Empirical cluster expansion models of cation order-disorder in $A(B'_{1/3},B''_{2/3})O_3$ perovskites

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Minimal cluster expansion models of *B*-site cation ordering in $A(B'_{1/3},B''_{2/3})O_3$ perovskites are evaluated. It is demonstrated that the linear triplet interaction is both necessary and sufficient to stabilize the $P\bar{3}m1$ 1:2 structure ground state that is observed in such compounds as $Ba(Zn_{1/3},Nb_{2/3})O_3$ and $Ba(Zn_{1/3},Ta_{2/3})O_3$. The linear triplet model exhibits a $P\bar{3}m1 \rightarrow Pm\bar{3}m$ transition at $kT_C/[-J_{(\bullet-\bullet-\bullet)}]=4.5184$. The addition of a nearest-neighbor pair interaction permits the transition sequence $P\bar{3}m1 \rightarrow Fm\bar{3}m1{:}1$ structure$\rightarrow Pm\bar{3}m$, which is observed in $Ca(Ca_{1/3},Nb_{2/3})O_3$, but not in a region of parameter space in which the lowest-energy ground state of the $AB'_xO_3-AB''_{1-x}O_3$ pseudobinary occurs at the $A(B'_{1/3},B''_{2/3})O_3$ composition. This latter condition can be satisfied by including a second many-body interaction, specifically, a cube minus the triangle of three second-neighbor pairs. Monte Carlo simulations with such a model generate microstructures of the type that are observed in $Pb(Zn_{1/3},Nb_{2/3})O_3$ and $Pb(Mg_{1/3},Nb_{2/3})O_3$. [S0163-1829(99)02509-6]

I. INTRODUCTION

Several $A(B'_{1/3},B''_{2/3})O_3$ perovskites, particularly those with Ba as the *A* cation (Table I), have the $P\bar{3}m1$ 1:2 structure[1] as their apparent ground state (g.s.). This structure is characterized by a 1:2 stacking modulation of $B'=B'^{(2+)}$ and $B''=B''^{(5+)}$ layers perpendicular to the $[111]_{cubic}$ vector of the $Pm\bar{3}m$ disordered (DIS) perovskite. Electrostatic calculations by Bellaiche and Vanderbilt[2] predict that the 1:2 structure is the natural g.s. for an idealized ionic model of an $A(B'_{1/3},B''_{2/3})O_3$ perovskite; i.e., for a 1:2 mixture of $(2-)$ and $(1+)$ point charges on a simple cubic $12\times12\times12$ supercell of *B* sites. They also considered alloying with neutral particles, and demonstrated that 10–50% neutral sites stabilize 1:1 ordering at low temperature. $A(B'_{1/3},B''_{2/3})O_3$ perovskites with Pb as the *A* cation, e.g., $Pb(Mg_{1/3},Nb_{2/3})O_3$ (PMN) (Refs. 3–6) and $Pb(Zn_{1/3},Nb_{2/3})O_3$ (PZN),[7] are typically described as having 1:1 ordered microregions, 2–5 nm,[8] in a disordered matrix. *Ideally*, the 1:1 structure is an $Fm\bar{3}m$ NaCl type ($a_{1:1}\sim2a_0$) in which one *B* site is occupied by Nb (Ta) while the other contains a disordered mixture of 2/3 Mg(Zn)+1/3 Nb (Ta). This structure has significant configurational entropy, which precludes it as a g.s. Therefore, the logical inference is that PZN and PMN fail to transform to their respective g.s.'s because of unfavorable kinetics. It should also be noted that

TABLE I. Data on order-disorder transitions in $A(B',B'')O_3$ perovskites.

