A model of cation ordering in A(B’\textsubscript{x}B”\textsubscript{1−x})O\textsubscript{3} relaxors

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Abstract

We have shown that the lattice-gas model with four repulsive pair interaction constants (corresponding to the four nearest coordination shells) on a simple cubic lattice is a sufficient model to describe the main types of cation ordering in relaxors. The phase diagram, obtained by the cluster variation method, shows the sequences of transitions between the phases 1 : 2 → 1 : 1 → disordered and 1 : 2 → disordered.

I. INTRODUCTION

Ferroelectric and piezoelectric properties of so-called relaxors, i. e. some complex mixed-metal perovskites with general chemical formulae A(B’\textsubscript{x}B”\textsubscript{1−x})O\textsubscript{3}, depend on the state of order in the (B’, B”) sublattice [1,2]. It is well-known that such relaxor materials as Pb(B’\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3} (B’=In and Yb) are ferroelectric when disordered and antiferroelectric when ordered [4]. The correlation between the order-disorder tendency of (B’, B”) ions and
the electromechanical \((e/m)\) coupling factor, an important parameter for fabrication of high-quality piezoelectric materials, is also known \([3]\). Thus the compositional ordering in the \((B', B'')\) sublattice might be essential for the different applications in which relaxor materials are nowadays used: the A=Pb-based relaxors are widely used in piezoelectric transducers for mostly medical diagnostic application, in actuators, capacitors, ultrasound and sonar listening devices, and the A=Ba-based relaxors are used in production of dielectric resonators and other high-frequency applications.

Apart from well-known examples, such as BaTiO\(_3\) with occupation of the \((B', B'')\) sublattice exclusively by 4-valent Ti ions \((x = 0)\), there are two other main stoichiometries of this sublattice with \(x = 1/2\) and \(x = 1/3\). While tetravalent \((B', B'')\) ions show no ordering (e.g. Pb\((\text{Zr}_x\text{Ti}_{1-x})\)O\(_3\) \([3]\)), samples made of heterovalent ions, i.e. 3-valent \(B' = \text{In, Sc, Yb}\) and 5-valent \(B'' = \text{Nb, Ta}\) or 2-valent \(B' = \text{Zn, Mg, Ni, Co}\) and 6-valent \(B'' = \text{W, Mo}\), in most cases exhibit long range order below an ordering transition temperature for \(x = 1/2\). The same is true for most of the 2-valent \(B'\) and 5-valent \(B''\) ions at \(x = 1/3\) (for experimental data on ordering types and temperatures see Tables in Refs \([3,7]\)).

Basically, two types of \((B', B'')\) sublattice ordering are found experimentally. For \(x = 1/2\) compounds the 1:1 stacking of \(B'\) and \(B''\) layers perpendicular to the \([111]\) axis of the simple cubic cell is observed in all A=Ba- and Pb-based A\((B'_xB''_{1-x})\)O\(_3\) materials. For \(x = 1/3\) the 1:2 structure with stacking of \(B'\), \(B''\), \(B''\) layers is found in all A=Ba-based relaxors with \(B' = \text{Zn, Mg}\) and \(B'' = \text{Nb, Ta}\). This type of ordering is the ground state for \(x = 1/3\) in a Coulomb-type of \(B'\)-\(B''\) interaction model \([2]\). However the same four materials with Ba fully substituted by Pb in the A sublattice demonstrate either short-range 1:1 ordering (e.g. Pb\((\text{Zn}_{1/3}\text{Nb}_{2/3})\)O\(_3\) (PZN), Pb\((\text{Mg}_{1/3}\text{Nb}_{2/3})\)O\(_3\) (PMN)) or long-range 1:1 ordering (Pb\((\text{Mg}_{1/3}\text{Ta}_{2/3})\)O\(_3\) (PMT)). This structure might be viewed as an alteration of \(B', B''\) sequence along the \([111]\) axis with the \(B''\) site occupied by Ta(Nb) and \(B'\) by a disordered mixture of \(2/3\text{Mg(Zn)} + 1/3\text{Nb(Ta)}\) \([3]\). Especially interesting is the type of \((B', B'')\) ordering observed in so-called relaxor ferroelectric alloys, for example \((1-y)\)Ba\((\text{Zn}_{1/3}\text{Ta}_{2/3})\)O\(_3+y\)BaZrO\(_3\) (BZT-BZ) or \((1 - y)\)Ba\((\text{Mg}_{1/3}\text{Nb}_{2/3})\)O\(_3+y\)BaZrO\(_3\) (BMN-BZ). For small values of \(y < 0.02\)
the 1:2 ordering is observed. At intermediate values (0.04 < \(y\) < 0.25 for BZT-BZ and 0.05 < \(y\) < 0.15 for BMN-BZ) the 1:1 ordering is observed in small microregions in a disordered matrix. At even higher \(y\) disordered structures are observed.

