Ferroelectric phase transition and spontaneous electric polarization in CaMn$_7$O$_{12}$ from first principles

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Abstract
The phase transition mechanism and ferroelectric polarization of CaMn$_7$O$_{12}$ are investigated by using the density functional theory. Our results show that the $P3$ space group should be the ground-state structure with $R3$ as the intermediate phase. It is the helicoidal magnetic order that induces the first transition to the $R3$ phase while the second transition to $P3$ structure results from soft modes under the constraint of the magnetic structure. The two phase transitions from $R3$ through $R3$ to $P3$ are second order and first order, respectively, which is consistent with experimental observations. Group theoretical analysis shows that the particular domain states and multi-domain structure of the $P3$ phase match with the observed coexistence of two magnetic modulations below $T_{N2} = 48$ K. Our calculated electric polarization is also in good agreement with experiment. By analyzing the polarization contributions from both mode and atomic-decomposition viewpoints, we find that the Raman-type distortions give rise to a significant contribution to the total polarization. This unexpected result can be understood through the asymmetric change of the Born effective charges caused by the particular helicoidal magnetic order, which leads to an abnormal infrared character of the purely Raman-active modes.

1. Introduction

Recent experimental and theoretical advances in multiferroic materials have greatly deepened understanding of coexistence and coupling of ferroelectric (FE) and magnetic orders, which is a subject attracting tremendous interest due to the technological importance in spintronics and information storage [1–5]. According to the classification by Khomskii [6], the FE polarizations of type-II multiferroics (or so-called magnetic multiferroics) are induced by some particular types of magnetic order and hence the intrinsic magnetoelectric couplings are strong. More recently, a large magnetically induced FE polarization (2870 $\mu$C m$^{-2}$ in a single crystal sample) has been reported in rhombohedral CaMn$_7$O$_{12}$ [7, 8]. Unlike the known cycloidal spin spiral or the $E$-type AFM order [5, 6], the magnetic structure of CaMn$_7$O$_{12}$ belongs to the unexpected helicoidal (or proper-screw) spin spiral [8, 9].

The room-temperature crystal structure of CaMn$_7$O$_{12}$ is the $R3$ (No 148) space group [10, 11], in which three types of Mn ion occupying the Wyckoff positions 9e, 9d, and 3b are labeled as Mn1, Mn2, and Mn3, respectively, as shown in figure 1. At 250 K, an isostructural charge-ordering transition gives the Mn2 and Mn3 ions nominal valences of $+3$ and $+4$, respectively [12]. In addition, CaMn$_7$O$_{12}$ shows two further magnetic phase transitions at $T_{N1} = 90$ K and $T_{N2} = 48$ K [13, 14]. In the temperature range $T_{N2} < T < T_{N1}$, an in-plane helical magnetic structure (shown in figure 1) with incommensurate propagation vector $k_i = (0, 0, 0.963)$ develops and results in a remarkable ferroelectricity along the $c$ axis of the rhombohedral conventional cell [8]. Below $T_{N2}$, the propagation vector $k_i$ splits into two branches with values of $k_{5,3} = k_1 \pm (0, 0, \delta) (\delta \approx 0.08)$, indicating the coexistence of two modulations along the same symmetry direction [8]. At the same time, a tiny change in electric polarization was observed at $T_{N2}$ [7, 8].
The discovery of large FE polarization in CaMn$_7$O$_{12}$, which persists up to a Néel temperature of 90 K, represents a significant development in the field of magnetic multiferroics. In order to explain the improper ferroelectricity, a phenomenological ferroaxial coupling mechanism has been proposed [8, 15]. The essential aspect of this scenario is the coupling among FE polarization, the chirality of the helical spin spiral, and the axial vector representing a homogeneous structural rotation of the $R\bar{3}$ structure with respect to its high-temperature cubic $Im\bar{3}$ space group. Based on first-principles calculations, Xiang et al [16] proposed that the microscopic origin of the giant FE polarization in CaMn$_7$O$_{12}$ is mainly due to the combined effect of the symmetric exchange striction and the antisymmetric Dzyaloshinskii–Moriya (DM) interaction. A subsequent theoretical work [17] confirmed the dominant role of the exchange-striction mechanism, and the spin-dependent p–d hybridization induced by the spin orbital coupling (SOC) also contributes a little polarization.

