CVM studies on the atomic ordering in complex perovskite alloys

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Abstract

The atomic ordering in complex perovskite alloys is investigated by the cluster variation method (CVM). For the 1/3{111}-type ordered structure, the order-disorder phase transition is the first order, and the order parameter of the 1:2 complex perovskite reaches its maximum near x=0.25. For the 1/2{111}-type ordered structure, the ordering transition is the second order. Phase diagrams for both ordered structures are obtained. The order-disorder line obeys the linear law.

PACS: 64.60.Cn, 77.84.Dy, 81.30.Hd, 81.30.Bx
I. INTRODUCTION

Complex perovskite alloys draw immense attention because of their exceptional dielectric and piezoelectric properties, which have great actual or potential uses. Examples are the so-called “super Q” mixed-metal perovskites with low losses, such as Ba(Zn\(_{1/3}\)Ta\(_{2/3}\))O\(_3\) (BZT) and Ba(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-BaZrO\(_3\) (BMN-BZ), and the relaxor ferroelectrics (relaxors) with extraordinarily high values of the relative permittivity and the piezoelectric constants, such as Pb(Sc\(_{1/2}\)Ta\(_{1/2}\))O\(_3\)-PbTiO\(_3\) (PST-PT) and Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PbTiO\(_3\) (PMN-PT).

An important aspect in complex perovskite alloys is the compositional atomic ordering, which is closely related to the desired properties. For example, it was indicated that the microwave-loss properties of 1:2 perovskite ceramics are very sensitive to the B-site cation ordering. In relaxors, it is widely accepted that the presence of the nanoscale ordered microregions is responsible for the relaxor behaviors. Some investigations have been done on the atomic ordering of complex perovskites. Considering the electrostatic interactions between the nearest B-site ions, Zhang et al. presented an available quantitative criterion of the order-disorder transition and successfully explained many experimental results in A(B\(_{1/2}^\prime\)B\(_{1/2}^\prime\prime\))O\(_3\). Recently, Bellaiche and Vanderbilt used the electrostatic model to satisfactorily reproduce the various types of ordered structures in BMN-BZ and other complex perovskites. In addition, the first-principle calculations were conducted to describe the ordering in some cases.

It has been revealed that the Fourier transforms of the atomic interactions play important roles in the atomic ordering. In this paper, we adopt the parameters in the reciprocal space of atomic interactions and conduct a cluster variation method (CVM) calculation to investigate the order-disorder transitions in complex perovskites.
II. METHOD

When considering the atomic ordering in complex perovskites, we can model \((1 - x)A(B'_cB''_{1-c})O_3-xAB'''O_3\) as a three-component system \((1 - x)(B'_cB''_{1-c})XB'''\) on a simple cubic Bravais lattice. \(c=1/3\) for 1:2 perovskites such as BMN-BZ, and \(c=1/2\) for 1:1 perovskites such as PST-PT.

The driving mechanism responsible for the ordering is mainly the electrostatic interaction. Introduce \(\sigma(R) = -1, 0, \text{ or } +1\) in the case of \(c = 1/2\) if \(R\) is occupied by \(B', B'''\) or \(B''\). In the case of \(c = 1/3\), introduce \(\sigma(R) = -2, 0, \text{ or } +1\) for \(B', B'''\) or \(B''\). The charge fluctuation of ions at \(R\), \(\Delta q(R)\), is proportional to \(\sigma(R)\).

The electrostatic energy between a pair of cations at \(R\) and \(R'\) is proportional to \(\Delta q(R)\Delta q(R')\) or \(\sigma(R)\sigma'(R')\), i.e.,

\[
E_{elec}(\sigma, \sigma', R, R') = W(R - R')\sigma(R)\sigma'(R'),
\]

where \(W(R - R')\) is the effective-interaction energy. In a purely Coulomb picture, \(W(R) \propto 1/R\). In the nearest-neighbor Coulomb picture, \(W(R)\) is equal to zero unless \(R\) is the nearest neighbor. Different from the two pictures, we do not make any assumption on the form of \(W(R)\) here. The energy of the system with a certain configuration \(\{\sigma(R)\}\) can be expressed as

\[
E(\{\sigma(R)\}) = E_0 + \frac{1}{2} \sum_{R, R'} W(R - R')\sigma(R)\sigma'(R'),
\]

where \(E_0\) is a constant independent on \(\{\sigma(R)\}\). The average value of the energy is \((E_0\) is neglected)

\[
E = \sum_{\{\sigma(R)\}} E(\{\sigma(R)\})P(\{\sigma(R)\})
= \frac{1}{2} \sum_{R, R', \sigma, \sigma'} W(R - R')\sigma(R)\sigma'(R')X_{\sigma\sigma'}(R, R'),
\]

where \(P(\{\sigma(R)\})\) is the statistic probability of the configuration \(\{\sigma(R)\}\), and \(X_{\sigma\sigma'}(R, R')\) is the pair occupation probability.
When the atomic interaction is long range, Eq. (3) is difficult to handle in CVM because a large cluster should be used to contain the long-range interaction. Therefore, some approximation should be made.

