Effects of temperature and electric field on order parameters in ferroelectric hexagonal manganites

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In Landau-Devonshire phase transition theory, the order parameter represents a unique property for a disorder-order transition at the critical temperature. Nevertheless, for a phase transition with more than one order parameter, such behaviors can be quite different and system-dependent in many cases. In this work, we investigate the temperature (T) and electric field (E) dependence of the two order parameters in improper ferroelectric hexagonal manganites, addressing the phase transition from the high-symmetry P63/mmc structure to the polar P63/mcm structure. It is revealed that the trimerization as the primary order parameter with two components: the trimerization amplitude Q and phase Φ, and the spontaneous polarization P emerging as the secondary order parameter exhibit quite different stability behaviors against various T and E. The critical exponents for the two parameters Q and P are 1/2 and 3/2, respectively. As temperature increases, the window for the electric field E enduring the trimerization state will shrink. An electric field will break the Z2 part of the Z2×Z3 symmetry. The present work may shed light on the complexity of the vortex-antivortex domain structure evolution near the phase transition temperature. Published by AIP Publishing.

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I. INTRODUCTION

Very different from typical ferroelectrics where spontaneous polarization is the primary order parameter,¹,² improper ferroelectrics usually have the ferroelectricity that is induced by phase transitions such as structural transitions, charge orders, and so on, rather than the primary displacive mode.³–⁸ Recently, these improper ferroelectrics have been receiving substantial attention due to the possible coexistence and inter-coupling of ferroelectricity and magnetism, i.e., multiferroicity.⁹ Among these improper ferroelectrics, hexagonal manganites (h-RMnO₃: R = rare earths) have been of particular concern, and the coupled lattice distortion and ferroelectric polarization are of high interest.¹⁰–¹² Especially, the finding of topological domain patterns in such systems,¹³,¹⁴ as shown in Fig. 1(c) for guiding the eye, makes h-RMnO₃ the focus of research on multiferroics. For the method used to obtain (c), the reader can refer to previous works.¹⁵,¹⁶

It is now well established that such a real space topological domain pattern in ferroelectric h-RMnO₃ essentially correlated with the trimerization-type structural phase transition.¹³,¹⁷,¹⁸ Such a trimerization occurs below certain temperature Tc and it originates from the periodic tilting of the MnO₃ trigonal bipyramids from the high-symmetry P63/mmc structure. This collective tilting leads to the lattice distortion with the effective unit cell being three times the basic unit cell in size. Consequently, the lattice symmetry is lowered to the polar P63/mcm space group which accommodates the three degenerate trimerization antiphases (α, β, γ). It is described by the Z3 symmetry. Here, each antiphase can accommodate two equivalent polarization states, marked P⁺ and P⁻ for the upward and downward polarizations along the c-axis, respectively. Consequently, there are generated six interlocked structural antiphase and ferroelectric domains satisfying the so-called Z2×Z3 symmetry. These domains would meet in a cloverleaf arrangement that can be characterized by two winding orders (α⁺, β⁺, γ⁺, α⁻, β⁻, γ⁻) and (α⁺, γ⁻, β⁺, α⁻, γ⁺, β⁻). Geometrically, these two orders correspond to a vortex and an antivortex which constitute a vortex-antivortex pair. This pair appears to be the basic unit for constructing the real space topological domain structure, as observed experimentally over the whole space. Such a topological domain pattern has been sufficiently discussed using the graph theory.¹⁹

In the past several years, various aspects of such interesting domain patterns have been intensively investigated, including the topological geometry, the microscopic mechanism, and the dynamics.¹⁶,²⁰–²⁵ Nevertheless, it is a bit strange that less comprehensive studies on the phase transitions in the space of temperature T and the electric field E in terms of order parameters have been reported. Landau theory on the structural and ferroelectric phase transitions in such systems must include two order parameters. One is the structural trimerization as described by the trimerization amplitude Q and the phase Φ and the other is the spontaneous polarization (P). For details, readers may refer to earlier literature.³,²⁶ Certainly, for a system with more than one order parameter, the temperature dependence of these order parameters and the critical behaviors have also been rarely investigated. It is of fundamental importance for understanding the mechanism of phase transitions occurring in such systems. In this paper, particular focus is placed on the T and E dependence of the two order parameters in a mode improper...
ferroelectric $h$-RMnO$_3$. The coupled behaviors of the two order parameters in the phase transition sequence can be illustrated to some extent.

