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Possible order–disorder phase transitions in $(A'_x A''_{1-x})BO_3$ and $A(B'_x B''_{1-x})O_3$ complex perovskites

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Abstract. The stabilities of different kinds of ordered structure in complex perovskites have been studied by the eight-point cluster variation method (CVM). The grand potentials of these structures have been calculated and compared with that of the disordered state. It has been proved that the $\frac{1}{2}\{111\}$ -type ordered structure will be stable in the system when the nearest-neighbour interaction is much stronger than other longer-distance interactions. The $\frac{1}{2}\{110\}$ - and $\frac{1}{2}\{100\}$ -type ordered structures result from the next-nearest- and the third-neighbour interactions respectively. The grand potentials of the $\frac{1}{2}\{111\}$ - and $\frac{1}{2}\{100\}$ -type ordered structures reach minima at the composition $x = 0.5$, whereas the grand potential of one of the $\frac{1}{2}\{110\}$ -type ordered structures reaches its minima at around $x = 0.25$ and $x = 0.75$. The formation of different kinds of ordered structure in real material systems has been discussed.

1. Introduction

Materials with the perovskite structure ABO_3 , such as $BaTiO_3$ and $PbTiO_3$, represent an important family of ferroelectrics. When two or more than two kinds of cation occupy the A-site or B-site lattice, the complex perovskite structure is formed. Some materials with this kind of structure manifest the properties of relaxor ferroelectrics, which are quite different from those of the normal ferroelectrics [1]. The relaxor characteristics were originally attributed to the chemical inhomogeneity arising from the cation disordering, i.e. the crystal structures of relaxors were considered to be disordered on the basis of the early microscopic observation [1, 2]. With the development of electron microscope techniques, many compounds previously accepted as disordered were found to be ordered on the nanoscale [3–5]. It has been realized that the special relaxor properties are closely related to the existence of nanoscale-ordered microregions in the complex perovskites [6–10]. The structures of these ordered microregions and the origins of their formation have caused a lot of interest.

By using the high-resolution electron microscope (HREM) in conjunction with selected-area electron diffraction, Krause *et al* [3] found that there existed 2–5 nm superlattice microregions in $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) in which Mg^{2+} and Nb^{5+} were ordered in alternating $\{111\}$ planes with the 1:1 composition. Such a nonstoichiometric structure was later confirmed by Jie Chen *et al* [5]. This $\frac{1}{2}\{111\}$ -type ordering (figure 1(a)) is most commonly observed in complex perovskites. Meanwhile, other kinds of ordered

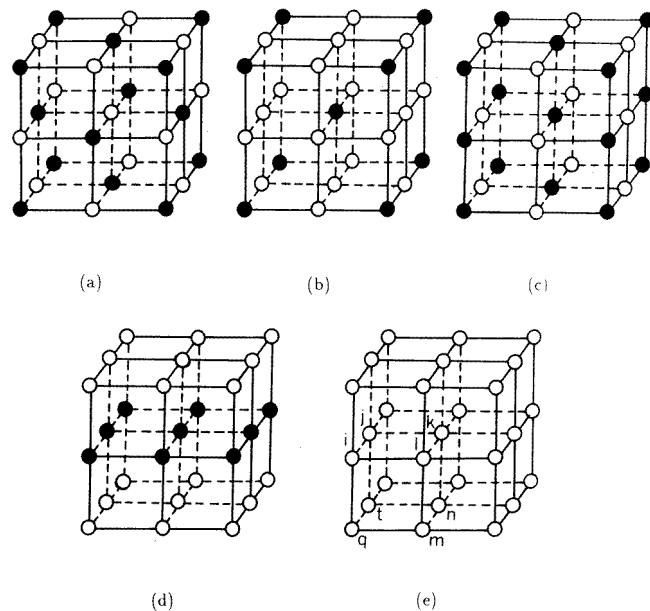


Figure 1. Ordered structures observed in complex perovskites together with the disordered structure. (a) The $\frac{1}{2}\{111\}$ -type ordered structure. (b) The $\frac{1}{2}\{110\}$ -type-I ordered structure. (c) The $\frac{1}{2}\{110\}$ -type-II ordered structure. (d) The $\frac{1}{2}\{100\}$ -type ordered structure. (e) The disordered structure.

