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.

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 Khan3 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 Ti2AlX 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 Ti2AlX 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 Ti50Al25Mo25 (at. %) in the Ti-Al-Mo system.

In the ternary Ti-Al-Mo, a B2 phase was first reported by Böhm and Löhberg7 although site occupancy was not mentioned. This phase was associated with an order-disorder B2→A2 second-order phase transition. Later, Hamajima, Luetjering, and Weissmann8 showed that for a Ti77Al16Mo7 (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 Vasu9 working on alloys around the composition Ti48Al47Mo5 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 Flanck11 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 Connelly-Williams12 for the disordered ones. A comparison between the formation energy of both phases in the same Ti50Al25Mo25 composition is shown as an application of the cluster expansion.
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 DO3 and ternary structures L21 and F43m 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. In order to choose a \( k \)-point mesh we calculated total energy for 8, 10, 12, 14, and 16 \( k \)-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 \( k \)-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:

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

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, Ti3AlDO3, and TiAl B2) are consistent with the phase diagram at \( T=0 \) K shown by Asta et al.

B. Calculation of cluster interactions

In order to compute the formation energy of the disordered states for the Ti2AlMo compound, we have to consider...
Relative stability of bcc structures in . . .

We considered all clusters within the tetrahedron approximation. In this work, the sum is extended over all possible clusters, although in practice it can be grouped leading to an expansion in 21 terms. The complete set of correlation functions adds up to 80 (K' = 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 \( \nu_i \) exhibit cluster symmetries 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 \( \nu_i \) of Eq. (1). These are shown in Tables II and III.

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

<table>
<thead>
<tr>
<th>Structure</th>
<th>( a ) (Bohr radius)</th>
<th>( E_T ) (mRy/atom)</th>
<th>( \Delta E_T ) (mRy/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al bcc</td>
<td>12</td>
<td>-484297.638</td>
<td>0</td>
</tr>
<tr>
<td>Ti bcc</td>
<td>12.1</td>
<td>-1704760.32</td>
<td>0</td>
</tr>
<tr>
<td>Mo bcc</td>
<td>12</td>
<td>-8091097.76</td>
<td>0</td>
</tr>
<tr>
<td>TiAl B2</td>
<td>11.85</td>
<td>-1094541.14</td>
<td>-12.16</td>
</tr>
<tr>
<td>TiMo B2</td>
<td>11.9</td>
<td>-4879738.46</td>
<td>-9.42</td>
</tr>
<tr>
<td>AlMo B2</td>
<td>11.8</td>
<td>-4287699.94</td>
<td>-2.25</td>
</tr>
<tr>
<td>TiAl B32</td>
<td>11.88</td>
<td>-1094541.14</td>
<td>-12.16</td>
</tr>
<tr>
<td>TiMo B32</td>
<td>11.9</td>
<td>-4879738.46</td>
<td>-9.42</td>
</tr>
<tr>
<td>AlMo B32</td>
<td>11.72</td>
<td>-4287720.49</td>
<td>-22.79</td>
</tr>
<tr>
<td>TiAl DO3</td>
<td>11.99</td>
<td>-1399663.66</td>
<td>-18.43</td>
</tr>
<tr>
<td>Ti3Al DO3</td>
<td>11.9</td>
<td>-789418.93</td>
<td>-5.63</td>
</tr>
<tr>
<td>Ti3Mo DO3</td>
<td>11.93</td>
<td>-6494526.48</td>
<td>-13.08</td>
</tr>
<tr>
<td>Mo3Ti DO3</td>
<td>12</td>
<td>-3301353.18</td>
<td>-8.5</td>
</tr>
<tr>
<td>Al3Mo DO3</td>
<td>11.7</td>
<td>-2385995.21</td>
<td>2.46</td>
</tr>
<tr>
<td>Mo3Al DO3</td>
<td>11.86</td>
<td>-6189402.95</td>
<td>-5.22</td>
</tr>
<tr>
<td>Ti2AlMo L21</td>
<td>11.9</td>
<td>-2996260.09</td>
<td>-31.09</td>
</tr>
<tr>
<td>TiAl2 Mo L21</td>
<td>11.77</td>
<td>-2691134.65</td>
<td>-21.31</td>
</tr>
<tr>
<td>TiAl2 Mo L21</td>
<td>11.83</td>
<td>-4592820.98</td>
<td>-7.61</td>
</tr>
<tr>
<td>Ti2Al Mo F43m</td>
<td>11.9</td>
<td>-2996265.32</td>
<td>-16.31</td>
</tr>
<tr>
<td>TiAl2 Mo F43m</td>
<td>11.81</td>
<td>-2691135.54</td>
<td>-21.21</td>
</tr>
<tr>
<td>TiAl2 Mo F43m</td>
<td>11.87</td>
<td>-4592831.99</td>
<td>-18.62</td>
</tr>
<tr>
<td>Ti2AlMo A2</td>
<td>-</td>
<td>-115.25</td>
<td>-26.4</td>
</tr>
<tr>
<td>Ti2AlMo B2</td>
<td>-</td>
<td>-115.25</td>
<td>-26.4</td>
</tr>
</tbody>
</table>

