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Erik Johansson,1,a) Annop Ektarawong,2,3 Johanna Rosen,4 and Björn Alling1

AFFILIATIONS
1Theoretical Physics Division, Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden
2Extreme Condition Physics Research Laboratory, Physics of Energy Materials Research Unit, Department of Physics, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
3Thailand Center of Excellence in Physics, Ministry of Higher Education, Science, Research and Innovation, 328 Si Ayutthaya Road, Bangkok 10400, Thailand
4Thin Film Physics Division, Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden

a)Author to whom correspondence should be addressed: erik.johansson@liu.se

ABSTRACT

Metastable ternary ceramic alloys with clustering tendencies are candidates for hard coating applications. In this work, mixing thermodynamics and structural parameters of ceramic $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ alloys are investigated with theoretical first-principles based techniques. Lattice dynamics and temperature dependent phase stability are explored. The effect of lattice vibrations on the total free energy is investigated and found to not significantly affect phase stability at temperatures below 1200 K. The isostructural phase diagram is derived using both cluster expansion-based Monte Carlo simulations and a mean field approach. The phase diagram shows a miscibility gap that does not close at temperatures below the melting or decomposition temperatures of the constituent binaries $\text{TiB}_2$ and $\text{AlB}_2$. The lattice mismatch between phases in the system is small regardless of their composition even at elevated temperatures. These findings support the prospect of age hardening due to coherent isostructural decomposition, such as spinodal decomposition, in coatings of $\text{Ti}_{1-x}\text{Al}_x\text{B}_2$ as diffusion is activated at elevated temperature.

I. INTRODUCTION

Boride compounds make up a class of ceramic materials, of which some exhibit exceptional properties useful for applications intended for tough environments. Transition metal borides, in particular, have high melting point, high hardness, and good thermal and electrical conductivity.1–3 Such attributes could make borides suitable for hard protective coatings on industrial cutting tools, or for instance, as electrically conducting coatings in demanding environments.

Titanium diboride, $\text{TiB}_2$, is a well-studied ceramic compound that is known for its hardness and resistance to wear.1,4 In the study of Mizuno et al., it was shown not only that $\text{TiB}_2$ outperforms its monoboride counterpart, $\text{TiB}$, in terms of hardness but also having the highest total covalent bond density among all considered titanium–Metalloid compounds.4 Vajeeston et al. investigated 12 transition metal diborides and found $\text{TiB}_2$ to be the strongest in terms of cohesive energy, as well as having the lowest value of heat of formation.4 This all relates to the remarkable properties of $\text{TiB}_2$, such as its high hardness, corrosion resistance,4 and high melting point. $\text{TiB}_2$ belongs to the $\text{P6/mmmm}$ hexagonal space group and its crystal structure is visualized in Fig. 1(a).

In a similar ceramic system titanium nitride, $\text{TiN}$, it was found that the materials performance as a protective coating on cutting
tools was improved when alloyed with AlN, forming cubic Ti1-xAlxN.\(^{7–12}\) This ternary compound has been used for cutting tool coatings since the 1980s and is the archetype material for such applications. At elevated temperatures, caused by operation, when diffusion is activated, Ti1-xAlxN undergoes spinodal decomposition, leading to the beneficial age-hardening phenomena.\(^{13–15}\) The promising mechanical and thermal properties of TiB\(_2\) and the technological success of the ternary Ti1-xAlxB2 further motivates research on the far less investigated ternary diboride systems.

Based on a previous theoretical investigation of a group of 45 ternary diboride alloys by Alling et al.,\(^{16}\) Ti1-xAlxB2, in particular, was predicted to show isostructural coherent decomposition, if diffusion could be activated in an alloy grown as a thin film.\(^{14}\) The prediction is based on the fact that Ti1-xAlxB2 exhibits a large positive mixing enthalpy, likely due to the aluminum atoms breaking the d–d electron bonds between titanium atoms, driving the phase separation. Additionally, its isostructural constituent binaries (TiB\(_2\) and AlB\(_2\)) have nearly perfectly matched lattice parameters based on room temperature experimental measurements and 0 K calculations.\(^{14–18}\) This means lattice strain will likely not act as a barrier for spinodal decomposition in this system. A positive mixing enthalpy implies a nonexistence of Ti1-xAlxB2 in equilibrium at 0 K. Nevertheless, initial experimental studies have proven that it can be synthesized as a metastable thin film in conditions where bulk diffusion is not yet activated.\(^{19,20}\) Furthermore, it was shown that age-hardening in Ti1-xAlxB2 indeed can be observed, but it was unclear if isostructural decomposition was involved as boron-rich tissue phases between grains was also observed which could be another explanation to hardening.\(^{19}\) An initial theoretical study of phonons indicated that vibrations may only weakly affect the mixing thermodynamics of Ti1-xAlxB2.\(^{21}\)

TiB\(_2\) is reported to be a line compound up to 3500 ± 20 K, where it congruently melts.\(^{22,23}\) AlB\(_2\) exists as a solid up to 1253 K, after which it decomposes into liquid Al and \(\alpha – \text{AlB}_{12}\).\(^{24}\) As pointed out in Ref. 24, the absolute value may differ between sources. The peritectic temperature at which L + AlB\(_{12}\) \(\rightarrow\) AlB\(_2\) ranges from 1223 to 1623 K depending on the investigator.\(^{25–28}\) Additionally, the melting point of AlB\(_2\) has elsewhere been reported to be 1928 ± 50 K.\(^{29}\) It is essential to investigate how the binaries, and also the alloy at different compositions, behave at these elevated temperatures.