However, the crystallographic characteristics and phase transition mechanism of the two phase transitions at $T_{N1}$ and $T_{N2}$ remain to be identified. The room-temperature $R\bar{3}$ space group includes spatial inversion ($R^\perp$) symmetry. In order to accommodate the FE polarization appearing at $T_{N1}$, it is necessary to break the inversion symmetry. Although the helical magnetic order itself breaks the spatial inversion symmetry [8], it is implausible that the giant improper ferroelectricity originates only from the purely electronic polarization mechanism [18, 19], i.e. without ionic displacements away from their centrosymmetric reference positions. In this respect an representative example is TbMn$_2$O$_5$, of which the ground-state structure is the $P6\bar{3}$ polar group instead of the nonpolar $Pbam$ symmetry [20, 21]. For the phase transition occurring at $T_{N2}$, the thermal hysteresis behavior indicates a first-order phase transition character [22], so the crystallographic symmetry below $T_{N2}$ should be distinct from that in the temperature range $T_{N2} < T < T_{N1}$. To our best knowledge, there are no experimental or theoretical works concerning the actual symmetry groups of CaMn$_7$O$_{12}$ and the underlying phase transition mechanisms in these two temperature ranges. Another closely related issue is to determine the effect of lattice distortion on FE polarization and distinguish the polarization contributions of purely electronic and lattice mechanisms. As we know, the purely electronic polarization, which is due to charge density redistribution induced by magnetic order in the absence of ionic displacements away from their centrosymmetric positions [18, 19], does not exist in traditional ferroelectrics. Similarly, the ingrained opinion that only zone-center infrared (IR)-active modes can be responsible for the appearance of polarization is only supplied from traditional ferroelectrics and should not be regarded as self-evident for all types of magnetic multiferroic, though it has been reiterated for the improper ferroelectricity of TbMnO$_3$ induced by the cycloidal spin spiral through the SOC effect [23, 24].

In the present work, we carry out a detailed first-principles study of the phase transition mechanism and spontaneous polarization in CaMn$_7$O$_{12}$ using the experimental helicoidal magnetic structure (denoted AFMI) determined in [8]. We will demonstrate that the ground-state structure of CaMn$_7$O$_{12}$ should be the $P3$ space group with $R\bar{3}$ as the intermediate phase, and that the phase transition sequence from $R\bar{3}$ through $R\bar{3}$ to $P3$ is driven first by the magnetically induced forces and then by soft modes at the boundary of the Brillouin zone under the constraint of the helicoidal magnetic structure. Although the magnetic structure below $T_{N1}$ is unresolved experimentally, the particular domain states and the single multi-domain structure of the $P3$ phase provides an alternative understanding of the coexistence of two different incommensurate magnetic modulations. The two phase transitions from $R\bar{3}$ through $R\bar{3}$ to $P3$ show second-order and first-order character, respectively, which are consistent with experimental observations at $T_{N1}$ and $T_{N2}$. By decomposing the FE polarization into individual modes and individual sites, we obtain the most unexpected feature of CaMn$_7$O$_{12}$, i.e. the dominant polarization contribution comes from the purely Raman-type structural distortion. We will...
illustrate that the abnormal IR character of the purely Raman-type distortion is due to the asymmetric changes of Born effective charges (BECs) caused by this uncommon helicoidal spin spiral.

2. Ferroelectric phase transition

For a hypothetical magnetic order denoted as AFMr (all the spins of Mn1 and Mn3 sites are parallel while all the Mn2 spins are antiparallel), we choose the most energetically favorable $R^3$ phase as the high-symmetry reference structure due not only to the satisfactory structural parameters but also to the insulating electronic behavior [25]. We first demonstrate that the ferroelectricity in CaMn$_7$O$_{12}$ can not be driven by soft modes as in traditional ferroelectrics since all the zone-center optical phonons are stable for different magnetic orders [25].

Then, for the AFMI helicoidal magnetic order, we provide the phonon-dispersion relations of the $R^3$ reference structure along the high-symmetry directions in the Brillouin zone of the 20-atom primitive cell, as shown in figure 2. It is evident that there exist unstable modes extended over quite a large area of the Brillouin zone. We find that the dominant instability originates from a singlet phonon at the $T$ point with an imaginary frequency of 65.3i cm$^{-1}$ and point symmetry $T^+_1$. It corresponds to the complex distortion pattern of the MnO$_6$ octahedra (including Mn1, Mn3, O1, and O2 ions). However, this type of distortion should be described in a 40-atom pseudocubic unit cell, which is incompatible with the AFMI helicoidal magnetic order. In spite of this, for the $(1/3, 1/3, 1/3)$ point along the $\Lambda$ direction, the less unstable doubly degenerate phonon ($\omega = 35.1i$ cm$^{-1}$ and $A_1$ symmetry) is just right for the 60-atom hexagonal unit cell and corresponds to displacements of all kinds of ion, which combines the distortion pattern of MnO$_6$ octahedra of the $T^+_1$ mode with the displacements consisting of Ca atoms and Mn1O$_4$ square planes. Finally, it should be noted that this structural instability at the $T$ point is not relevant to the magnetic order (82.3i cm$^{-1}$ and 32.2i cm$^{-1}$ for the AFMr and ferromagnetic order, respectively).