System	Structure, $x-$, T range	Ref.
$Ca(Ca_{1/3},Nb_{2/3})O_3$	1:2$\rightleftharpoons$1:1	10,11
	$1300<T_C<1425$ °C	
$Ba(Ni_{1/3},Nb_{2/3})O_3$	1:2 $\rightleftharpoons$ disordered	12
	$1350<T_C<1400$ °C	
$Ba(Zn_{1/3},Nb_{2/3})O_3$	1:2 $\rightleftharpoons$ disordered	13
	$1350<T_C<1400$ °C	
$Ba(Co_{1/3},Nb_{2/3})O_3$	1:2 $\rightleftharpoons$ disordered	13
	$T_C \approx 1500$ °C	
$Ba(Mg_{1/3},Ta_{2/3})O_3$	1:2 $\rightleftharpoons$ disordered	14,15
	$T_C \approx 1655$ °C	
$(1-x)Ba(Zn_{1/3},Ta_{2/3})O_3$-$(x)BaZrO_3$	1:2, $0<x<0.02$, $T=1425$ °C	16
	1:1, $0.04<x<0.25$	
	DIS, $0.25<x$	
$(1-x)Ba(Mg_{1/3},Nb_{2/3})O_3-(x)BaZrO_3$	1:2, $0<x<0.02$, $T=1350$ °C	17
	1:1, $0.05<x<0.15$	
	DIS, $0.15<x$	
$Ba_{1-x},La_x(Zn_{(1+x)/3},Ta_{(2-x)/3})O_3$	1:2, $0<x<0.02$, $T=1500$ °C	18
	1:1, $0.02<x<0.20$	
$Ba_{1-x},K_x(Zn_{(1-x)/3},Ta_{(2+x)/3})O_3$	1:2, $0<x\leqslant0.10$, $T=1500$ °C	18

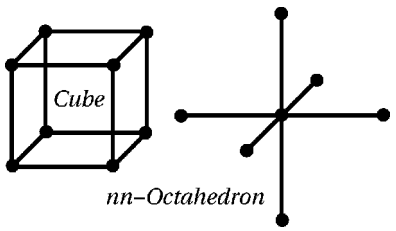

FIG. 1. The unit cube and the nn octahedron clusters.

pseudopotential calculations by Wensell and Krakauer[9] predict that the g.s. of $Pb(Zn_{1/3},Nb_{2/3})O_3$ is not 1:2, but rather the ''six-triangle'' structure, an $Imm2$ 30-atom cell in which there is a stacking sequence of $(111)_{cubic}$ planes of the form β',β'' where β' is $[Zn_{2/3},Nb_{1/3}]$ and β'' is [Nb]. Although the six-triangle structure may be the true g.s. of PZN, this has not been demonstrated experimentally, whereas the full 1:2 g.s.$\rightarrow$1:1$\rightarrow$DIS transition sequence is actually observed in $Ca(Ca_{1/3},Nb_{2/3})O_3$ (CCN). Therefore, the working hypothesis adopted here is that CCN is the prototype system, and 1:2 is the presumed g.s. As indicated in Table I, 1:2 perovskites may transform to 1:1 structure phases in response to *either* an increase in temperature, *or* alloying with a very small amount ($\sim$2%) of a (4+) ion such as $Zr^{(4+)}$.

The experimental data compiled in Table I indicate a close competition between 1:2 and 1:1 phases in $A(B'_{1/3},B''_{2/3})O_3$ perovskites, and suggest the following three constraints for a *sufficient* model for order-disorder phenomena in these materials: (1) yield, or at least permit, the correct g.s. (presumably 1:2), (2) permit the transition sequences 1:2 g.s.$\rightarrow$1:1$\rightarrow$DIS and 1:2 g.s.$\rightarrow$DIS, and (3) have its lowest g.s. at the $x=1/3$ composition in the $AB'_xO_3-AB''_{1-x}O_3$ pseudobinary.

Constraint (3) obtains because $x=1/3$ is the only composition at which all ions may have their normal valences (A^{2+}, $B'^{(2+)}$, $B''^{(5+)}$, O^{2-}) and the only composition at which compounds form experimentally. Also, this *appropriate g.s. hierarchy* ($\Delta E_{(1:1)}>\Delta E_{(1:2)}=$minimum) for the $AB'_xO_3-AB''_{1-x}O_3$ pseudobinary is supported by first-principles calculations.[19] None of the previous statistical models of order-disorder phenomena in PMN (Refs. 20 and 21) satisfy all three conditions. The purpose of this paper is to identify a minimal Ising-type model that is sufficient to treat order-disorder phenomena in these systems and to demonstrate that such a model produces microstructures of the type observed in $Pb(Mg_{1/3},Nb_{2/3})O_3$.[8]

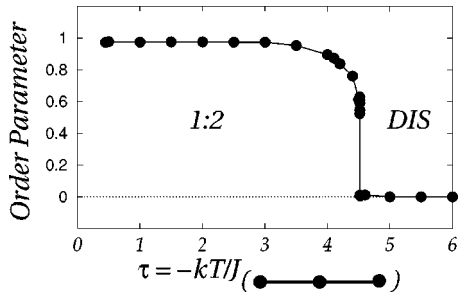

FIG. 2. Phase diagram for the linear triplet model at $x=1/3$.