Therefore it is interesting and important to find the appropriate model and from this model obtain the phase diagram (PD) which would account for known experimental facts including the disordered phase at high temperatures and the 1:1 and 1:2 phases at their corresponding stoichiometries. This problem is closely related to the problem of finding a minimal set of interaction constants in an Ising-type model for a simple cubic lattice.

One of the first models, proposed to simulate the images found in HRT EM experiments for PMN, accounted for the nearest neighbor (NN) and next-nearest neighbor (NNN) interactions between (B', B'') ions supplemented by an electrostatic (Coulomb) energy term \(E_{el}\). At \(E_{el} = 0\) this Monte Carlo simulation yields the separation of initial 1:2 system into locally ordered negative 1:1 (\(\text{Pb(Mg}_{1/2}\text{Nb}_{1/2}\text{O}_{3})^{1-}\)) domains surrounded by positive regions of (\(\text{PbNbO}_{3}\))\(^{1+}\). The minimization of electrostatic energy between these domains, realized by the inclusion of \(E_{el}\), leads to much smaller 1:1 regions percolating the lattice. The obtained texture, which gives the superlattice reflections much closer to those seen in experiments, might be interpreted as a vanishing of the two-phase segregation. Another Monte Carlo simulation [2], used the Coulomb interaction as the only type of interaction energy present in an ideal system of ionic charges. The comparison of the results of this model to different types of long-range structures in relaxors with \(x = 1/2\) and \(x = 1/3\) supported very much the viewpoint that the Coulomb interaction between ions might be the driving force of the ordering.

There are also known several studies of the ground states of a simple cubic lattice using the Ising model with just few short-range interaction constants taken into account [3-11]. However, the range of interaction of these models was not sufficient for the occurrence of the ground states found in relaxors, the 1:2 phase in particular. Namely, the number of interaction constants were limited either to those three corresponding to the three main distances of the cube (i.e. NN, NNN and third-nearest neighbor (3NN)) [3,10] or to a very
particular set of NN, NNN and fourth-nearest neighbour (4NN) interactions as well as to the
smallest triangle interaction and linear triplet, but omitting 3NN interaction [11]. Therefore
much more important to the studies of stability of ordered phases in relaxors were the works
of Burton [3] and McCormack and Burton [12] where the stability conditions for the 1:2
phase were investigated in particular. These authors have concluded that using simple pair
interactions in the Ising-type Hamiltonian up to fourth-nearest neighbors is not sufficient
to obtain the experimentally observed superstructures as ground states. They obtained the
PD with phase transition sequences 1 : 2 → 1 : 1 → disordered and 1 : 2 → disordered
using many-body interactions such as linear triplet and, so-called, cube-222. However the
values of these interaction constants, chosen [3] for the calculation of the PD, cannot be
reconciled with the relative energies for several of the most probable phases obtained from
first-principles calculation by the same authors [12].

In this work we present the PD of a lattice-gas model with four repulsive pair interaction
constants (NN, NNN, 3NN and 4NN) taken into account in a simple cubic lattice. Our calcu-
lations, performed by the cluster variation method (CVM), show that this model is sufficient
to explain the main ordering features of relaxors, and that no multi-point interactions are
really necessary.