structure have also been reported. Randall *et al* [11] observed the $\frac{1}{2}\{110\}$ superlattice reflections in PMN, $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PST), $(\text{PbLa})(\text{ZrTi})\text{O}_3$ (PLZT), $(\text{Ba}_{1-x}\text{Pb}_x)\text{TiO}_3$, etc, and associated the superstructure with the ordering of Pb^{2+} and lead-site vacancies ($\text{V}_{\text{Pb}^{2+}}$). Recently, the lattice image of this kind of superstructure in PLZT had been shown via HREM [12]. $\text{V}_{\text{Pb}^{2+}}$ and La^{3+} are assumed to occupy the corner and the body-centred positions (figure 1(b)). What is more interesting is that the $\frac{1}{2}\{111\}$, $\frac{1}{2}\{110\}$ and $\frac{1}{2}\{100\}$ superlattice reflections were found to exist simultaneously in $(\text{PbCa})\text{TiO}_3$ [13, 14]. King and co-workers proposed that only the $\frac{1}{2}\{111\}$ reflections result from the chemical ordering of Pb^{2+} and Ca^{2+} while the other two are due to electrical ordering caused by the atomic shuffling. Most recently, Fei Fang and Xiaowen Zhang [15] postulated, on the basis of an HREM study, that the three types of superlattice reflection were all of chemical ordering origin (figure 1(a), 1(c), 1(d)).

By using the probability wave theory of the atomic configuration (PWAC), Binglin Gu *et al* [16] studied the ground-state structures in complex perovskites theoretically. Seven kinds of ground-state ordered structure have been predicted, including the ordered structures observed in experiments (figure 1(a)–1(d)). This means that one of these structures will have the lowest energy at $T = 0$ K under the proper interaction conditions and is possible to observe in experiments. However, since the entropy is not considered in the PWAC theory, it remains unclear how different kinds of ordered structure are formed in complex perovskites with the decrease of temperature. In this contribution, we use the cluster variation method (CVM) [17] to investigate the stability of various ordered structures in complex perovskites. The grand potentials of the ordered structures together with the disordered structure are calculated and compared in order to determine the stable structure with the lowest energy.

The influences of effective ionic interactions on the formation of different kinds of ordered structure have been discussed.

2. The method

The A site and B site in ABO_3 form simple cubic lattices. We focus our attention on the site which more than one kind of cation occupies. The influences of the other site and the O site are included in the effective-interaction parameters. Thus the order–disorder transition in $(A'_x A''_{1-x})BO_3$ and $A(B'_x B''_{1-x})O_3$ complex perovskites is modelled as one problem, i.e. the order–disorder phase transition of a two-component system $C'_x C''_{1-x}$ on a sc Bravais lattice. In order to study the ordered structures shown in figures 1(a)–1(d), an eight-point basic cluster ($ijklmntq$) is chosen (figure 1(e)). It can be seen that when C' and C'' occupy the eight points randomly, the system is in the disordered state. When the occupation probabilities of i, k, m, t and j, l, n, q are identical respectively, the system is in the $\frac{1}{2}\{111\}$ -type ordered structure. When the occupation probabilities of i and n are equal while the other points are equivalent, the structure of figure 1(b) is formed. When the occupation probabilities of i, k, n, q and j, l, m, t are identical respectively, we get the ordered structure shown in figure 1(c). When the occupation probabilities of i, j, k, l and m, n, t, q are identical respectively, the system is in a $\frac{1}{2}\{100\}$ -type ordered structure. Therefore the occupation probabilities of the eight-point cluster can describe all of the structures shown in figure 1. Notice that the two ordered structures shown in figures 1(b) and 1(c) both present $\frac{1}{2}\{110\}$ superlattice reflections. We call them the $\frac{1}{2}\{110\}$ -type-I and $\frac{1}{2}\{110\}$ -type-II ordered structures, respectively. According to the PWAC theory, these two kinds of structure are degenerate in energy in the ground state [16]. We will show in the following that the degeneracy is broken by considering entropy at $T \neq 0$ K. The grand potentials are different, so the structures may be formed in different systems.

Define $W_{ijklmntq}$ as the eight-point cluster occupation probability, where i, j, \dots, q are equal to 1 or -1 , according to whether or not the point is occupied by C' or C'' ions. S_{ijkl} , $S_{ij tq}$, S_{jknt} , S_{klmn} , S_{ilmq} , S_{mntq} are the four-point subcluster occupation probabilities; X_{ij} , X_{il} , \dots , X_{tq} are the pair occupation probabilities; P_i , P_j , \dots , P_q are the point occupation probabilities. These satisfy the self-consistent relations

$$S_{ijkl} = \sum_{mntq} W_{ijklmntq}, \dots X_{ij} = \sum_{kl} S_{ijkl}, \dots P_i = \sum_j X_{ij}, \dots \quad (1)$$

