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Relative stability of bcc structures in ternary alloys with $Ti_{50}Al_{25}Mo_{25}$ composition

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In reviewing the literature that concerns the CsCl-type intermetallic compound Ti_2AlMo (B2), the question arises if this compound is preferably formed with respect to the high-temperature bcc completely disordered structure (A2). Our present work takes an *ab initio* approach to this subject. The first-principles linear-muffin-tin-orbital method was used to calculate the total energy of a series of bcc structures in the ternary system Ti-Al-Mo. Second, a cluster expansion in the tetrahedron approximation was calculated for each formation energy. Finally, a Connolly-Williams-like inversion scheme was used to obtain the formation energy of both the A2 phase and the partially ordered structure B2. From the calculations, the B2 formation energy came out to be aprox 10 mRy/atom lower than the A2 energy, suggesting a relative greater stability. The relative stability of other possible structures with the same global composition $Ti_{50}Al_{25}Mo_{25}$ is discussed.

I. INTRODUCTION

To improve the performances of aircraft engines and of some nuclear devices, it is necessary to increase the service temperature of hot components working in high-temperature environments, typically from 1100 to 1900 K. In this context, research and development activities are underway on a wide range of intermetallics-based alloys systems. However, ordered intermetallics in monolithic form have limited the prospects of providing the required balance of mechanical properties because they suffer from inadequate ductility and extremely low fracture toughness at low temperature. Numerous attempts have therefore been made to overcome these limitations both through grain-size refinement or grain-boundary suppression and by micro or macroalloying.[1]

Following a different approach inspired by the outstanding mechanical performance of nickel-base superalloys which results from an excellent phase compatibility between their constituent γ and γ' phases, Naka and Khan[2] have attempted to create a γ-γ' type microstructure in a refractory metal-base alloy. Since refractory metals have a bcc (A2) lattice, a suitable second phase might be of the ordered-cubic-centered B2 type. However, among about 300 binary B2 compounds listed in the literature, no binary B2 compound can be formed with refractory metals. Therefore, they extended the proposal to ternary and quaternary systems. A survey of the literature indicates that there are some ternary B2 compounds of the Ti_2AlX type, where X is molybdenum, iron, chromium, or niobium. Their lattice parameters are not well known but seem to be of an order that might lead to a high compatibility with the A2 matrix.

The field of existence of these Ti_2AlX type compounds in terms of both concentration and temperature is not well known, still demanding research efforts. For example, Rubin and Finel,[3] M. Asta *et al.*,[4] and also Chaumat *et al.*,[5,6] recently have investigated, through the cluster variation method (CVM) and experimental studies, the B2/A2 phase boundary, the ordering temperature, and the probabilities of sites around the composition $Ti_{50}Al_{25}Nb_{25}$ (at. %) in the Ti-Al-Nb system.

In the ternary Ti-Al-Mo, a B2 phase was first reported by Böhm and Löhberg[7] although site occupancy was not mentioned. This phase was associated with an order-disorder $B2 \rightarrow A2$ second-order phase transition. Later, Hamajima, Luejtering, and Weissmann[8] showed that for a $Ti_{77}Al_{16}Mo_7$ (at. %) alloy a structure with B2 particles, having a diameter of approximately 160 Å, surrounded by an A2 matrix was produced upon quenching from 1273 K. However, Banerjee, Krishnan, and Vasu,[9] working on alloys around the composition $Ti_{48}Al_{47}Mo_5$ and annealing treatments up to temperature of 1573 K followed by quenching in water, did not find the B2 phase although x-ray and electron diffraction characterization were employed. A review of these publications has been presented by Budberg and Schmid-Fetzer;[10] there the presence of a miscibility gap was suggested between the B2 and A2 phases, giving rise to a two-phase field $A2+B2$ below 1273 K. Concerning the crystallography of this B2 compound, Sikora, Hug, and Flanck[11] arrived at the conclusion through extended x-ray-absorption fine structure (EXAFS) studies that Ti atoms fill one sublattice in the bcc cell while Al and Mo atoms occupy randomly the other. Figure 1 shows the A2 and B2 structures.

The aim of this paper is to calculate the ternary cluster expansion of the formation energy of A2 and B2 phases as a first step in the calculation of the Ti-Al-Mo phase diagram by the CVM. We use a first-principles method to calculate the total energy for the ordered structures and a structure inversion method (SIM) based on an idea of Connolly-Williams[12] for the disordered ones. A comparison between the formation energy of both phases in the same $Ti_{50}Al_{25}Mo_{25}$ composition is shown as an application of the cluster expansion.