Based on the findings of Norrby et al.,\(^{30}\) Ti0.6Al0.4N cutting tool coatings in operation can reach maximum temperatures of slightly below 1200 K.\(^{31}\) Therefore, the interval 1000–1500 K will be treated as extra important and highlighted throughout this work.

The aim of the present theoretical work is to further investigate fundamental properties and alloy stability of Ti1-xAlxB2 as a function of temperature. We focus in our study on the effects of temperature, through lattice vibrations, thermal expansion, and configurational effects, on the alloying behavior and structural parameters as calculated from first-principles. A pseudobinary isostructural alloy phase diagram is derived in the mean field approximation and presents a miscibility gap. Furthermore, it is first investigated whether or not lattice vibrations affect the general prediction of clustering in the present alloy system, and second, the same for short-range clustering effects. In both cases, the mean field phase diagram is found robust in predicting clustering at the specific temperature range of practical relevance.

**II. METHODS**

The theoretical framework is based upon first-principles density functional theory (DFT), which is used to derive the ground state electronic structure and total energy of the materials. Calculations are performed using the Vienna \textit{Ab initio} Simulation Package (VASP),\(^{31,32}\)\(^{31,32}\) with a plane wave approach using the Projector-Augmented-Wave (PAW) method.\(^{33}\) The generalized gradient approximation (GGA) functional is used for calculating the exchange-correlation energies, as proposed by Perdew, Burke, and Ernzerhof (PBE96).\(^{34}\)

To ensure sufficient convergence, a plane wave energy cut-off of 600 eV is used for all structures. For the binary TiB\(_2\) and AlB\(_2\) unit cells, and all ordered Ti1-xAlxB2 primitive cells, a \(k\)-point mesh of 15 × 15 × 15 is used when sampling the Brillouin zone in the Monkhorst–Pack scheme,\(^{35}\) and a 5 × 5 × 5 mesh is used for the large ternary alloy supercells.

Equilibrium volume is obtained by first calculating the total energy for a set of fixed volumes, where cell shape and all atomic coordinates within the cell are allowed to relax. The data are then fitted to the third-order Birch–Murnaghan equation of state\(^{36,37}\) upon which minimizing the total energy gives the equilibrium volume at zero pressure.

When investigating mixing and clustering thermodynamics of alloys computationally, it is common practice to consider disordered structures, as well as ordered. In this work, the large positive mixing enthalpy of Ti1-xAlxB2 means that such ternary alloys are
not possible to synthesize as solid solutions in equilibrium growth processes. However, as reported by Mockute et al., they can be synthesized under typical physical vapor deposition (PVD) conditions as metastable solid solutions. Analogously there are other metastable alloys in nitride, oxide, and carbide systems.

By the inherent nature of the PVD process, allowing metastable growth, the Ti$_{1-x}$Al$_x$B$_2$ alloys will obtain a disordered metal sublattice. Due to the relatively low deposition temperature, the Ti and Al atoms remain mixed as they are not allowed to cluster by means of diffusion, until the films are annealed. It is of interest to understand the alloy stability and thermal properties from its as-deposited state and how they evolve with temperature. Based on these arguments, it becomes clear that it is a necessity to model the Ti$_{1-x}$Al$_x$B$_2$ alloys by constructing disordered supercells.

In this study, configurational disorder is modeled by the special quasi-random structure (SQS) approach for the Ti$_{1-x}$Al$_x$B$_2$ alloys, obtained with Andrei V. Ruban’s SPCM program, as previously used in the work of Alling et al. This method ensures a good model for disorder on the metal sublattice. It distributes the metal atoms in such a way that, on average, the short-range order parameters vanish on several close-range coordination shells, mimicking the ideal random alloy with the corresponding composition. Due to being limited to a finite size cell in the modeling, a possible weak point of the SQS model is the challenge of generating an atomic configuration that ensures vanishing of long distant neighbor correlation functions and not only the first few neighboring shells.

A sufficiently large 192 atom supercell size, consisting of 4 x 4 x 4 unit cells, was chosen to model the disordered alloys with compositions $x = 0.125, 0.25, 0.375, 0.50, 0.625, 0.75,$ and 0.875. Figure 1(b) shows different views of a disordered Ti$_{0.5}$Al$_{0.5}$B$_2$ alloy used as one of the structures in this study.

PHONOPY is used to derive lattice vibration effects. Finite displacements of 0.01 Å of the atoms from their equilibrium positions are performed using the Parlinski-Li-Kawazoe method. 192 atom supercells are used when calculating the forces from the subsequent energy response, resulting in 1152 total displacements per composition for disordered Ti$_{1-x}$Al$_x$B$_2$ alloys. We calculate vibrational contributions to the free energy in both the harmonic approximation (HA) and the quasi-harmonic approximation (QHA) to evaluate the impact of lattice vibrations on the phase stability and thermal expansion of Ti$_{1-x}$Al$_x$B$_2$ alloys. HA vibrational free energies are calculated for $x = 0, 0.25, 0.50, 0.75,$ and 1. For vibrations within the QHA, they are calculated for $x = 0, 0.75, 1,$ and 1. It is worthy to point out that the force constant matrices are evaluated with atoms at their ideal static lattice positions, and consequently, as a possible shortcoming of this method, there can be inaccuracies at very high temperatures for crystal structures with strong anharmonicity. However, it is considered a sufficient descriptor at the temperatures of interest in this study.