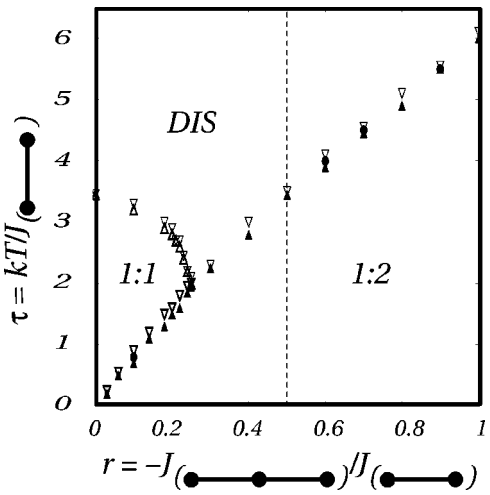

FIG. 3. Phase diagram for the {nn pair + linear triplet} model at $x=1/3$. Triangles bracket phase boundaries: solid triangles are 1:2 phase, open triangles are 1:1 or disordered phase. Solid circles indicate two-phase coexistence associated with the strongly first-order 1:2$\rightleftharpoons$DIS and 1:2$\rightleftharpoons$1:1 transitions. Right of the dashed line at $r=1/2\Delta E(1:2)_{x=1/3}<\Delta E(1:1)_{x=1/2}$, which is the appropriate g.s. hierarchy for $A(B'_{1/3},B''_{2/3})O_3$ perovskites.

II. SIMPLE ISING MODELS

The cluster expansion Hamiltonian is of the form

$$E=\sum_{\alpha} m_\alpha \xi_\alpha J_\alpha ,$$

where E is total enetgy, α indexes all clusters in the expansion, m_α are the multiplicities of clusters α in a simple cubic lattice, ξ_α are site and multisite correlation functions, and J_α are effective cluster interactions [ECI's (Ref. 22)].

In a previous discussion[23] of the simple cubic g.s. problem[23–27] it was reported that a sufficient Ising Hamiltonian could be obtained by including the ECI's contained within the unit cube plus the linear triplet. It was noted, however, that some *undetermined* subset of the 22 ECI's in the cube plus linear triplet set might be sufficient. Ground-state analyses for each of the 33 ECI's in the unit cube plus the centered-octahedron [nn (nearest-neighbor) octahedron, Fig. 1] demonstrate that further simplification is possible. Specifically, the linear triplet alone is sufficient to stabilize the 1:2 g.s.

A. Linear triplet model

Within the {cube+nn octahedron} ECI set, only the linear triplet interaction $J_{(\bullet-\bullet-\bullet)}$ is both necessary and sufficient to stabilize the 1:2 g.s.; i.e., only $J_{(\bullet-\bullet-\bullet)}$ yields a 1:2 g.s. at $x=1/3$. The finite-temperature behavior of the linear triplet model (Fig. 2) was determined by Monte Carlo (MC) simulations[28] performed on a $30\times30\times30$ simple cubic

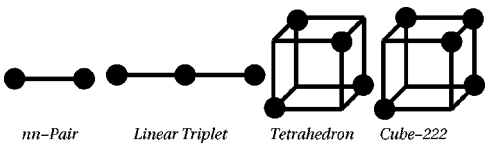

FIG. 4. The nn pair, linear triplet, tetrahedron, and cube-222 clusters.