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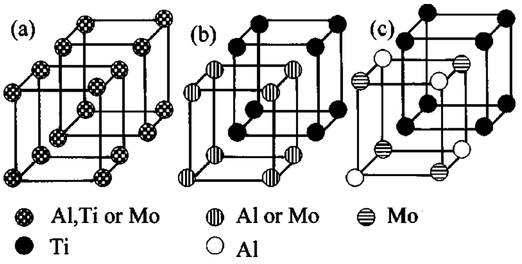

FIG. 1. (a) High-temperature A2 phase, completely disordered bcc, (b) B2 phase (CsCl type), and (c) completely ordered $L2_1$ structure.

II. TOTAL AND FORMATION ENERGY CALCULATIONS

A. Ordered compounds

Total energy calculations were performed for all pure constituents in the bcc structure, binary structures B2, B32, and DO_3 and ternary structures $L2_1$ and $F\bar{4}3m$ of the ternary system Ti-Al-Mo. The tight-binding linear-muffin-tin-orbital first-principles method was used in the atomic-sphere approximation (TB-LMTO-ASA), including scalar relativistic corrections.[13] In order to choose a *k*-point mesh we calculated total energy for $8^3, 10^3, 12^3, 14^3$, and 16^3 *k* points, setting the convergence in total energy to within 0.06 mRy/atom in all cases. The precision of the total energy with respect to *k*-point sampling was within 0.03 mRy/atom for the 8^3 *k*-point mesh (152 irreducible *k* points in the Brillouin zone). It being acceptable, we preferred this size to gain in machine time. Relaxation curves of energy vs lattice parameter were obtained varying the volume while keeping constant the cell shape. The curves were successfully fitted to cubic polynomials (Fig. 2). The equilibrium energy for each compound was taken as the minimum in these curves (Table I).

The formation energy is defined as the total energy of the structure at its equilibrium volume minus the concentration-weighted average of the pure elements total energies at their equilibrium volumes:[14]

$$\Delta E_F = E_T - c_A E_A - c_B E_B - c_C E_C .$$

It should be observed that even though some of the compounds show a positive formation energy, this fact does not imply instability by itself. The ordering or phase separation tendency should be evaluated taking into account the formation energy of the compound together with the formation energies of all possible phases which could be present at that composition. In Ref. 4, Asta *et al.* have presented the ground-state phase diagram for Ti-Al-Nb resulting from such considerations. In particular, the Ti-Al ground-state binary structures resulting from our computations (Ti bcc, Al bcc, Ti_3AlDO_3, and TiAl B2) are consistent with the phase diagram at $T = 0$ K shown by Asta *et al.*[4]

B. Calculation of cluster interactions

In order to compute the formation energy of the disordered states for the Ti_2AlMo compound, we have to consider

