Application of an axial next-nearest-neighbor Ising model to the description of $M_{n+1}AX_n$ phases

T. Ouisse[*] and D. Chaussende

LMGP, UMR CNRS 5628, Grenoble INP, Minatec, 3, parvis Louis Néel, BP257, 38016 Grenoble Cedex 1, France
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We show that some important features characterizing the $M_{n+1}AX_n$ phases, a family of hexagonal-structure ternary carbides and nitrides (X) including a transition metal (M) and an A-group element (A), can be reproduced by modifying the spin model known as the axial next-nearest-neighbor Ising model into a form where pseudospin inversion changes the system energy and requires the inclusion of single- and three-spin products. We describe the various *MAX* phases in terms of M-A or M-X bilayer stacking along the c axis. We discuss the dependence of the cohesive energy and phase stability on coupling parameters which characterize the first- and second-neighbor interactions between those bilayers. We also address the case of "hybrid" *MAX* phases.

I. INTRODUCTION

In this paper we wish to apply the axial next-nearest-neighbor Ising (ANNNI) model to the case of *MAX* phases,[1,2] which are formed by a stacking of M-A or M-X bilayers. M is a transition metal, A is an element of the A group, and X is either C or N.[1–4] Such phases form a class of materials which are expected to play a major role in applications requiring resistance to oxidation and corrosion, high-temperature operation, good electrical conduction, and good mechanical properties, since they combine many of the positive characteristics of ceramics to that of metals.[1,4] These lamellar compounds, about 60 of which have already been experimentally reported,[2] can be synthesized in different ways, either by bulk synthesis methods such as, e.g., hot isostatic pressing[5] and pulse discharge sintering,[4] or by thin-film methods such as physical vapor deposition (PVD) by sputtering,[6] chemical vapor deposition (CVD),[7,8] or solid-state reactions[9] (for an exhaustive review of such methods one can consult Refs. 1–4). Recently, we have shown that they could be obtained in a single-crystalline form by using high-temperature solution growth.[10,11] *MAX* phases are not an example of polytypism in the strict sense, since changing n in $M_{n+1}AX_n$ also modifies the stoichiometry. However, in this paper we wish to show that their formation might be interpreted by using tools quite similar to those already developed for studying polytypism. Besides, real polytypism can also occur and should be discussed, since different *MAX* phases, the "conventional" and the "hybrid" ones,[2,6,7] may exhibit the same stoichiometry.

The phenomenon of polytypism is frequently encountered in close-packed structures,[12–14] and silicon carbide (SiC) is probably the most famous example.[15–18] Why some compounds exhibit polytypism and others do not has been the subject of intensive research. In short, polytypism with long-range stacking periods has been explained either in terms of crystal growth assisted by defects (screw dislocations with a very large Burgers vector[16]), by energy considerations (which phase has the lowest energy?),[19,20] or by a mixture of arguments appealing to thermodynamics, kinetics, and defect-assisted formation.[21] Although the longstanding debate between the proponents of the various models is still far from being closed, a useful tool for investigating polytypism has been revealed to be the ANNNI model.[22,23] When applied to polytypism, it

describes the energy of the system in terms of pseudospins and interaction parameters between the various layers which form a stacking periodic sequence of the investigated lattice.[24] The interaction between a given layer and the ones next to it is accounted for by the use of a Hamiltonian of the form

$$H_{\text{ANNNI}} = E_0 - J_1\sigma_n\sigma_{n-1} - J_2\sigma_n\sigma_{n-2} - J_3\sigma_n\sigma_{n-3} - K\sigma_n\sigma_{n-1}\sigma_{n-2}\sigma_{n-3}, \qquad (1)$$

where n is the bilayer index, the J_i's and K are interaction parameters characterizing the investigated compound, and the pseudospins σ_n's describe a binary property of the corresponding layer, as further detailed below.

Depending on the structure, the pseudospin can describe the orientation of a bond which can only point in two possible directions within a bilayer (the case of SiC),[24–26] or the shift in position of a substructure resulting from the existence of antiphase boundaries (TiAl$_3$).[22] In all cases, two conditions have to be fulfilled: First of all, any structure must correspond to only one spin sequence. Second, inversion of all spins of a given sequence should not change the energy. The latter point prohibits the existence of spin products with an odd number of spins in the Hamiltonian. By using the ANNNI model, various authors have shown that the occurrence of the most common SiC polytypes could be explained in a plausible way.[24–26] This is due to the fact that, for a given set of coupling parameters between the bilayers, there is a degeneracy point in the phase diagram, and for a system located close to this point, many polytypes exhibit almost the same energy.[24] SiC was presumed to be in such a case, and detailed *ab initio* and density functional theory (DFT) calculations have confirmed this.[27] Compounds exhibiting coupling constants far from this degeneracy point cannot exhibit polytypism, at least from the point of view of the possible equilibrium phases. Therefore, calculating these constants from first principles allows one to assess whether polytypism is possible in principle. It can also be applied to surface problems such as epitaxial growth of a given polytype,[28–30] or to the estimation of stacking fault energy.[31] Despite its intrinsic tendency to oversimplify, the ANNNI model has proven to be successful in explaining the formation of the most common SiC polytypes, even if it is clear that obtaining one of them clearly relies upon other conditions (nature of the seed surface, thermodynamic conditions during growth, etc.).
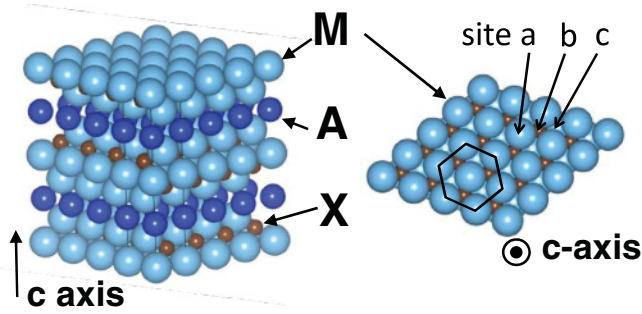
FIG. 1. (Color online) Atomic structure of the M_3AX_2 phase (drawn with the VESTA software).