Clustering expansion (CE) formalism, as proposed by Sanchez, Ducastelle, and Gratias and implemented in the Alloy-Theoretic Automated Toolkit (ATAT), is used to derive a model of effective pair, three-site, and four-site interactions between the metal atoms that accurately predicts the total energy of Ti$_{1-x}$Al$_x$B$_2$ alloys, with any arbitrary configuration of Ti and Al atoms, at any fixed atomic composition $x$. For any atomic configuration $\sigma$ on the metal sublattice, the total energy may be decomposed in the following way:

$$E(\sigma) = \sum_a f^a(\phi^a(\sigma)),$$

Here, the correlation functions of symmetrically inequivalent clusters $a$ are given by $\phi^a(\sigma)$, where the superscript $(n)$ specifies that the cluster contains $n$ sites. These are weighted with their corresponding effective cluster interactions (ECIs) $f^a$, which are obtained using structure inversion. The CE model is trained using 1200 structures, containing up to 40 atoms per primitive unit cell, whose energies are derived from DFT calculations. The structures were generated using the MIT Abinitio Phase Stability (MAPS) subroutine implemented in ATAT, based on the algorithm developed by Hart and Forcade. The training is done for the entire composition range from pure TiB$_2$ to pure AlB$_2$. The CE model containing 66 two-site, 116 three-site, and 18 four-site clusters was found satisfactory in describing the energies of both included and excluded structures. It had the lowest cross-validation score (CVS), the assessment of the model accuracy, out of around 3000 total considered CEs, defined as

$$CVS = \left(\frac{1}{N_0} \sum_{i=1}^{N_0} \left(\frac{E_{i,DFT} - E_{i,CE}}{E_{i,CE}}\right)^2\right)^{1/2}.$$

It sums the square error made in predicting the energy for structures not included in the fit. Here, $E_{i,CE}$ is the “leave-one-out” estimated energy based on a least squares fit of the remaining ($N_0 - 1$) structures included in the CE fit, and $E_{i,DFT}$ is the first-principles reference value of structure $i$. The maximum diameter (length of longest pair within the cluster) is 17.4 Å, 10.3 Å, and 6.2 Å for two-, three-, and four-site clusters, respectively. The CE model fits the 1200 input structures with the cross-validation score of 3.26 meV/f.u.

Figure 2 visualizes the predictive power of the CE. It graphs the mixing enthalpy, as fitted (blue crosses) and predicted (red crosses) by the CE, vs calculated DFT values. The straight black line corresponds to a perfect fit or prediction. All structures lie in close proximity to this line, which is also reflected in the low CVS of 3.26 meV/f.u. and CVS of 3.30 meV/f.u., where the latter follows the idea of Eq. (2), but the sum is run over all predicted structures instead.

The CE is used as the Hamiltonian in canonical Monte Carlo (MC) simulations using the Easy Monte Carlo Code (EMC2) subroutine implemented in ATAT. Simulation boxes of $16 \times 16 \times 13$ primitive unit cells (9984 atoms) are used. The simulations are performed at fixed compositions $x$, where $0 \leq x \leq 1$ with $\Delta x = 0.0625$. For each simulation, the Ti$_{1-x}$Al$_x$B$_2$ alloy starts in a disordered configuration at 6000 K, is cooled using simulated annealing, first to 4000 K using $\Delta T = 100$ K, and then down to 0 K using $\Delta T = 25$ K. At each simulated temperature, the system is equilibrated with 20 000 steps and an additional 14 000 steps sample an average energy for evaluating thermodynamic quantities.

Phase stability of Ti$_{1-x}$Al$_x$B$_2$ as a function of temperature is derived from the Gibbs mixing free energy with respect to its constituent binaries TiB$_2$ and AlB$_2$. To model the configurational thermodynamics we use two different approaches for $\Delta G$, mean field (MF) calculations and Connolly-Williams type CE combined with canonical MC simulations.
In the former approach, we express it as
\[
\Delta G^{MF}(x, T) = \Delta H(x, T = 0, p = 0) - T \Delta S^{MF}_{\text{mix}}(x),
\]
where zero pressure \(\Delta H\) is calculated using DFT and configurational entropy of mixing of random alloys, as modeled by the SQS approach, is given per formula unit (1 metal site with mixing, two boron sites without mixing) by
\[
\Delta S^{MF}_{\text{mix}}(x) = -k_B \ln(x) + (1 - x) \ln(1 - x),
\]
assuming the metal sublattice takes on a \(T \to \infty\) property, namely, an ideal random solution.

In the latter approach, Gibbs mixing free energy is derived from canonical MC simulations and is expressed as
\[
\Delta G^{MC}(x, T) = \Delta H^{MC}(x, T, p = 0) - T \Delta S^{MC}(x, T),
\]
where now the mixing enthalpy has a temperature dependence, taken directly from the MC simulations, meanwhile the configurational mixing entropy is obtained through downward thermodynamic integration from infinite temperature
\[
\Delta S^{MC}(x, T) = \Delta S^{MF}_{\text{mix}}(x) + \int_{x_0}^{x} \frac{C_V(x', T)}{T} \, dx'.
\]

The first term is the mean field configurational entropy assuming an ideal solid solution, Eq. (4), and the second term gives the temperature dependent entropy contribution from the canonical MC simulation box. For practical reasons, the integral from infinite temperature has to be truncated. Given the very high initial temperature of the MC simulation boxes, 6000 K is a suitable truncation such that the initial mixing entropy of the disordered state reduces to \(\Delta S^{MC}(x, 6000 \text{ K}) = \Delta S^{MF}_{\text{mix}}(x)\).