On the other hand, there are remarkable Hellmann–Feynman forces appearing on the ions as the AFMI helicoidal magnetic order is turned on (with the structural parameters clamped in the AFMr reference structure). The forces induced by the change of the spin ordering are undoubtedly due to the change of electronic structure. However, the detailed tridimensional electronic structure is averaged so much in the DOS presentation that it is hard to explain the atomic forces only with respect to the current DOS presentation. Another work of ours [26] provides detailed analysis of the AFMI spin ordering induced forces from the electronic density difference between different spin orderings: The helicoidal magnetic order induces strong charge redistributions on all types of Mn and O ions in the reference structure. Projecting the forces onto the 20-atom primitive cell of the reference structure along the high-symmetry directions in the Brillouin zone of the 20-atom primitive cell, we find that, in the range of numerical precision, the forces can be entirely classified into (i) 97.5% of the symmetry-preserving Raman-active $A_g$ ($\Gamma^+_1$) irreps and (ii) 2.5% of the infrared-active $A_u$ ($\Gamma^-_1$) irreps, both of which have order parameters along the $c$ axis of the 60-atom conventional cell. The decomposed forces in the 20-atom primitive cell are collected in table 1. For the Raman-active $A_g$ modes, we see that the forces on O ions along the direction of the lattice vector can achieve a value as high as 230 meV Å$^{-1}$. Even for the IR-active $A_u$ irreps, the
forces are still several times larger than that of the IR-active state structure has polarization direction parallel to the random pattern, and the other is starting from the possible intermediate phases such as 2.56, 2.48, and 1.86, which are in good agreement with the experimental values reported in high as 673.2 meV. In addition, the calculated magnetic moments of Mn1, Mn2, and Mn3 ions are respectively 56 meV lower in energy per 60-atom unit cell. If we employ the total energy of the energy difference between the AFMr state as the reference point, the energy difference increases to 417.2 meV. Further turning on the SOC effect, the induced forces, we cannot search for the ground-state structure only by freezing the unstable mode deducing the ionic displacements from these forces. Due to the dual nature of structural instability originated from the soft magnetic order. For this mechanism, the unstable phase as the intermediate structure, which triples the 20-atom primitive cell and results from the subgroup relation \( \bar{R}_3 \) rules out this easy path because of the compatibility of atomic displacements at this \( q \) point with the helicoidal magnetic order. For this mechanism, the unstable \( \Lambda_1 \) phonon is the primary order parameter, which single-handedly leads to the final distorted \( P3 \) symmetry and triples the 20-atom primitive cell [29]. The resulting primitive cell of \( P3 \) symmetry is just the 60-atom hexagonal unit cell of the \( R3 \) phase. On the other hand, although the \( A_1 \) and \( A_3 \) modes at the \( \Gamma \) point receive significant forces due to the AFMI magnetic order (shown in table 1), they still serve as the secondary order parameters because of their incapacity of lowering the symmetry enough to the \( P3 \) group. However, the group–subgroup relation [30] between the two space groups of \( R3 \) and \( P3 \) rules out this easy path (1); instead we have the following two possibilities. Path (2) denotes the transition sequence with the nonpolar \( P3 \) phase as the intermediate structure, which triples the 20-atom primitive cell and results from the primary order parameter of the \( \Lambda_1 \) phonon but with no other secondary order parameter than the \( A_2 \) modes. The

### Table 1. For the \( R3 \) phase with AFMI magnetic order, the calculated Hellmann–Feynman forces (meV Å\(^{-1}\)) projected onto the 20-atom primitive cell and decomposed into Raman-active \( A_u \) and IR-active \( A_g \) irreps.