First of all, we note that since the A layers of a *MAX* phase are always obtained in a locally hexagonal stacking with respect to the M planes, whereas the X layers are locally cubic (see Fig. 1), any phase can be uniquely defined just by specifying the sequence of A and X monolayers successively intercalated in between M monolayers over a unit cell (A or X). Knowledge of this sequence thus suffices to reconstruct the full structure. However, in the case of *MAX* phases, passing from a MA to a MX bilayer clearly changes the energy, so that defining a bilayer pseudospin as up ($\uparrow$ or $\sigma = +1$) for MX and down ($\downarrow$ or $\sigma = -1$) for MA cannot lead to invariance under spin inversion. We will justify in Sec. II how this can be accounted for by introducing a Hamiltonian of the form

$$H_{ANNNI} = E_0 + L_1\sigma_n + L_2\sigma_n\sigma_{n-1} + L_3\sigma_n\sigma_{n-2} + K\sigma_n\sigma_{n-1}\sigma_{n-2}. \quad (2)$$

In Eq. (2) we now included a single-spin term, as in the conventional ANNNI model in the presence of a magnetic field, where invariance under spin inversion is broken by application of the field.[32] But, as demonstrated in this paper, the necessary inclusion of the three-spin term causes this Hamiltonian to differ as well from the ANNNI model with a field. Using this Hamiltonian, we shall calculate in Sec. III the energy of $M_{n+1}AX_n$ phases with varying n to establish a pseudophase diagram as a function of the characteristic coupling parameters. Depending on the nature and hence on the location of a given ternary family in the pseudophase diagram, one can predict the phases which have the lowest energy at $T = 0$ K. In particular, we will show that there is a degeneracy point where all phases have the same ground-state energy, and that the pseudophase diagram is mostly occupied by the 211 and 312 phases.

Our model is not expected to replace *ab initio* and other detailed numerical calculations: Just to mention but one argument, such calculations would be required anyway to establish the coupling constants we introduce, so as to be able to put a point corresponding to a particular set of M, A, and X atoms on the phase diagram. However, it may form a useful frame of interpretation, most particularly to predict, for a particular compound, which *MAX* phases have the lowest energy, and thus as a starting point to assess their stability. More detailed considerations of this kind are produced in Sec. IV. Of course, we do not claim that these simple energy considerations are enough to determine

which phase must be formed. This clearly relies not only upon determining the energy of one phase, but on finding the relevant competing phases, on determining the energy difference between the *MAX* phase and its decomposition products, and taking into account temperature.[33] Obtaining one *MAX* phase depends on many additional factors, such as, e.g., the stoichiometry of a melt, the thermodynamic conditions during growth and/or solidification, the partial pressures of the various species for growth from the vapor phase, the presence of defects, etc. These factors can give rise to the growth of a particular metastable phase, or even systematically prohibit the growth of the more stable one. However, we propose our approach as a useful point of view to investigate those aspects: More specifically, the model leads to qualitatively different predictions, depending on whether the structure of the *MAX* phase is essentially determined by first-neighbor bilayer interactions, or also affected by second- and third-neighbor bilayer interactions. As for other systems, ANNNI-like models are a tool of choice in the ones available to the solid-state physicist in order to investigate the stability and complexity of layered structures with long periodic sequences, as is the case, e.g., of a 413 phase (eight bilayers per unit cell), or, even worse, of a hybrid 725 phase (21 bilayers per unit cell).

II. MODEL

$M_{n+1}AX_n$ phases can be described by a hexagonal-close-packed stacking of atomic layers including only M, A, or X atoms, each A or X layer being surrounded by M layers (see Fig. 1). The atoms of a hexagonal-close-packed crystal lie in three different kinds of sites which we label as a, b, and c (see Fig. 2), and all atoms lying in a plane perpendicular to the c axis belong to the same kind of site. In the case of the *MAX* phases each X layer is in a "locally cubic environment": If layer X is of type b, it is, e.g., in between an M layer of type a and an M layer of type c. Besides, if several X planes are successively encountered without any A plane in between, they keep the same cubic orientation, that is to say, the stacking of X and M planes can be defined with the same $abcabc$, etc., succession of atomic planes (in other words, each X atom lies at the center of a M_6X octahedron). In contrast, each A layer is in a "locally hexagonal environment," i.e., the atoms belonging to the planes below and above a given A plane occupy the same kind of sites
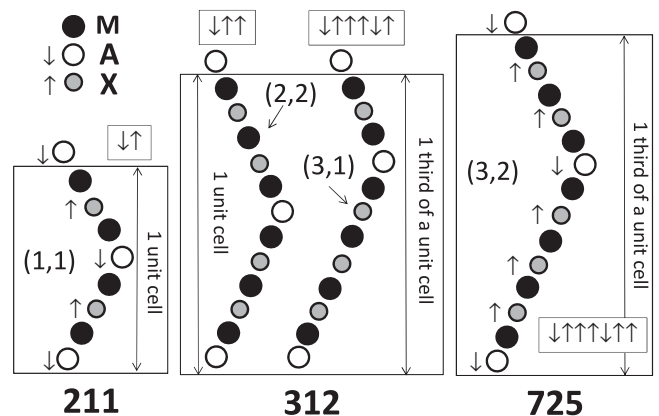

FIG. 2. Atomic stacking of the 211, 312, and 725 *MAX* phases along the c axis and in a $(10\bar{2}0)$ plane.

TABLE I. Definition and numbering of all possible pseudospin sequences describing the stacking of three successive MA or MX bilayers in a MAX phase. Spin-down stands for an MA bilayer and spin-up stands for an MX bilayer.

Configuration No.	$(n-2)$th bilayer pseudospin	$(n-1)$th bilayer pseudospin	nth bilayer pseudospin	Energy value
1	↑	↑	↑	E_1
2	↓	↑	↑	E_2
3	↑	↓	↑	E_3
4	↓	↓	↑	E_4
5	↑	↑	↓	E_5
6	↓	↑	↓	E_6
7	↑	↓	↓	E_7
8	↓	↓	↓	E_8

(e.g., the MAM sequence is of the kind aba). Therefore, plotting the atomic site as a function of the layer can be represented by a schematic as in Fig. 2. In this paper, we will take those rules for granted. It must therefore be clear that our assumption excludes the possibility to study a polymorphism as described, e.g., in Ref. 34, or observed in Ref. 35, but which for MAX phases seems to be closer to an exception than to a rule. To assume those two hypotheses, rough though this procedure is, brings forth a comfortable advantage: A mere knowledge of the succession of A and X planes over a unit cell is enough to reconstruct the full crystal structure. The latter can thus be simply described by associating to each A or X layer the M layer below it so as to group all layers into bilayers, and then by assigning a pseudospin to the bilayer type: $\sigma = +1$ for MX and $\sigma = -1$ for MA. This will allow us to build an ANNNI model for describing the MAX phases.