III. RESULTS

A. Structural parameters

Presented below in Fig. 3 are the results from structural calculations of Ti\(_{1-x}\)Al\(_x\)B\(_2\). The lattice parameters \(a\) [3(a)] and \(c\) [3(b)] as a function of composition are plotted at different temperatures, ranging from 0 K (black curve) up to 2000 K (red curve) in steps of 500 K with the additional inclusion of room temperature. The 0 K curves are obtained from static DFT without zero-point motion (ZPM) correction to the lattice parameters, which otherwise amounts to an increase of 0.5% or less. The other curves are obtained within the QHA where ZPM is included. In this way, one can trace the thermal expansion of the system.

QHA calculations were only carried out for the alloy with \(x = 0.50\), together with the binaries \(x = 0\) and 1, and a quadratic polynomial fitting has been chosen to give an approximative trend.
throughout the composition range. From the composition dependence of the lattice parameters, one can see that this alloy system is almost lattice matched. That is, as the crystal structure is the same across the compositions, and the lattice spacings are not changing much, any two compositions can form coherent phase boundaries with the lattice planes crossing the boundary without misfit dislocations. We thus predict that the system can preserve interface coherency, and consequently also its hardness, even at elevated temperatures. Figure 3(a) shows how the \( a \) lattice parameter of the \( \text{Ti}_{0.5}\text{Al}_{0.5}\text{B}_2 \) alloy is below those of the constituent binaries \( \text{TiB}_2 \) and \( \text{AlB}_2 \), for all considered temperatures. On the other hand, the \( c \) lattice parameter of the alloy is in between that of the binaries, as can be seen in Fig. 3(b). Although not explicitly shown here, the consequence is that the mixing volume \( \Delta V \) of the \( \text{Ti}_{0.5}\text{Al}_{0.5}\text{B}_2 \) alloy is negative at all considered temperatures.

It is not until elevated temperatures beyond 1000 K that a mismatch between the binaries \( \text{TiB}_2 \) and \( \text{AlB}_2 \) is manifested, most notable in the \( c \)-direction. Looking at the different values at 0 K and 2000 K, for \( \text{TiB}_2 \), the \( c \) lattice parameter goes from 3.24 Å to 3.30 Å, an increase of 1.9%, whereas \( \text{AlB}_2 \) expands from 3.30 Å to 3.50 Å corresponding to an increase of 6.1%. The difference in thermal expansion between the binaries is made apparent by the lattice parameter ratio \( c/a \) and its slope, shown in Fig. 4. Here, the 0 K (black curve) is again without ZPM correction to the lattice parameters.

As the ratio is larger than unity for all compositions and temperatures, it readily shows the anisotropy of the thermal expansion in \( \text{Ti}_{1-x}\text{Al}_x\text{B}_2 \) aluminum rich alloys, in particular. This can be understood from considering the different types of bonds in the crystal structure. The three most dominant types of bonds present throughout the composition range are, in descending strength, M–B ionic bonding, B–B covalent interaction, and M–M metallic bonding (although weakened due to electron donation from both Ti and Al to B).\(^6\),\(^{14,58,59}\) Mutual to both \( c \)- and \( a \)-directions are the M–M and the diagonal M–B bonds. However, the anisotropy comes from the in-plane B–B bonds adding strength only to the \( a \)-direction of the crystal. In the \( c \)-direction, the separation between adjacent boron layers is roughly 1.9 times the nearest-neighbor distance within the boron sublattice, resulting in very weak interlayer B–B interaction, and thus allowing for a larger degree of thermal expansion.

By comparing the results present here with, the theoretical work of Zhang et al.,\(^{128} \) the cell parameters of the binary \( \text{TiB}_2 \) is in good agreement at 1073 K. The same goes for the \( a \) lattice parameter of \( \text{AlB}_2 \), although for \( c \) there is a discrepancy. For close to isoatomic \( \text{Ti}_{1-x}\text{Al}_x\text{B}_2 \) alloys, the \( c \) lattice parameter of Zhang et al. is underestimated. Looking at the \( c \) lattice parameter of \( \text{Ti}_{0.5}\text{Al}_{0.5}\text{B}_2 \), they report a value of \( c = 3.36 \) Å at 1073 K, while our calculations would suggest \( c \approx 3.33 \) Å at a similar temperature. Even more evident is the difference in the \( c/a \)-ratio at the same x = 0.50 composition. Zhang et al. report a value of \( c/a = 1.107 \) at 1073 K, while our calculations estimate 1.096.

To further compare our results with Zhang et al., we present the lattice parameters where experimental values are available. To the best of our knowledge, the literature is lacking experimental measurements of thermal expansion in \( \text{AlB}_2 \). As such, we present the \( a \) and \( c \) lattice parameters for \( \text{TiB}_2 \) alone in Fig. 5. Here, the compilation allows us to compare the lattice parameters from room temperature up to 1073 K. The results in this work, as well as from Zhang et al., are in good agreement with experiments. The temperature trend, however, is slightly more accurately captured by our calculations. This comparison suggests that the methodology used by Zhang et al. is credible, but that the discrepancy in the ternary \( \text{Ti}_{1-x}\text{Al}_x\text{B}_2 \) alloys originates in differences in the configurational modeling. In their work, small ordered structures are used. This implies that one has to be careful when constructing disordered \( \text{Ti}_{1-x}\text{Al}_x\text{B}_2 \) supercells to model configurational disorder in systems like the present one.