\[ \Delta E_T = \sum_i \nu_i x_i, \]

where \( \nu_i \) 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 \( \Delta E_T \) 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 \( \nu_i \). Therefore, the \( \nu_i \) 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 \( \nu_i \). This is the SIM based on the idea of Connolly and Williams.

For the computation of the \( x_i \) functions we followed the formalism described by Inden and Pitsch. The first step is to define a site operator \( \sigma_n \) 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 \( \sigma_n \) has three values. Therefore, to fully specify a function of \( \sigma_n \), 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 \( \sigma_n(1, \sigma a^2) \). Cluster functions formed from products of the set \( \{1, \sigma a^2\} \) are proposed as a possible basis of functions for describing the ternary alloy problem. 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

\[ x_i = \langle \sigma_n^{i-1} \sigma_m^{i-1} \sigma_o^{i-1} \sigma_p^{i-1} \rangle, \]

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, DO3, L21, and F43m.

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

\[
\langle \sigma_n^{i_1-1} \sigma_m^{i_2-1} \sigma_o^{i_3-1} \sigma_p^{i_4-1} \rangle = \sum_{k_1=1}^{3} \sum_{k_2=1}^{3} \sum_{k_3=1}^{3} \sum_{k_4=1}^{3} M_{k_1 k_2} M_{k_2 k_3} M_{k_3 k_4} M_{k_4 k_1} \delta_{n m o p}^{k_1 k_2 k_3 k_4},
\]

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

\[
M = \begin{pmatrix}
1 & 1 & 1 & 0 & -1 \\
1 & 0 & 0 & 1 & 1
\end{pmatrix}
\]
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

\[ \langle \sigma \rangle = c_{Ti}^{-1} c_{Mo} \quad \text{and} \quad \langle \sigma^2 \rangle = c_{Ti}^{-1} c_{Mo}. \]

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

\[ \rho_{nmop}^{2.11} = \rho_{nmop}^{3.11} = \rho_{nmop}^{2.211} = \frac{1}{2} \]

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 (Ti33Mo) 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 \( \Delta E = E_I - E_{LMTO} = 0.04 \text{ mRy/atom} \). 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 Flanck11 showing that the Ti3AlMo phase should be named Ti3(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. With this aim, we considered one structure (Ti3AlMo) 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 \( \Delta E = E_I - E_{LMTO} = 0.04 \text{ mRy/atom} \). 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 Flanck11 showing that the Ti3AlMo phase should be named Ti3(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...
RELATIVE STABILITY OF bcc STRUCTURES IN . . .

Typically, the ordering energy is of the order of 18–0.1 mRy/atom, indicating a possible ordering in a L21 phase. The L21 phase at low temperatures is more stable than the A2 phase. In our case, the A2 ordering energy consists in a large value of the order of 11.2 mRy/atom, thus indicating that this compound could be formed at high temperatures. The L21 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 explicitly 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 at lower temperatures.

As an application of these results, the formation energy of A2 and B2 phases in the same Ti50Al25Mo25 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 \( \gamma - \gamma' \) 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.

ACKNOWLEDGMENTS

P.R.A. was supported by the CNEA. We greatly appreciate interaction with J. M. Sánchez and wish to thank him for his clarifying remarks. P.R.A. is also grateful to L. M. Gribaudo, M. Ortiz Albuixech, and S. Arico for helpful and interesting discussions as well as for reading the manuscript.