The system's grand potential is written approximately in terms of the above occupation probabilities; the equilibrium properties of the system are then determined by minimizing the energy. The iteration equation without any limitation on the symmetry of the eight-point cluster has been obtained by such a process [18]:

$$\begin{aligned} W_{ijklmntq} = & \exp(\lambda/k_B T) \exp(-E_{ijklmntq}/k_B T) \exp(\mu a_{ijklmntq}/k_B T) \\ & \times (P_i P_j P_k P_l P_m P_n P_t P_q)^{1/8} \\ & \times (X_{ij} X_{il} X_{iq} X_{jk} X_{jt} X_{kl} X_{kn} X_{lm} X_{mn} X_{mq} X_{nt} X_{tq})^{-1/4} \\ & \times (S_{ijkl} S_{ij tq} S_{jknt} S_{klmn} S_{ilmq} S_{mntq})^{1/2} \end{aligned} \quad (2)$$

where $E_{ijklmntq}$ represents the interaction energy of a eight-point cluster made up of i, j, \dots, q species:

$$\begin{aligned} E_{ijklmntq} = & \frac{1}{4} J_1 (ij + il + iq + jk + jt + kl + kn + lm + mn + mq + nt + tq) \\ & + \frac{1}{2} J_2 (ik + im + it + jl + jn + jq + km + kt + ln + lq + mt + nq) \end{aligned}$$

$$+J_3(in + jm + kq + lt) \quad (3)$$

where J_1 , J_2 , J_3 are the nearest-, next-nearest- and third-neighbour effective-interaction parameters. In the following calculation, J_1 is included in the reduced temperature $k_B T/J_1$ and two other parameters are introduced: $u = J_2/J_1$ and $v = J_3/J_1$. They represent the relative strength of the next-nearest- and third-neighbour interactions with respect to the nearest-neighbour interaction. Interactions over longer distances than the third-neighbour distance have been neglected. $a_{ijklmntq}$ is the number of C' ions in the eight-point cluster, μ is the chemical potential, and λ is the Lagrange multiplier introduced in the minimization procedure for the energy. It can be solved for via the normalization condition:

$$\begin{aligned} \exp\left(\frac{-\lambda}{k_B T}\right) &= \sum_{ijklmntq} \exp(-E_{ijklmntq}/k_B T) \exp(\mu a_{ijklmntq}/k_B T) \\ &\times (P_i P_j P_k P_l P_m P_n P_t P_q)^{1/8} \\ &\times (X_{ij} X_{il} X_{iq} X_{jk} X_{jt} X_{kl} X_{kn} X_{lm} X_{mn} X_{mq} X_{nt} X_{tq})^{-1/4} \\ &\times (S_{ijkl} S_{ijtq} S_{jknt} S_{klmn} S_{ilmq} S_{mntq})^{1/2}. \end{aligned} \quad (4)$$

The grand potential of the system is [17]

$$G = N\lambda \quad (5)$$

where N is the number of lattice points in the system. The composition of C' ions in the system is

$$x = \frac{1}{8}(P_i(1) + P_j(1) + \dots + P_q(1)). \quad (6)$$

In principle, given the reduced temperature and interaction parameters, the stable structure with the lowest energy could be determined from equations (1)–(6). However, since they are deduced without any restriction on the occupation probabilities [18], some uncertainties exist in the calculation. For example, there is more than one kind of occupation configuration of the eight-point cluster corresponding to one kind of ordered structure, and a complex and ambiguous result will be obtained by the iteration. Furthermore, if we do not make any prior assumption regarding the symmetry of the structure, the choice of initial values has great uncertainty. The iteration will probably not stop at the minimum, and may stop at other extrema or saddle-points. Therefore in order to obtain clear information from the CVM calculation, restriction conditions on the symmetry must be imposed upon the iteration equation. This means that we first find out the minimum point under the restricted conditions, then determine the stable structure with the lowest energy by comparing the minima. In the disordered structure, we have

$$P_i = P_j = \dots = P_q \quad X_{ij} = X_{il} = \dots = X_{tq} \quad S_{ijkl} = S_{ijtq} = \dots = S_{mntq}. \quad (7)$$

On substituting the above symmetry conditions into equation (2), a simplified iteration equation is obtained, via which the occupation probabilities can be calculated for the corresponding structure. The grand potential and composition can be subsequently obtained using equation (5) and equation (6). It is the extreme point of the system's free energy under the restricted condition of equation (7). Similarly, the grand potential of the ordered structures can be calculated. The symmetry conditions are:

(i) for the $\frac{1}{2}\{111\}$ -type ordered structure:

$$\begin{cases} P_i = P_k = P_m = P_t \\ P_j = P_l = P_n = P_q \end{cases} \quad X_{ij} = X_{il} = \dots = X_{tq} \quad S_{ijkl} = S_{ijtq} = \dots = S_{mntq} \quad (8)$$