In the \( \text{Ti}_{1-x}\text{Al}_x\text{B}_2 \) system, the lattice mismatch is very small, also at elevated temperature, but for other materials systems it might be interesting to study lattice mismatch as a function of...
temperature. It could give information about the miscibility in isostructural alloys, or be used to investigate if there exists some critical temperature for which crack formation may appear, or to understand coherent to semi-coherent interface transitions. Building further on Ref. 14, the lattice mismatch can be quantified by studying the temperature dependent misfit parameter \( \delta \) between two arbitrary phases \( \alpha_A \) and \( \alpha_B \),

\[
\delta_z(T) = \frac{z_{\alpha_A}(T) - z_{\alpha_B}(T)}{\bar{z}_{\alpha_A}(T)}. \tag{7}
\]

In Eq. (7), the subscript \( z \) is either volume or lattice parameter \( a \) or \( c \). As an illustrative example, in Fig. 6, we present the case of \( \alpha_A = \text{TiB}_2 \)-\( \text{Al}_5\text{B}_3 \) and \( \alpha_B = \text{TiB}_2 \). It shows how the equiatomic \( \text{TiB}_2\)-\( \text{Al}_5\text{B}_3 \) alloy has a smaller \( a \) lattice parameter (\(<1\%) compared to the binary \( \text{TiB}_2 \), at all temperatures within the range 0 to 2000 K. On the other hand, the spacing in the \( c \)-direction is larger than that of \( \text{TiB}_2 \). The overall volume mismatch is only around 1% in the temperature range of interest for cutting tool operation, with its largest contribution coming from the mismatch in the \( c \)-direction. Even so, by studying Fig. 6, one can predict that the process of decomposing a \( \text{Ti}_{1-x}\text{Al}_x\text{B}_2 \) alloy can lead to a non-zero but small compressive stress in the \( a \)-direction and tensile stress in the \( c \)-direction in Ti-rich regions.

B. Mean field thermodynamics and the effect of lattice vibrations

Figure 7 shows the composition and temperature dependence of the Gibbs mixing free energy of \( \text{Ti}_{1-x}\text{Al}_x\text{B}_2 \) in the mean field approximation. It can be explained as follows:

Solid lines represent the static lattice approximation, which only includes configurational contributions to the free energy. It is the DFT ground state energy of the SQS models for a random alloy where temperature is introduced together with configurational entropy, i.e., \( \Delta G_{\text{mix}}^{\text{MF}} \) [Eqs. (3) and (4)]. Black circles represent the mixing energies of all considered disordered SQSs and can be directly compared with the gray squares from the small ordered structures from Zhang et al. Dashed lines represent the HA, for which harmonic phonons are added to the static lattice free energy, resulting in \( \Delta G_{\text{QHA}}^{\text{MF}} \). Finally, the dotted lines represent the QHA, for which the harmonic phonons have quasi-harmonic corrections added to them in order to incorporate effects of ZPM and thermal expansion to the total free energy, resulting in \( \Delta G_{\text{QHA}}^{\text{MF}} \).

For clarity, the data points used for each lattice approximation have been marked with symbols in Fig. 7. Again, the black circles mark the SQSs used for \( \Delta H \) in the static lattice approximations, for which calculations have been performed for the compositions \( x = 0, 0.125, 0.25, 0.375, 0.50, 0.625, 0.75, 0.875, \) and 1.0. The other two levels of approximations are marked only for the case \( T = 2000 \) K. For HA, crosses are used to mark the data points for the compositions \( x = 0, 0.25, 0.50, 0.75, \) and 1.0. Stars are used for QHA, for which calculations have been performed for the compositions \( x = 0, 0.50, \) and 1.0.

For the static lattice approximation and HA, the data points are interpolated using fourth order polynomials to derive both the continuous configurational and vibrational free energy curves. For the quasi-harmonic correction term, second order polynomials are used to interpolate over the whole composition range.

The analytical form of the three different lattice approximations are given below,

\[
\Delta G_{\text{static}}^{\text{MF}}(x, T) = \Delta H_{\text{static}}(x, T = 0, p = 0) - T\Delta S_{\text{mix}}^{\text{MF}}(x),
\]

\[
\Delta G_{\text{QHA}}^{\text{MF}}(x, T) = \Delta G_{\text{static}}^{\text{MF}}(x, T) + \Delta F_{\text{QHA}}^{\text{HF}}(x, T),
\]

\[
\Delta G_{\text{QHA}}^{\text{MF}}(x, T) = \Delta G_{\text{static}}^{\text{MF}}(x, T) + \Delta F_{\text{QHA}}^{\text{HF}}(x, T) + \Delta F(x, T).
\]

Here, \( \Delta F(x, T) \) is the quasi-harmonic correction term that we define as

\[
\Delta F(x, T) = \delta F(x, T) - (1 - x) \cdot \delta F(\text{TiB}_2) - x \cdot \delta F(\text{AlB}_2),
\]
where

$$\delta F(x, T) = F^{\text{QHA}}(x, T) - F^{\text{HA}}(x, T). \quad (10)$$

From the temperature dependence shown in Fig. 7, one can see in the range 0–1000 K that the three lattice approximations practically lie on the top of each other. Hence, it is not until temperatures beyond 1000 K that the vibrational free energies contribute significantly, compared to the configurational part, to the total Gibbs mixing free energy. It is, therefore, made apparent that it is important to include the effect of lattice vibrations when investigating phase stability of Ti$_{1-x}$Al$_x$B$_2$ mainly at elevated temperature.