Expand $X_{\sigma\sigma'}(\mathbf{R}, \mathbf{R}')$ in a Fourier transform:

$$X_{\sigma\sigma'}(\mathbf{R}, \mathbf{R}') = \sum_{k, k'} Q_{\sigma\sigma'}(k, k') \exp[i(k \cdot \mathbf{R} + k' \cdot \mathbf{R}')],$$

and substituting it into Eq. (3) yields

$$E = \frac{N}{2} \sum_{\sigma, \sigma', k} V(k)\sigma\sigma'Q_{\sigma\sigma'}(k, -k),$$

where $V(k)$ is the Fourier transform of $W(\mathbf{R})$:

$$V(k) = \sum_{\mathbf{R}} W(\mathbf{R}) \exp(i k \cdot \mathbf{R}).$$

For a certain ordered structure, only a few $Q_{\sigma\sigma'}(k, -k)$ in Eq. (5) are nonzero under the single-particle approximation. We assume that this property is still valid in CVM. The assumption is not absurd since in experiments there are only a few superlattices for a certain ordered structure. Thus Eq. (5) can be simplified. For example, for the 1/2\{111\}-type-ordered structure [Fig. 1(a)], all lattice sites are divided into two nonequivalent groups. Only the superlattice $Q_{\sigma\sigma'}(k = 1/2\{111\})$ are nonzero. Then the energy is reduced to

$$E = \frac{N}{2} V(k = 1/2\{111\}) \sum_{\sigma, \sigma'} \sigma\sigma'Q_{\sigma\sigma'}(k = 1/2\{111\}).$$

By using the symmetry of the ordered structure, we can evaluate $Q_{\sigma\sigma'}(k = 1/2\{111\})$ from a small cluster and deal with Eq. (7) in CVM. It is noted that $V(k = 1/2\{111\})$ involves any long distance interactions. For the 1/3\{111\}-type ordered structure, lattice sites are divided into three groups,

$$E = \frac{N}{2} V_{1/3} \sum_{\sigma, \sigma'} \sigma\sigma' [Q_{\sigma\sigma'}(k = 1/3\{111\}) + Q_{\sigma\sigma'}(k = 2/3\{111\})],$$

where $V_{1/3} \equiv V(k = 1/3\{111\}) = V(k = 2/3\{111\})$.

Four-point basic clusters (Fig. 1) are chosen in our CVM calculation.
III. RESULTS

The 1/2\{111\}-type ordered structure occurs in both 1:2 and 1:1 complex perovskites. $V_{1/2} \equiv V(k = 1/2\{111\}) < 0$ is required since it is a necessary condition for the 1/2\{111\}-type ordered structure to appear.

First, the ordering transition type is specified. The long-range order parameters (LRO) are defined as

$$\eta = |P_i - P_j|,$$

which represent the occupation-probability difference between nonequivalent sites. $\eta$ for $B'$, $B''$, and $B'''$ as functions of the reduced temperature $T^*$ are plotted in Fig. 2 when $c = 1/3$ and $x = 0.25$. (The reduced temperature is defined as $T^* = k_B T/|V_{1/2}|$ in this figure and the following Fig. 3.) It shows that $\eta$ decreases gradually to zero when increasing temperature. So the ordering transition is the second order. For 1:1 complex perovskites ($c=1/2$), the transition is also the second order.

Fig. 3 depicts the curves of $\eta$ as functions of the composition $x$ when $c=1/3$ and $T^* = 0.5$. It shows that $\eta_{B'}$ increases when decreasing $x$, while $\eta_{B''}$ and $\eta_{B'''}$ reach their maxima near $x = 0.25$. The appearance of the maximum in LRO is consistent with the experimental findings in BZT-BZ\textsuperscript{3} and previous theoretical work\textsuperscript{10}. For 1:1 complex perovskites ($c = 1/2$), $\eta_{B'}$ and $\eta_{B''}$ are equal to each other and increase with decreasing $x$, but $\eta_{B'''}$ keep equal to zero in all range of $x$.

The critical temperatures of the phase transition, $T_c$, can be determined at different $x$ values. Approximately, $T_c$ decrease linearly with increasing $x$.