II. MODEL AND PHASE DIAGRAMS

We consider a lattice-gas model which is described by the Hamiltonian

$$\mathcal{H} = \sum_{i<j} v_{ij} n_i n_j - \mu \sum_i n_i, \quad (1)$$

where $n_i = 1$ when the site is occupied by the atom $B'$ and 0 when it is occupied by $B''$.
It can be shown [13] that the effective interaction constant $v_{ij} = v_{ij}^{BB'} + v_{ij}^{BB''} - 2v_{ij}^{B'B''}$,
where $v_{ij}^{MN}$ is the interaction energy between the atoms $M$ and $N$, and $\mu = \mu_B' - \mu_B'' + $ $v_{i}^{BB'} - v_{ij}^{BB''} (v_{ij}^{MN} = \sum_i v_{ij}^{MN})$ is the chemical potential of the system expressed via the
chemical potentials of the different cations. The lattice gas model can be mapped to the
more common Ising model in an external field via the relation between \( n_i \) and the Ising spin variables \( s_i = \pm 1, s_i = 2n_i - 1 \), which implies the simple relation \( v_{ij} = 4J_{ij} \) between the Ising interaction constants \( J_{ij} \) and \( v_{ij} \).

We are going to show that repulsive pair interactions in the four nearest coordination shells are sufficient to describe the experimentally observed 1:1 and 1:2 phases and the phase transitions between these phases. This statement contradicts earlier ground-state analysis [12], thus the Appendix is devoted to show that our approach is justified. Here we just want to give a simple indirect argument supporting our choice.

According to the ground-state analysis [10] for repulsive \( v_1, v_2, v_3 > 0, v_4 = 0 \) and the case \( v_3 < v_2/2, v_2 < v_1/4 + v_3 \), four ordered ground-states take place at \( x = \langle n_i \rangle = 1/2, 3/8, 1/4 \) and 1/8. The ground-state structure is \( S(0, 6, 0; \frac{1}{2}) \) or 1:1 at \( x = 1/2 \), \( S(0, 4, 0, \frac{3}{8}) \) (hereafter labelled as 3/8) at \( x = 3/8 \), \( S(0, 0, 4, \frac{1}{4}) \) (1/4) at \( x = 1/4 \) and \( S(0, 0, 0, \frac{1}{8}) \) (1/8) at \( x = 1/8 \). The structure notations here, \( S(p_1, p_2, p_3; x) \), are taken from Ref [10], and \( p_i \) means the number of B'-B' bonds per B' atom in the \( i \)-th coordination shell of the B"-B' \( 1-x \) structure (\( i=1, 2, 3 \) corresponds to NN, NNN and 3NN respectively). The phases are shown schematically in Fig 1. The 1/4 phase is bcc with a size of a new unit cell \( a = 2a_0 \), the 1/8 phase is sc with \( a = 2a_0 \), and the 3/8 phase could be regarded as 1:1 phase with substracted 1/8 structure (atoms are removed from the sites which are part of \( a = 2a_0 \) cubic structure). Here \( a_0 \) is the lattice parameter of the initial sc unit cell. The ground-state at \( x = 1/3 \) (the stoichiometric value for the 1:2 structure) is a mixture of 1/4 and 3/8 structures taken with proper weights. One can easily check that for \( v_4 = 0 \) the energy of the 1:2 structure at \( x = 1/3 \) is exactly the same as that of the mixture, i.e. the 1:2 phase is just marginally unstable. By introducing an arbitrarily small \( v_4 > 0 \) one can make the 1:2 structure stable albeit only at very low temperatures. This is because the energy of the mixture increases with \( v_4 \), but the energy of the 1:2 phase is independent of \( v_4 \).

When choosing the empiric values of the interaction constants we assume \( v_1 = 1 \), since the negative value would cause decomposition rather than ordering and the absolute value just gives the energy scale which can always be adjusted to the experiment. It would be
interesting to explore all possible situations in the remaining three-dimensional space of $v_2$, $v_3$, and $v_4$ for which the ground state is the 1:2 structure at $x = 1/3$. This is too ambitious however, since not much is known about the PDs for the simple cubic lattice even for $v_4 = 0$. Thus to simplify our task, we base our choice on the results of Ref. [2], that the interactions might be of electrostatic nature (similar atoms tend to repel each other) and take all $v_i$ to be positive.