In particular, at 1500 K, there is a clear onset of a difference between harmonic and quasi-harmonic lattice approximations. Then, at 2000 K, the red dotted QHA curve is considerably higher than both the static and HA curves. In fact, it lies on top of the QHA curve of the case $T = 1500$ K shown by the orange dotted curve. This is explained by a balancing between the configurational entropy and the mixing vibrational free energy within QHA, preventing the curve from shifting downward at this high temperature. The black 0 K curve shows the mixing enthalpy of Ti$_{1-x}$Al$_x$B$_2$, which has a maximum value of 0.125 eV/f.u. at the composition $x = 0.55$. Zhang et al. reports a much higher maximum value of 0.196 eV/f.u. for their small ordered structures compared to our disordered supercells.

Figure 8 shows the theoretical mean field phase diagram constructed by applying the common tangent method on the total Gibbs mixing free energy mean field curves. The binodal lines are shown in solid, indicating the boundary between the region where active, spinodal decomposition occurs throughout the material. There is no nucleation barrier and, as soon as atomic diffusion is significant, of the SQSs from Sec. III B, superimposed on 1500 ordered Ti$_{1-x}$Al$_x$B$_2$ structures generated with the MAPS subroutine of ATAT, whose energies were derived from DFT calculations. The blue colored boxes correspond to the 1200 randomly included structures used to train the CE, and in red are the 300 ones left out from the fit. All calculated ordered structures also show positive $\Delta H$ indicating the clustering tendencies at zero Kelvin. The CE used to describe both included and excluded structures contains 66 pair, 116 triplet, and 18 quadruplet clusters.

C. Configurational thermodynamics beyond the mean field

Figure 9 shows the zero Kelvin mixing enthalpies, at zero pressure, of the SQSs from Sec. III B, superimposed on 1500 ordered Ti$_{1-x}$Al$_x$B$_2$ structures generated with the MAPS subroutine of ATAT, whose energies were derived from DFT calculations. The blue colored boxes correspond to the 1200 randomly included structures used to train the CE, and in red are the 300 ones left out from the fit. All calculated ordered structures also show positive $\Delta H$ indicating the clustering tendencies at zero Kelvin. The CE used to describe both included and excluded structures contains 66 pair, 116 triplet, and 18 quadruplet clusters.
and second-nearest neighbor distances as longest pair. The ECIs of the quadruplets might be hard to distinguish on this scale, but they are all non-zero. The magnitude of the ECIs decay to zero as a function of both distance and number of sites it contains, i.e., neither adding more pairs, triplets or quadruplets, nor introducing new five- and six-site ECIs will considerably improve the CE.

This CE is used as a Hamiltonian for canonical MC simulations using the EMC2 subroutine of ATAT to derive the free energy as a function of temperature and concentration. Figure 11 shows the zero pressure Gibbs mixing free energy, Eq. (5), as a function of the Al concentration for select temperatures, as derived from the CE+MC approach, as well as for SQS+MF. The simulations were carried out at fixed compositions between 0 and 1 in steps of 0.0625, and the composition range was then made continuous with spline interpolation. In the very high temperature limit (6000 K, the highest simulated temperature), the mixing enthalpy $\Delta H$ of the MC simulation box in its initial disordered configuration overlaps with the SQS 0 K DFT results (not presented here). As Fig. 11 shows, even as the configurational entropy contribution is included, there is excellent agreement between the two approaches as temperature is lowered from the red curve at 6000 K to the olive green curve at 3000 K. This point, simulation temperature is still far above the critical temperature for transitioning from mixing to clustering inside each canonical MC simulation box for all compositions. Consequently, the temperature independent MF entropy of the SQSs proves valid here.

As temperature is lowered below the heat capacity peak of each said simulation boxes in the Monte Carlo run, the clustering introduces boundaries between Ti-rich and Al-rich phases whose surface energies depend on the simulation box size. Moreover, to continue deriving free energies in this temperature region by thermodynamic

![Figure 9](image-url)  
**FIG. 9.** Mixing enthalpies at zero pressure, $\Delta H$. Black circles show the SQS values previously used for interpolation in Fig. 7. Blue squares are structures included in the CE, while the red are left out and used to test the predictive power of the fit. The gray curve shows zero pressure $\Delta H$ from Zhang et al.\textsuperscript{55}

![Figure 10](image-url)  
**FIG. 10.** Effective cluster interactions as a function of length of the longest pair within the cluster. In brackets are the number of $n$-site clusters.

![Figure 11](image-url)  
**FIG. 11.** Gibbs mixing free energy, $\Delta G$, for select temperatures: (a) 0 K (black) to 6000 K (red) in steps of 1000 K, capturing the whole temperature range simulated in MC. Solid lines are those of CE+MC, and dashed are from the SQS+MF approach. (b) 0 K to 2300 K in steps of 50 K, only for CE+MC, to highlight what happens in the mixing region. The red dots mark the edges of miscibility for $T = 1000$ K, 2000 K, and 2300 K. No vibrations included.
integration across the heat capacity peak can be unfavorable depending on the nature of the phase transition. For first order phase transitions, integrating across a non-differentiable energy is inaccurate in principle, and for second order, integrating over a high magnitude, or diverging, peak in heat capacity can make the free energy unreliable in practice.