| Atoms | \( a \) | \( b \) | \( c \) | \( A_u \) irreps | \( A_g \) irreps |
|-------|-------|-------|-------|----------------|----------------|
|       | \( F_a \) | \( F_b \) | \( F_c \) | \( F_a \) | \( F_b \) | \( F_c \) |
| Ca    | 0     | 0     | 0     | 2.6   | 2.6   | 2.6   |
| Mn1   | 0     | 0.5   | 0.5   | 4.5   | -9.8  | -8.5  |
| Mn1   | 0.5   | 0     | 0.5   | -8.5  | 4.5   | -9.8  |
| Mn1   | 0.5   | 0.5   | 0     | -9.8  | -8.5  | 4.5   |
| Mn2   | 0     | 0     | 0     | -12.4 | 31.1  | 5.9   |
| Mn2   | 0     | 0.5   | 0     | 5.9   | -12.4 | 31.1  |
| Mn2   | 0     | 0     | 0.5   | 31.1  | 5.9   | -12.4 |
| Mn3   | 0.5   | 0     | 0.5   | -45.7 | -45.7 | -45.7 |
| O1    | 0.8081 | 0.3055 | 0.1306 | -153.8 | -158.1 | -75.5 |
| O2    | 0.3055 | 0.3055 | 0.8081 | -75.5  | -155.8 | -158.1 |
| O2    | 0.6945 | 0.1919 | 0.1919 | 158.1  | 75.5   | 155.8 |
| O2    | 0.8694 | 0.1919 | 0.6945 | 75.5   | 155.8  | 158.1 |
| O2    | 0.1919 | 0.6945 | 0.8694 | 158.1  | 158.1  | 75.5  |
| O3    | 0.3159 | 0.4768 | 0.1815 | -151.2 | 57.6   | -228.7 |
| O3    | 0.4768 | 0.1815 | 0.3159 | 57.6   | -228.7 | -151.2 |
| O3    | 0.1815 | 0.3159 | 0.4768 | -228.7 | -151.2 | 57.6  |
| O3    | 0.8185 | 0.6841 | 0.5232 | 228.7  | 151.2  | -57.6 |
| O3    | 0.5232 | 0.8185 | 0.6841 | 57.6   | 228.7  | 151.2 |
| O3    | 0.6841 | 0.5232 | 0.8185 | 151.2  | -57.6  | 228.7 |

In order to verify the above results, we have attempted two alternative strategies to determine the ground-state structure. One is relaxing the lowest \( P1 \) space group obtained by displacing ions from their high-symmetry positions in an entirely random pattern, and the other is starting from the possible intermediate phases such as \( R3 \) (No 143) and \( R3 \) (No 146) symmetry. Excellent agreement between these different strategies is achieved.
nonpolar $P\overline{3}$ to polar $P3$ phase transition occurs due to the IR-active $A_u$ ($\Gamma_1$) phonon as the order parameter, and hence one expects a distinct change in the FE polarization. However, there is definite experimental evidence [7, 8] that the giant FE polarization appears due to the first phase transition at $T_{N1}$ and that the change in polarization is tiny when CaMn$_2$O$_{12}$ undergoes the second transition at $T_{N2}$. The disagreement with experiments also rules out path (2). Then path (3), the transition sequence with the $R3$ phase as the intermediate structure, is the one and only choice, of which the first transition is driven by the magnetically induced forces (the primary and secondary order parameters are the forces with IR $A_u$ irrep and Raman $A_g$ irrep, respectively) and the second transition originates from the $\Lambda$ mode at the $(1/3, 1/3, 1/3)$ point.

Now we try to estimate the phase transition temperature. As mentioned above, our results show that the energy difference between the AFMr $R3$ phase and the AFMI $P3$ phase with the SOC effect is about 673.2 meV per 60 atoms. This is about 11.2 meV/atom and roughly corresponds to the temperature of 129 K, which is qualitatively consistent with the phase transition temperature of $T_{N1}$ (90 K). The relatively large error is likely due to the hypothetical AFMr spin order used in our calculations instead of the practical paramagnetic spin state. In addition, as shown in figure 2, the soft phonon at the $\Lambda$ $(1/3, 1/3, 1/3)$ point has the frequency of 35.11 cm$^{-1}$, which is equivalent to 4.35 meV. The converted temperature is about 50 K, which is in good agreement with the value of $T_{N2} = 48$ K. Therefore our first-principles results do demonstrate the existence of the $R3$ intermediate phase and indicate that path (3) can account very well for both the FE transition due to the helicoidal magnetic order at $T_{N1} = 90$ K and the observed second phase transition at $T_{N2} = 48$ K [7, 8]. As shown in [25], a majority of ionic displacements from $R3$ to $R3$ phase can achieve an about $10^{-5}$ order of magnitude of the lattice constants, whereas all the displacements from $R3$ to $P3$ remain in the order of $10^{-4}$ of the lattice constants. So far as we know, despite the evident change in lattice parameters at $T_{N2}$ [14, 31], no direct evidence of the $R3$ and the $P3$ structures has yet been reported because the atomic displacements are extremely small. Our results stimulate further careful investigations of the temperature dependence of selected structural parameters to explore the anomalies of the atomic displacement parameters (ADPs) at $T_{N1}$ and $T_{N2}$, as has been done in TbMn$_2$O$_5$ [32]. Here we propose a novel diffraction technique [33], of which the amplitude and phase of the ionic displacements are encoded due to the interference between charge and magnetic x-ray scattering, to directly determine the internal atomic coordinates of the intermediate $R3$ phase and the ground-state $P3$ structure because of the very high precision, up to several femtometers.

