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A New Model of Ferroelectric Phase Transition with Neglectable Tunneling Effect *

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Due to the obvious deviations of the existing theoretical models from the experimental results of ferroelectric phase transition, a new model is proposed on the basis of the coupling between spontaneous polarization and spontaneous strain in ferroelectrics. The spontaneous polarization and specific heat of ferroelectric phase transition predicted by the model are in better agreement with the corresponding data of triglyceride sulfate, a typical ferroelectric. In addition, the model predicts a new type of ferroelectric in which a phase transition and a phase-like transition coexist.

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Ferroelectrics have a wide range of applications, including random access memories,[1,2] pyroelectric detectors,[1] electrocaloric devices,[1] piezoelectric transducers,[1,3] manipulation of light devices,[4] tunable microwave devices,[5] bypass capacitors,[1,6] dynamic access memory capacitors,[1] electron emitters,[1] photovoltaic devices,[7] visible-light-absorbing devices,[7] filtering devices,[8] etc.,[1–18] and these applications are more or less related to ferroelectric phase transitions (FPTs).

After long-term theoretical exploration, the theoretical models of FPTs have achieved great advances, such as (1) Landau phenomenological theory,[19,20] Weiss molecular field theory,[21] Ising model of pseudospin (equivalent of permanent dipole orientation),[22,23] transverse field Ising model of pseudospin,[24–26] and soft-mode theory of 2nd-order phase transition (PT),[27] (2) Devonshire phenomenological theory of 1st-order PT,[28] and (3) compressible Ising models,[29–32] and transverse field Ising model including four-pseudospin interaction (abbreviated as WQL model) of 1st or 2nd order PT.[33] However, for triglycine sulfate, a typical ferroelectric with 2nd-order PT,[34–36] the existing theoretical models still have obvious deviations from the experimental results of the spontaneous polarization (P_s) and specific heat (c_s) per dipole of FPT versus temperature (T) as shown in Fig. 1.

Therefore, it is undoubtedly valuable to explore more precise theories or models of FPTs. In this work, based on the coupling between spontaneous polarization and spontaneous strain in ferroelectrics, a new model of FPTs with neglectable tunneling effect is proposed.

Traditionally, there are two microscopic schemes, i.e., pseudospin and soft-mode, to describe FPTs. For example, the FPT of TGS and KH_2PO_4 families can be investigated by the pseudospin scheme[22–26] while that of ABO_3 ferroelectrics needs to be described by soft-mode theory.[27] However, Cohen found that, in $BaTiO_3$, a typical ABO_3 ferroelectric, the hybridization between the titanium 3d states and the oxygen 2p states is essential for ferroelectricity.[37] In other words, the phase transitions of ABO_3 ferroelectrics can also be investigated by covalent pseudospins, such as the Ising model of pseudospins.