If we are interested in interactions up to second-nearest-neighbor bilayers (that is to say, up to fourth-nearest-neighbor atomic interactions), we can restrict ourselves to the study of the different combinations which can be formed by stacking three bilayers. As is clear from Table I, there are only eight possible spin configurations. However, in great contrast to the usual ANNNI models, inverting the spins is equivalent to turning all A layers into X layers, and vice versa. This operation clearly leads to a change in energy, so that a configuration as, e.g., ↑↓↓, is certainly not equivalent to the inverted configuration ↓↑↑. This means that if one is interested in enumerating all possible configurations of a MAX phase surface, limiting its description to three bilayers, we have $2^3 = 8$ different possible values of energy (the system is the MAX phase substrate + one newly attached bilayer). Let us define those energies as E_1, E_2, etc., up to E_8 (see Table I). Then, building an ANNNI-like model is nothing but finding a convenient analytical expression of the spins to obtain again those eight energies as a function of spin configuration, and to apply this expression to an infinite stacking sequence so as to calculate the energy of the bulk materials (as a side note, and although not frequently mentioned, previous ANNNI-like models are implicitly built in the same way, and this is, for instance, the reason why four-spin terms are required in the case of SiC, whose description in terms of four adjacent

bilayers leads to eight different possible configurations, now taking invariance under spin inversion into account[26]).

To derive a correct formula, to be used either in surface or bulk problems, we thus require a mathematical expression depending only on the E_i's and on spin configuration, so that for configuration number i the formula is equal to E_i. Such an expression is quite easily derived by weighting each energy value E_i by a function of the spins equal to 1 if the spin configuration is i, to zero otherwise, and then by summing all the different energy terms so obtained (i.e., we write $H_{\mathrm{NNN}} = f_1(\sigma_n, \sigma_{n-1}, \sigma_{n-2})E_1 + f_2(\sigma_n, \sigma_{n-1}, \sigma_{n-2})E_2 + \cdots + f_8(\sigma_n, \sigma_{n-1}, \sigma_{n-2})E_8$ with $f_j(\sigma_n, \sigma_{n-1}, \sigma_{n-2}) = 1$ if $j = i$ and 0 if $j \neq i$. A possible function f_1 corresponding to E_1 is given by $(1 + \sigma_n)(1 + \sigma_n\sigma_{n-1})(1 + \sigma_n\sigma_{n-2})E_1/8$ (see configuration 1 in Table I). It can be straightforwardly expanded into a simpler expression, taking into account that terms of the form σ_i^2 are equal to 1:

$$H_1 = \frac{E_1}{8}(1 + \sigma_n + \sigma_{n-1} + \sigma_{n-2} + \sigma_n\sigma_{n-1} + \sigma_n\sigma_{n-2}$$
$$+ \sigma_{n-1}\sigma_{n-2} + \sigma_n\sigma_{n-1}\sigma_{n-2}). \quad (3)$$

The next term, corresponding to E_2, is calculated in the same way from configuration 2 and is equal to

$$H_2 = \frac{E_2}{8}(1 + \sigma_n + \sigma_{n-1} - \sigma_{n-2} + \sigma_n\sigma_{n-1} - \sigma_n\sigma_{n-2}$$
$$- \sigma_{n-1}\sigma_{n-2} - \sigma_n\sigma_{n-1}\sigma_{n-2}). \quad (4)$$

Repeating this calculation for all E_i's and summing all terms gives an energy

$$H = E_0 + I_1\sigma_n + I_2\sigma_{n-1} + I_3\sigma_{n-2} + J_1\sigma_n\sigma_{n-1}$$
$$+ J_2\sigma_n\sigma_{n-2} + J_3\sigma_{n-1}\sigma_{n-2} + K\sigma_n\sigma_{n-1}\sigma_{n-2} \quad (5)$$

where

$$E_0 = \tfrac{1}{8}(E_1 + E_2 + E_3 + E_4 + E_5 + E_6 + E_7 + E_8),$$
$$I_1 = \tfrac{1}{8}(E_1 + E_2 + E_3 + E_4 - E_5 - E_6 - E_7 - E_8),$$
$$I_2 = \tfrac{1}{8}(E_1 + E_2 - E_3 - E_4 + E_5 + E_6 - E_7 - E_8),$$
$$I_3 = \tfrac{1}{8}(E_1 - E_2 + E_3 - E_4 + E_5 - E_6 + E_7 - E_8),$$
$$J_1 = \tfrac{1}{8}(E_1 + E_2 - E_3 - E_4 - E_5 - E_6 + E_7 + E_8), \quad (6)$$
$$J_2 = \tfrac{1}{8}(E_1 - E_2 + E_3 - E_4 - E_5 + E_6 - E_7 + E_8),$$
$$J_3 = \tfrac{1}{8}(E_1 - E_2 - E_3 + E_4 + E_5 - E_6 - E_7 + E_8),$$
$$K = \tfrac{1}{8}(E_1 - E_2 - E_3 + E_4 - E_5 + E_6 + E_7 - E_8).$$

We obtain simple-spin, double-spin, and triple-spin terms. Equation (5) is the formula which should be used in surface problems (for instance, to study epitaxial growth), so that if one wants to calculate the energy corresponding to a given surface configuration, knowledge of all eight energies is a prerequisite. To obtain the bulk formula, we need to sum energies of the kind given in Eq. (5) over an infinity of unit cells, since we build the bulk phase by stacking bilayers up to infinity. It is straightforward to factorize all terms in front of the spin of a given bilayer of index n, limiting the collected terms to all three-layer blocks with an upper bilayer index larger than n. We therefore obtain the energy per M-X and A-X pair after summing over the N bilayers forming a unit cell and dividing

by N:

$$H_{\text{ANNNI}} = E_0 + \frac{1}{N}\sum_n [(I_1 + I_2 + I_3)\sigma_n + (J_1 + J_3)\sigma_n\sigma_{n-1}$$
$$+ J_2\sigma_n\sigma_{n-2} + K\sigma_n\sigma_{n-1}\sigma_{n-2}]. \quad (7)$$

Taking into account the dependence of the I_i's and J_i's over the E_i's, we can then express the energy as a function of the E_i's under the form

$$E_{MAX} = E_0 + \frac{1}{N}\sum_n (L_1\sigma_n + L_2\sigma_n\sigma_{n-1} + L_3\sigma_n\sigma_{n-2}$$
$$+ K\sigma_n\sigma_{n-1}\sigma_{n-2}), \quad (8)$$

with

$$L_1 = \tfrac{1}{8}(3E_1 + E_2 + E_3 - E_4 + E_5 - E_6 - E_7 - 3E_8),$$
$$L_2 = \tfrac{1}{4}(E_1 - E_3 - E_6 + E_8), \quad (9)$$
$$L_3 = J_2 = \tfrac{1}{8}(E_1 - E_2 + E_3 - E_4 - E_5 + E_6 - E_7 + E_8).$$

Equation (8) is our bulk ANNNI formula. Due to the presence of products with an odd number of pseudospins, it is formally different from that obtained in the frame of the "conventional" ANNNI model. The energy of any M_nAX_{n+1} phase can be deduced from knowledge of only five different parameters (one more than, e.g., in the case of SiC with third-neighbor bilayer interactions). Besides, if one assumes that configurations 4, 7, and 8 are highly improbable (succession of two A bilayers), one can get rid of all the energy values with the same indices in Eq. (9).