To further shed light on the underlying physics, we have determined the orders of the two phase transitions and their possible domain states. According to the Landau phase transition theory, a phase transition is allowed to be continuous only if both the Landau condition and the Lifshitz condition are satisfied for the primary order parameter. On the other hand, a phase transition must be first order as long as the Lifshitz condition is violated. In the case of the first transition from $R3$ to $R3$, it is obvious that the $R3$ symmetry is a subgroup of the $R3$ space group and that the $A_{u}$ mode is just the single irreducible representation corresponding to this phase transition. If we expand the free energy of the crystal in terms of components of the $A_u$ order parameter, we find that the third-degree invariant polynomials are vanishing. In other words, the Landau condition is satisfied. Furthermore, theoretical analysis [29, 30] also shows that the low-symmetry $R3$ phase will retain the macroscopic uniformity because the Lifshitz invariant is excluded from the symmetry considerations. The above analysis demonstrates that the Landau condition and Lifshitz condition are both satisfied for the primary order parameter of the $A_u$ irrep, which indicates the second-order characteristic of this phase transition. In addition, the analysis also demonstrates that this phase transition is allowed to be continuous even in the renormalization-group theory. This conclusion is also supported by the clear lambda character of the specific heat (figure 2(a) in [7]) and the absence of thermomagnetic irreversibility [22] around $T_{N1}$. In the case of the second transition from $R3$ to $P3$, we find that the primary order parameter of the doubly degenerate $\Lambda_1$ mode is incapable of meeting the...
Lifshitz condition, which demonstrates that this phase transition cannot be continuous. In fact, experimental observation of the thermal hysteresis behavior \cite{22} around $T_{N2}$ has confirmed the first-order character of this phase transition.

As we all know, collection of coherent domains, which are symmetrically and energetically equivalent structures differing only in their orientation and possibly position, often occurs when a crystal undergoes a phase transition. For more information concerning the possible domain states associated with the R3 to P3 phase transition, group theory analysis shows that there are three domain states which have the same basis vectors but different origins. Careful inspection shows that the common basis vectors for the three single-domain states are $(1, 1, 0), (-1, 0, 0),$ and $(0, 0, 1)$. On the other hand, the three different origins are respectively $(0, 0, 0), (-1/3, 1/3, 1/3)$ and $(1/3, 2/3, 2/3)$, which are just the three Wyckoff positions of Ca ions in the 60-atom crystallographic unit cell. Furthermore, the three single-domain states of the P3 phase are only applicable to form a single multi-domain structure of which the basis vectors are $(-1, -1, 0), (1, 0, 0),$ and $(0, 0, 1)$ while the origin is at the $(0,0,0)$ point. It is important to note that the average symmetry of the single multi-domain structure is the R3 space group. Our result is consistent with the experimental observation \cite{7, 8} that the propagation vector of the AFMI spin ordering splits into two symmetric branches, which indicates the coexistence of two modulations along the same symmetry. In other words, the particular domain states and the single multi-domain structure in the P3 phase may provide an alternative understanding of the helicoidal magnetic order below $T_{N2}$, which is characterized by two propagation vectors split symmetrically from that of the AFMI phase \cite{8, 34}.

### Table 2. Mode decomposition of the FE polarization in terms of different distortion patterns.

The $P_{xy}$ and $P_{xz}$ represent the polarizations along the $z$ axis which are induced by the atomic displacements with respect to the $xy$ plane and the $z$ direction, respectively. The summation of $P_{xy}$ and $P_{xz}$ represents all values in unit of $10^3 \mu C m^{-2}$. The Born effective charges (BECs) used here are those calculated in the R3 phase with the AFMI magnetic order.