The remaining part of this article is organized in the following. In Sec. II, the phenomenological Landau theory used in this paper is introduced. The main results on the variation of the order parameters against varying $T$ and $E$ will be presented in Sec. III with relevant discussions, including the critical behaviors, although the critical behaviors as predicted by Landau theory on second-order phase transitions are not accurate. A brief conclusion is given in Sec. IV.

II. LANDAU THEORY

We start from the well-established phenomenological Landau theory in which the two order parameters, trimerization and polarization ($P$), are included. As mentioned above, the trimerization can be described by its amplitude $Q$ and phase $\Phi$, with $Q$ describing the tilting amplitude of a bipyramidal triangular from the $c$-axis and $\Phi$ the azimuthal angle of the tilting, as shown in Fig. 1(b). Here, only the amplitude $Q$ is discussed and the phase $\Phi$ is found to be independent of stimuli in many cases. In fact, it is understood that the phase $\Phi$ is determined by the trimerization geometry and it may take one of the six constant values ($0, \pm \pi/3, \pm 2\pi/3, \pi$). A combination of the two order parameters can characterize the lattice distortion from the high-symmetry $P6_3/mmc$ structure to the polar $P6_3cm$ structure.\textsuperscript{11,12} In the framework of lattice dynamics, the trimerization can be viewed as the condensation of the zone-boundary $K_3$ mode and the ferroelectric polarization as the secondary order parameter can be characterized by the amplitude of the polar $\Gamma_{2}^-$ mode. So, $Q$ and $P$ can also represent the amplitude of the zone-boundary $K_3$ mode and the zone-center $\Gamma_{2}^-$ mode, respectively. The nonlinear coupling between the $K_3$ and $\Gamma_{2}^-$ modes induces ferroelectricity in $h$-RMnO$_3$.\textsuperscript{11,12,18} This is the reason why the ferroelectricity in $h$-RMnO$_3$ is categorized as the improper ferroelectricity. For many improper ferroelectrics, the two polarization states may not be degenerate, but here they are.

The expression of the system free energy (density) for an $h$-RMnO$_3$ system has been well established according to the transformation properties of the trimerization and the polarization based on Landau theory.\textsuperscript{11,12} In consideration of the effect of the electric field along the $z$-axis, the free energy can be written in the following form:

$$F = -\frac{a_0}{2T_0}(T - T_0)Q^2 + \frac{b_0}{4}Q^4 + \frac{c_0}{6}Q^6 + \frac{c_0'}{6}Q^6 \cos 6\Phi - gQ^3P \cos 3\Phi + \frac{b'}{2}Q^2P^2 + \frac{d_0P^2}{2} - E_zP,$$

where the term $-E_zP$ is the electrostatic energy that is rooted in the fact that only the polarization along the $c(z)$-axis exists in these ferroelectric hexagonal manganites and it is sufficient to consider the effect of the electric field along the $z$-axis $E_z$.\textsuperscript{13,16} According to Artyukhin et al., $Q$ and $P$ in Eq. (1), respectively, represent the amplitude of the zone-boundary $K_3$ mode and the zone-center $\Gamma_{2}^-$ mode. Both $Q$ and $P$ were measured in displacement, while the unit used in this work is pm. The real polarization $P_c$ is related to the amplitude of the polar zone-center $\Gamma_{2}^-$ mode $P$ by $P_c = V^{-1}Z^*P$, where $Z^*$ is the effective charge of the polar mode $\Gamma_{2}^-$ and $V$ is the volume of the unit cell. For the sake of simplification, the amplitude of the polar zone-center $\Gamma_{2}^-$ mode $P$ is used to scale the polarization in this work. Parameters $a_0$, $b_0$ and $c_0$ are the constants for the free energy polynomial on $Q$ extended up to...
the sixth-order, $c'_0$ is the anisotropic coupling factor between $Q$ and $\Phi$, $g$ is the nonlinear coupling factor between mode $K_i$ and mode $\Gamma_2^*$, $g'$ is the coupling factor between $Q$ and $P$, and $a_p$ is the self-energy factor of $P$.

We discuss the measure of the external electric field as done in earlier work.\textsuperscript{16} Here, $E_z = E . E_0$ is set, where $E_0 = 1.0 \text{ eV/Å}$ and $E$ is a dimensionless number. The realistic electric field $E_z$ is obtained by $E_z = 2E.E_0(9.03) = 22146$ $E$ with the unit of kV/cm. In this work, hexagonal YMnO$_3$ is taken as the representative of hexagonal manganites RMnO$_3$, and the parameter values for YMnO$_3$ given by Artyukhin et al.\textsuperscript{12} based on the first-principles calculations are taken in practical calculations. These parameters are shown in Table I. For hexagonal YMnO$_3$, the structural phase transition temperature is about 1270 K, which is used as the value of $T_s$ in the following calculations.

