



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



A. Thore*, M. Dahlqvist, B. Alling, J. Rosén

Department of Physics, Chemistry, and Biology, Thin Film Physics Division, Linköping University, SE-581 83 Linköping, Sweden

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ABSTRACT

Methods based on first-principles calculations have proven effective for predicting the thermodynamic stability of materials that have not previously been considered. However, the vast majority of these predictions are based on 0 K calculations, which means that little is known about the effects of temperature on their accuracy. This causes considerable uncertainty with respect to stability predictions of new hypothetical phases.

In this work we combine first-principles calculations with an optimization procedure to calculate the phase stability as a function of temperature for Ti_2AlC , Ti_3AlC_2 and Ti_4AlC_3 MAX phases with respect to their most competing phases in the Ti–Al–C phase diagram, in a temperature interval from 0 to 2000 K. To model nonzero temperatures, we include effects from the electronic and vibrational free energies to the Gibbs free energy for all relevant competing phases. We show that, due to a mutual cancellation of the temperature dependent energy terms, the results of neither the harmonic nor the quasiharmonic calculations differ significantly from the calculated 0 K formation energies. We thus provide a plausible explanation for the success of previous 0 K predictions, an explanation which also serves as evidence for the hypothesis that the phase stability in many materials systems is primarily governed by the 0 K energy terms.

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1. Introduction

Since its discovery in the 1960s by Nowotny [1], the class of so-called MAX phases has been subjected to extensive theoretical and experimental research. The general formula of these nanolaminated, hexagonally structured materials is $M_{n+1}AX_n$, where M is a transition metal, A is an A-group element, and X is most commonly carbon and/or nitrogen. Due to the metallic M – A bonds and ionic-covalent like M – X bonds, MAX phases possess both properties typical of metals such as good machinability and high electrical as well as high thermal conductivity, and ceramic properties such as high hardness and resistance against corrosion and the wearing effects of high temperatures [2,3]. Because of this, MAX phases show potential for, e.g., electrical contacts, tool coatings, and as structural material in demanding environmental conditions.

A useful tool in the search for new and not yet experimentally verified materials – and in this particular case, MAX phases – is a computational method described in detail in two papers by

Dahlqvist et al. [4,5]. It combines first-principles calculations with a linear optimization procedure to find the set of most competing phases at any compositional point of interest in a multinary space. Equivalent approaches have also been used to search for new thermodynamically stable phases in other multicomponent systems such as Heusler alloys and oxynitrides [6,7]. The method has been used to retrodict and to successfully predict the existence of several MAX phases, and also to explain failed synthesis attempts of hypothetical MAX phases. The number of retrodicted MAX phases include, e.g., Cr_2AlC , Ti_2AlC , Ti_3AlC_2 , Ti_2AlN , Ti_4AlN_3 , Ti_3SiC_2 , V_2AlC , V_3AlC_2 and $V_4AlC_{3-\delta}$ [5,8]. Examples of predicted and later experimentally verified phases are Nb_2GeC , $(Cr_{1-x}Mn_x)_2AlC$, $(Cr_{1-x}Mn_x)_2GeC$, and Mn_2GaC [9–12]. However, while this serves as evidence that the method is reliable, there are potential pitfalls that need to be considered.

As in the above examples, most first-principles based phase stability calculations are performed at 0 K. This means that neither the electronic nor the vibrational (i.e., phonon) entropic contributions to the total energy are taken into account. However, configurational entropy is sometimes considered in the case of alloys [11,13]. Considering temperature induced excitations could be necessary if the difference in energy between the investigated

* Corresponding author. Tel.: +46 70 3212109.

E-mail addresses: andth@ifm.liu.se (A. Thore), madah@ifm.liu.se (M. Dahlqvist), bjoal@ifm.liu.se (B. Alling), johro@ifm.liu.se (J. Rosén).

phase and its most competing phases is otherwise small enough to be comparable in size to the errors introduced by the finite accuracy of the calculations. As is noted by Dahlqvist et al. [5], for the hypothetical case of Ti_4AlC_3 , including temperature dependent contributions in the calculations might play an essential role in determining whether this phase is stable or not. Another case could be if a particular phase, which is thermodynamically or even dynamically unstable at low temperatures, is stabilized and becomes important as a competing phase at high temperatures.

Calculations of various physical properties of crystals at nonzero temperatures are not nearly as commonly reported in the literature as 0 K calculations due to the higher theoretical complexity and much higher computational demands, stemming mainly from the vibrational contribution to the formation energy. Nevertheless, due to technological advances such calculations are rapidly becoming practically feasible, and in recent years several MAX phase related theoretical studies dealing with temperature dependence have been published. While most of these studies have been dedicated to the characterization of thermodynamic properties such as heat capacity, thermal expansion, and bulk modulus [14–18], some of them have indeed focused on phase stability. However, their scopes have been limited to investigations of the relative stability between α and β MAX phase polymorphs [19–21].