| Atom | $\mathbf{A}_2$ modes | $\mathbf{A}_3$ modes | $\mathbf{A}_4$ modes |
|------|----------------------|----------------------|----------------------|
| Ca   | $p^a_{z}$ $p^b_{z}$ $p^c_{z}$ | $p^a_{z}$ $p^b_{z}$ | $p^c_{z}$ |
| Mn1  | $1.0097$ $-2.1561$ $-1.1464$ | $0$ $0$ $0$ | $0$ $-0.0316$ $-0.0316$ |
| Mn2  | $0.0434$ $-1.0716$ $-1.0283$ | $0$ $0$ $0$ | $-0.0812$ $-0.0114$ $-0.0926$ |
| Mn3  | $0$ $0.8758$ $0.8758$ | $0$ $0$ $0$ | $0$ $0.1226$ $0.1226$ |
| O1   | $-0.1052$ $0.0915$ $-0.0137$ | $0.4580$ $3.7251$ $4.2101$ | $0.2649$ $-0.0091$ $0.2558$ |
| O2   | $0.3328$ $-0.1823$ $-0.5151$ | $2.3950$ $0.0580$ $2.4530$ | $-0.0223$ $-0.2284$ $-0.2506$ |
| $\Sigma$ | $0.2047$ $-1.0622$ $-0.8574$ | $-2.3473$ $-0.0265$ $-2.3738$ | $0.3900$ $-0.2234$ $0.1666$ |

### 3. Spontaneous electric polarization

We now determine the spontaneous polarization of CaMn$_2$O$_{12}$ by using the Berry phase method \cite{35}. The total FE polarization of the ground-state P3 structure in the AFMI helicoidal magnetic order is parallel to the $c$ axis with a value of $3230 \mu C m^{-2}$ from the DFT + $U$ calculations. Our calculated FE polarization is in excellent agreement with the experimental value of $2870 \mu C m^{-2}$ \cite{8}. In order to estimate the influence of the phase transition from R3 to P3 on the FE polarization, we artificially construct a P3 structure by only freezing in the unstable $A_2$ mode of the R3 phase, and the polarization becomes $-48.7 \mu C m^{-2}$ in this case. Thus, it is the first transition from R3 to P3 that results in the giant FE polarization and the second transition from R3 to P3 has negligible effect, which is consistent with experiments \cite{7, 8}. When the SOC is turned on, the FE polarization of the ground-state R3 phase is $3002 \mu C m^{-2}$, which is reduced by 7% in comparison with that without SOC. Therefore, our results as well as previous theoretical works \cite{16, 17} demonstrate that the giant FE polarization of CaMn$_2$O$_{12}$ is almost completely determined by the exchange-striction mechanism rather than by the SOC effect.

To understand the polarization contributions from different Wyckoff coordinates for each distorted mode, we perform mode decomposition \cite{28} of the ground-state P3 structure in terms of the AFMI R3 reference phase. As a matter of course, besides the tiny $A_3$ -symmetry distortion, the atomic displacements from R3 to P3 are composed of the Raman-active $A_2$ and the IR-active $A_4$ modes. As shown in table 2, polarization contributions from these three types of atomic displacement sum up to $-3065 \mu C m^{-2}$, which is in good agreement with the value obtained by using the Berry phase method. The negative sign denotes that the direction of polarization is opposite to the forward direction of the $z$ axis. The small change in polarization induced by the $A_1$ -irep distortion, $P \approx 167 \mu C m^{-2}$, is also consistent with our previous theoretical estimate and the experimental results \cite{7, 8}.
Table 3. Mode decomposition of the FE polarization using the BECs calculated in the R3 phase with the AFMr magnetic order. $P_{xy}$ and $P_{xz}$ denote the z-direction polarizations induced by the atomic displacements in the $xy$ plane and along the $z$ axis, respectively. The values of BECs for the AFMr state, as well as the differences between AFMI and AFMr magnetic order in the $P_{xy}$ and $P_{xz}$ polarizations and the BECs are given in units of $10^3 \mu$C m$^{-2}$ and $\epsilon$, respectively.