The calculations of the PDs have been performed using the CVM [14], a powerful variational method to treat phase transition problems. In this method the local interactions between a particular group of spins (cluster) are exactly taken into account. The interaction of the cluster spins with those being outside the cluster are accounted for by the, so-called, effective fields which are the variational parameters in the version [15] of the CVM used here. The PD for $v_2 = 0.2, v_3 = 0.06$ and $v_4 = 0$ obtained using the 8+7-point (cube + octahedron) approximation of the CVM is presented in Fig. 2. The values of interactions were chosen to obtain the 1:1 phase down to $x < 1/3$ at intermediate temperatures (which are below the maximum of the 1:1 phase at $x = 1/3$, but above all other ordered phases). This PD could describe those A(B’$_{1/3}$B”$_{2/3}$)O$_3$ materials, which do not exhibit 1:2 ordering, but the ground state in this case would be a mixture of 1/4 and 3/8 phases. By setting $v_2 = v_3 = 0$ we could make other structures disappear arriving at the classical antiferromagnetic Ising result with only 1:1 ordering. As was already mentioned, there is no 1:2 phase in this PD, since at $x = 1/3$ the energy of the 1:2 structure is equal to that of the proportional mixture of 1/4 and 3/8 phases.

For $v_4 > 0$ the 1:2 phase becomes energetically favourable with respect to the mixture of neighboring phases. The higher $v_4$, the higher temperatures the 1:2 phase would reach. Other consequences of $v_4 > 0$ on the PD are as follows. First, the domain of the 1:1 phase at intermediate temperatures should shrink at higher $x$, since the inclusion of $v_4$ increases the energy of the 1:1 phase. Second, the degeneracy of the 1/8 and 3/8 phases is removed at $v_4 > 0$ (at $v_4 = 0$ any [100] or equivalent plane of the 1/8 phase can be moved along any vector in that plane and the depleted [100] planes of the 3/8 phase can be moved along $v_2$ in
that plane without change of energy). Actually, for small $v_4 > 0$ the ground state at $x = 3/8$ is a new 3/8 phase (3/8’), which is obtained from the “original” 3/8 phase by shifting every second depleted [100] plane along the (011) direction (see Fig.[4]). Also at $x = 1/8$ the ground state for $v_4 > 0$ is different from the “original” 1/8 phase (we do not examine this phase as it has no relevance to the vicinity of $x = 1/3$). Third, a number of ordered structures with longer period should appear below $x = 1/8$ and above $x = 3/8$, which we also do not consider here. For small $v_4 > 0$, the transition from 1:2 to 3/8’ phase takes place between $x = 1/3$ and $x = 3/8$. Another transition from 1/4 to 1:2 occurs between $x = 1/4$ and $x = 1/3$. The PD for $v_2 = 0.2, v_3 = 0.06$ and $v_4 = 0.02$ is presented in Fig.[3]. The PD is not complete as the phases to the left of the 1/4 phase and to the right of the 3/8’ phase are not considered. We obtain a rather narrow 1:2 phase in $(T, x)$ coordinates. Meanwhile in the $(T, \mu)$ diagram, there is quite a large domain of chemical potential corresponding to the 1:2 structure. It should be also noted that for $v_4 = 0.02$ we could not obtain the 3/8’ phase by the CVM, since the mixture of the 1:2 and off-stoichiometric 1:1 phase has lower energy. We calculated the high-temperature metastability limit of the 3/8’ phase by Monte Carlo simulations only (see Fig.[3b]). Still we can conclude that if the 3/8’ phase exists, it exists only below $T \approx 0.08$.