The 1/3\{111\}-type ordered structure is observed only in 1:2 complex perovskites. The calculated curves of the long-range order parameters $\eta$ as functions of the reduced temperature $T^*$ when $x=0.25$ are shown in Fig. 4. (In this figure and thereafter, $T^*$ is defined in $T^* = k_B T/|V_{1/3}|$ where $V_{1/3} < 0$.) It can be seen that LRO of the 1/3\{111\}-type ordered structure suddenly drop to zero at the transition temperature, which indicates that the transition is the first order.
The 1/2{111}- and 1/3{111}-type ordered structures are separately discussed above. In actual cases, which ordered phase to appear is determined by the free energy, i.e., at a certain composition, the ordered phase with the minimal free energy will become the equilibrium phase and can be observed in experiments.

In the investigations above, the model is parameter-free in the sense that $V_{1/2}$ and $V_{1/3}$ define the temperature scale. When we consider the 1/2{111}- and 1/3{111}-type ordered phases at the same time, a ratio $V_{1/2}/V_{1/3}$ should be introduced. For the purely Coulombic interactions, $|V_{1/2}| \approx |V_{1/3}|$; for the nearest neighbor interaction, $|V_{1/2}| = 2|V_{1/3}|$. Adopting $|V_{1/2}| = 1.4|V_{1/3}|$, we plot in Fig. 5 the free energy curves of the 1/2{111}- and 1/3{111}-type ordered structures for $c = 1/3$. It shows that the 1/3{111}-type ordered phase appears at small $x$ values, and the 1/2{111}-type phase favors larger $x$ values, which agrees with results in BMN-BZ. The boundary of $x$ values for the 1/2{111}- and 1/3{111}-type ordered phases is determined by the crossing of the curves. The combined phase diagram of the system is shown in Fig. 6. The phase region of the 1/3{111}-type ordered phase near $x = 0$ is located inside the region of the 1/2{111}-type ordered phase.

When $|V_{1/3}|$ decreases, the phase region of the 1/3{111}-type ordered structure gets smaller and smaller, and vanishes at last. This may be the cases in PMN and PMT in which only the 1/2{111}-type ordered phase is observed. Of course, the source of the small $|V_{1/3}|$ cannot be solved in the theoretical framework of this paper. The effective energy parameters are affected by the A-site and O-site ions. Perhaps the different effects of the Pb and Ba can provide some clues on this problem.

For 1:1 complex perovskites ($c = 1/2$), the chemical formula is favorable to form the 1/2{111}-type ordered structure, so the situation is different from that of $c = 1/3$. The free energy curves are depicted in the inserted graphics of Fig. 9 when $c = 1/2$. The curve of the 1/3{111}-type ordered structure wholly lies above that of the 1/2{111}-type phase. It suggests that the 1/3{111}-type ordered phase is impossible (or difficult) to form in 1:1 complex perovskites such as Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$ and Pb(Mg$_{1/2}$W$_{1/2}$)O$_3$. 
IV. CONCLUSIONS

The 1/2{111}- and 1/3{111}-type atomic ordering in complex perovskites have been studied by the cluster variation method. For the 1/2{111}-type ordered phase, the transition is the second order, and the order parameter reaches its maximum near $x=0.25$ for 1:2 complex perovskites. For the 1/3{111}-type ordered phase, the transition is the first order. The order-disorder transition line is found to obey the linear law. The phase diagram containing both ordered structures is obtained.

ACKNOWLEDGMENT

This work was supported by the Chinese National Science Foundation. We acknowledge Dr. Hui Zheng for many very useful discussions.
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FIGURES

FIG. 1. Lattice site occupations and basic clusters used in CVM for: (a) the 1/2{111}-type ordered structure; (b) the 1/3{111}-type ordered structure.

FIG. 2. LRO of the 1/2{111}-type ordered structure as functions of reduced temperature $T^* = k_B T / |V_{1/2}|$ at $x = 0.25$ and $c = 1/3$.

FIG. 3. LRO of the 1/2{111}-type ordered structure as functions of $x$ at $T^* = 0.5$ and $c = 1/3$.

FIG. 4. LRO of the 1/3{111}-type ordered structure as functions of reduced temperature at $x = 0.25$ and $c = 1/3$. The reduced temperature is defined as $T^* = k_B T / |V_{1/3}|$.

FIG. 5. Reduced free energies of the 1/2{111}-type (solid line) and 1/3{111}-type (dashed line) ordered structures as functions of $x$ when $c = 1/3$. $V_{1/2} = -1.4$, $V_{1/3} = -1.0$, and $k_B T = 0.6 |V_{1/3}|$. Inserted graphics is the case of $c = 1/2$.

FIG. 6. Combined phase diagram when $c = 1/3$. $\alpha$, $\beta$, and $\gamma$ designate disordered, 1/2{111}-type and 1/3{111}-type ordered phases, respectively. $V_{1/2} = -1.4$, $V_{1/3} = -1.0$. The reduced temperature is defined as $T^* = k_B T / |V_{1/3}|$. 