| Atom | $A_g$ modes | $A_u$ modes | BECs (AFMr) | $\Delta$BECs (AFMI–AFMr) |
|------|-------------|-------------|-------------|-----------------|
|      | $p^A_{xy}$  | $p^A_{xz}$  | $p^u_{xy}$  | $Z^A_{xx}$ | $Z^A_{xy}$ | $Z^A_{xz}$ | $Z^u_{xx}$ | $Z^u_{xy}$ | $Z^u_{xz}$ | $\Delta Z^A_{xx}$ | $\Delta Z^A_{xy}$ | $\Delta Z^A_{xz}$ | $\Delta Z^u_{xx}$ | $\Delta Z^u_{xy}$ | $\Delta Z^u_{xz}$ |
| Ca   | 0           | 0           | 0           | 1.4450 | 0   | 0   | 2.812 | −0.011 | 0.004 | 0.138 |
| Mn1  | 0           | 0           | 1.7872     | −2.9278 | 0   | 0   | 4.460 | −0.020 | 0.009 | −1.176 |
| Mn2  | 0           | 0           | −0.5929    | −1.4256 | 0   | 0   | 5.286 | 0.007 | 0.014 | −1.313 |
| Mn3  | 0           | 0           | 0          | 1.1480 | 0   | 0   | 4.800 | −0.044 | 0.035 | −1.138 |
| O1   | −0.7962     | 5.0867     | −0.2514    | 0.1240 | 0   | 0   | −4.055 | −0.039 | 0.021 | 1.044 |
| O2   | 0.7964      | −5.0752    | −0.2368    | 0.1444 | 0   | 0   | −4.064 | 0.044 | −0.031 | 1.066 |
| O2   | −5.5600     | −0.0740    | 0.4142     | −0.2643 | 0   | 0   | −2.078 | 0.033 | −0.008 | 0.169 |
| O2   | 5.5467      | 0.0745     | 0.4534     | −0.2343 | 0   | 0   | −2.093 | −0.006 | −0.019 | 0.465 |
| Σ    | −0.0130     | 0.0120     | 1.5738     | −1.9906 |

For the $A_g$-type distortion, the dominant contribution of $-1062 \mu$C m$^{-2}$ comes from atomic displacements along the $z$ direction, while the displacements within the $xy$ plane partially counteract the total contribution of the $A_g$ modes. A close look at the contributions $P^A_{xy}$ from different Wyckoff coordinates reveals that each type of ion except O1 has considerable influence, among which the Ca and Mn3 give rise to contributions opposite to the net polarization. In addition, the large counteracting contribution from Ca cations (1516 $\mu$C m$^{-2}$) has not been reported in previous theoretical investigations [16, 17] and, indeed, it cannot be explained by any existing model that takes only account of Mn–O–Mn exchange interactions. It should be pointed out that a similar result has been reported in the TbMnO$_3$ system although the ferroelectricity is induced by a cycloidal spin spiral via the SOC effect [23, 36]. In that case, the displacements of Tb cations, which are uninvolved in the usual scenario of nearest-neighbor Mn–Mn spin interactions, contribute about 20% of the lattice polarization [23]. Finally, it is crucial to pay attention to the fact that the contribution from the IR-active $A_g$ modes is only responsible for $-857 \mu$C m$^{-2}$, which is far less than the overall value of $-3065 \mu$C m$^{-2}$.

The most unexpected outcome is that the dominant contribution up to about 77.5% ($-2374 \mu$C m$^{-2}$) of the total polarization is due to the purely Raman-type $A_g$ distortion, which, for the traditional ferroelectrics, is not concerned with the appearance of ferroelectricity. Due to the ionic displacement pattern of the $A_g$ modes, displacements of all the cations (Ca and three types of Mn) are vanishing and hence have no contributions to the polarization. Within the range of numerical precision, the extremely large contribution to the polarization is found to result entirely from the displacements of O ions within the $xy$ plane. Among these contributions, it is evident that the O2 ions play a decisive role. As regards the polarizations of O ions along the $z$ direction, we find that the large contributions from two types of O1 anion almost cancel each other out.

The fact that the giant FE polarization of CaMn$_2$O$_4$ is mainly due to the purely Raman-type distortion will lead to serious conflict with our ingrained concept that ferroelectricity originates only from the zone-center IR-active modes instead of the Raman-active modes. As we know, the purely Raman-active modes belong to the symmetry-preserving irreps and the ionic displacement pattern can not lower the crystallographic symmetry. However, we should not ignore the fact that the dominating contribution of a Raman mode to electric polarization implies the following hypothesis: the local electric dipoles induced by these ionic displacements are equal in magnitude and opposite in direction and hence entirely cancel each other out, which requires that the symmetry of atomic BECs is consistent with the crystallographic symmetry. This is true for traditional ferroelectrics, but the case of improper ferroelectricity deserves careful analysis. As we know, for the magnetic multiferroics driven by the exchange-striction mechanism, the magnetic order itself breaks the spatial inversion symmetry, which can lead to a remarkably asymmetric change in BECs. One possible consequence of the mismatch between the BECs and the lattice symmetry is that local electric dipoles induced by the symmetry-preserving ionic displacements can not be completely canceled out, and then the ferroelectricity comes into being, i.e. the purely Raman-active modes exhibit abnormal IR-active character.