For $2.01 < \mu < 2.06$ and $0.13 < T < 0.25$ the 8+7 - point approximation of the CVM has unexpectedly shown some instability resulting in the gap on the phase boundary between 1:1 and 1:2 phases and the strange reentrance of the second order transition line between disordered and 1:1 phase. It is interesting to note, that reducing the variational space of the CVM by omitting all the correlations with more than two sites, the problems related to the second order phase transition line disordered - 1:1 disappear (dotted line in Fig.[4]), but those related to the transition 1:1 - 1:2 become worse. Such a behavior of the 8+7 - point approximation is clearly related to the increased range of interactions which can not be properly accommodated within the cube and octahedron clusters. It seems that these problems appear at any $v_4 > 0$ (we checked the values between 0.01 and 0.04, also slightly varying $v_2$ and $v_3$). At $v_4 = 0$ we had no similar problems with the
8+7-point approximation. To be sure, we have performed calculations with a 27-point
(2a₀ × 2a₀ × 2a₀ cube) approximation of the CVM. Besides the increase of accuracy due to
larger basic cluster (a general feature of the CVM), the 27-point cluster has an advantage
of including all interactions into single basic cluster, thus avoiding occasional breakdowns,
sometimes observed when basic clusters are too small. Unfortunately, the minimisation of
the free energy then becomes more complicated, since the number of variational parameters
drastically increases. Since it is not feasible to treat all 2^{27} \approx 134 \text{ mln configurations of the}
27-point cluster, we excluded the possibility for the NN sites to be occupied (v₁ = \infty).
This NN exclusion makes a big difference at high temperatures, as the 1:1 phase is always
present above some critical concentration. However we expect only small changes at low
temperatures, where 1:2 and the rest of ordered phases exist, since due to v₁ \gg T the
probability of the NN being occupied is very low, especially for small concentrations. The
NN exclusion decreases the number of configurations of the 27-point cluster down to 70663,
which is tractable with some effort. The results of the 27-point CVM are presented by
dashed lines in Figs. 2 and 3. Indeed, while there are large discrepancies between the results
obtained by the 8+7- and 27-point approximations at higher temperatures due to the
exclusion, at low temperatures the lines are pretty close. It is rather difficult to compare
accuracies of the two approximations, since formally they describe different models. The
27-point approximation does not suffer from the problems of the 8+7-point one and
confirms its results by filling the gap in the PD. To be sure, we have also applied the NN
exclusion to the 8+7-point approximation (to check whether the exclusion itself could hide
the problems with the CVM), but the problems remained.

To support our CVM calculations, we have performed some limited Monte Carlo simula-
tions using a simple Metropolis algorithm on a 24 × 24 × 24 lattice with periodic boundary
conditions and around 50000 sweeps for each point. These points are plotted in Fig.3 with
circles. First-order transitions are difficult to locate accurately by the Monte Carlo method,
so the points on the first-order phase transition lines are actually metastability limits of the
corresponding low-temperature phase, a true phase transition should be slightly below. It
is much easier to find metastability limits, if one starts from a perfectly ordered structure at low temperatures and gradually increases the temperature until the order changes or is destroyed. We show in Fig.4 that the metastability limits obtained by the CVM and Monte Carlo calculations are quite close, thus we expect the location of the true first-order phase transition to be correct too. It is seen that these results nicely confirms our CVM data.

In summary, a lattice gas model for a simple cubic lattice with four nearest repulsive pair interaction constants was proposed. The presented PD possesses all features of cations ordering observed in relaxor compounds, namely, a phase transition sequence 1 : 2 → 1 : 1 → disordered at $x = 1/3$. The increase of $v_4$ from 0.02 to 0.03 shifts the phase boundary between disordered and 1:1 phases to the region $x > 1/3$, thus resulting at $x = 1/3$ in a phase transition 1 : 2 → disordered, which was also observed in a number of relaxor materials. Another interesting feature of the PD is that a pure 1:2 phase reaches its stoichiometric concentration only at $T = 0$, while at any finite temperature it separates into a mixture of the 1:2 phase with a slightly lower concentration and a small amount of adjacent phase (e.g. 1:1). This indicates that a slightest increase in concentration above stoichiometric value tends to destroy the 1:2 ordering, making it favorable for the excess ions to form islands of another higher concentration phases. Could this be an explanation of the nanoregions, which are observed in some A(B’$^{1/3}$B’’$^{2/3}$)O$_3$ compounds and, most likely, are responsible for the relaxor properties, besides the electrostatic arguments?