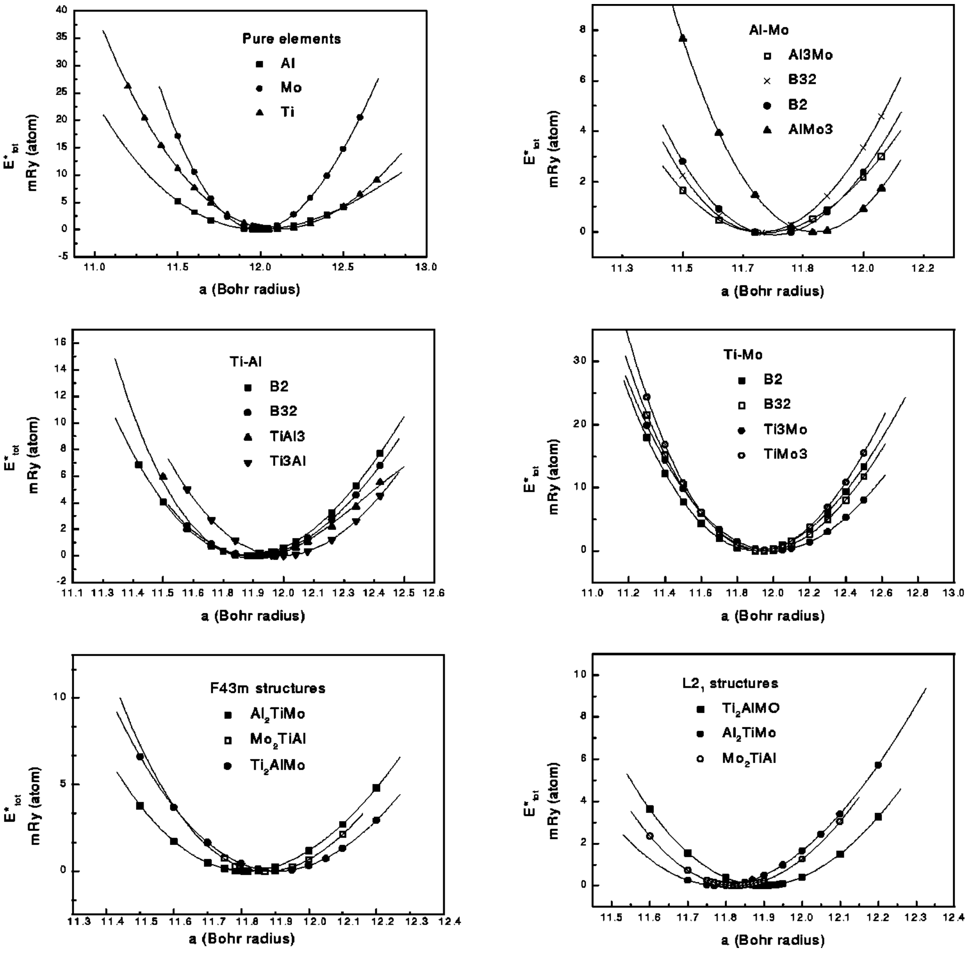

FIG. 2. Total energies of ordered compounds vs crystalline parameters. E_T^* stands for $E_T - E_{T\min}$.

TABLE I. TB-LMTO-ASA results for bcc ordered structures total energies.

Structure	a (Böhr radius)	E_T (mRy/atom)	ΔE_F (mRy/atom)
Al bcc	12	-484297.638	0
Ti bcc	12.1	-1704760.32	0
Mo bcc	12	-8091097.76	0
TiAl B2	11.85	-1094559.84	-30.87
TiMo B2	11.9	-4897938.46	-9.42
AlMo B2	11.8	-4287699.94	-2.25
TiAl B32	11.88	-1094541.14	-12.16
TiMo B32	11.95	-4897941.34	-12.31
AlMo B32	11.72	-4287720.49	-22.79
Ti_3Al DO_3	11.99	-1399663.08	-18.43
Al_3Ti DO_3	11.9	-789418.938	-5.63
Ti_3Mo DO_3	11.93	-6494526.48	-13.08
Mo_3Ti DO_3	12	-3301353.18	-8.5
Al_3Mo DO_3	11.7	-2385995.21	2.46
Mo_3Al DO_3	11.86	-6189402.95	-5.22
Ti_2AlMo $L2_1$	11.9	-2996260.09	**-31.09**
$TiAl_2Mo$ $L2_1$	11.77	-2691134.65	-21.31
$TiAlMo_2L2_1$	11.83	-4592820.98	-7.61
Ti_2AlMo $F\bar{4}3m$	11.9	-2996245.32	-16.31
$TiAl_2Mo$ $F\bar{4}3m$	11.81	-2691134.54	-21.21
$TiAlMo_2F\bar{4}3m$	11.87	-4592831.99	-18.62
Ti_2AlMo A2	-	-	**-15.25**
Ti_2AlMo B2	-	-	**-26.4**

it as a cluster expansion. In this method, the formation energy is written as

$$\Delta E_F = \sum_i \nu_i x_i , \tag{1}$$

where ν_i are cluster interaction parameters depending on the lattice type (i.e., fcc, bcc, etc.) for an alloy system and x_i are cluster-occupation-dependent correlation functions. The sum is extended over all possible clusters, although in practice it is usually limited to a certain approximation. In this work, we considered all clusters within the tetrahedron approximation (Fig. 3).

Since the energies ΔE_F for a set of ordered structures can be obtained, for example, through a first-principles method, and x_i can be calculated for each of them, we can have a set of linear equations on the parameters ν_i. Therefore, the ν_i can be obtained by inversion. Now, the energy for another structure with the same lattice type can be calculated writing the proper functions x_i for it and considering the same calculated ν_i. This is the SIM based on the idea of Connolly and Williams.