(ii) for the $\frac{1}{2}\{110\}$ -type-I ordered structure:

$$\begin{cases} P_i = P_j = P_l = P_m = P_n = P_t \\ P_k = P_q \\ \begin{cases} X_{ij} = X_{il} = X_{jt} = X_{lm} = X_{mn} = X_{nt} \\ X_{iq} = X_{jk} = X_{lk} = X_{nk} = X_{mq} = X_{tq} \end{cases} \\ S_{ijkl} = S_{ijtq} = \dots = S_{mntq} \end{cases} \quad (9)$$

(iii) for the $\frac{1}{2}\{110\}$ -type-II ordered structure:

$$\begin{cases} P_i = P_k = P_n = P_q \\ P_j = P_l = P_m = P_t \\ \begin{cases} X_{iq} = X_{kn} \\ X_{jt} = X_{lm} \\ X_{ij} = X_{il} = X_{jk} = X_{kl} = X_{mn} = X_{mq} = X_{nt} = X_{tq} \end{cases} \\ \begin{cases} S_{ijkl} = S_{mntq} \\ S_{ijtq} = S_{jknt} = S_{klmn} = S_{ilmq} \end{cases} \end{cases} \quad (10)$$

(iv) for the $\frac{1}{2}\{100\}$ -type ordered structure:

$$\begin{cases} P_i = P_j = P_k = P_l \\ P_m = P_n = P_t = P_q \\ \begin{cases} X_{ij} = X_{il} = X_{jk} = X_{kl} \\ X_{mn} = X_{mq} = X_{nt} = X_{tq} \\ X_{iq} = X_{jt} = X_{kn} = X_{lm} \end{cases} \\ S_{ijtq} = S_{jknt} = S_{klmn} = S_{mntq} \end{cases} \quad (11)$$

Comparing the grand potentials of the above five kinds of structure, the minimum point of the system's free energy is determined. Then it can be made clear which is the stable structure actually existing in the material.

The order parameter M is defined as

$$M = |P - P'| \quad (12)$$

where P and P' represent the occupation probabilities of C' cations on the two superlattices in the ordered structures. It reflects the degree of ordering of the corresponding ordered structure. When $M = 1$, the system is in a completely ordered state, whereas $M = 0$ corresponds to the disordered state.

3. Results

The grand potentials of the structures shown in figure 1 are calculated under various effective-interaction conditions. First we consider three typical cases. For $(u, v) = (0, 0)$, the system is studied under the nearest-neighbour approximation. The difference between the grand potentials of the disordered and ordered symmetry at different reduced temperatures is depicted in figure 2. The result shows that the energy of the $\frac{1}{2}\{110\}$ - and $\frac{1}{2}\{100\}$ -type ordered structures remains equal to that of the disordered structure, while the energy of the $\frac{1}{2}\{111\}$ -type ordered structure becomes lower in a certain range of chemical potential when the temperature is lowered to some extent. The order parameter M of the $\frac{1}{2}\{111\}$ -type ordered structure begins to have nontrivial values when the grand potential becomes lower (figure 3). At the same time, the order parameters of the $\frac{1}{2}\{110\}$ - and $\frac{1}{2}\{100\}$ -type ordered

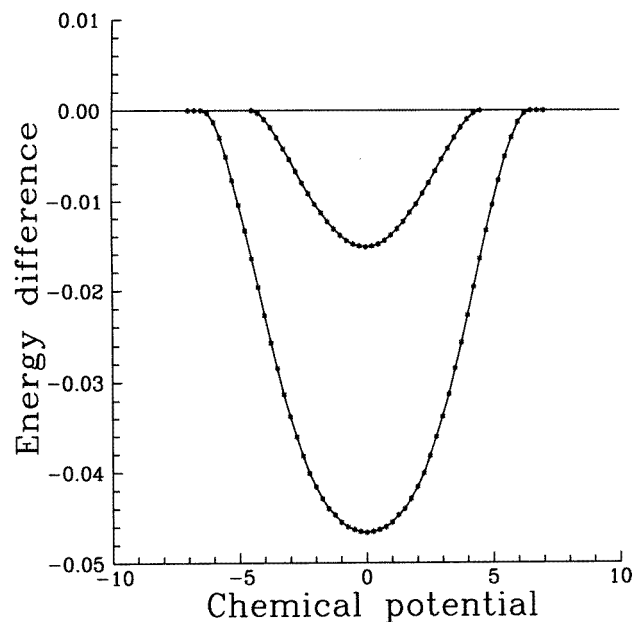


Figure 2. The difference between the grand potentials of the disordered and ordered symmetry at $k_B T / J_1 = 4.0$ and 4.3 when $(u, v) = (0, 0)$. The energy of the $\frac{1}{2}\{110\}$ - and $\frac{1}{2}\{100\}$ -type ordered structures remains equal to that of the disordered structure, while the energy of the $\frac{1}{2}\{111\}$ -type ordered structure becomes lower in a certain range of the chemical potential and temperature.