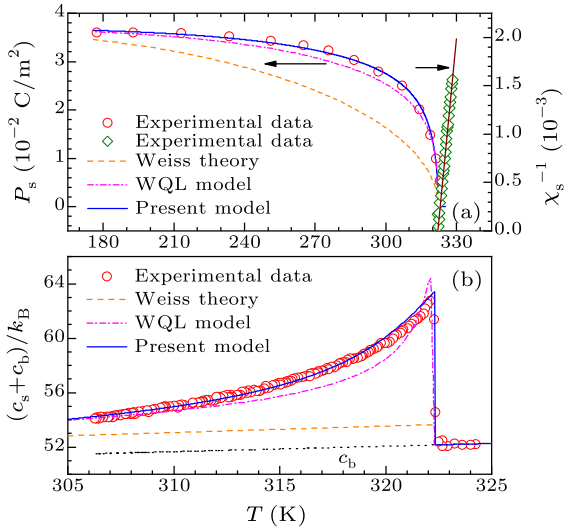

Fig. 1. Here circles and diamonds are the experimental results of P_s,[34] the reciprocal of static susceptibility (χ_s^{-1}) of the paraelectric phase,[35] and specific heat (c_s+c_b)[36] for triglycine sulfate crystal versus temperature T, with c_b being the background irrelevant to FPTs. Solid lines ($J_0 = 322.3k_B$, $\alpha = 0.289$, $\beta = 0.135$, $\mu = 1.32\times10^{-29}$ Cm, $N = 2.80\times10^{27}$ m^3), dash-dotted line ($J_0 = 322.3k_B$, $\alpha = 0.301$, $\mu = 1.32\times10^{-29}$ Cm, and $N = 2.80\times10^{27}$ m^3), and dotted line ($J_0 = 322.3k_B$, $\mu = 1.32\times10^{-29}$ Cm, and $N = 2.80\times10^{27}$ m^3) correspond to the present model, WQL model, and Weiss theory, respectively.

In the pseudospin scheme, there are the transverse-field Ising model[26] (KH_2PO_4 families with obvious tunneling effect) and the Ising model (TGS and ABO_3 families with neglectable tunneling effect).[23] To simplify the mathematical representation, the Ising model

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of pseudospins is chosen as the starting point of the present study.[22,23] In fact, the results of this work can be easily extended to the transverse-field Ising model.[24–26] The Hamiltonian of the Ising model is

$$H = -\frac{J}{2}\sum_{i\neq j}^{\{nn\}} s_i s_j, \tag{1}$$

where J is the interaction energy constant between pseudospins, s_i is the ith pseudospin in ferroelectrics, $s_i = \pm 1$, and $\{nn\}$ represents the sum over all the nearest neighbors.

In ferroelectrics, P_s is always accompanied by spontaneous strain (changes in lattice parameters and symmetry versus T),[9,38] i.e., there is coupling between spontaneous polarization and spontaneous strain, while the strain inevitably leads to the variation of J, i.e., J is related to P_s.

In view of the inversion symmetry of P_s, the relationship between J and P_s is expanded as $J = J_0(1+\alpha p_s^2+\beta p_s^4)$ in this work, where J_0, α, and β are constants independent of T, and $p_s \equiv \frac{P_s}{N\mu}$ with μ being the permanent electric dipole moment of pseudospins and N the dipole density per unit volume. In the following, we show that the αp_s^2 term is equivalent to the linear coupling of J to the lattice spontaneous strain (δ_s) of the compressible Ising models,[29–32] which may originate from the electrostriction ($\delta_s \propto p_s^2$). Further, it could be imagined that the βp_s^4 term is equivalent to the quadratic coupling of J to δ_s, i.e., the elastic energy that is proportional to $\delta_s^2 \propto p_s^4$, and its influences on FPTs have not been reported as far as we know.

Therefore, the FPT Hamiltonian including the coupling between spontaneous polarization and spontaneous strain up to p_s^4 is

$$H = -\frac{J_0(1+\alpha p_s^2+\beta p_s^4)}{2}\sum_{i\neq j}^{\{nn\}} s_i s_j, \tag{2}$$

which is an extended form of the three-dimensional Ising model, and it can be imagined that it is extremely difficult to solve it exactly. In this work, the single pseudospin mean field has been used,[39,40] i.e., $s_i s_j \approx s_i\langle s_j\rangle$, where $\langle s_j\rangle$ is the statistical average of s_j, and obviously, $p_s \equiv \langle s_j\rangle$. In this way, the Hamiltonian can be expressed as

$$H \approx -J_0 p_s(1+\alpha p_s^2+\beta p_s^4)\sum_{i=1}^{\infty} s_i. \tag{3}$$

Using Eq. (3) and based on the Boltzmann principle, p_s, the average internal energy u_s per dipole, and c_s, as well as the static polarizability χ_s of ferroelectrics versus T are

$$p_s = \tanh[\frac{T_0}{T}p_s(1+\alpha p_s^2+\beta p_s^4)], \tag{4}$$

$$u_s = -\frac{J}{2}(1+\alpha p_s^2+\beta p_s^4)p_s^2, \tag{5}$$

$$c_s \equiv \frac{\partial u_s}{\partial T}, \tag{6}$$

$$\chi_s = \frac{aC_w}{T - T_0 a(1+3\alpha p_s^2+5\beta p_s^4)}, \tag{7}$$

where $T_0 \equiv \frac{J}{k_B}$, $C_w \equiv \frac{N\mu^2}{k_B\varepsilon_0}$ is the Curie–Weiss constant, k_B is the Boltzmann constant, ε_0 is the vacuum permittivity, and $a \equiv 1-\tanh^2[\frac{T_0}{T}(1+\alpha p_s^2+\beta p_s^4)]$. The detailed calculation of χ_s can be found in Appendix A.