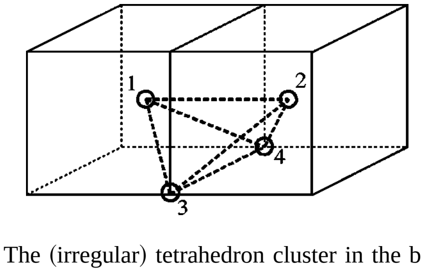

FIG. 3. The (irregular) tetrahedron cluster in the bcc cell. Four different sites (labeled n, m, o, and p) are considered to describe the cell with twice the lattice constant.

For the computation of the x_i functions we followed the formalism described by Inden and Pitsch.[15] The first step is to define a site operator σ_n which takes the values $+1$, 0 or -1 if site n is occupied by a Ti, Al, or Mo atom, respectively. The domain of the point variable σ_n has three values. Therefore, to fully specify a function of σ_n, it is necessary to choose three-point functions, products of which form the corresponding cluster functions. A set of three-point functions (from which an orthonormal basis is constructed) is the first three polynomials of $\sigma_n : \{1,\sigma,\sigma^2\}$. Cluster functions formed from products of the set $\{1,\sigma,\sigma^2\}$, are proposed as a possible basis of functions for describing the ternary alloy problem.[16] The averages of these products over all equivalent clusters in the crystal are called the correlation functions.

Taking the tetrahedron as the largest cluster, for a ternary bcc alloy they take the form

$$x_i = \langle \sigma_n^{i_1-1} \sigma_m^{i_2-1} \sigma_o^{i_3-1} \sigma_p^{i_4-1} \rangle , \tag{2}$$

where n, m, o, and p denote the site of the tetrahedron and $i_1, i_2, i_3, i_4 = 1$, 2, or 3. The distinction among the four types of sites is necessary to the description of the occupancy in the superstructures B2, B32, DO_3, $L2_1$, and $F\bar{4}3m$.

The right-hand side of Eq. (2) can be computed from the probabilities of finding atoms k_1, k_2, k_3, and k_4 on sites n, m, o, and p as

$$\langle \sigma_n^{i_1-1} \sigma_m^{i_2-1} \sigma_o^{i_3-1} \sigma_p^{i_4-1} \rangle = \sum_{k_1=1}^{3} \sum_{k_2=1}^{3} \sum_{k_3=1}^{3} \sum_{k_4=1}^{3} M_{i_1k_1} M_{i_2k_2} M_{i_3k_3} M_{i_4k_4} \rho_{n\,m\,o\,p}^{k_1k_2k_3k_4} , \tag{3}$$

where $k_1, k_2, k_3, k_4 = 1$, 2 or 3 for atoms Ti, Al, or Mo, respectively. The matrix M in this equation contains information from the site occupation operator and has the form

$$M = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 0 & -1 \\ 1 & 0 & 1 \end{pmatrix} .$$

The complete set of correlation functions adds up to 80 ($K^r - 1$, with $K = 3$, the number of elements in the alloy and $r = 4$ the largest cluster). This would lead to an expansion of the energy in 80 terms. Although as the interaction parameters ν_i exhibit cluster symmeties of atomic sites and cluster decoration symmetries by the point functions, only 21 of them remain distinct. In consequence correlation functions can be grouped leading to an expansion in 21 terms (see the Appendix).

To apply the inversion method, we calculated the values of the correlation functions for the 21 ordered structures mentioned above and obtained by inversion the values for the interaction parameters ν_i of Eq. (1). These are shown in Tables II and III.

TABLE II. Values of the correlation functions for the 21 structure set.