This work was supported by The Swedish Academy of Sciences, The Swedish Institute, The Swedish Natural Research Council and SSF (Swedish Foundation for Strategic Research). SL is indebted to The Royal Institute of Technology, Stockholm for kind hospitality.

**APPENDIX A:**

Here we apply the partial vertex enumeration (PVE) procedure for interaction clusters to our four two-point clusters corresponding to NN, NNN, 3NN and 4NN pairs. The
PVE technique for the ground state problem is based up on the more general vertex enumeration of the configuration polyhedron method [13]. It is easier described in terms of the Ising model and the outline is as follows. Consider a cluster $\alpha$ of $|\alpha|$ lattice sites which includes all interactions of the Hamiltonian. It is shown [13] that the probability function $\rho_\alpha(\{s\})$ for the configuration $\{s\}$ (the set of Ising spins $s_i$ at every site $i$) of the cluster $\alpha$ is a linear function of the spin products $s_\beta = \prod_{i \in \beta} s_i$ of all subclusters $\beta$ of the cluster

$$\rho_\alpha = \frac{1}{2^{|\alpha|}} (1 + \sum_{\beta \subset \alpha, \beta \neq \emptyset} \nu_\beta s_\beta),$$

where $\nu_\beta = \langle s_\beta \rangle$ are cluster correlation functions. The requirement $0 \leq \rho \leq 1$ imposes constraints for the allowed values of $\nu_\beta$, and equations

$$\rho_\alpha(\{s\}) = 0$$

(A2)

for each symmetry distinct configuration $\{s\}$ define hyperplanes in the space spanned by $\nu_\beta$. These hyperplanes are boundaries in a space of allowed values of $\nu_\beta$ which is a configurational polyhedron (CP). The possible ground states of the model reside in the vertices of the CP, because the energy is a linear function of $\nu_\beta$, and the extremum of the linear function is reached on the boundary of its domain of definition. Since not all $\nu_\beta$ necessarily contribute to the energy $E = \langle H \rangle$, one needs to project the CP on the subspace of those $\nu_\beta$, which contribute to the energy.

However it may be impractical to make a full vertex enumeration for large clusters, when interactions beyond the 3NN are considered. Therefore the PVE is used (see Ref [12]) to determine whether in the space of $\nu_\beta(\beta \subset \alpha)$ included in a certain cluster $\alpha$ (or several clusters), the point, corresponding to the given structure, is a vertex of the CP. It is a vertex if the number of faces it belongs to is not less than the dimensionality of the space (number of distinct $\nu_\beta$). Then for a given (periodic) structure one obtains values of $\nu_\beta$ by averaging over the unit cell of the structure, and checks how many equations (A2) are satisfied by these values. It is found [12] that at least some many-body interactions in the cube and a linear triplet are necessary for the 1:2 phase to be a vertex.
Consider PVE for our four pair clusters ($\alpha = 1, 2, 3, 4$). The configuration probabilities for each cluster are 
\[ \rho_\alpha = \frac{1}{4}[1 + m(s_i + s_j) + r_\alpha s_i s_j], \]
or
\[ \rho_\alpha(\pm\pm) = \frac{1}{4}(1 \pm 2m + r_\alpha) \geq 0, \quad \rho_\alpha(+-) = \rho_\alpha(-+) = \frac{1}{4}(1 - r_\alpha) \geq 0. \tag{A3} \]

Here $m = \langle s_i \rangle$ is a magnetization, $r_\alpha = \langle s_i s_j \rangle_{i,j \in \alpha}$ is a pair-correlation function of the cluster $\alpha$, and these five parameters span a 5-dimensional space. For the $1:2$ structure $m = r_1 = r_4 = -1/3, r_2 = 1/3, r_3 = 0$, and two configuration probabilities are zero, namely $\rho_1(++)$ and $\rho_4(++)$. This accounts for 2 faces of the 5-dimensional space. If there are no other constraints on the $m, r_\alpha (\alpha = 1, \ldots, 4)$, the structure cannot be a vertex. But there are other constraints. The point is, that $\rho \geq 0$ are sufficient conditions only if all $\nu_\beta$ are defined on the same cluster. This is not the case here and neither it was in Ref [12]. There are in general additional relations between the probabilities for configurations defined on different clusters, since one can imagine these clusters being parts of a single larger cluster.