We first concentrate on the possible ground states as given by Landau theory. According to the usually used analyzing method in Landau theory,\textsuperscript{13,14,16} the equilibrium state of order parameters can be determined from the standard procedure by evaluating the conditions for minimization of free energy density $F$ with respect to parameters $Q$, $\Phi$, and $P$. Mathematically, this procedure is equivalent to solving the following set of equations:

$$\frac{\partial F}{\partial Q} = -\frac{a_0}{T_s} (T - T_s) + b_0 Q^2 + (c_0 + c'_0 \cos 6 \Phi) Q^4 - 3gQ p \cos 3 \Phi + g' P^2 = 0,$$

$$\frac{\partial F}{\partial \Phi} = -gQ^3 \cos 3 \Phi + (g' Q^2 + a_p) P - E_z = 0.$$  \hspace{0.5cm} (2)

The solution of Eq. (2) can be written in the following form:

$$\left\{ \begin{array}{l}
-\frac{a_0}{T_s} (T - T_s) + b_0 Q^2 + (c_0 + c'_0) Q^4 - 3gQ \cos 3 \Phi \\
\times \frac{gQ^3 \cos 3 \Phi + E_z}{g' Q^2 + a_p} + g' \left( \frac{gQ^3 \cos 3 \Phi + E_z}{g' Q^2 + a_p} \right)^2 = 0, \\
\Phi = 0, \pm \pi/3, \pm 2\pi/3, \pi, \\
P = \frac{gQ^3 \cos 3 \Phi + E_z}{g' Q^2 + a_p},
\end{array} \right.$$  \hspace{0.5cm} (3)

which can be divided into two types: one with upward polarization ($P_\uparrow$) and the other with downward polarization ($P_\downarrow$), as shown below

$$-\frac{a_0}{T_s} (T - T_s) + b_0 Q^2 + (c_0 + c'_0) Q^4 - 3gQ \frac{gQ^3 + E_z}{g' Q^2 + a_p}$$

$$+ g' \left( \frac{gQ^3 + E_z}{g' Q^2 + a_p} \right)^2 = 0,$$

$$\Phi = 0, \pm \pi/3, \pi,$$

$$P = \frac{gQ^3 + E_z}{g' Q^2 + a_p} \quad (P_\uparrow, P > 0),$$

$$-\frac{a_0}{T_s} (T - T_s) + b_0 Q^2 + (c_0 + c'_0) Q^4 - 3gQ \frac{gQ^3 - E_z}{g' Q^2 + a_p}$$

$$+ g' \left( \frac{gQ^3 - E_z}{g' Q^2 + a_p} \right)^2 = 0,$$

$$\Phi = 0, \pm \pi/3, \pi,$$

$$P = - \frac{gQ^3 - E_z}{g' Q^2 + a_p} \quad (P_\downarrow, P < 0).$$  \hspace{0.5cm} (4)

It can be seen from Eq. (4) that the variation of $Q$ in the $P_\uparrow$ state exposed to a positive electric field is exactly the same as that in the $P_\downarrow$ state exposed to a negative electric field, corresponding to a reversal of polarization $P$. It accords with the fact that the $P_\uparrow$ and $P_\downarrow$ states are the two degenerate states described by the $Z_2$ symmetry.

III. RESULTS AND DISCUSSION

A. Temperature dependence of order parameters

As the electric field is absent, the following relationship between $Q$ and $T$ can be obtained from Eq. (4)

$$-\frac{a_0}{T_s} (T - T_s) + b_0 Q^2 + (c_0 + c'_0) Q^4 - 3gQ \frac{gQ^3}{g' Q^2 + a_p}$$

$$+ g' \left( \frac{gQ^3}{g' Q^2 + a_p} \right)^2 = 0,$$  \hspace{0.5cm} (5)

which is applicable to the $P_\uparrow$ and $P_\downarrow$ states. The $T$-dependence of parameter $Q$ can be obtained by numerically solving Eq. (5), and the corresponding $T$-dependence of parameter $P$ can be evaluated from Eq. (4).

Taking the $P_\uparrow$ state as an example, we check the $T$-dependences of parameters $Q$ and $P$ in the absence of an electric field, and the results are plotted in Figs. 2(a) and 2(b) where the solid dots are numerically calculated data and the solid lines represent the fitting using the scaling relationship for a second-order phase transition.