Compound	x_0	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8	x_9	x_{10}	x_{11}	x_{12}	x_{13}	x_{14}	x_{15}	x_{16}	x_{17}	x_{18}	x_{19}	x_{20}
Al	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ti	1	4	4	2	4	4	8	2	4	4	8	4	4	8	4	1	4	2	4	4	1
Mo	1	-4	4	2	4	-4	-8	2	4	-4	8	4	-4	-8	4	1	-4	2	4	-4	1
TiAl B2	1	2	2	1	0	2	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
TiMo B2	1	0	4	2	-4	0	0	2	4	0	-8	4	0	0	4	1	0	2	-4	0	1
AlMo B2	1	-2	2	1	0	-2	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
TiAl B32	1	2	2	0	1	0	2	0	1	0	0	0	0	0	0	0	0	0	0	0	0
TiMo B32	1	0	4	-2	0	0	0	2	4	0	0	-4	0	0	4	1	0	-2	0	0	1
AlMo B32	1	-2	2	0	1	0	-2	0	1	0	0	0	0	0	0	0	0	0	0	0	0
Ti$_3$Al DO$_3$	1	3	3	1	2	2	4	1	2	1	2	1	1	2	1	0	0	0	0	0	0
Al$_3$Ti DO$_3$	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
TiMo$_3$DO$_3$	1	-2	4	0	0	-2	-4	2	4	2	0	0	-2	-4	4	-1	2	0	0	-2	1
Ti$_3$Mo DO$_3$	1	2	4	0	0	2	4	2	4	-2	0	0	2	4	4	-1	-2	0	0	2	1
Al$_3$Mo DO$_3$	1	-1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
AlMo$_3$DO$_3$	1	-3	3	1	2	-2	-4	1	2	-1	2	1	-1	-2	1	0	0	0	0	0	0
Ti$_2$AlMo L1$_2$	1	1	3	1	-2	1	0	1	2	-1	-2	1	-1	2	1	0	0	0	0	0	0
TiAl$_2$Mo L1$_2$	1	0	2	-1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
TiAlMo$_2$ L1$_2$	1	-1	3	1	-2	-2	0	1	2	1	-2	1	1	-2	1	0	0	0	0	0	0
Ti$_2$AlMo F$\bar{4}$3m	1	1	3	-1	0	0	2	1	2	-1	0	-1	1	-1	1	0	0	0	0	0	0
TiAl$_2$Mo F$\bar{4}$3m	1	0	2	0	-1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
TiAlMo$_2$F$\bar{4}$3m	1	-1	3	-1	0	0	-2	1	2	1	0	-1	-1	0	1	0	0	0	0	0	0
Ti$_2$AlMo A2	1	1	3	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{3}{2}$	$\frac{9}{8}$	$\frac{9}{4}$	$\frac{1}{16}$	$\frac{3}{8}$	$\frac{3}{16}$	$\frac{9}{16}$	$\frac{9}{8}$	$\frac{27}{16}$	$\frac{1}{256}$	$\frac{3}{64}$	$\frac{9}{128}$	$\frac{9}{64}$	$\frac{27}{64}$	$\frac{81}{256}$
Ti$_2$AlMo B2	1	1	3	$\frac{5}{4}$	-2	$\frac{3}{2}$	0	$\frac{5}{4}$	2	$-\frac{1}{2}$	-3	$\frac{1}{2}$	$-\frac{1}{2}$	1	$\frac{3}{2}$	$\frac{1}{4}$	0	$\frac{1}{2}$	-1	0	$\frac{1}{4}$

C. Disordered structures

The formation energy of the A2 and B2 structures can be obtained through Eq. (1) writing suitable correlation functions.

For the A2 phase we made use of the fact that all sites are equivalent and computed the correlation functions for large clusters as products of the point ones, being the point correlation functions in this case[15] $\langle\sigma\rangle = c_{Ti} - c_{Mo}$ and $\langle\sigma^2\rangle = c_{Ti} + c_{Mo}$.

Following the experimental results of Sikora *et al.*[11] concerning the site occupation in the B2 compound, we considered equivalent sites in the sublattice occupied by Al and Mo, while the other sublattice was considered to be fully occupied by Ti. Correlations functions were calculated using Eq. (3), taking the probabilities $\rho^{2\,2\,11}_{nmop} = \rho^{2\,3\,11}_{nmop} = \rho^{3\,2\,11}_{nmop} = \rho^{3\,3\,11}_{nmop} = \frac{1}{4}$ and the rest equal to zero.

The resulting values for the formation energies and for the correlation functions of both phases are included in Table I and Table II, respectively.

III. DISCUSSION

As we have already mentioned, the computation of the formation energy via the inversion method is based on a cluster expansion within the irregular tetrahedron. That is, we restrict the expansion to a certain size and choose a set of ordered structures to perform the inversion. The particular choice of this set may be regarded as a source of imprecision. It is thus worthwhile to evaluate the accuracy of the inversion computation. With this aim, we considered one structure (Ti$_{15}$Mo) not used in the inversion set. Its total energy was calculated through the LMTO method (E_{LMTO}) and through the inversion method (E_I). The energy difference turned out to be $\delta E = E_I - E_{LMTO} = 0.04$ mRy/atom. This quantity is lower than 0.1 mRy/atom, our chosen convergence limit, thus proving the reliability of the procedure.