Therefore, we halt thermodynamic integration in any given canonical MC simulation box, at a certain fixed composition, as its transition temperature is approached from above. From our results, below 2300 K is when these phenomena start coming into play. The free energy curves are drawn in the mixing region where single phase Ti$_{1-x}$Al$_x$B$_2$ solid solutions are stable. Thus, the CE+MC derived 2000 K (blue) free energy curve has been partially cut, along with 1000 K (purple) and 0 K (black). In order to visualize the introduction of clustering across all compositions in greater detail, Fig. 11(b) presents the CE+MC derived free energy curves from 2300 K down to 0 K in steps of 50 K. Temperatures 2000 K, 1000 K, and 0 K have been given the same colors as in Fig. 11(a). Here, it is evident that the unstable region quickly opens up across the compositional range.

However, our main interest is still phase stability of Ti$_{1-x}$Al$_x$B$_2$ alloys, and thus we apply thermodynamic stability condition on the CE+MC derived free energies. As these curves are more “flat” in comparison to the mean field ones, matching derivatives through common tangent construction is sensitive to small fluctuations and statistical noise from the MC simulations. Instead, linear optimization is found more robust, where for each temperature, it is investigated if there exists a compositional range where the continuous $\Delta G$ can be decreased by decomposing the single phase Ti$_{1-x}$Al$_x$B$_2$ solid solution into a linear combination of two other compositions, i.e., a miscibility gap. The red points in Fig. 11(b) correspond to such linear combination of new compositions that mark the end points of the miscibility gap. Repeating this procedure for all temperatures derives the phase diagram, as presented in Fig. 12.

The red curve shows the phase diagram as derived from the chosen CE. It is cut when crossing the order-disorder temperature from above, for any fixed composition, to avoid thermodynamic integration across $C_V$ peaks. It predicts that the miscibility gap closes at 2420 K, in contrast to the mean field approach in black (identical to the black curve in Fig. 9) that closes at 3120 K. Thus, the critical temperature for closing the miscibility gap is reduced by 22.4%, which is in line with what can be expected with respect to a mean-field approximation of the Ising-like alloy problem. The maximum temperature of the miscibility gap is shifted upward more Ti-rich compositions in the CE+MC method as compared to the MF approximation. In fact, the maximum is found around $x = 0.4$ in CE+MC as compared to $x = 0.7$ in MF. One reason for this difference is that the top of the miscibility gap in a MC simulation of any Ising-like model is very flat and thus the exact composition of the maxima is sensitive to the details of the cluster expansion. In our case, we tested by performing a CE with only 2-site and 3-site clusters included and obtained a CVS of 4.79 meV/f.u. This expansion obtained the top of the miscibility at $x = 0.8$ at T = 2620 K. This illustrates the challenge of quantitatively converge predicted phase diagrams using our type of standard CE procedure, but it does not influence our ability to draw qualitative conclusions: The Ti$_{1-x}$Al$_x$B$_2$ system is predicted to be subject to isostructural phase separation at the practically relevant temperatures, 1000–1500 K across almost the entire composition range, even if short range clustering effects are taken into account, as is done in the CE+MC simulations.

IV. DISCUSSION

Based on previous calculations of Alling et al., and those presented in this study, it is apparent that a solid solution of Ti$_{1-x}$Al$_x$B$_2$ cannot exist in equilibrium bulk form. Nevertheless in the previous experimental study by Mockute et al., the possibility of synthesizing these ternary alloys as metastable thin films was realized. In their work, age-hardening in Ti$_{1-x}$Al$_x$B$_2$ was observed, although it was never resolved if it could be attributed to isostructural spinodal decomposition as theory predicts.

In this study, the focus has been to further reveal fundamental properties of Ti$_{1-x}$Al$_x$B$_2$ alloys and their phase stability. For the first time, lattice dynamics have been extensively investigated for this system. It has revealed that the lattice parameters remain almost matched throughout the composition range even at elevated temperature. Consequently, the overall volume misfit is minute, meaning that lattice strain is unlikely to act as an activation barrier for isostructural spinodal decomposition. The isostructural mean field phase diagram of Ti$_{1-x}$Al$_x$B$_2$ has been derived, showing a wide miscibility gap that in the temperature range of interest is not greatly affected by lattice vibrations in the HA and QHA. We acknowledge that AlB$_2$ as a solid phase beyond 2000 K is unstable, but for academic interest and completeness we assume that AlB$_2$ remains stable all the way and go beyond the melting point in order to close the miscibility gap in the phase diagram.

As the mean field phase diagram predicts, an experimentally synthesized metastable Ti$_{1-x}$Al$_x$B$_2$ thin film will decompose into two phases with widely different compositions, one rich in Ti and the other rich in Al. This clustering on the metal sublattice occurs only at elevated temperature when atomic diffusion is activated.
instance, suppose a cutting tool coated with metastable Ti$_{0.5}$Al$_{0.5}$B$_2$ is operating at 1250 K and diffusion is activated within the coating. Then, the phase diagram in Fig. 12 predicts that the films will decompose into domains of Ti$_{5.95}$Al$_{0.05}$B$_2$ and Ti$_{8.01}$Al$_{0.99}$B$_2$ compositions. Our theory predicts spinodal decomposition, which for the related ceramic alloy Ti$_{1-x}$AlN leads to a more distinct age-hardening effect, as compared to nucleation and growth type decomposition.