Let’s take a simple example. Consider the 4NN pair ($\alpha = 4$) and mark its sites with $(+)$ if $s_i = +1$, $(-)$ if $s_i = -1$, and $\cdot$ for the site in the middle (to make it different from the NN pair). Also consider for a moment a linear triplet which contains a 4NN pair and two NN pairs. Since $\rho(s_i, s_j) = \sum_{s_k = \pm 1} \rho(s_i, s_j, s_k)$ and all probabilities are non-negative, it is obvious that $\rho(+-) = \rho(+-) + \rho(--) \leq \rho(++) + \rho(---)$, which using (A3) gives a relation
\[ 1 - r_4 \leq 2 + 2r_1. \tag{A4} \]

This relation defines a new constraint and a new hyperplane, which is not equivalent to any of the constraints in (A3). It is not that simple to obtain all the constraints. In general one has to consider clusters large enough to contain all the interaction clusters (e.g. a double-cube), then to project the resulting CP on the space of $m, r_\alpha (\alpha = 1, \ldots, 4)$, and see if the vertex corresponding to the desired structure survives. Fortunately, here we can use the result [12] that the cube+4NN pair interaction cluster is missing one constraint for the 1:2 phase to be a vertex. Since the constraint (A4), which is not equivalent to those already
considered in Ref. [12], applies here also, and the corresponding hyperplane includes the 1:2 phase, we conclude that the 1:2 structure is a possible ground state.
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FIGURES

FIG. 1. Schematic view of ordered phases mentioned in the text. The structures are projected onto the (001) plane. Open circles indicate a sequence of B” atoms along the [001] direction. Half-filled black-white (white-black) circles represent B’, B” (B”, B’) atoms alternating along the [001] direction.

FIG. 2. Phase diagrams ($T, x$) (a) and ($T, \mu$) (b) obtained by the CVM with the interaction constants $v_2 = 0.2$, $v_3 = 0.06$ and $v_4 = 0$. Solid line - 8+7 - point approximation ($v_1 = 1$), dashed line – 27-point approximation ($v_1 = \infty$). The two-phase regions, marked by numbers are: 1 - disordered+1/4 and 2 - 1:1+3/8.

FIG. 3. Phase ($T, x$) (a) and ($T, \mu$) (b) diagrams obtained by the CVM with the interaction constants $v_2 = 0.2$, $v_3 = 0.06$, and $v_4 = 0.02$. Solid and dashed lines - same as in Fig.2, dotted line – 8+7-point approximation with the variational space, reduced to one- and two-point correlation functions only. Monte Carlo results are shown by circles. Phases to the right of the 3/8’ phase and to the left of the 1/4 phase are not shown. The two-phase regions, marked by numbers are: 1 - disordered+1/4 and 2 - disordered+1:2.

FIG. 4. The metastability limits of 2:1 and 1:1 phases at $\mu = 2.1$ obtained with the CVM (solid lines) and Monte Carlo calculations (circles). The energy $E = \langle H \rangle$ per site is presented for $v_2 = 0.2$, $v_3 = 0.06$, and $v_4 = 0.02$. The dashed lines are CVM free-energies which intersect at the first-order phase transitions (pointed to by an arrow).
$v_2 = 0.2, v_3 = 0.06, v_4 = 0$

(a) Disordered

$T$ vs $x$

- $1/8$
- $1/4$
- $1/4 + 1:1$
- $1/4 + 3/8$
- $3/8$
- $1:1$
$v_2 = 0.2$, $v_3 = 0.06$, $v_4 = 0$

Disordered
\( v_2 = 0.2, v_3 = 0.06, v_4 = 0.02 \)

Disordered

(a)
$v_2 = 0.2$, $v_3 = 0.06$, $v_4 = 0.02$