We have been comparing until now the formation energy of A2 and B2 structures, being, respectively, completely and partially disordered. It arises the question if a completely ordered phase could take place. Taking into account EXAFS results from Sikora, Hug, and Flanck[11] showing that the Ti$_2$AlMo phase should be named Ti$_2$(Al,Mo), that is, a B2-like structure with Ti atoms filling one sublattice, we have evaluated the various possible distributions of Al and Mo atoms in the other sublattice forming a superstructure. The total energy of each of the resulting structures was calculated through the TB-LMTO-ASA method with the same procedure that was explained before. The crystallographic description of the evaluated structures and their formation energies are given in Table IV, where we follow the nomenclature of

TABLE III. Interaction parameters calculated via the inversion scheme.

v_0	v_1	v_2	v_3	v_4	v_5	v_6	v_7	v_8	v_9	v_{10}	v_{11}	v_{12}	v_{13}	v_{14}	v_{15}	v_{16}	v_{17}	v_{18}	v_{19}	v_{20}
0	-4.05	-1.58	2.39	1.88	-3.09	6.70	-15.76	-16.17	2.23	0.39	-0.70	-8.24	-4.52	34.80	1.13	-2.80	0.91	-1.48	11.61	-46.31

TABLE IV. Evaluated superstructures for the $Ti_2(Al,Mo)$ B2 compound. (For Wickoff positions see Ref. 17).

Pearsonś symbol	$tP4$	$tP32$	$aP16$	$cP16$	$tP4$	$cF16$
Spatial group	$P4/mmm$	$P4mm$	$P1$	$P2/m3$	$P4/mmm$	$\mathrm{Fm}\overline{3}\mathrm{m}$
Spacial group No.	123	99	1	200	123	225
Axial relationship	$c=2a=2b$	$c=2a=2b$	$a=c=2b$		$a=b=\sqrt{2}c$	
Angles between axis			$\alpha=\beta=60°,\ \gamma=90°$			
Ti positions (Wickoff positions)	$2h\ z=1/4$	$4d\ x=1/4\ z=1/8$ $4d\ x=1/4\ z=3/8$ $4d\ x=1/4\ z=5/8$ $4d\ x=1/4\ z=7/8$	$1a\ x=1/2\ y=1/2\ z=1/4$ $1a\ x=3/4\ y=0\ z=1/4$ $1a\ x=1/4\ y=0\ z=1/4$ $1a\ x=3/4\ y=0\ z=3/4$ $1a\ x=1/2\ y=1/2\ z=3/4$ $1a\ x=0\ y=1/2\ z=3/4$ $1a\ x=1/4\ y=0\ z=3/4$ $1a\ x=0\ y=1/2\ z=1/4$	$8i\ x=0.25$	$2e$	$8c$
Al positions (Wickoff positions)	$1b$	$1a\ z=0$ $1a\ z=1/2$ $1b\ z=1/4$ $1b\ z=3/4$ $2c\ z=1/4$ $2c\ z=3/4$	$1a\ x=0\ y=0\ z=0$ $1a\ x=1/2\ y=0\ z=0$ $1a\ x=3/4\ y=1/2\ z=0$ $1a\ x=3/4\ y=1/2\ z=1/2$	$1b$ $3c$	$1a$	$4a$
Mo positions (Wickoff positions)	$1a$	$1a\ z=1/4$ $1az=3/4$ $1b\ z=0$ $1b\ z=1/2$ $2c\ z=0$ $2c\ z=1/2$	$1a\ x=1/4\ y=1/2\ z=0$ $1a\ x=0\ y=0\ z=1/2$ $1a\ x=1/2\ y=0\ z=1/2$ $1a\ x=1/4y=1/2z=1/2$	$1a$ $3d$	$1c$	$4b$
ΔE_F (mRy/atom)	-28.52	-29.19	-28.33	-28.57	-29.09	$\mathbf{-31.09}$

Ref. 17. As can be seen from the referred values, the more stable structure among them, and in consequence, the appropiate superstructure, should be the $L2_1$ phase (Fig. 1). We can indeed observe that the formation energy of the $L2_1$ phase is also lower than that of the $\mathrm{F}\overline{4}3\mathrm{m}$ phase, as it can be seen in Table I.