Figure 1 shows the fits of the present model to the experimental results of P_s,[34] χ_s^{-1} of the paraelectric phase[35] (because the values of χ_s in the ferroelectric phases are related to domain walls,[41,42] they are not fitted here), and c_s[36] (c_b is the background irrelevant to FPT) of triglycine sulfate crystal. The fitting parameters used are shown in Fig. 1. It can be seen that, compared with the Weiss theory and the WQL model, the present model coincides better with the data.

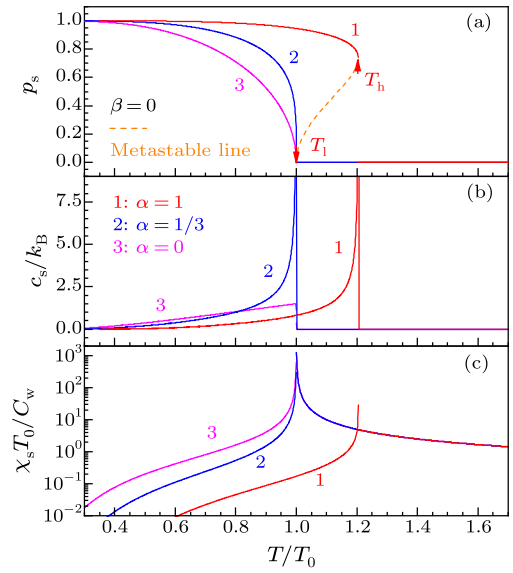

Fig. 2. The values of p_s, c_s and χ_s versus T for $\beta = 0$ and serial α.

Obviously, the Weiss theory completely ignores the coupling of spontaneous polarization and spontaneous strain. Mathematically, the results (Eqs. (4)–(7)) of the present model when $\beta = 0$ are equivalent to the compressible Ising models[29–32] and the WQL model[33] under the single pseudospin mean-field approximation. In other words, the αp_s^2 term in Eq. (2) is equivalent to the linear coupling of J to the lattice strain of the compressible Ising models[29–32] and the four-pseudospin interaction of the WQL model.[33]

To further study the effect of the βp_s^4 term on FPTs, p_s, c_s, and χ_s of the model system with T are shown in Figs. 2–7, which indicate that: (1) For $\beta = 0$ (Fig. 2), the results are consistent with those reported in Refs. [22-26]. That is: (i) when $\alpha \leqslant \frac{1}{3}$, a 2nd-order PT occurs, and the PT temperature (T_c) is equal to T_0 (see Appendix B for details), and (ii) when $\alpha > \frac{1}{3}$, a 1st-order PT appears, i.e., there is a temperature range of the transition (here the highest and the lowest temperatures of the range are expressed as T_h and T_l), and $T_l = T_0$. (2) For $\alpha = 0$, in addition to the

2nd-order PT at T_0, (i) when β is large (Fig. 6), a sharp peak of c_s and χ_s appears at lower temperature, while p_s jumps from a nonzero value to another one, which is called a phase-like transition here. It is a 1st-order phase-like transition when the jump value is nonzero, or a 2nd-order phase-like transition when the jump value is zero but the slope tends to infinity, and (ii) when β is small (Figs. 2–5), there is a diffuse peak of c_s, while a diffuse or shoulder peak of χ_s and a rapid change of p_s appears at lower temperature. This process and the temperature corresponding to the maximum value of c_s are called a diffuse phase-like transition and the transition temperature (T_d) in this work, respectively.