Apparently, the $T$-dependence of $Q$ clearly demonstrates the typical second-order phase transition, while the
continuous decaying near the critical temperature \(T_c\) can be well described by the well-established scaling law. Here, \(Q\) as the primary order parameter does fit well the power law with the scaling exponent \(\beta_Q = 0.4966 \pm 0.0003\), as shown in Fig. 2(a), consistent with the theoretical prediction of 1/2 for a typical second-order phase transition. This consequence is reasonable considering the nature of \(Q\) as the primary order parameter, while this prediction seems not well applicable to the secondary order parameter \(P\). In fact, if one looks at the \(P(T)\) data, as shown in Fig. 2(b), the best fitting can be obtained only in the \(T\)-range far below the critical point \(T_c\), noting that the critical point for \(P\) must be the same as that for \(Q\) in the absence of an electric field \((E = 0)\). It seems that the data at \(T \to T_c\) exhibit a behavior different from the 1/2-exponential behavior. We consider two specific cases in the absence of an electric field \((E = 0)\)

\[
\begin{align*}
\{ & P \sim \pm \frac{g}{g'}Q \sim \pm (T_c - T)^{\beta_P} \\
& (E = 0, \ Q \neq 0 \ \text{and} \ g'Q^2 \gg \alpha_P) \\
& P \sim \pm \frac{g}{\alpha_P}Q^{1/2} \sim \pm (T_c - T)^{\beta_Q} = \pm (T_c - T)^{\beta_r}, \\
& \beta_P = 3\beta_Q \quad (E = 0, \ Q \to 0)
\end{align*}
\]

where \(\beta_P\) is the scaling exponent for order parameter \(P\). It is thus clearly shown that the order parameter \(P\) follows the same scaling behavior as \(Q\) if \(g'Q^2 \gg \alpha_P\) and \(Q \neq 0\). However, as \(T \to T_c\), one has \(Q \to 0\), leading to the second scaling law given in Eq. (6). In this case, one has the scaling exponent for \(P\), \(\beta_P = 3\beta_Q = 3/2\) in the absence of an electric field.

In fact, the calculated \(P(T)\) data over a broad \(T\)-range below \(T_c\), as shown in Fig. 2(b), can be approximately fitted using the power law, with the scaling exponent \(\beta_P = 0.5984 \pm 0.0011\). It is noted that this fitting produces big uncertainties, and such an exponent is not common for a typical second-order phase transition. Subsequently, we come to the data very close to \(T_c\) and the data are re-plotted in Fig. 2(c), and the fitting using the power scaling relationship gives an exponent \(\beta_P = 1.5 \sim 3/2\), very well consistent with the prediction of Eq. (6).

Here, it noted that Landau theory itself may be inaccurate for correctly describing the critical behavior of a second-order phase transition. The scaling exponent of 1/2 is either not correct. The significance of the present results is to unveil a scaling behavior of the secondary order parameter different from that of the primary order parameter. In the qualitative sense, this is not strange since the two order parameters follow different symmetries on one hand, and on the other hand, polarization \(P\) as the secondary order parameter is coupled with the primary order parameter \(Q\) via the specific term given in Eq. (1), resulting in a different critical behavior. Another point that is noticeable is that the critical exponents for \(Q\) and \(P\) are connected by the scaling law. In fact, the scaling behavior of the secondary order parameter in the system that has more one order parameter has rarely been investigated before. The result of this section provides a clue for answering such questions.

Here, it should also be mentioned that no \(T\)-dependence of parameter \(\Phi\) is available, and this consequence is straightforward since no such dependence is considered in Eq. (3). Therefore, the trimerization phase \(\Phi\) is independent of \(T\). Such a prediction may not be correct in the quantitative sense, but correct qualitatively.

**B. Electric field dependence of order parameters**

Now, we investigate the effect of \(E\) on the two order parameters. The calculated results at three different temperatures in the case of two polarization states \((P_1\) and \(P_\perp\)) are plotted in Figs. 3(a) and 3(b). Two features can be highlighted. First, it is clearly seen that for each \(T\) parameter \(Q\) as a function of \(E\) shows a distorted semi-cycle pattern and it is easy to understand that such a semi-cycle pattern shifts toward the \(E > 0\) side for the \(P_1\) state and toward the \(E < 0\) side for the \(P_\perp\) state. Second, the \(E\)-window for stable \(Q\)-states becomes narrow with increasing \(T\). This is also understandable since \(Q\)
decreases gradually and the $E$-range in which a real solution of $Q$ in Eq. (5) exists shrinks with increasing $T$.