III. APPLICATION OF THE MODEL TO THE *MAX* PHASES

Let us first give a short description of the existing *MAX* phases, as well as of the nomenclature which we will apply in this paper, and how we connect this nomenclature to the already published ones: One can subdivide the *MAX* phases into "conventional" ones, of the form $M_{n+1}AX_n$, and into "hybrid" ones.[2] Hybrid phases are more an exception than the rule. The conventional phases are usually noted 211 for M_2AX, 312 for M_3AX_2, 413 for M_4AX_3, etc. As an example, the crystal structure of the conventional 312 phase is shown in Fig. 1. As illustrated by Fig. 2, the atom lines in a $(11\bar{2}0)$ plane exhibit a zigzag structure along the c axis, with an equal number of X bilayers in both zigzag sides. In this paper we label them as (n,n), where n is the number of X planes in one "zig." The corresponding energy is $E_{n,n}$. Hybrid phases, less frequently observed, have a rhombohedral structure and are characterized by a different number of X planes for the "zig" (let us say m) and for the "zag" (let us say n), with three repetitions of the same zigzag over one unit cell, as depicted in Fig. 2 (this is formally quite similar to the case of the SiC rhomboedral polytypes). We will label them (m,n), with energy $E_{m,n}$. This notation, although less complete than that proposed by Fisher and Selke to define a spin sequence,[23] is sufficient for describing the *MAX* phase structure. It permits to define both the usual and hybrid phases in a unified way, and offers the advantage of suppressing the ambiguity which may exist when describing a hybrid phase by giving the number of X and A atoms over one zigzag. For instance, a hybrid phase usually defined as 725 can indeed correspond to two different

structures, either 413 for the "zig" and 312 for the "zag," or 514 for the "zig" and 211 for the "zag." With our notation these two structures are clearly differentiated and defined as the (3,2) and (4,1) phases, respectively.

The expressions of energy given below are all derived by applying Eq. (8) to a given *MAX* phase, and obtained after some tedious but in no way heroic bout of algebra. They allow one to describe any usual or hybrid phase as defined above. The different formulas correspond to the MX and MA phases (which are not *MAX* phases in the strict sense), the conventional (2,2) phase (211 with the usual notation), the (m,n) and (n,n) phases with $m,n \geqslant 2$, and the hybrid phases $(n,1)$ with $n \geqslant 2$, respectively:

$$E_{MX} = E_0 + L_1 + L_2 + L_3 + K, \quad (10a)$$

$$E_{MA} = E_0 - L_1 + L_2 + L_3 - K, \quad (10b)$$

$$E_{1,1} = E_0 - L_2 + L_3 = E_{MX} - L_1 - 2L_2 - K, \quad (10c)$$

$$E_{m,n} = E_{MX} - \frac{4}{m+n+2}(L_1 + 2L_2 + 2L_3 + 3K)$$
$$\text{if} \quad m,n \geqslant 2, \quad (10d)$$

$$E_{n,n} = E_{MX} - \frac{2}{n+1}(L_1 + 2L_2 + 2L_3 + 3K) \quad \text{if} \quad n \geqslant 2, \quad (10e)$$

$$E_{n,1} = E_{MX} - \frac{2}{n+3}(2L_1 + 4L_2 + 3L_3 + 4K) \quad \text{if} \quad n \geqslant 2. \quad (10f)$$

Equations (10) represent the central result of this paper. Equation (10c) corresponds to the conventional 211 phase, and Eq. (10e) to all other conventional *MAX* phases. As a verification, it is easily seen that the expression of $E_{m,n}$ converges toward that of E_{MX} as m or n tend to infinity, i.e., as the fraction of A atoms is reduced down to zero. In Eq. (10), it is worth noticing that all energies can be normalized by dividing them by L_1. Besides, MA compounds are usually known for being unstable in front of compounds exhibiting another stoichiometry (e.g., TiSi and TiSi$_2$). This indicates that L_1, which is roughly twice the difference in energy between the MA and MX compounds and thus probably the largest term, is negative. A pseudophase diagram can therefore be plotted on the basis of the three reduced parameters $l_2 = L_2/L_1$, $l_3 = L_3/L_1$, and $k = K/L_1$, and by determining for each set of interaction parameters which phase exhibits the lowest energy. Such a plot is given in Fig. 3 as a function of l_2 and l_3, with k as a parameter, and taking into account all *MAX* phases described by Eq. (10).

Figure 3 can be interpreted easily by noting that the interaction parameters L_1, L_2, L_3, and K have a straightforward physical meaning: (1) $L_1 + K$ is twice the difference in energy between the hypothetical MA and MX compounds, with K being smaller than L_1. (2) A large L_2 value indicates that the difference of interaction energy between identical (MX and MX) and different (MA and MX) neighbor bilayers is high. $L_2 > 0$ means that the binding between the nearest bilayers is enhanced if they are of a different type, and this lowers the overall energy. (3) A large L_3 value means that there is a
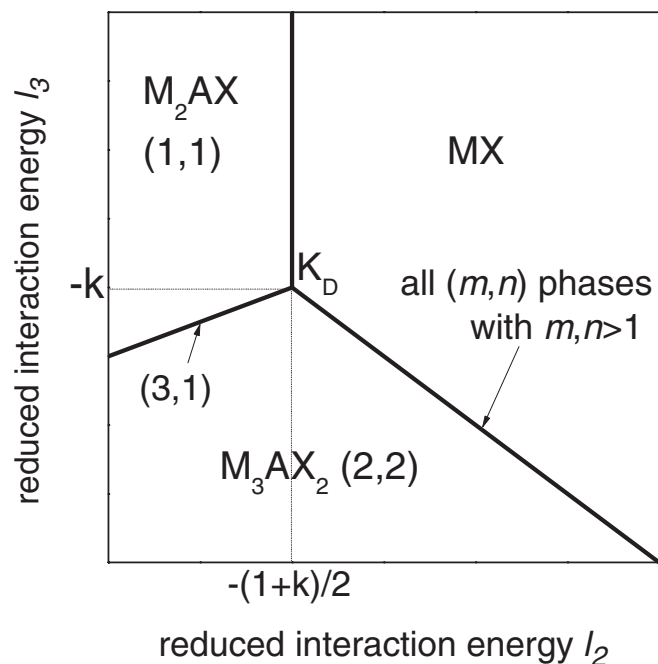
FIG. 3. Pseudophase diagram indicating the *MAX* phases with the lowest energy per atom as a function of the reduced bilayer interaction parameters l_2 and l_3.