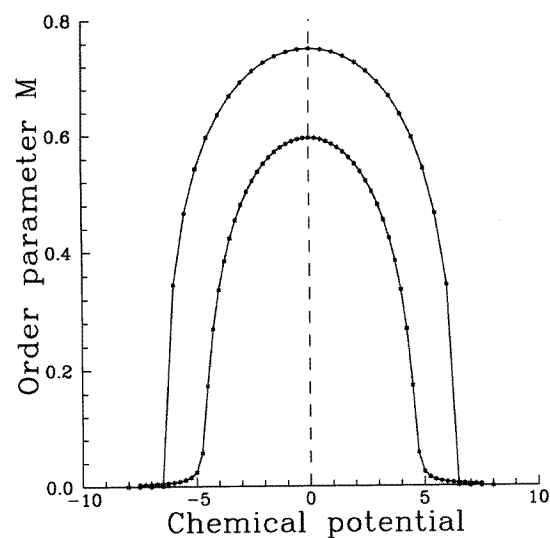


Figure 3. A diagram of the order parameter M of the $\frac{1}{2}\{111\}$ -type ordered structure versus the chemical potential at $k_B T / J_1 = 4.0$ and 4.3 when $(u, v) = (0, 0)$.

structures remain very small ($< 10^{-5}$) over the whole calculation range of the chemical potential and reduced temperature. This shows that when the nearest-neighbour interaction is much stronger than other longer-distance interactions, the $\frac{1}{2}\{111\}$ -type ordered structure is the state of minimum energy in a certain range of temperature and composition.

Next we take the interaction parameters $(u, v) = (1, 0)$ to study the cases under the next-nearest-neighbour approximation. A diagram showing the grand potential difference is given in figure 4. In this case, the grand potentials of the $\frac{1}{2}\{111\}$ -type and $\frac{1}{2}\{100\}$ -type ordered structures remain equal to that of the disordered structure, while the energy of the $\frac{1}{2}\{110\}$ -type ordered structure becomes lower. The solid lines represent the grand potential

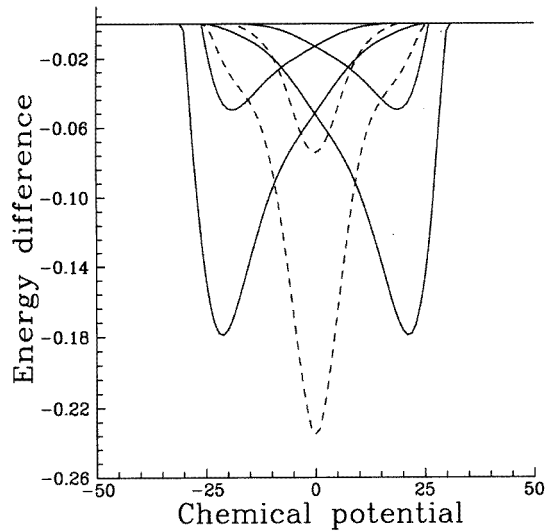


Figure 4. The difference between the grand potentials of the disordered and ordered symmetry at $k_B T/J_1 = 3.0$ and 3.5 when $(u, v) = (1, 0)$. The energy of the $\frac{1}{2}\{111\}$ - and $\frac{1}{2}\{100\}$ -type ordered structures remains equal to that of the disordered structure, while the energy of the $\frac{1}{2}\{110\}$ -type ordered structure becomes lower in a certain range of the chemical potential and temperature. The solid and dashed lines correspond to the $\frac{1}{2}\{110\}$ -type-I and $\frac{1}{2}\{110\}$ -type-II ordered structures respectively.

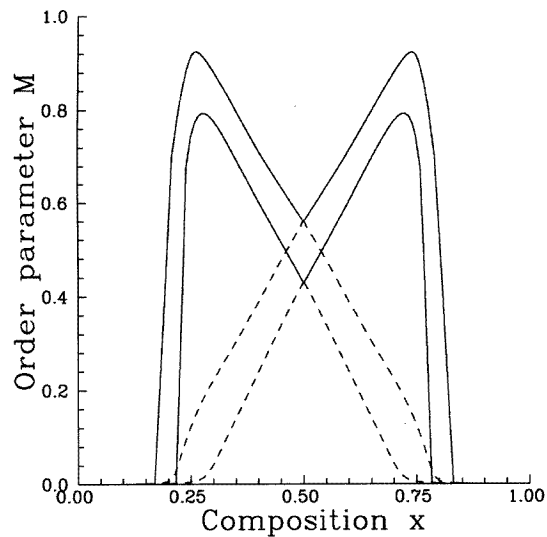


Figure 5. A diagram of the order parameter M of the $\frac{1}{2}\{110\}$ -type-I ordered structure versus the composition x at $k_B T/J_1 = 3.0$ and 3.5 when $(u, v) = (1, 0)$.