From our formation energy results it is found that both $L2_1$ and B2 phases are more stable than the A2 phase. The comparison between B2 and $L2_1$ results in a difference of about 4.7 mRy/atom, indicating a possible ordering in a $L2_1$ phase at low temperatures. If this phase happens to exist at low temperatures, the ordering in a $Ti_{50}Al_{25}Mo_{25}$ alloy would follow the transitions $A2 \rightarrow B2 \rightarrow L2_1$. It is worth mentioning that such transformations have already been suggested in an analogous system. Asta *et al.*[4] and Chaumat, Colinet and Moret[5] have investigated the Ti-Al-Nb system through the CVM, finding an ordering in the same sequence, although experimental work from some of these authors[6] gives no evidence for the formation of an $L2_1$ compound.

A final comment on the ordering energy could be placed here. The difference between the energy of the completely random state and that of the ordered compound at the same concentration is referred to as the ordering energy. This is typically[18] of 0.1–0.01 eV (7.4–0.74 mRy). As has been pointed out by Wolverton *et al.*,[19] a large value of this energy implies that the compound will be strongly ordered and hence will only disorder at high temperatures. In our case, the B2 ordering energy consists in a large value (aproximately 11.2 mRy/atom), thus indicating that this compound could be formed at high temperatures. The $L2_1$ ordering energy, on the other hand, exhibits the intermediate value of 4.7 mRy/atom, meaning that this completely ordered compound could be formed at relative lower temperatures.

IV. CONCLUSIONS

In this study, a ternary cluster expansion of the formation energy in a body-centered-cubic structure was obtained for the Ti-Al-Mo system. We considered the ternary basis functions $\{1,\sigma,\sigma^2\}$ from which the correlation functions in the tetrahedron approximation were explicitily written. Having computed the 21 ternary interaction parameters through the SIM, we are able now to obtain the formation energy of any given composition alloy in this system. The SIM has proved its reliability by reproducing the energy value for a compound not used in the inversion set.

As an application of these results, the formation energy of A2 and B2 phases in the same $Ti_{50}Al_{25}Mo_{25}$ composition was evaluated showing, at $T=0$ K, a higher stability of the B2 compound when compared with the A2 disordered phase. It's also possible that an ordering in a L21 compound could take place.

In order to generate a two-phase γ-γ' type microstructure in the Ti-Al-Mo system, as proposed by Naka and Khan,[2] evidence of a miscibility gap between the B2 and A2 phases giving rise to a two-phase field A2+B2 has to be given. The ternary phase diagram calculation at a given temperature using input from our 21 ternary interaction parameters can theoretically reveal this evidence. We are now undertaking these calculations together with experimental work.

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APPENDIX

Correlation functions in the tetrahedron approximation:

$$x_0 = \text{empty cluster},$$

$$x_1 = \langle\sigma_n\rangle + \langle\sigma_m\rangle + \langle\sigma_o\rangle + \langle\sigma_p\rangle,$$

$$x_2 = \langle\sigma_n^2\rangle + \langle\sigma_m^2\rangle + \langle\sigma_o^2\rangle + \langle\sigma_p^2\rangle,$$

$$x_3 = \langle\sigma_n\sigma_m\rangle + \langle\sigma_o\sigma_p\rangle,$$

$$x_4 = \langle\sigma_n\sigma_o\rangle + \langle\sigma_m\sigma_p\rangle + \langle\sigma_n\sigma_p\rangle + \langle\sigma_m\sigma_o\rangle,$$

$$x_5 = \langle\sigma_n^2\sigma_m\rangle + \langle\sigma_o^2\sigma_p\rangle + \langle\sigma_n\sigma_m^2\rangle + \langle\sigma_o\sigma_p^2\rangle,$$

$$x_6 = \langle\sigma_n^2\sigma_o\rangle + \langle\sigma_m^2\sigma_p\rangle + \langle\sigma_n^2\sigma_p\rangle + \langle\sigma_m^2\sigma_o\rangle + \langle\sigma_n\sigma_o^2\rangle + \langle\sigma_m\sigma_p^2\rangle + \langle\sigma_n\sigma_p^2\rangle + \langle\sigma_m\sigma_o^2\rangle,$$

$$x_7 = \langle\sigma_n^2\sigma_m^2\rangle + \langle\sigma_o^2\sigma_p^2\rangle,$$