large difference in the second-neighbor interactions between bilayers of the same and of a different kind. $L_3 > 0$ means that the interaction between next-nearest bilayers lowers the overall energy if they are of a different type (i.e., $L_3 > 0$ means that second-neighbor interactions favor cohesion).

To give an example, let us have a look at Fig. 3 (note that $L_1 < 0$ implies that if $l_2 = L_2/L_1$ is negative, then L_2 is positive). The domain where M_2AX has a lower energy is located to the left of the domain where MX has the lower energy (i.e., for positive and larger values of L_2). This can be easily explained in terms of a first-neighbor bilayer interaction: Although a MA bilayer has an energy that is higher than a MX bilayer, increasingly good bonding between MA and MX bilayers (i.e., for positive and large values of L_2) makes the insertion of MA bilayers favorable. The domain with M_2AX could not appear to the right of the MX domain. And M_2AX does not appear at the bottom of Fig. 3, even for $L_2 > 0$, because then second-neighbor interactions with $L_3 < 0$ act in a way opposite to that of the first-neighbor ones, and partially compensate them, so that a *MAX* phase with a lower amount of MA layers (M_3AX_2) now has the lowest energy.

It is remarkable that whatever is the value of k, none of the phases with $n \geqslant 3$ exhibit the smallest energy over nonzero areas, as compared to phases with a lower order. However, from Eq. (10), it is obvious that *all* conventional *MAX* phases with $n \geqslant 2$ possess the same energy if the condition $2l_3 + 2l_2 + 3k + 1 = 0$ is verified. This represents a plane in (l_1, l_2, k) space, and for a given k value, a line. It is also obvious that all hybrid phases (m,n) with $m,n \geqslant 2$ belong to the same pseudocoexistence line. The equation of the boundary line between the 211 and 312 phases is $2l_2 - 4l_3 - 3k + 1 = 0$, and the equation of the boundary line between the MX and 211 phases is $2l_2 + k + 1 = 0$. All those lines are defined in Fig. 3.

Besides, whatever is the value of k, there is a single degeneracy point K_D for which *all* phases have the same energy, equal to $(L_1 - K)/2$. The reduced coordinates of this point are

$$\left. \begin{array}{l} l_2 = -\frac{1+k}{2} \\ l_3 = -k \end{array} \right\} \quad \text{at the degeneracy point.} \qquad (11)$$

Concerning hybrid phases such as $(n,1)$, none of them occupy a nonzero area in the phase diagram. The simplest one [(2,1) with our notation] possesses the lowest energy on the pseudocoexistence line between the 211 and 312 phases (i.e., all three phases have the same minimum energy along this line), whereas all others can only be found to be minimum at the degeneracy point K_D.

It follows from these calculations that, depending on the nature of the M and A atoms, which fix the value of the coupling constants, several features can be obtained: If the corresponding point lies far from the degeneracy point and from the two-phase boundary between the 211 and 312 phases, only one phase has an energy lower than that of all others. However, for a set of coupling constants making the point to lie at or close to the two-phase boundary, three phases (211, 312, and 523) should be close to a minimum energy. This implies that all three phases might be obtained, provided that the energy difference between these compounds and their assumed decomposition products remains negative (we discuss that point in Sec. IV). For a point lying at or very close to the highly degenerated point, *all* conceivable phases are close to a minimum value. As discussed in Sec. III, where we take into account some competing phases and discuss stability, the model can predict that some *MAX* systems should exhibit only the (211) phase, some others only the (312) and higher-order phases, and still others all possible *MAX* phases. Here we note that we did not try to incorporate the influence of temperature, which could substantially modify our pseudophase diagram (and sometimes in a very complex manner, as exemplified by previous work on the conventional ANNNI model[22]). However, as simple as our model is, our almost back-to-the-envelope calculations depict a frame which is in agreement with what is actually known from the already observed *MAX* phases. Although first-order interactions should favor the addition of MX rather than MA bilayers (for instance, TiC planes are more tightly bounded than TiSi planes), the introduction of first- and second-order interactions and the absence of more stable competing phases make the apparition of more complex structures energetically favorable, and gives rise to the apparition of the various *MAX* phases. A comparison with observed phases and previous *ab initio* calculations is conducted in the next section.

IV. DISCUSSION AND COMPARISON WITH OBSERVED *MAX* PHASES

A. Energy variation with the amount of A layers per M layer

To identify the interaction parameters of a given family, it is necessary to compute the energy of several phases belonging to a given M-A-X system, and to withdraw from it the energy of the MX phase. We note that due to the form of Eq. (10), (m,n) phases with $m,n \geqslant 2$ are not independent and only one of them can be used. The same is true for the $(n,1)$ phases.

Besides, computing one $E_{m,n}$ value with $m,n \geqslant 2$, one $E_{n,1}$ value with $n \geqslant 2$, and $E_{1,1}$ gives only three equations for four unknowns. It is thus necessary to add the computed value of an additional hypothetical phase such as, e.g., MA to solve the resulting system. We did not find such a set in the literature, but hope that our paper will stimulate future work by research groups involved both in the realm of *MAX* phases and *ab initio* calculations. Nonetheless, and as detailed below, it is still possible to make some comparison between our model and existing theory or experimental data, either to justify some of the model assumptions or to assess the validity of some of its predictions.