Furthermore, the mean field phase diagram is derived in the absence of strain fields. If the lattice misfit is to be taken into account, the effective shifts of the free energy curves would result in a phase diagram with a tightened coherent miscibility gap as well as a coherent spinodal within the chemical spinodal. Although the difference ought to be small in this system due to the small lattice misfit, and the presence of strain fields is beyond the scope of this study. Another factor of uncertainty is that our theoretical model assumes fully stoichiometric boron and metal sublattices, while experimental samples might include some degree of vacancies. Off-stoichiometry has been noted to be of importance for phase stability in borides, and influence metal-site clustering in Ti–Al–N. Moreover, decomposition in experiments might not be complete due to other reasons than strain or stress. For instance, if atomic diffusion is limited, heat treatment may not have been long enough for equilibrium to be reached.

The ECIs used for capturing short-range clustering effects with the CE+MC approach, are in this study temperature and concentration independent. As the (Q)HA study has revealed, the inclusion of vibrations is not important at reasonable temperatures, and as such the usage of temperature independent ECIs are for this system justified. There is, however, a quantitative uncertainty in the CE+MC approach, originating from the exact details of choosing CE basis functions, which as already mentioned can affect the temperature and composition of phase diagram miscibility peaks. Therefore, it could be of future interest to study phase stability using concentration dependent ECIs. Nevertheless, it is important to point out that qualitative conclusions regarding phase stability based on concentration independent ECIs are still credible. For temperatures relevant for cutting tool applications, the MF approach proves to work reasonably well in predicting the extent of the miscibility gap, as SQS+MF and CE+MC both predict virtually the same miscibility boundaries; two dilute alloy compositions.

As was visualized in Fig. 11(b), short-range clustering effects come into effect below 2300 K. In order to further concretize this, the correlation functions for the first, second, and third NN clusters as function of temperature is presented in Fig. 13 for equiaxotropic Ti$_{0.5}$Al$_{0.5}$B$_2$, using two vastly different MC simulation boxes. The solid lines are those of a 31 × 31 × 25 supercell, plotted all the way down to 0 K. On the other hand, the dashed lines correspond to the 16 × 16 × 13 supercell used to derive the results in Sec. III C, whose correlation functions have been plotted down to the temperature for which the CE+MC miscibility gap closes, i.e., 2420 K. Above this temperature, the pair correlation functions of the three smallest shells, for both depicted MC simulation box sizes, overlap perfectly. Therefore, varying the MC simulation box size would only marginally affect the phase diagram, as it is dictated by the correlation functions at temperatures above the miscibility limit.

The choice of MC simulation box size only affects the total energy at lower temperatures with initiated clustering, as surface effects between Ti and Al boundaries are sensitive to the surface-volume ratio of the whole MC simulation box. However, as thermodynamic integration is halted at the onset of clustering, the choice of the smaller 16 × 16 × 13 supercell remains robust. Regardless of box size, the fact that the initial configuration of atoms at the 6000 K starting point in the MC simulation box is disordered, is reflected by the vanishing correlation functions of all depicted shells. By going down in temperature, the correlation functions start to increase prior to the critical temperature being reached. This shows how short-range clustering in fact slowly manifests in the system, before the distinct order-disorder transition, otherwise marked by the peak in heat capacity. The slope of each curve reaches its maximum near 2300 K, and then the correlation functions tend close toward 1.0 as 0 K is approached, but not quite due to finite size limitations. Note, they all would have converged and become identical to 1.0 in the limit of infinite MC simulation box size. Nevertheless, the results shown in Fig. 13 reinforces the onset of short-range clustering within the canonical MC simulation box at 2300 K. The exact onset temperature would of course slightly vary for other compositions, but $x = 0.50$ was considered to be the most pedagogical and illustrative example.

V. CONCLUSION

In this work, we have derived a theoretical isostructural mean field phase diagram for Ti$_{1-x}$Al$_x$B$_2$, showing a wide miscibility gap that does not close at temperatures below the melting temperatures of its constituent binaries TiB$_2$ and AlB$_2$. We have shown that phonon vibrational free energies within harmonic and QHA affect the phase diagram very little at application-relevant temperatures.

From vibrational studies within the QHA, we have calculated how the lattice parameters expand when temperature is increased. Throughout the composition range, the lattice remains almost matched even at elevated temperature. By studying the lattice misfit between Ti$_{0.5}$Al$_{0.5}$B$_2$ and TiB$_2$ as function of temperature, it has
been shown that it can be expected to be less than 1% in the \( a \)-direction and less than 3% in the \( c \)-direction at all studied temperatures. It is therefore unlikely that coherency strain energies will hinder \( \text{Ti}_{1-x}\text{Al}_x\text{B}_2 \) alloys from undergoing isostuctural spinodal decomposition.

Furthermore, by explicitly letting Ti and Al atoms change their configuration on the metal sublattice, using the CE+MC approach, short-range clustering effects were captured and found to come into effect below 2300 K. Based on the best considered CE candidate containing up to 4-site clusters, short-range clustering is found to lower the closing of the miscibility gap by 22.4%, as compared to the MF estimate. At temperatures relevant to cutting tool applications, especially 1000–1200 K, both SQS+MF and CE+MC predict similar phase stability of \( \text{Ti}_{1-x}\text{Al}_x\text{B}_2 \) alloys.

The findings in this work further support and extend upon the initial prediction of Alling et al.\(^{14}\) that \( \text{Ti}_{1-x}\text{Al}_x\text{B}_2 \) should exhibit the same type of isostuctural phase separation as in the archetype \( \text{Ti}_{1-x}\text{Al}_x\text{N}_y \), giving rise to age-hardening. Ultimately, the structural and thermodynamic properties of metastable \( \text{Ti}_{1-x}\text{Al}_x\text{B}_2 \) alloys make them potential candidates for thin film applications where age-hardening is desirable.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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