To confirm the above argument, we recalculate the polarization contributions of Raman-active $A_g$ and IR-active $A_u$ modes using the BECs of the R3 phase in the AFMr magnetic order. The results are given in table 3. This time, we can see that the local electric dipoles caused by O displacements of the Raman-type $A_g$ distortions counteract each other and the net contribution to polarization is vanishing. More than this, the change in polarization for the IR-active $A_u$ modes is also distinct not only for the net polarization ($-417 \mu$C m$^{-2}$) but also for the contribution from each Wyckoff coordinate. Since the ionic displacements remain invariant, the significant difference in polarization contributions can only be attributed to the change in BECs and, in the final analysis, to the electronic charge redistribution induced by different magnetic orders. For CaMn$_2$O$_4$, the
The asymmetric change in BECs for the AFMI helicoidal magnetic order with respect to the AFMr magnetic structure is also collected in table 3. It is clear that, for the AFMr magnetic order, the zx and zy components of BECs are zeros because the magnetic order is in accordance with the crystallographic symmetry, which results in the vanishing polarization contribution of the ionic displacements within the xy plane for the $A_g$-type distortion. In the case of CaMn$_7$O$_{12}$, the improper ferroelectricity originates mainly from the exchange-striction mechanism, of which the magnetic point group of 31' breaks the inversion symmetry and leads to strong asymmetry in hybridization of electronic orbitals. This electronic effect induced by the helicoidal magnetic order will inevitably be reflected in the asymmetric change of the BECs, which mismatches the BECs with the crystallographic symmetry. As shown in table 3, besides the distinct changes in $Z_{2-3}$, we also identify that the zx and zy components of BECs possess nonzero values due to the AFMI helicoidal magnetic order. Thus we conclude that, for the $A_g$-type distortion, it is the nonzero zx and zy components of BECs that give rise to significant contributions to the FE polarization.

For CaMn$_7$O$_{12}$, with regard to the purely electronic polarization, we freeze the ionic positions in the $R^3$ reference structure while switching the magnetic order from AFMr to AFMI state and calculate the polarization to be $-4787 \mu C m^{-2}$. This value is much larger than the actual theoretical value of $-3230 \mu C m^{-2}$, suggesting that the ionic displacements provide an opposite contribution of 1557 \mu C m^{-2} to partially counteract the pure electronic polarization. Finally, the AFMI helicoidal magnetic order in CaMn$_7$O$_{12}$ results not only in strong coupling of the BECs with the incommensurate structural modulation along the c axis appears below this temperature, producing a continuous variation in Mn–O bond lengths, and this corresponds to the onset of a novel form of orbital ordering, which may be crucial for the emergence of the unusual helicoidal spin order in CaMn$_7$O$_{12}$. In our present work, we just adopt the experimental helicoidal spin order without respect to the origin of such a magnetic structure. The charge-ordering transition and the consequent incommensurate structural modulation, which are apparently not captured by our first-principles calculations, deserve further investigations.

Finally, we should point out that, as mentioned above, an isostructural charge-ordering transition develops gradually below 250 K. According to [15], an incommensurate structural modulation along the c axis appears below this temperature, producing a continuous variation in Mn–O bond lengths, and this corresponds to the onset of a novel form of orbital ordering, which may be crucial for the emergence of the unusual helicoidal spin order in CaMn$_7$O$_{12}$. In our present work, we just adopt the experimental helicoidal spin order without respect to the origin of such a magnetic structure. The charge-ordering transition and the consequent incommensurate structural modulation, which are apparently not captured by our first-principles calculations, deserve further investigations.

4. Conclusions

In summary, for the magnetic multiferroic CaMn$_7$O$_{12}$, the ground-state structure should be the $P3$ space group with $R^3$ symmetry as the intermediate phase. The two phase transitions from $R3$ through $R3$ to $P3$ are driven by the helicoidal spin spiral and soft modes but under the constraint of the helicoidal magnetic order, respectively. The initial second-order and then first-order character of this phase transition sequence is also consistent with experimental observations. Mode decomposition of the ferroelectric polarization demonstrates the dominant contribution from the purely Raman-type lattice distortion. This unexpected outcome is in conflict with the ingrained concept in traditional ferroelectrics, which can be understood by the abnormal IR-active character of the purely Raman modes caused by asymmetric changes of the BECs in the helicoidal magnetic order. The possibility of improper ferroelectricity induced by the Raman-type ionic displacements opens an avenue to search for or design novel magnetic multiferroics.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (grant Nos. 51162019 and 51462019).
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New J. Phys. 17 (2015) 113038