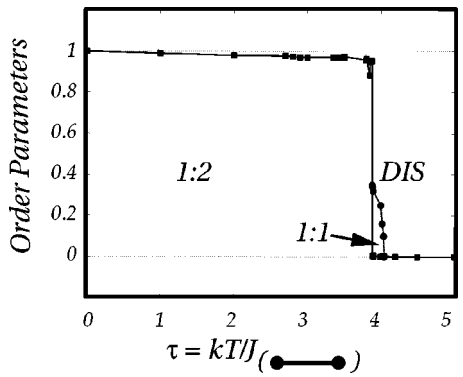

FIG. 5. Phase diagram at $x=1/3$ for the {nn pair + linear triplet + cube-222} model.

array of sites, in a canonical ensemble, via pairwise distant-neighbor exchange (ions closer than five lattice spacings were not exchanged). At least 5000 iterations were performed at a given temperature before the calculations were considered to have converged. The linear triplet model yields a first-order 1:2 g.s.$\rightarrow$ DIS transition at $4.5183< -kT_c/[J_{(\bullet-\bullet-\bullet)}]<4.5185$.

B. *nn* pair + linear triplet model

Obviously, the simplest Hamiltonian that will yield a 1:2 g.s.$\rightarrow$1:1$\rightarrow$ DIS transition sequence must combine $J_{(\bullet-\bullet-\bullet)}$ with another ECI that stabilizes the 1:1 phase at $x=1/3$, e.g., the {*nn* pair + linear triplet} model, $\{J_{(\bullet-\bullet)}+J_{(\bullet-\bullet-\bullet)}\}$. The phase diagram for this model at $x=1/3$ (Fig. 3) was determined by MC simulations (triangular symbols). For values of $r=-J_{(\bullet-\bullet-\bullet)}/J_{(\bullet-\bullet)}\leqslant 0.25$ this model yields the desired g.s. and transition sequence at $x=1/3$, but only in a region of ECI space where the formation

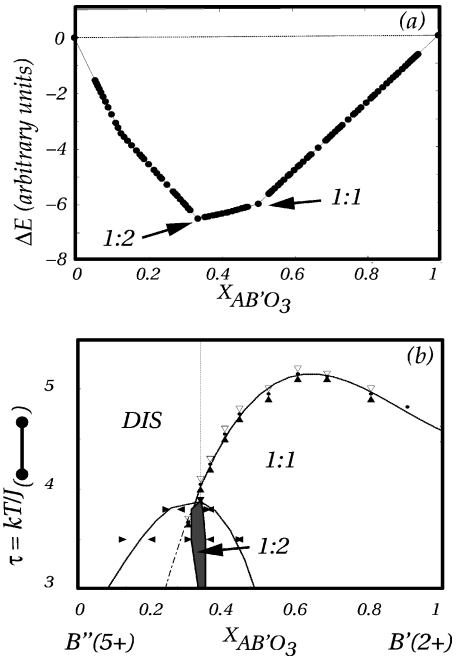

FIG. 6. (a) Ground-state diagram for the mostly metastable $AB'_xO_3-AB''_{1-x}O_3$ pseudobinary system in the {nn pair + linear triplet + cube-222} model. (b) The corresponding pseudobinary phase diagram.

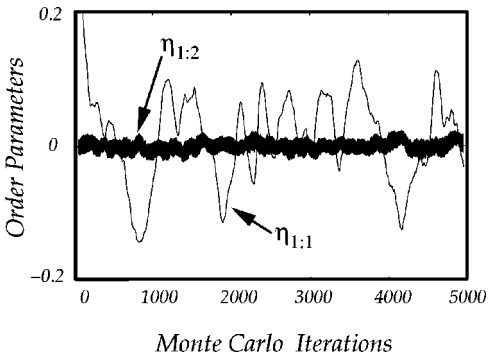

FIG. 7. Results of a MC simulation at $x=1/3$ and $T/T_C(1:1\rightleftharpoons\mathrm{DIS})=1.1$ for the {nn pair + linear triplet + cube-222} model.

energy $[\Delta E(1:2)]$ for the 1:2 phase is greater than that for the 1:1 phase at $x=1/2, \Delta E(1:2)_{x=1/3}>\Delta E(1:1)_{x=1/2}$ (left of the dotted vertical line in Fig. 3). This g.s. hierarchy is contrary to both experiment and to first-principles calculations.[19] Note the distinction between the 1:1 phase at $x=1/3$ and the fictive $A(B'_{1/2},B''_{1/2})O_3$ phase with NaCl-type ordering, for which the formation energy is $\Delta E(1:1)_{x=1/2}$. The former is observed experimentally, but the latter is not.