difference between the disordered structure and the $\frac{1}{2}\{110\}$ -type-I ordered structure. The two wells symmetrical about $\mu = 0$ are obtained by iterations starting from different initial values which are symmetrical about $x = 0.5$. They correspond to the two kinds of $\frac{1}{2}\{110\}$ -type-I ordered structures with C' and C'' ions exchanged. When the crystal is completely ordered, the compositions x of these two kinds of structure are 0.25 and 0.75 respectively. For clarity, we converted the x -axis from the chemical potential to the composition via

equation (6) when giving the diagram of the order parameter M and found that M reaches maxima at around $x = 0.25$ and $x = 0.75$ corresponding to the grand potential's minimum (figure 5). The dashed lines in figure 4 represent the grand potential difference between the disordered structure and the $\frac{1}{2}\{110\}$ -type-II ordered structure. It can be seen that the grand potential of the $\frac{1}{2}\{110\}$ -type-II ordered structure reaches a minimum at $\mu = 0$ which corresponds to $x = 0.5$.

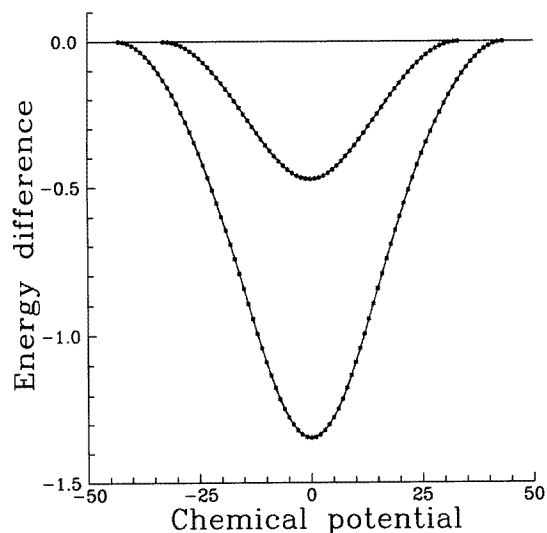


Figure 6. The difference between the grand potentials of disordered and ordered symmetry at $k_B T/J_1 = 4.0$ and 6.0 when $(u, v) = (1, 1)$. The energy of the $\frac{1}{2}\{111\}$ - and $\frac{1}{2}\{110\}$ -type ordered structures remains equal to that of the disordered structure, while the energy of the $\frac{1}{2}\{100\}$ -type ordered structure becomes lower in a certain range of the chemical potential and temperature.

When the interaction parameters are taken to be $(u, v) = (1, 1)$, the grand potential difference diagram is as shown in figure 6. Now the grand potentials of the $\frac{1}{2}\{111\}$ - and $\frac{1}{2}\{110\}$ -type ordered structures remain equal to that of the disordered structure, while the energy of the $\frac{1}{2}\{100\}$ -type ordered structure becomes lower. The variation of the order parameter M as a function of the chemical potential in the $\frac{1}{2}\{110\}$ -type-II and the $\frac{1}{2}\{100\}$ -type ordered structures is similar to that in the $\frac{1}{2}\{111\}$ -type ordered structure (figure 3), so the diagrams are no longer given here.

The above calculations show that in the three typical cases, i.e. $(u, v) = (0, 0)$, $(1, 0)$ and $(1, 1)$, the stable ordered structures in the system within a certain range of temperature and composition should be of the $\frac{1}{2}\{111\}$ -, $\frac{1}{2}\{110\}$ - and $\frac{1}{2}\{100\}$ -type structures, respectively. Thus it is interesting to investigate the cases where the effective-interaction parameters change as variables. First, let u vary from $0 \rightarrow 1$ while $v = 0$; the maximum values of the order parameter in the $\frac{1}{2}\{111\}$ - and $\frac{1}{2}\{110\}$ -type ordered structures as functions of u at one reduced temperature are shown in figure 7. The order parameter of the $\frac{1}{2}\{100\}$ -type ordered structure is neglected since it takes trivial values under these interaction conditions. The symbols $+$ and Δ represent M_{max} in the $\frac{1}{2}\{110\}$ -type-I and $\frac{1}{2}\{110\}$ -type-II ordered structures respectively. It can be seen that the M_{max} for these two kinds of structure vary in almost the same manner; hence they are no longer specified in the following. Figure 7 shows that M_{max} for the $\frac{1}{2}\{111\}$ -type ordered structure decreases sharply as the value of u increases, whereas M_{max} for the $\frac{1}{2}\{110\}$ -type ordered structure begins to be nontrivial at $u = 0.64$ and then increases rapidly until reaching a saturated value when u is approaching unity. When $0.13 < u < 0.64$ at $k_B T/J_1 = 3.0$, the order parameters of both kinds of structure remain trivial, implying that the next-neighbour interaction is sufficient