In this work, we extend the 0 K method described in Ref. [5] into a temperature dependent phase stability criterion based on the Gibbs free energy within the so-called harmonic and quasiharmonic approximations (HA and QHA). We investigate the phase stability of the $\text{Ti}_{n+1}\text{AlC}_n$ (for $n=1-3$) MAX phases with respect to competing phases in the Ti–Al–C phase diagram, in a temperature interval from 0 to 2000 K. The HA is used to model all phases, and for a carefully selected subset we also use the QHA for comparison. We show that despite the inclusion of both the electronic and the vibrational contributions to the Gibbs free energies, neither within the HA nor the QHA are the calculated phase stabilities significantly affected as compared to the 0 K case. This result thus provides further evidence that it is mainly the 0 K energy terms that govern phase stability, or, stated differently, that 0 K calculations can indeed be used for confident predictions of the existence of new MAX phases.

2. Methodology

2.1. Thermodynamic phase stability

If the electron–phonon interactions are assumed to be negligible, the Gibbs free energy can be written as

$$G(p, T) = E_0(V) + F_{el}(T, V) + F_{vib}(T, V) + F_c(T) + pV, \quad (1)$$

where $E_0(V)$ is the zero-temperature energy of the crystal, i.e., the energy that the phase would have at 0 K at volume V , and F_{el} , F_{vib} , and F_c are the free electronic, vibrational and configurational energies, respectively. The last term in Eq. (1) has been neglected in the present work, as the ambient pressure was set to 0 GPa.

The free electronic energy F_{el} is given by the difference between the electronic excitation energy, E_{el} , and the entropic contribution, TS_{el} :

$$F_{el}(V, T) = E_{el}(V, T) - TS_{el}(V, T). \quad (2)$$

E_{el} can be found by subtracting the total electronic energy in the excited state with the electronic ground state energy,

$$E_{el}(V, T) = \int_0^\infty n(\varepsilon, V) \varepsilon f(\varepsilon) d\varepsilon - \int_0^{\varepsilon_F} n(\varepsilon, V) \varepsilon d\varepsilon, \quad (3)$$

where $n(\varepsilon, V)$ is the electronic density of states, $f(\varepsilon)$ the Fermi–Dirac distribution, and ε_F the Fermi energy.

The electronic entropy S_{el} can be expressed as

$$S_{el}(V, T) = -k_B \int n(\varepsilon, V) [f(\varepsilon) \ln f(\varepsilon) + (1 - f(\varepsilon)) \ln(1 - f(\varepsilon))] d\varepsilon. \quad (4)$$

The vibrational free energy in Eq. (1) is given by

$$F_{vib}(V, T) = \frac{1}{2} \sum_{q,v} \hbar \omega_{q,v} + k_B T \sum_{q,v} \ln [1 - \exp(-\hbar \omega_{q,v}/k_B T)], \quad (5)$$

where ω is the phonon frequency, q is the wave vector, and v is the band index [14].

Finally, the free configurational energy F_c can be written as

$$F_c(T) = E_c(T) - TS_c(T), \quad (6)$$

for which the mean field approximation (MF) often gives a good estimate, with $E_c = E_{random} - E_0$ and

$$S_c^{MF} = -k_B \sum_i^n y_i \ln y_i, \quad (7)$$

where y_i is the mole fraction of species i . Here E_{random} is the energy of an ideally disordered random alloy that can be modeled with, e.g., the special quasirandom structure (SQS) technique while S_c^{MF} is the corresponding configurational entropy of an ideal solid solution. However, with one single exception the phases included in this work are compositionally ordered, which means that F_c is zero.

In the harmonic approximation, the volume dependence of G (i.e., thermal expansion) is neglected. Using the HA speeds up the calculations significantly, but the results are less accurate as compared to the quasiharmonic approximation, under which the volume dependence of G is included.

Once the Gibbs free energy for all relevant phases have been calculated, a linear optimization procedure is employed in order to determine whether the phase of interest is stable or not with respect to any combination of other competing phases. This procedure works by identifying the set of competing phases for which the sum of the respective Gibbs free energies is minimized. Thus, if the stability of a MAX phase is investigated we get

$$\min G_{cp}(b^M, b^A, b^X) = \sum_i^n x_i G_i, \quad (8)$$

where $b^{M,A,X}$ is the amount of species M , A , and X in the MAX phase, x_i is the amount of compound i , and G_i its free energy. The weighting factors x_i must be chosen so that the total amount of each atomic species in the set of competing phases is the same as in the MAX phase. The constraint put on x_i is such that

$$x_i \geq 0; \quad \sum_i^n x_i b_i^M = b^M, \quad \sum_i^n x_i b_i^A = b^A, \quad \sum_i^n x_i b_i^X = b^X.$$

The condition for thermodynamical stability is that

$$\Delta G_{cp} = G_{MAX} - G_{cp} < 0, \quad (9)$$

i.e., the difference between the Gibbs free energy of the investigated phase and the Gibbs free energy for the identified set of most competing phases is less than zero. Here we note that some authors use the convention that the investigated phase itself is included in the set of competing phases, giving $\Delta G_{cp} = 0$ for all stable phases and a positive “instability energy” for all other cases. However, such a procedure hides useful information of how stable, in terms of the magnitude of negative values of ΔG_{cp} , the investigated phase is with respect to other phases. As all computational approaches involve approximations, a value of ΔG_{cp} that is just below zero might not guarantee successful experimental synthesis while a case where ΔG_{cp} is well below zero with several tenths of meV/atom is more

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