From Eq. (10) we can infer that the energy difference between the MX phase and a (m,n) phase is proportional to $2/(m + n + 2)$. It is worth noticing that this factor is nothing more but the amount of A layers per M layer. We thus find that the energy of a (m,n) *MAX* phase with $m,n \geqslant 2$ is proportional to this amount, with an intercept equal to the energy of the MX phase. Cancellation of the slope would give the same energy for all phases, and this corresponds to the degeneracy condition already found in Sec. II. The smaller is the slope, the closer is the considered family from the degeneracy condition, and the easier it should be to obtain a larger number of phases. From Eq. (10e), we expect that by plotting the energy of the MX and of the conventional 312 and 413 phases as a function of the number of A layers per M layers, the three values should be aligned. However, depending on the interaction parameters, the ANNNI model states that the energy of the conventional 211 phase, as given by Eq. (10c), does not necessarily fall on the same line. This is thus a way to compare the predictions of the ANNNI model with first-principles calculations, and to assess to which extent the second-neighbor interactions contribute to the cohesive energy. An interesting reference is the paper by Dahlqvist *et al.*,[36] who computed the energy per atom for the first three *MAX* phases and for a wide number of elements. It is indeed the best reference we found for comparing *ab initio* calculations to our speculative ANNNI model. In Fig. 4 are incorporated the numerical values they obtained for the energy of the MX, 211, 312, and 413 phases of the Ti-Al-N, V-Al-N, Ti-Al-C, and Sc-Al-N families. These values are plotted as a function of the number of A layers per M layer. For the four considered families, linear regression over the first three points (MX, M_4AX_3, and M_3AX_2 compounds) gives regression coefficients of 1, 0.987, 0.996, and 0.998, respectively, and the corresponding points are effectively aligned (see Fig. 4). The slight departures probably come from the overall accuracy of the numerical calculation. In contrast, one can also see that the points corresponding to the 211 phase are not necessarily aligned with the others, even if for one of them (TiAlN) the last three points might be fitted as well by a single line with a regression coefficient close to one (to a lesser extent, the same can be said of the Sc-Al-N system). These data seem therefore to be in agreement with the predictions of the ANNNI model, and support our assumption that second-neighbor bilayer interactions are essential for determining the cohesive energy. However, it must also be noted that, in the same paper, this property does not hold for the Mn-Al-C, Mn-Al-N, Cr-Al-C, and Cr-Al-N systems, which include magnetic atoms, and the Sc-Al-C and V-Al-C systems. For these ternary systems, the energy of the MX compound
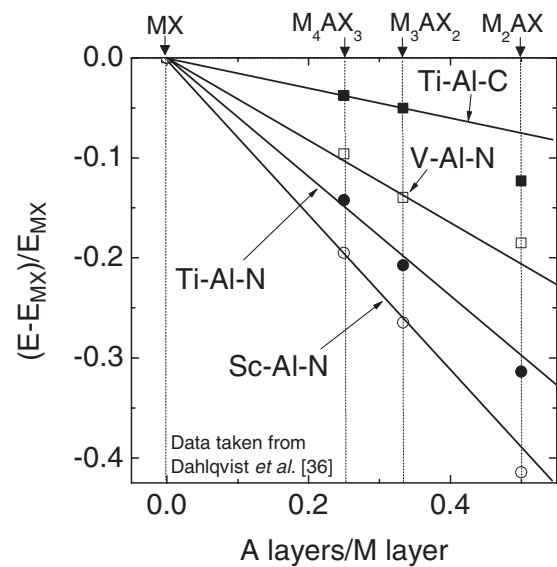

FIG. 4. Energy per atom of the MX, M_2AX, M_3AX_2, and M_4AX_3 phases as a function of the number of A layers per M layer; data points are reproduced from the article by Dahlqvist *et al.* and were computed using DFT calculations (Ref. 36). Energy is referenced to that of the MX phase and normalized; each curve is for a different ternary system. Numerical values were communicated by the authors of Ref. 36.

does not align with that of the M_3AX_2 and M_4AX_3 compounds (numerical values were provided to us by the authors of this reference). Therefore the ANNNI model seems not to be relevant for *MAX* phases including magnetic elements (at least for predicting the energy of the MX phase, even if it might still be relevant to study the energy of the *MAX* phases themselves). We do not know whether this is due to a modification of the magnetic contribution to the energy when one adds the A atoms, or if for such elements the structure of the MX phase is different after relaxation of the atomic positions.

The predicted linear relationship between $E_{m,n}$-E_{MX} and the amount of A layers per M layers with $m,n \geqslant 2$ is also in agreement with the numerical findings of Palmquist *et al.*[33] They performed local density approximation–density functional theory (LDA-DFT) calculations for six *MAX* phases of the Ti-Si-C family, and found that the cohesive energy of all six *MAX* phases was proportional to this ratio, the curve intercept of $E_{m,n}$-E_{TiC} being equal to zero. However, among those six phases are included the 211 and 523 phases. According to our model this means that for the Ti-Si-C system both L_3 and K are small. We should therefore conclude that for this family the structure is dominated by nearest-neighbor interactions between bilayers, whereas second-neighbor interactions are negligible. In our opinion, this is hard to admit as a general property, independent of the ternary system, and it would be important to repeat the same calculations with other ternary systems for two reasons: First, if this property is general (a point which we are not inclined to believe), this would lead to a considerable simplification in modeling (in our case, reducing the *MAX* phase description to the knowledge of two parameters, L_1 and L_2). Second, and as detailed below, such calculations might allow one to answer to the apparent contradiction between this property and the fact that (3,1)

phases were, to the best of our knowledge, never reported in the literature, and most particularly in the case of the Ti-Si-C system. Keast *et al.* have also computed the energy of *MAX* phases for a large number of systems.[37] In their paper, the energy of all systems is almost perfectly linear with the amount of *A* layers per *X* layer. However, the relative numerical departure of the energy of a particular *MAX* phase from a linear relationship is exactly the same, whatever is the ternary system, so that all sets can be deduced from one another by a simple multiplication, which sounds rather strange. Besides, their data seem not to be in agreement with that of Ref. 36.