APPENDIX

Correlation functions in the tetrahedron approximation:

\[ x_0 = \langle \sigma \rangle + \langle \sigma_m \rangle + \langle \sigma_o \rangle + \langle \sigma_p \rangle, \]

\[ x_1 = \langle \sigma \sigma_m \rangle + \langle \sigma_o \sigma_p \rangle + \langle \sigma_p \sigma_o \rangle, \]

\[ x_2 = \langle \sigma^2 \rangle + \langle \sigma_o \sigma_p \rangle + \langle \sigma_p \sigma_o \rangle, \]

\[ x_3 = \langle \sigma \sigma_m \rangle + \langle \sigma_o \sigma_p \rangle, \]

\[ x_4 = \langle \sigma \sigma_m \rangle + \langle \sigma_o \sigma_p \rangle + \langle \sigma_m \sigma_o \rangle, \]

\[ x_5 = \langle \sigma^2 \sigma_m \rangle + \langle \sigma_o \sigma_p \rangle + \langle \sigma_m \sigma_o \rangle, \]

\[ x_6 = \langle \sigma^2 \sigma_m \rangle + \langle \sigma_o \sigma_p \rangle + \langle \sigma_m \sigma_o \rangle + \langle \sigma_o \sigma_o \rangle, \]

\[ + \langle \sigma_m \sigma_p \rangle + \langle \sigma_o \sigma_p \rangle + \langle \sigma_m \sigma_o \rangle, \]

\[ x_7 = \langle \sigma^2 \sigma_m \rangle + \langle \sigma^2 \sigma_p \rangle, \]

\[ x_8 = \langle \sigma^2 \sigma_m \rangle + \langle \sigma^2 \sigma_p \rangle + \langle \sigma^2 \sigma_o \rangle + \langle \sigma^2 \sigma_o \rangle, \]

\[ x_9 = \langle \sigma \sigma_m \sigma_o \rangle + \langle \sigma \sigma_m \sigma_p \rangle + \langle \sigma \sigma_o \sigma_p \rangle + \langle \sigma \sigma_o \sigma_o \rangle, \]

\[ x_{10} = \langle \sigma \sigma_m \sigma_o \rangle + \langle \sigma \sigma_m \sigma_p \rangle + \langle \sigma \sigma_o \sigma_p \rangle + \langle \sigma \sigma_o \sigma_o \rangle, \]

\[ + \langle \sigma \sigma_o \sigma_p \rangle + \langle \sigma \sigma_o \sigma_o \rangle, \]

\[ x_{11} = \langle \sigma \sigma_m \sigma_o \rangle + \langle \sigma \sigma_m \sigma_p \rangle + \langle \sigma \sigma_o \sigma_p \rangle + \langle \sigma \sigma_o \sigma_o \rangle, \]

\[ + \langle \sigma \sigma_o \sigma_p \rangle + \langle \sigma \sigma_o \sigma_o \rangle, \]

\[ x_{12} = \langle \sigma \sigma_m \sigma_o \rangle + \langle \sigma \sigma_m \sigma_p \rangle + \langle \sigma \sigma_o \sigma_p \rangle + \langle \sigma \sigma_o \sigma_o \rangle, \]

\[ + \langle \sigma \sigma_o \sigma_p \rangle + \langle \sigma \sigma_o \sigma_o \rangle, \]

\[ x_{13} = \langle \sigma \sigma_m \sigma_o \rangle + \langle \sigma \sigma_m \sigma_p \rangle + \langle \sigma \sigma_o \sigma_p \rangle + \langle \sigma \sigma_o \sigma_o \rangle, \]

\[ + \langle \sigma \sigma_o \sigma_p \rangle + \langle \sigma \sigma_o \sigma_o \rangle, \]

\[ x_{14} = \langle \sigma \sigma_m \sigma_o \rangle + \langle \sigma \sigma_m \sigma_p \rangle + \langle \sigma \sigma_o \sigma_p \rangle + \langle \sigma \sigma_o \sigma_o \rangle, \]

\[ + \langle \sigma \sigma_o \sigma_p \rangle + \langle \sigma \sigma_o \sigma_o \rangle, \]

\[ x_{15} = \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle, \]

\[ x_{16} = \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle, \]

\[ + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle, \]

\[ x_{17} = \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle, \]

\[ x_{18} = \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle, \]

\[ + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle, \]

\[ x_{19} = \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle, \]

\[ + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle, \]

\[ x_{20} = \langle \sigma \sigma_m \sigma_o \sigma_p \rangle + \langle \sigma \sigma_m \sigma_o \sigma_p \rangle. \]