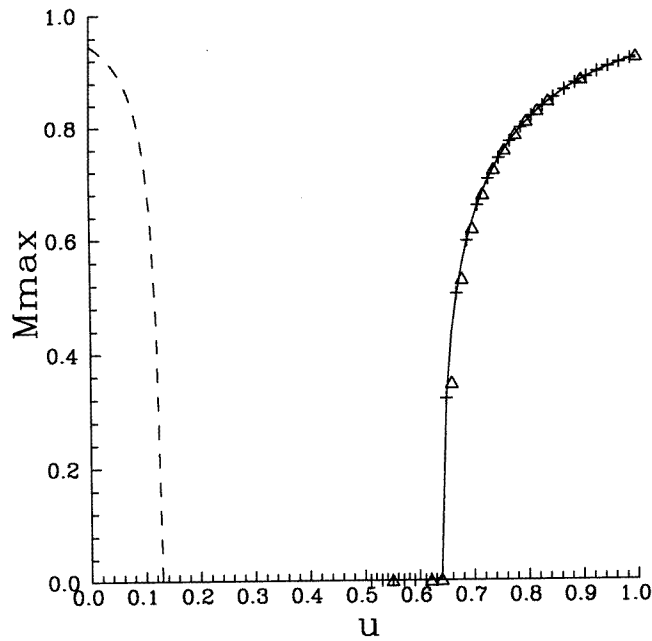


Figure 7. M_{max} of the $\frac{1}{2}\{111\}$ -type (dashed) and $\frac{1}{2}\{110\}$ -type (solid) ordered structures as functions of u when $(u, v) = (u, 0)$ at $k_B T/J_1 = 3.0$. Symbols + and Δ represent M_{max} in the $\frac{1}{2}\{110\}$ -type-I and $\frac{1}{2}\{110\}$ -type-II ordered structures respectively.

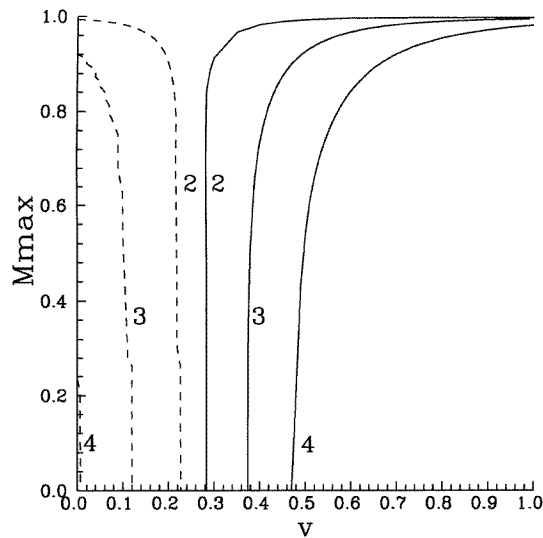


Figure 8. M_{max} of the $\frac{1}{2}\{110\}$ -type (dashed) and $\frac{1}{2}\{100\}$ -type (solid) ordered structures as functions of v when $(u, v) = (1, v)$ at $k_B T/J_1 = 2.0, 3.0$ and 4.0 (marked near the corresponding curves).

to destroy the $\frac{1}{2}\{111\}$ -type ordering but is not strong enough to sustain the $\frac{1}{2}\{110\}$ -type ordered structure as yet. The stable structure under this interaction condition is disordered at the corresponding temperature. An ordered structure will be formed ultimately with the decreasing of temperature. The boundary point between the $\frac{1}{2}\{111\}$ - and $\frac{1}{2}\{110\}$ -type ordered structures at $T = 0$ K is $u_0 = 0.25$ (see figure 3 in [16]). This means that when

the temperature is lowered, the range of u -values corresponding to the disordering shrinks until in the ground state, the $\frac{1}{2}\{111\}$ -type ordered structure will have the lowest energy at $u < 0.25$ and the $\frac{1}{2}\{110\}$ -type ordered structure will have the lowest energy when $u > 0.25$. When $u = 0.25$, the two kinds of ordered structure are degenerate in energy. In figure 8 such a tendency is demonstrated more clearly. When $u = 1$ and v is varied from $0 \rightarrow 1$, M_{max} for the $\frac{1}{2}\{110\}$ -type ordered structure decreases with the increase of v , whereas M_{max} for the $\frac{1}{2}\{100\}$ -type ordered structure increases. The range of v -values corresponding the disordering dwindles, approaching the boundary point between the $\frac{1}{2}\{110\}$ - and the $\frac{1}{2}\{100\}$ -type ordered structures in the ground state $v_0 = 0.25$ (see figure 3 in [16]).