Other combinations of two ECI's that include $J_{(\bullet-\bullet-\bullet)}$ also stabilize the 1:1 structure, but none were found that did so with an acceptable g.s. hierarchy.

C. *nn* pair + linear triplet + cube-222 model

Investigations of three parameter models of the form $\{J_{(\bullet-\bullet-\bullet)}+J_{(\bullet-\bullet)}+\text{a third ECI}\}$ revealed only one combination that satisfied all three constraints listed above. The third ECI is the cube-222 interaction, which is associated with the cluster that remains after one removes a triangle of three second *nn* pairs from a unit cube (Fig. 4).

Figure 5 is the $x=1/3$ phase diagram for this model, with ECI values $J_{(\bullet-\bullet)}=1, J_{(\bullet-\bullet-\bullet)}=-0.23$, and $J_{(cube-222)}=-0.2$. Figure 6(a) is the g.s. diagram, and Fig. 6(b) is a portion of the *mostly metastable* $AB'_xO_3-AB''_{1-x}O_3$ pseudobinary, metastable because $x=1/3$ is the only composition at which phases are observed experimentally. Each solid circle on the convex hull (solid line) indicates a different ordered structure that is stable at 0 K, but only the 1:2 and 1:1 structure phases persist to high temperatures. With these ECI values, the 1:2$\rightleftharpoons$1:1 and 1:1$\rightleftharpoons$DIS transitions are very

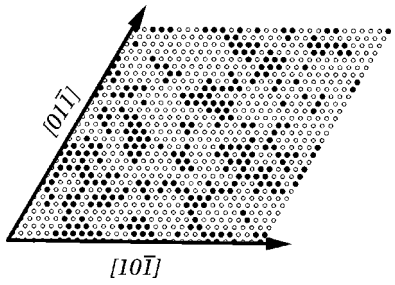

FIG. 8. A (111) plane through the MC box after 5000 MC iterations at $x=1/3$ and $T/T_C(1:1\rightleftharpoons\mathrm{DIS})=1.1$,{nn pair + linear triplet + cube-222} model. Solid circles (●) represent $B'^{(2+)}$ions. Open circles (○) represent $B''^{(5+)}$ions.

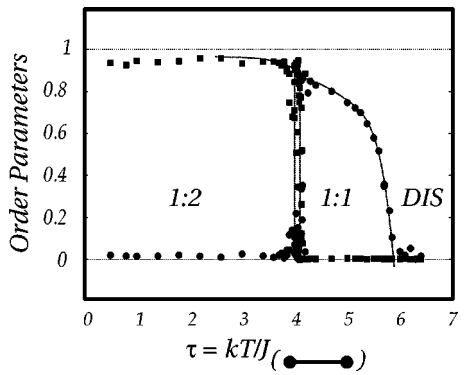

FIG. 9. Phase diagram at $x=1/3$ for the {nn pair + linear triplet + tetrahedron + cube-222} model.

close together [$\tau_c(1{:}2)=kT/J_{\bullet-\bullet}\sim 3.885$ and $\tau_c(1{:}1)\sim 4.05$]. A more negative value of $J_{(cube\text{-}222)}$ increases the temperature range in which 1:1 phase is stable, but this range can only be expanded slightly before the g.s. at $x=1/2$ becomes lower than that at $x=1/3$. A less negative value of $J_{(cube\text{-}222)}$ will decrease the 1:1-phase field. The $1{:}2\rightarrow 1{:}1$ transition is predicted to be strongly first order, but the $1{:}1 \rightleftharpoons$ DIS transition is predicted to have a critical point. Because the $1{:}2 \rightleftharpoons 1{:}1$ transition is strongly first order, it will, in general, traverse a $(1{:}2+1{:}1)$ two-phase field, unless the congruent point is exactly at $x=1/3$. Within the precision of this calculation, however, no such field is resolved.