For parameter $P$, it is a monotonously increasing function of $E$, as shown in Fig. 3(b). This function could be roughly linear in the $E$-range where $Q$-variation is insignificant. In the two ends, where $Q$ varies sharply, the $E$-dependence of $P$ becomes severely nonlinear, and eventually the switching of $P$ occurs when no more real solution of $Q$ is available at the two ends.

C. Energy contours in the parameter space

Furthermore, it would be beneficial to discuss the variations of order parameters in the free energy space. This energy contour allows us to have an overall understanding of these variations. By substituting the solutions of $Q$ and $P$ given in Eq. (3) into Eq. (1), the free energy has the following form:

$$F = -\frac{a_0}{T_s} (T - T_s) Q^2 + \frac{b_0}{4} Q^4 + \frac{1}{6} (c_0 + c'_0 \cos 6\Phi) Q^6$$

$$-\frac{1}{2} \left( gQ^3 \cos 3\Phi + E_z \right)^2.$$  

(7)

By transforming the polar coordinates $Q$ and $\Phi$ into Cartesian coordinates $(Q_x, Q_y)$ where $Q_x = Q \cos \Phi$ and $Q_y = Q \sin \Phi$, Eq. (7) can be rewritten as

$$F = -\frac{a_0}{2 T_s} (T - T_s) (Q_x^2 + Q_y^2) + \frac{b_0}{4} (Q_x^2 + Q_y^2)^2 + \frac{c_0}{6} (Q_x^2 + Q_y^2)^3$$

$$+ \frac{c'_0}{6} (Q_x^6 - 15 Q_x^4 Q_y^2 + 15 Q_x^2 Q_y^4 - Q_y^6)$$

$$-\frac{1}{2} \left( g(Q_x^3 - 3 Q_x Q_y^2) + E_z \right)^2.$$  

(8)

The calculated energy contours in the $(Q_x, Q_y)$ planes at different $T$ and $E$ are summarized in Fig. 4. First, the six-fold

FIG. 3. The order parameters $Q$ (a) and $P$ (b) as a function of electric field $E$ at different temperatures.

FIG. 4. The energy contours in the order parameter space for different temperatures and electric fields.
symmetry of the contours at $E = 0$ can be clearly shown, and the six minima appear, corresponding to the six trimerization phases ($\Phi = 0, \pm \pi/3, \pm 2\pi/3, \pi$). Second, the contour shrinks gradually with increasing $T$ in terms of the energy depth and $(Q_1, Q_2)$ values of the six valleys, which accords with the previous statement that the trimerization-type structural phase transition starts from the undistorted $P6_3/mmc$ structure. Third, for a positive field ($E > 0$), the alternative three of the six valleys, corresponding to the three domains with negative polarization ($P_1$), are equivalently lifted up, damaging the stability of these domains. This character is reversely shown if a negative field is applied. Therefore, the electric field would break the $Z_2$ part of the $Z_2 \times Z_2$ symmetry of $h$-RMnO$_3$.

Finally, it should be remarked that all the discussions on the phase transition in $h$-RMnO$_3$ manganites against temperature $T$ and electric field $E$ are based on Landau theory described by Eq. (1). This theory represents a simplified version of the system energy in the framework of spatial symmetry and antiphase-ferroelectric coupling. In recent works, it has been proposed that further symmetry breaking subsequent to the phase transition from the high-symmetry $P6_3/mmc$ structure to the polar $P6_3/mcm$ structure is possible. Alternatively, other symmetry breaking paths from the $P6_3/mmc$ structure to the polar $P6_3/mcm$ structure may be favored. The corresponding Landau theory remains yet to be developed, due to insufficient experimental data on the physical properties. These possibilities deserve additional investigations in near future.

IV. CONCLUSION

The temperature and electric field dependence of the two order parameters for improper ferroelectric phase transitions in hexagonal YMnO$_3$ have been investigated by numerical calculations based on the phenomenological Landau theory. It has been revealed that the temperature dependence of the trimerization amplitude $Q$ as the primary order parameter follows the scaling behaviors near the critical point of a typical second order phase transition and the scaling exponent is 1/2, while the secondary order parameter $P$ has a different $T$-temperature dependence, giving rise to a critical exponent 3/2. This difference is suggested to be related to the coupling of the secondary order parameter $P$ to the trimerization-like lattice distortion. The electric field window for the stabilized trimerization state becomes narrow as the temperature rises. The $Z_2$ part of the $Z_2 \times Z_2$ symmetry in $h$-RMnO$_3$ may be broken by applying an external electric field.

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