4. Discussion

Based on the above CVM calculations, it can be seen that the nearest-neighbour interaction favours the formation of the $\frac{1}{2}\{111\}$ -type ordered structure, while the $\frac{1}{2}\{110\}$ - and $\frac{1}{2}\{100\}$ -type ordered structures result from the next-nearest- and third-neighbour interactions respectively. Since most complex perovskites have the dielectric properties of normal ferroelectrics or relaxors, the dielectric constants are very high (10^3 – 10^4). This means that the screening effect in the crystal is so strong that the nearest-neighbour approximation is valid in most complex perovskites. This may be why the $\frac{1}{2}\{111\}$ -type ordered structure is most commonly observed in this kind of material. Furthermore, when the $\frac{1}{2}\{111\}$ -type order–disorder phase transition takes place, the grand potential reaches a minimum at the composition $x = 0.5$ (figure 2). Therefore although the composition in some complex perovskites deviates from 0.5, a nonstoichiometric ordered structure is formed in order to achieve the lowest free energy. The nonstoichiometric ordering causes the charge imbalance in the ordered domains and the surrounding disordered matrix; hence the static electric energy increases with the ordered domains. When the decrease of the free energy is compensated by the increase of the static electric energy, the growth of the ordered domains stops. So the space charge caused by the nonstoichiometric ordering is the main reason for the formation of nanoscale-ordered microregions in systems like PMN [19].

When ordering of Pb^{2+} and $\text{V}_{\text{Pb}^{2+}}$ takes place on an A-site lattice, the charge imbalance may play a more important role in determining the crystal structure. The $\frac{1}{2}\{110\}$ -type-I ordered structure is preferred because the system has the smallest charge imbalance at the minimum point of the grand potential with $\text{V}_{\text{Pb}^{2+}}$ (or $\text{V}_{\text{Pb}^{2+}} + \text{La}^{3+}$ in PLZT) occupying the corner and the body-centred positions (figures 4 and 5). When the other kinds of ordered structure are formed, the grand potentials reach minima at $x = 0.5$. This will lead to a tremendous charge assembling, which causes a large static electric energy.

The coexisting of three kinds of ordered structure in $(\text{Pb}_x\text{Ca}_{1-x})\text{TiO}_3$ is believed to be caused by the fluctuation of effective ionic interactions. The CVM calculations suggest that different kinds of ordered structure may appear when the values of the effective interactions vary from one case to another. Defined as the averages of the formation energies over all atomic configurations, the effective interactions vary as functions of the average atomic volume [20, 21]. The Pb element in $(\text{PbCa})\text{TiO}_3$ has a complicated electronic structure, so there may be a relatively large elastic energy caused by its change in atomic volume. When the crystal is in a completely disordered state, the average atomic volume of every local region varies due to the composition inhomogeneity. A possible way for an ordered domain to grow is if its average atomic volume matches best to the original one of the local region in the disordered state. The elastic energy is therefore made minimal. The variation of the average atomic volume and the elastic energy lead to a fluctuation of the

effective-interaction parameters, so different kinds of ordered structure result in different regions. It can be seen that the order–disorder phase transition in complex perovskites is influenced by many factors. The CVM calculations give the free energy in an ideal crystal. The ordered structure actually formed in the real material system is the one that makes the total energy of the system minimal.

5. Conclusion

The order–disorder phase transition in complex perovskites has been studied by the eight-point CVM. The grand potentials of various ordered structures which have been observed in experiments are calculated and compared with that of the disordered state. It has been proved that the $\frac{1}{2}\{111\}$ -, $\frac{1}{2}\{110\}$ - and $\frac{1}{2}\{100\}$ -type ordered structures will be stable under the effective-interaction conditions $(u, v) = (0, 0), (1, 0)$ and $(1, 1)$ respectively. The calculations of order parameters as functions of the effective-interaction parameters further demonstrate that the nearest-neighbour interaction favours the formation of the $\frac{1}{2}\{111\}$ -type ordered structure, while the $\frac{1}{2}\{110\}$ - and $\frac{1}{2}\{100\}$ -type ordered structures result from the next-nearest- and third-neighbour interactions. The grand potentials of the $\frac{1}{2}\{111\}$ - and $\frac{1}{2}\{100\}$ -type ordered structures reach minima at the composition $x = 0.5$, whereas the grand potential of the $\frac{1}{2}\{110\}$ -type-I ordered structure reaches a minimum at around $x = 0.25$ and $x = 0.75$. The ordered structure actually formed in real materials is determined from the grand potential together with other factors, such as the static electric energy and the elastic energy.

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