Figure 7 is a plot of the running average, over the preceeding 100 MC iterations, of the order parameters for the 1:2 and 1:1 phases ($\eta_{1:2}$ and $\eta_{1:1}$, respectively) at $x=1/3$ and $T/T_C(1{:}1\rightleftharpoons \text{DIS})=1.1$. Fluctuations of $\eta_{1:1}$ are just what one would expect from a microstructure characterized by 1:1-type short-range order (SRO) that manifests itself as ordered microregions in a (long-range) disordered crystal. Figure 8 is a (111) plane through the MC box after 5000 MC iterations at $T/T_c(1{:}1\rightleftharpoons\text{DIS})=1.1$ and $x=1/3$. This gives some idea of the predicted domain size, up to $\sim 5-10$ unit cells, $\sim 2-4$ nm, which is within the range ($\sim 2-5$ nm) observed experimentally[8] in crystals that were grown from a melt at 1150 °C.[29] Note, however, that MC simulations with larger system sizes should be performed to evaluate finite-size effects on calculated domain size.

D. nn pair + linear triplet + tetrahedron + cube-222 model

A four-ECI model that greatly expands the stability field of the 1:1 phase at $x=1/3$, while retaining an appropriate g.s. hierarchy, is obtained by adding the tetrahedron ECI's (Fig. 4) to the three-parameter model discussed above. Figure 9 is the $x=1/3$ phase diagram for $J_{(\bullet-\bullet)}=1$, $J_{(\bullet-\bullet-\bullet)}=-0.23$, $J_{(tetrahedron)}=-0.25$, and $J_{(cube\text{-}222)}=-0.3$. Qualitatively, the phase diagram is similar to that for the {nn pair + linear triplet + $cube$-222} model, but in this case a $(1{:}2+1{:}1)$ two-phase field is clearly present. Figure 8 is not compelling in this respect, but MC calculations at a reduced temperature $\tau=kT/J_{(\bullet-\bullet)}=4$ produce very stable $(1{:}2+1{:}1)$ two- phase assemblages, stable in the sense that $\eta_{1:2}$ and $\eta_{1:1}$ do not change sign during as many as 10 000 MC iterations.

III. DISCUSSION

The models described above suggest a simple interpretation for observed cation order-disorder phenomena in $Pb(Mg_{1/3},Nb_{2/3})O_3$.

(i) The g.s. is 1:2 or some other ordered structure, but unfavorable kinetics cause the disordered phase to persist metastably at low temperatures.

(ii) A 1:1-phase field may be stable at intermediate temperatures, but if such a field exists, it is below the temperature at which an equlibrium cation distribution can be achieved.

(iii) As shown in Fig. 6(b), the $1{:}1\rightleftharpoons 1{:}2$ transition may be close to the $x=1/3$ composition over a substantial temperature range, which implies that enhanced 1:1-type SRO is stable within that broad range.

IV. CONCLUSIONS

A sufficient Ising model to describe *B*-site order-disorder phenomena in $A(B'_{1/3},B''_{2/3})O_3$ perovskites must permit both the 1:2 g.s. and the transition sequence $1{:}2$ g.s.$\rightarrow 1{:}1\rightarrow$ DIS, and it must do so with the minimum g.s. in the $AB'_x,B''_{1-x}O_3$ pseudobinary at $x=1/3$. The linear triplet interaction is both necessary and sufficient to stabilize the 1:2 g.s. and the { linear triplet +nn pair} model is sufficient to generate the $1{:}2$ g.s.$\rightarrow 1{:}1\rightarrow$ DIS transition sequence, but only with an inappropriate g.s. hierarchy. The {nn pair + linear triplet + cube-222} model is the simplest one that satisfies all three sufficiency constraints. Finite-temperature MC simulations with $J_{(\bullet-\bullet)}=1, J_{(\bullet-\bullet-\bullet)}=-0.23$, and $J_{(cube\text{-}222)}=-0.2$ yield the $1{:}2$ g.s.$\rightarrow 1{:}1\rightarrow$ DIS transition sequence with the 1:1 phase stable over a very narrow temperature range ($3.885\leqslant\tau=kT/J_{\bullet-\bullet}\leqslant 4.05$). The simulated microstructure is qualitatively consistent with experiment, but finite-size effects on the calculated domain size should be analyzed in greater detail.

ACKNOWLEDGMENTS

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