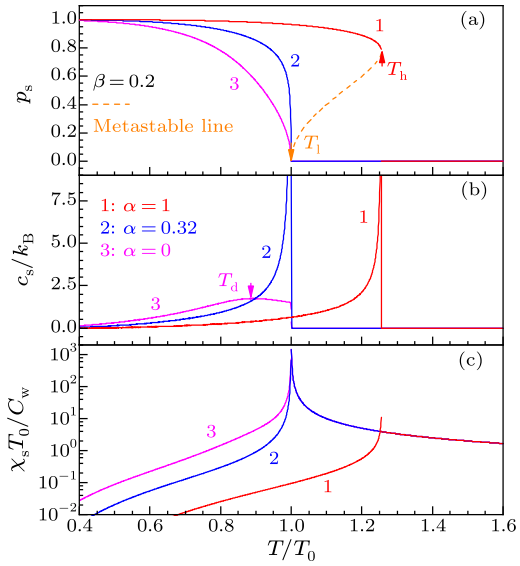

Fig. 3. The values of p_s, c_s and χ_s versus T for $\beta = 0.2$ and serial α.

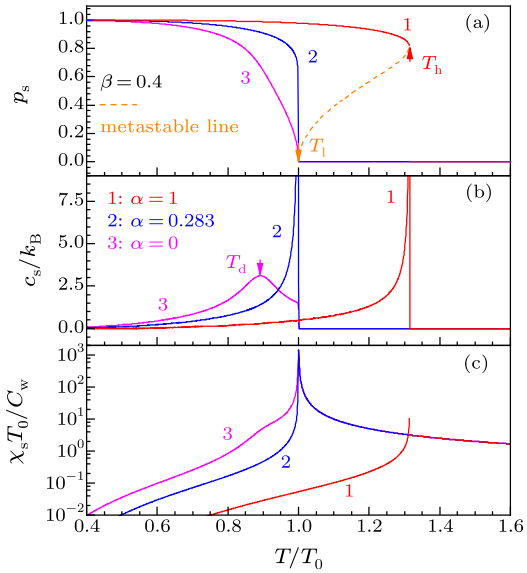

Fig. 4. The values of p_s, c_s and χ_s versus T for $\beta = 0.4$ and serial α.

Figures 8 and 9 show the phase diagrams predicted by the present model, i.e., the changes of T_c, T_h, T_l, and T_d with α and β. It can be seen that the model system exhibits: (1) a 2nd-order PT and a diffuse phase-like transition when α and β are smaller; (2) a 2nd-order PT, and a 1st- or 2nd-order phase-like transition when α is smaller but β is relatively larger; and (3) only a 1st-order PT when both α and β are larger.

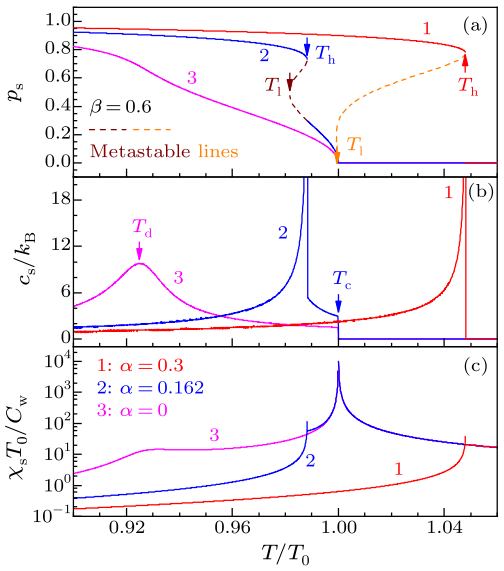

Fig. 5. The values of p_s, c_s and χ_s versus T for $\beta = 0.6$ and serial α.

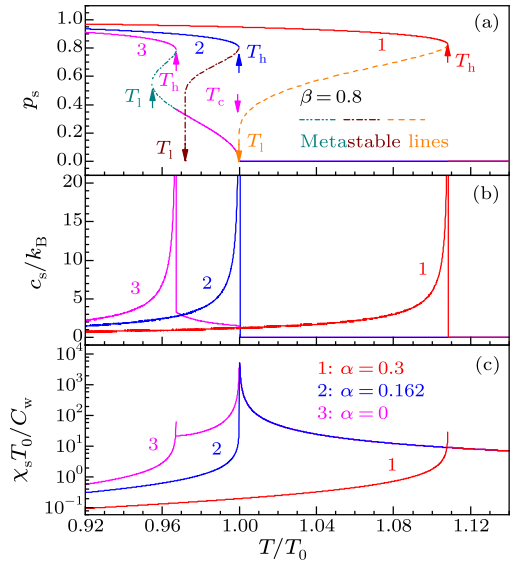

Fig. 6. The values of p_s, c_s and χ_s versus T for $\beta = 0.8$ and serial α.