B. Polytypism

A simple calculation of its energy is obviously not enough to predict if a *MAX* phase is more stable than another: The possible competing phases and their energy must also be known.[33,36] However, the situation changes if one is interested in real polytypism, i.e., if we compare *MAX* phases with the same stoichiometry, so that they exhibit the same $(m + n)$ value. Then our model predicts which polytype is thermodynamically stable (at $T = 0$ K), and this allows us to directly compare hybrid and conventional phases. For $m,n \geqslant 2$ and from Eq. (10), conventional and hybrid phases with the same stoichiometry are equally stable. If one is experimentally obtained, thermodynamics does not prohibit the existence of the other and, more importantly, this holds true even if second-neighbor bilayer interactions are substantial. To find a difference between conventional and hybrid phases with $m,n \geqslant 2$ would require to take into account third-neighbor bilayer interactions. But we note that these additional interactions cannot make a difference between polytypes with $m,n \geqslant 3$, and since the (3,2) *MAX* phase can present polytypism only with the (4,1) phase (which is treated below), it is rather useless to add these interactions. Comparing the energies of a hybrid $(p,1)$ phase to a (n,n) conventional phase with $p = 2n - 1$ (i.e., the same stoichiometry) leads to an energy difference given by

$$E_{n,n} - E_{2n-1,1} = -\frac{1}{n+1}\left(L_3 + 2K\right). \qquad (12)$$

It is worth noting that in some sense, K also includes the way by which second-neighbor interactions are modified by the bilayer inserted in between two next-nearest bilayers. This is the reason why, in Eq. (12), the difference in energy between two polytypic forms, where first-neighbor interactions do not change with polytype, depends only on L_3 and K. It is thus only in the absence of second-neighbor bilayer interactions (negligible L_3 and K), or if by chance $L_3 = -2K$, that both phases should be equally stable. If the sum $L_3 + 2K$ is appreciable, one phase should prevail if its formation is driven by thermodynamics. Most interesting is the case of the 312 phase, which in theory is polytypic, and includes the conventional (2,2) phase and the hypothetical hybrid (3,1) phase (see Fig. 2). The energy difference between these two polytypes exhibits the largest attainable value for a given family, equal to $(L_3 + 2K)/3$. As far as we know, the (3,1) phase has not yet been observed. This would tend to indicate that second-neighbor bilayer interactions do exist and make it unstable with respect to its alternative polytype (the conventional 312 phase). In the case of the Ti-Si-C system,

from the linear relationship between the cohesive energy and the ratio of Si on Ti atoms calculated by Palmquist *et al.*,[33] we deduce vanishing second-neighbor interactions, and thus a negligible energy difference between the (3,1) and (2,2) phases. Therefore, it comes as a surprise that the (3,1) polytype of Ti_3SiC_2, to the best of our knowledge, has never been observed,[2] a fact which is at variance with the prediction that it should be equally stable with the usual form, as deduced from the calculations by Palmquist *et al.*[33] and the ANNNI model. One might infer from these authors' results that Ti_3SiC_2 should be full of stacking faults, or consist of a mixture of (2,2) and (3,1) phases. Since, to the best of our knowledge, (3,1) phases have not been reported for any ternary family, whereas (2,2) phases are quite common, we suspect that second-order neighbor interactions between the bilayers do exist, even for the Ti-Si-C system. It seems highly dubious that among two polytypes with exactly the same energy and not too long a periodic sequence, only one has been observed. We thus hope that our remarks will stimulate both further theoretical and practical work, because these considerations are in partial contradiction with the calculations by Palmqvist *et al.*[33]

The rule used for the model (no zigzag between the *MX* planes and mandatory zigzag for the *A* planes) prohibits its use for estimating stacking fault energies resulting from the glide of a single bilayer in the basal plane. However, it is worth noticing that previous reports about stacking faults in *MAX* phases conclude that these planar defects consist in the addition of a few *MX* bilayers in a given sequence, so that the zigzag rule is not violated.[38–40] This is a good empirical argument in favor of its use. *Ab initio* calculations should confirm that the stacking fault energy of such defects must be high in order to fully justify our ANNNI model. Besides, even if it is rather difficult to define a stacking fault energy when the defect modifies the stoichiometry of the compound, energy considerations can still be conducted by estimating, e.g., the energy required to add a plane differing from the one expected at the top surface during 2D growth.

C. Stability trends

Figure 3 is a pseudophase diagram, because we did not consider the possible competing phases. Therefore it cannot be used to predict stability trends. It is also clear that each different ternary *MAX* system possesses different stable binary compounds in the ternary phase diagram, which make the determination of those competing phases a nontrivial task, and requires proper use of both experimental and theoretical data (for instance, the Ti-Si-C system involves the $TiSi_2$, TiSi, Ti_5Si_4, Ti_3Si, SiC, TiC binary, and $Ti_5Si_3C_x$ ternary compounds[41]). Such considerations are detailed, e.g., in the paper by Dalhqvist *et al.*[36] Besides, our model cannot say anything about the energy of binary compounds but *MA* and *MX*, which are the only ones being located on the same line as all possible *MAX* phases in the ternary phase diagram (see Fig. 5), corresponding to an *M* fraction $x_M = 0.5$. So is it still possible to write something about the *MAX* phase stability using this simple model? As detailed below, the answer is positive, provided that we restrict the analysis to the *MA* and *MX* competing phases. In other words, the model cannot predict if the investigated *MAX* phases
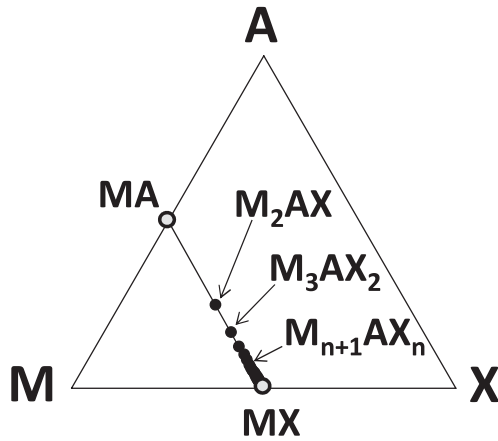
FIG. 5. M-A-X ternary diagram showing the line $x_M = 0.5$ which includes all MAX phases.

are really thermodynamically stable, since this obviously requires an investigation of all possible binary and ternary compounds with a structure different from that of the MAX phases. However, it can predict which phases are necessarily unstable, because their decomposition in the form of MA and MX compounds is energetically favorable. It must be noted that this approach does not require the MA phase to exist in reality, and in general this compound is not stable. But if for some set of interaction parameters a MAX phase is shown to be more unstable than its decomposition into products which are themselves unstable, then it is rigorous to state that this MAX phase must also be unstable. As crude though it is (still reinforced by the fact that we make the temperature $T = 0$ K), this restriction nevertheless allows one to explain why the M_2AX and MAX phases with a higher n index are not equally stable, depending on the value of the coefficients corresponding to the first- and second-neighbor bilayer interactions.