$$x_8 = \langle\sigma_n^2\sigma_o^2\rangle + \langle\sigma_m^2\sigma_p^2\rangle + \langle\sigma_n^2\sigma_p^2\rangle + \langle\sigma_m^2\sigma_o^2\rangle,$$

$$x_9 = \langle\sigma_n\sigma_m\sigma_o\rangle + \langle\sigma_n\sigma_m\sigma_p\rangle + \langle\sigma_n\sigma_o\sigma_p\rangle + \langle\sigma_m\sigma_o\sigma_p\rangle,$$

$$x_{10} = \langle\sigma_n^2\sigma_m\sigma_o\rangle + \langle\sigma_n^2\sigma_m\sigma_p\rangle + \langle\sigma_n\sigma_o^2\sigma_p\rangle + \langle\sigma_m\sigma_o^2\sigma_p\rangle + \langle\sigma_n\sigma_m^2\sigma_o\rangle + \langle\sigma_n\sigma_m^2\sigma_p\rangle + \langle\sigma_n\sigma_o\sigma_p^2\rangle + \langle\sigma_m\sigma_o\sigma_p^2\rangle,$$

$$x_{11} = \langle\sigma_n\sigma_m\sigma_o^2\rangle + \langle\sigma_n\sigma_m\sigma_p^2\rangle + \langle\sigma_n^2\sigma_o\sigma_p\rangle + \langle\sigma_m^2\sigma_o\sigma_p\rangle,$$

$$x_{12} = \langle\sigma_n^2\sigma_m^2\sigma_o\rangle + \langle\sigma_n^2\sigma_m^2\sigma_p\rangle + \langle\sigma_n\sigma_o^2\sigma_p^2\rangle + \langle\sigma_m\sigma_o^2\sigma_p^2\rangle,$$

$$x_{13} = \langle\sigma_n\sigma_m^2\sigma_o^2\rangle + \langle\sigma_n\sigma_m^2\sigma_p^2\rangle + \langle\sigma_n^2\sigma_o\sigma_p^2\rangle + \langle\sigma_m^2\sigma_o^2\sigma_p\rangle + \langle\sigma_n^2\sigma_m\sigma_o^2\rangle + \langle\sigma_n^2\sigma_m\sigma_p^2\rangle + \langle\sigma_n^2\sigma_o^2\sigma_p\rangle + \langle\sigma_m^2\sigma_o\sigma_p^2\rangle,$$

$$x_{14} = \langle\sigma_n^2\sigma_m^2\sigma_o^2\rangle + \langle\sigma_n^2\sigma_m^2\sigma_p^2\rangle + \langle\sigma_n^2\sigma_o^2\sigma_p^2\rangle + \langle\sigma_m^2\sigma_o^2\sigma_p^2\rangle,$$

$$x_{15} = \langle\sigma_n\sigma_m\sigma_o\sigma_p\rangle,$$

$$x_{16} = \langle\sigma_n^2\sigma_m\sigma_o\sigma_p\rangle + \langle\sigma_n\sigma_m^2\sigma_o\sigma_p\rangle + \langle\sigma_n\sigma_m\sigma_o^2\sigma_p\rangle + \langle\sigma_n\sigma_m\sigma_o\sigma_p^2\rangle,$$

$$x_{17} = \langle\sigma_n^2\sigma_m^2\sigma_o\sigma_p\rangle + \langle\sigma_n\sigma_m\sigma_o^2\sigma_p^2\rangle,$$

$$x_{18} = \langle\sigma_n^2\sigma_m\sigma_o\sigma_p^2\rangle + \langle\sigma_n^2\sigma_m\sigma_o^2\sigma_p\rangle + \langle\sigma_n\sigma_m^2\sigma_o\sigma_p^2\rangle + \langle\sigma_n\sigma_m^2\sigma_o^2\sigma_p\rangle,$$

$$x_{19} = \langle\sigma_n^2\sigma_m^2\sigma_o^2\sigma_p\rangle + \langle\sigma_n^2\sigma_m^2\sigma_o\sigma_p^2\rangle + \langle\sigma_n\sigma_m^2\sigma_o^2\sigma_p^2\rangle + \langle\sigma_n^2\sigma_m\sigma_o^2\sigma_p^2\rangle.$$

$$x_{20} = \langle\sigma_n^2\sigma_m^2\sigma_o^2\sigma_p^2\rangle.$$

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