibrational, and electronic properties of the magnetic nanolaminate Mn_2GaC

In this paper, selected properties of one of the first magnetic MAX phases to be synthesized, Mn_2GaC , were studied.

The electronic properties were investigated by evaluating the electronic band structure and electronic density of states. The energy bands cross the Fermi level in the horizontal directions in reciprocal space, but not in the vertical directions, indicating that electrical conduction in Mn_2GaC might be anisotropic, occurring mostly in-plane. Furthermore, the electronic Mn and Ga density of states differs for different Mn-Ga-Mn trilayers depending on whether the Mn magnetic moments are parallel or antiparallel over the Ga layer. This effect is also seen in the distribution of the vibrational Mn and Ga states.

We further investigated the elastic properties, which were derived from the five elastic constants C_{11} , C_{12} , C_{13} , C_{33} , and C_{44} . Evaluated elastic properties were compared to theoretical and experimental results for $M_2\text{AC}$ phases where $M=\text{Ti, V, Cr, Zr, Nb, Ta}$, and $A=\text{Al, S, Ge, In, Sn}$. The Voigt bulk modulus was determined to be 157 GPa, the Voigt shear modulus 93 GPa, the Young's modulus 233 GPa, and the Poisson's ratio 0.25. As compared to other $M_2\text{AC}$ phases, the bulk and shear moduli are concluded to be fairly low, whereas the Young's modulus is intermediate, and the Poisson's ratio high. Furthermore, Mn_2GaC was found relatively elastically isotropic, with a compression anisotropy factor of 0.97, and shear anisotropy factors of 0.9 and 1, respectively. Two machinability indices were also calculated, which indicate that Mn_2GaC is machinable.

For all properties here investigated, the choice of magnetic configuration affects the results significantly. This underlines the importance of identifying the most relevant magnetic configuration, i.e. the ground state for low temperatures and disordered paramagnetic states at higher temperatures, before evaluating physical MAX phase properties.

7 Bibliography

- [1] A. Mockute, M. Dahlqvist, J. Emmerlich, L. Hultman, J.M. Schneider, P.O.Å. Persson, J. Rosen, *Physical Review B*, 87 (2013) 094113.
- [2] S. Dubois, G.P. Bei, C. Tromas, V. Gauthier-Brunet, P. Gadaud, *International Journal of Applied Ceramic Technology*, 7 (2010) 719-729.
- [3] M.W. Barsoum, T. El-Raghy, M. Ali, *Metall and Mat Trans A*, 31 (2000) 1857-1865.
- [4] P. Eklund, M. Beckers, U. Jansson, H. Högberg, L. Hultman, *Thin Solid Films*, 518 (2010) 1851-1878.
- [5] M. Naguib, V.N. Mochalin, M.W. Barsoum, Y. Gogotsi, *Advanced Materials*, 26 (2014) 992-1005.
- [6] W. Jeitschko, H. Nowotny, F. Benesovsky, *Journal of the Less Common Metals*, 7 (1964) 133-138.
- [7] W. Jeitschko, H. Nowotny, *Monatshefte für Chemie*, 98 (1967) 329-337.
- [8] H. Wolfsgruber, H. Nowotny, F. Benesovsky, *Monatshefte für Chemie*, 98 (1967) 2403-2405.
- [9] M.W. Barsoum, T. El-Raghy, *American Scientist*, 89 (2001) 334-343.
- [10] M.W. Barsoum, T. El-Raghy, *Journal of the American Ceramic Society*, 79 (1996) 1953-1956.
- [11] M.W. Barsoum, M. Radovic, *American Ceramic Society Bulletin*, 92 (2013) 28.
- [12] S&S Cycle Inc, <http://www.sscycle.com/>.
- [13] Laser Design Inc, <http://laserdesign.com/>.
- [14] SANDVIK Coromant, <http://www.sandvik.coromant.com/>.
- [15] J. Frodelius, E.M. Johansson, J.M. Córdoba, M. Odén, P. Eklund, L. Hultman, *International Journal of Applied Ceramic Technology*, 8 (2011) 74-84.
- [16] D.J. Tallman, B. Anasori, M.W. Barsoum, *Materials Research Letters*, 1 (2013) 115-125.
- [17] P. Hohenberg, W. Kohn, *Physical Review*, 136 (1964) B864-B871.
- [18] W. Kohn, L.J. Sham, *Physical Review*, 140 (1965) A1133-A1138.
- [19] K. Burke, J.P. Perdew, M. Ernzerhof, *The Journal of Chemical Physics*, 109 (1998) 3760-3771.
- [20] C.S. Wang, B.M. Klein, H. Krakauer, *Physical Review Letters*, 54 (1985) 1852-1855.
- [21] J. Kübler, *Solid State Communications*, 72 (1989) 631-633.
- [22] F.O. Kannemann, A.D. Becke, *Journal of Chemical Theory and Computation*, 5 (2009) 719-727.
- [23] J.P. Perdew, K. Burke, M. Ernzerhof, *Physical Review Letters*, 77 (1996) 3865-3868.
- [24] A.E. Mattsson, P.A. Schultz, M.P. Desjarlais, T.R. Mattsson, K. Leung, *Modelling and Simulation in Materials Science and Engineering*, 13 (2005) R1.
- [25] P.E. Blöchl, *Physical Review B*, 50 (1994) 17953-17979.
- [26] G. Trimarchi, A. Zunger, *Physical Review B*, 75 (2007) 104113.
- [27] J.P. Palmquist, S. Li, P.O.Å. Persson, J. Emmerlich, O. Wilhelmsson, H. Högberg, M.I. Katsnelson, B. Johansson, R. Ahuja, O. Eriksson, L. Hultman, U. Jansson, *Physical Review B*, 70 (2004) 165401.
- [28] V.J. Keast, S. Harris, D.K. Smith, *Physical Review B*, 80 (2009) 214113.
- [29] W. Luo, R. Ahuja, *Journal of Physics: Condensed Matter*, 20 (2008) 064217.

- [30] M. Dahlqvist, B. Alling, J. Rosén, *Physical Review B*, 81 (2010) 220102.
- [31] X. Gonze, C. Lee, *Physical Review B*, 55 (1997) 10355-10368.
- [32] S. Baroni, S. de Gironcoli, A. Dal Corso, P. Giannozzi, *Reviews of Modern Physics*, 73 (2001) 515-562.
- [33] A. Zunger, S.H. Wei, L.G. Ferreira, J.E. Bernard, *Physical Review Letters*, 65 (1990) 353-356.
- [34] L. Fast, J.M. Wills, B. Johansson, O. Eriksson, *Physical Review B*, 51 (1995) 17431-17438.
- [35] M. Dahlqvist, B. Alling, J. Rosén, *Journal of Applied Physics*, 113 (2013) 216103.

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