It is worth mentioning that smaller α and larger β correspond to the strong nonlinear spontaneous polarization-strain coupling, and whether this kind of ferroelectrics exists or not still needs further experimental exploration.

As stated above, P_s is coupled with δ_s, thus the Hamiltonian describing ferroelectric phase transition

can be expressed in the form

$$H_{\text{total}} = -\frac{J(\delta_{\text{s}})}{2}\sum_{i\neq j}^{\{nn\}} s_i s_j + H_{\text{strain}}(\delta_{\text{s}}), \qquad (8)$$

where $J(\delta_{\text{s}})$ is a function of δ_{s}, and $H_{\text{strain}}(\delta_{\text{s}})$ is the Hamiltonian related to δ_{s}.

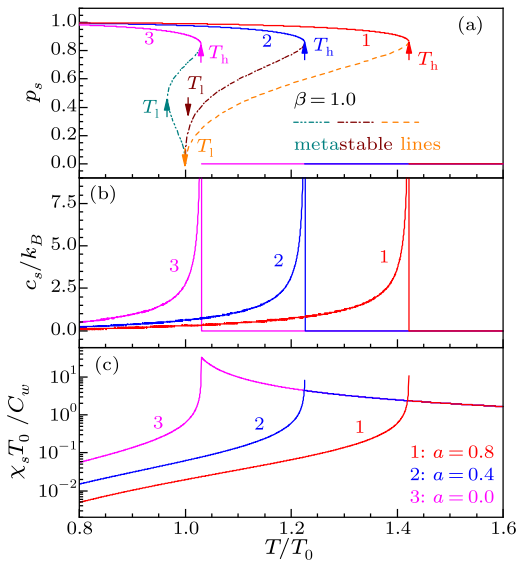

Fig. 7. The values of p_{s}, c_{s} and χ_{s} versus T for $\beta = 1.0$ and serial α.

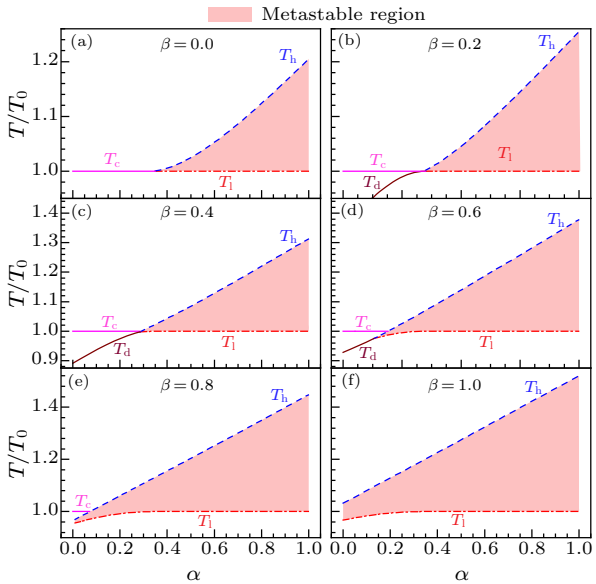

Fig. 8. The phase diagrams predicted by the present model, i.e., T_{c}, T_{h}, T_{l}, and T_{d} with versus α for serial β.

If we know the functions of $J(\delta_{\text{s}})$ and $H_{\text{strain}}(\delta_{\text{s}})$ with δ_{s} in a specific ferroelectric material, in principle we can calculate the change of P_{s} and δ_{s} of the material with temperature by H_{total}, that is, we can obtain the information of the ferroelectric phase transition related to the structure. However, it could be imagined that the mathematical description of the Hamiltonian is complex and difficult to solve.