Assuming that the MA and MX phases are intrinsically stable, the possible decomposition schemes of a given (n,n) MAX phase are depicted in Fig. 6. Since the MA phase is in
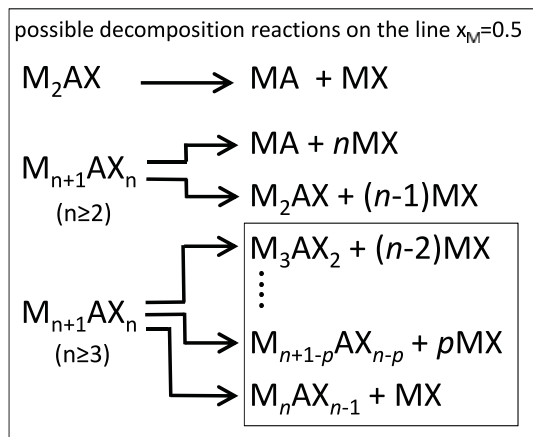

FIG. 6. Possible decomposition reactions of a MAX phase when the reaction products lie on the line $x_M = 0.5$. Note that those reactions are not the ones occurring in practice, because the MA compound is most often unstable (see the comments in Sec. IV C).
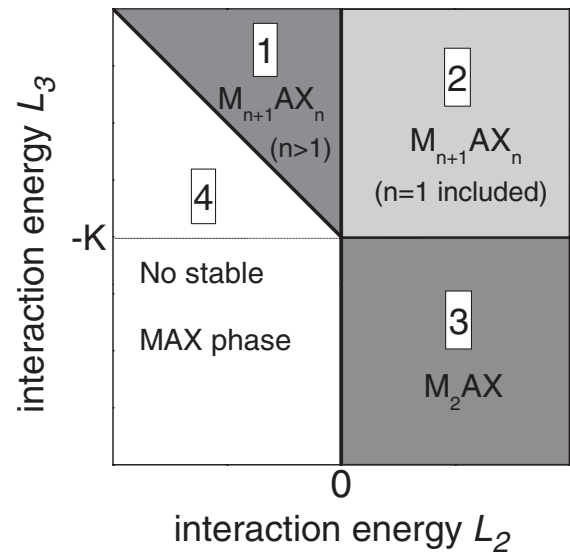

FIG. 7. Potentially stable areas of the MAX phases in the (L_2, L_3) plane, with K as a parameter, as determined from consideration of the hypothetical decomposition into the MA and MX competing phases. When taking into account all competing phases, part of the stable domains would become unstable and the areas defining the unstable domains of a given phase would increase.

general not stable, let us stress once again that these reactions do not happen in practice, because they would be replaced by reactions involving phases not only lying on the line $x_M = 0.5$ and resulting in a still larger variation of energy. For each of those pseudoreactions, we can easily calculate an energy variation from the ANNNI model. As a matter of fact, we must distinguish four different cases. The first is the decomposition of an (n,n) phase $(M_{n+1}AX_n)$ with $n \geqslant p + 2$, p being an integer, giving as a reaction product another MAX phase with index $(n-p, n-p)$. The energy variation is easily found to be equal to zero. The second possibility is the decomposition of an (n,n) phase with $n \geqslant 2$ into the $(1,1)$ (i.e., M_2AX) phase and MX compound, with the corresponding energy variation being

$$\Delta E = \frac{2}{n+1}(L_3 + K).\tag{13}$$

The third corresponds to the decomposition of an (n,n) phase with $n \geqslant 2$ into MA and MX compounds, resulting in an energy variation equal to

$$\Delta E = \frac{4}{n+1}(L_2 + L_3 + K).\tag{14}$$

The last case corresponds to the decomposition of the M_2AX phase into the MA and MX binary compounds, which leads to

$$\Delta E = 2L_2.\tag{15}$$

Stability of the considered MAX phase requires $\Delta E > 0$. From Eqs. (13)–(15) and the relation $\Delta E = 0$ of the first case, it is straightforward to plot the phase diagram of the MAX phases as a function of L_2, L_3, and K, as illustrated by Fig. 7. It is remarkable that none of Eqs. (13)–(15) involve the L_1 parameter, but only interaction energies (L_2, L_3, and K). This

diagram shows that, depending on the particular strength of those interaction energies, one can find ternary systems for which all *MAX* phases are potentially stable, others for which only the (n,n) phases with $n \geqslant 2$ are potentially stable, still others for which only the $(1,1)$ phase is potentially stable, and, finally, systems for which all *MAX* phases are necessarily unstable. It is also interesting to note that even when Eqs. (13) and (14) give positive values, ΔE decreases with n, and thus stability decreases as n increases, making the existence of *MAX* phases with a high index improbable not only because of the difficulty inherent in the reproduction of a complex and long stacking periodic sequence, but also for thermodynamic reasons. We speculate that the Ti-Si-C system, for which both Ti_3SiC_2 and Ti_4SiC_3, but no Ti_2SiC phase have been observed,[2] belongs to domain No. 1 in the phase diagram, that many systems for which only the 211 phase has been observed belong to the third domain (see, e.g., Table 1 in Ref. 2), and that a system such as V-Al-C, for which V_2AlC, V_3AlC_2, and V_4AlC_3 *MAX* phases have all been observed,[2] belongs to domain No. 2 in Fig. 7.

V. CONCLUSION

We have shown that the energy of any *MAX* phase can be estimated by using a particular ANNNI-like model, so that the description of any phase belonging to a given ternary family is reduced to the knowledge of four energy parameters, which characterize the interaction between first- and second-neighbor bilayers. Knowing a particular set, it is possible to assess which phases exhibit the lowest energy. Besides, since their physical meaning is straightforward, their determination from first-principles calculations could be used as a measure of the

extent to which first-neighbor and second-neighbor bilayer interaction contribute to material cohesion. We found that the possibility of real polytypism, which can theoretically happen between conventional and hybrid phases possessing the same stoichiometry, is determined by the strength of second-neighbor interactions between bilayers. The fact that the (3,1) phase, to the best of our knowledge, has never been reported seems to be in favor of the existence of such interactions, and the ANNNI model should therefore help in explaining why hybrid phases remain an exception. This preliminary report is restricted to a temperature $T = 0$ K, and further studies should include the influence of temperature. However, even at this stage, calculation of the interaction parameters corresponding to various *MAX* phases might give a unified view of their behavior and explain possible variations between different ternary systems. Phase stability can be partially discussed: Studying the pseudodecomposition of a *MAX* phase into the *MA* and *MX* compounds suffices to explain why for some *M-A-X* ternary systems the M_2AX phase cannot be stable, why for others it is the only possible stable compound (if there is any), and why for a third class of ternary systems, all $M_{n+1}AX_n$ phases are potentially stable, stability progressively reducing as n increases. The belonging of a given *MAX* system to any of those three families is determined by a set of only three interaction energies between bilayers, which can be numerically computed using, e.g., *ab initio* DFT techniques.

*Thierry.Ouisse@phelma.grenoble-inp.fr

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