This study chooses a self-consistent approximation of H_{total}, i.e., the influence of $H_{\text{strain}}(\delta_{\text{s}})$ and δ_{s} on J is equivalent to the contribution of P_{s} to J by the approximation (Eq. (2)). This approximation is mainly for the conciseness of mathematical description and physical image.

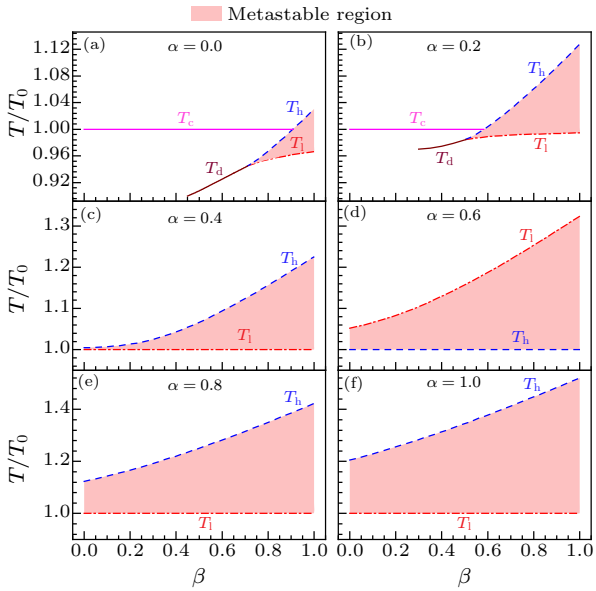

Fig. 9. The phase diagrams predicted by the present model, i.e., T_{c}, T_{h}, T_{l}, and T_{d} versus β for serial α.

Appendix A

When an external electric field ($E \to 0$) is applied to ferroelectrics along the direction of dipole moments, the FPT Hamiltonian becomes

$$H_E \approx -[J_0 p(1+\alpha p^2+\beta p^4)+\mu E]\sum_{i=1}^{\infty} s_i, \quad \text{(A1)}$$

where $p = \frac{P}{N\mu}$, with p the polarization of ferroelectrics.

Using Eq. (A1) and based on the Boltzmann principle, it is easy to obtain

$$p = \tanh\left[\frac{J_0 p(1+\alpha p^2+\beta p^4)+\mu E}{k_{\text{B}}T}\right]. \quad \text{(A2)}$$

From Eq. (A2)

$$\frac{\partial p}{\partial E}\Big|_{E\to 0} = \alpha\frac{J(1+3\alpha p_{\text{s}}^2+5\beta p_{\text{s}}^4)\frac{\partial p}{\partial E}+\mu}{k_{\text{B}}T}, \quad \text{(A3)}$$

where $\alpha \equiv 1-\tanh^2[\frac{T_0}{T}p_{\text{s}}(1+\alpha p_{\text{s}}^2+\beta p_{\text{s}}^4)]$. According to the definition, i.e., $\chi_{\text{s}} \equiv \frac{N\mu}{\varepsilon_0}\frac{\partial p}{\partial E}|_{E\to 0}$, we obtain

$$\chi_{\text{s}} = \frac{aC_{\text{w}}}{T - T_0 a(1+3\alpha p_{\text{s}}^2+5\beta p_{\text{s}}^5)}. \quad \text{(A4)}$$

Appendix B

When $\beta = 0$ and $p_{\text{s}} \to 0$, from Eq. (3) and $\tanh(x) \approx x - \frac{x^3}{3}$, we obtain

$$p_{\text{s}} = \frac{T_0}{T}p_{\text{s}} + \alpha\frac{T_0}{T}p_{\text{s}}^3 - \frac{1}{3}\left(\frac{T_0}{T}p_{\text{s}}\right)^3. \quad \text{(B1)}$$

That is,

$$p_{\rm s}^2 = \frac{1-\frac{T}{T_0}}{\frac{1}{3}(\frac{T_0}{T})^2 - \alpha}. \tag{B2}$$

Thus $p_{\rm s}$ only has a nonzero real solution below T_0 when $\alpha \leqslant \frac{1}{3}$, i.e., a 2nd-order PT occurs in the system.

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