

ON THE LOW-SYMMETRY ORBITAL PHASES IN $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ MANGANITE

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On the basis of the free energy expansion, the low-symmetry orbital phases originating from the high-temperature crystal phase with the $Pnma(D_{2h}^{16})$ symmetry in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.3 \leq x \leq 0.5$) manganite are investigated. The free order parameter susceptibilities and elastically clamped ones in these phases are calculated.

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1. Introduction

In references [1, 2] on the basis of symmetry analysis the phenomenological theory of the orbital phase transition (PT) proceeding from the high-temperature phase with $Pnma(D_{2h}^{16})$, the symmetry in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.3 \leq x \leq 0.5$) manganite is developed. It is shown that the two states reported in [3] and [4,5] correspond to the two types of orbital ordering of a single orbital order parameter (OP) (for a given OP, three types of orbital ordering are possible). The temperature dependencies of the elastic coefficients in the low-symmetry orbital phases are also calculated in reference[2].

The aim of this study is to present, in an unified form, results concerning the low- symmetry orbital phases in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.3 \leq x \leq 0.5$) manganite [1,2], and in addition to calculate the free order parameter susceptibilities and elastically clamped ones in these phases.

2. Free energy expansion

The free energy expansion describing the orbital PT in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.3 \leq x \leq 0.5$) manganite, in terms of the two invariants, $I_1 = \varphi_1^2 + \varphi_2^2$ and $I_2 = \varphi_1^2 \varphi_2^2$, has the form [2]:

$$\begin{aligned}
 F = & \frac{1}{2} r (\varphi_1^2 + \varphi_2^2) + \frac{1}{4} u (\varphi_1^2 + \varphi_2^2)^2 + \frac{1}{6} u_1 (\varphi_1^2 + \varphi_2^2)^3 + \frac{1}{8} u_2 (\varphi_1^2 + \varphi_2^2)^4 + \frac{1}{4} v \varphi_1^2 \varphi_2^2 + \frac{1}{8} v_1 \varphi_1^4 \varphi_2^4 + \\
 & + \beta_1 (\varphi_1^2 - \varphi_2^2) \psi + \frac{1}{2} r_1 \psi^2 + \beta_2 \varphi_1 \varphi_2 \xi + \frac{1}{2} r_2 \xi^2 + \beta_3 (\varphi_1 \eta_1 + \varphi_2 \eta_2) + \frac{1}{2} r_3 (\eta_1^2 + \eta_2^2) + \\
 & + \sum_{i=1}^3 \alpha_i e_i (\varphi_1^2 + \varphi_2^2) + \alpha_5 e_5 (\varphi_1^2 - \varphi_2^2) + \frac{1}{2} \sum_{i=1}^6 C_{ii} e_i^2 + \sum_{i<j,i,j=1}^3 C_{ij} e_i e_j .
 \end{aligned} \tag{1}$$

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Here $\{\varphi_1, \varphi_2\}$ is the main orbital two-component OP with wave vector $k_1=(1/2,0,0)$; $\{\eta_1, \eta_2\}$ is an OP characterized by the wave vector $k_1=(1/2,0,0)$ and the symmetry of the main OP, which may be a phonon Jahn-Teller OP; ξ and ψ are the secondary OPs with the wave vector $k_2=(0,0,0)$; C_{ij} , e_i are the elastic coefficients and the strain tensor components, respectively, in Voight's notation; $r = \alpha(T - T_c)$, where T_c is the bare PT temperature, and $\alpha > 0$, α_i , β_i , $r_i > 0$, u_i , v_i are phenomenological parameters independent on temperature.

The free energy expansion (1) describes the PT from the $Pnma(D_{2h}^{16})$ high-temperature phase to some of the three low-temperature phases of the $P2_1/m(C_{2h}^2)$, $Pmn2_1(C_{2v}^7)$ and $Pm(C_s^1)$ symmetry at nonzero components of OP: $\varphi_1 \neq 0$, $\eta_1 \neq 0$, $\psi \neq 0$, $e_i \neq 0$, $i=1,2,3,5$; $\varphi_1 = \varphi_2 \neq 0$, $\eta_1 = \eta_2 \neq 0$, $\xi \neq 0$, $e_i \neq 0$, $i=1,2,3$, and $\varphi_1 \neq \varphi_2 \neq 0$, $\eta_1 \neq \eta_2 \neq 0$, $\psi \neq 0$, $\xi \neq 0$, $e_i \neq 0$, $i=1,2,3,5$, respectively.

Using the polar representation $\varphi_1 = \rho \cos(\varphi)$, $\varphi_2 = \rho \sin(\varphi)$, one can rewrite Eq. (1) as a function of ρ and φ instead φ_1 and φ_2 . From the equilibrium conditions, $\partial F / \partial \psi = 0$, $\partial F / \partial \xi = 0$, $\partial F / \partial \eta_i = 0$, $i=1,2$ and $\partial F / \partial e_j = 0$, $j=1,2,3,5$, one gets expressions for the secondary order parameters. Substituting these into Eq. (1) in polar representation, we obtain the free energy minimized in the secondary order parameters:

$$F_{eff.} = f(\rho) + \alpha(\rho) \sin^2(2\varphi) + \beta(\rho) \sin^4(2\varphi), \quad (2)$$

where

$$f(\rho) = \frac{1}{2} \tilde{r} \rho^2 + \frac{1}{4} \tilde{u} \rho^4 + \frac{1}{6} u_1 \rho^6 + \frac{1}{8} u_2 \rho^8, \quad \alpha(\rho) = \frac{1}{4} \tilde{v} \rho^4, \quad \beta(\rho) = \frac{1}{8} \tilde{v}_1 \rho^8. \quad (3)$$

In Eq. (3), $\tilde{r} \equiv r - \beta_3^2 / r_3$, $\tilde{u} \equiv u - 2\beta_1^2 / r_1 - 2\alpha_5^2 / C_{55} + 2 \sum_{i=1}^3 (C_{ii} A_i^2 + 2\alpha_i A_i) + 4 \sum_{i < j; i, j=1}^3 C_{ij} A_i A_j$, $\tilde{v}_1 \equiv v_1 / 16$ and $4\tilde{v} \equiv v - 2\beta_2^2 / r_2 + 8\beta_1^2 / r_1 + 8\alpha_5^2 / C_{55}$.

The polar angle φ in Eq. (2) determines the low-symmetry phase. In the case of $\alpha(\rho) / \beta(\rho) < 0$, $\beta(\rho) \neq 0$ there are three low-symmetry phases in general [2]:

(a) at $\varphi = \frac{\pi}{4}$ we have $\varphi_1 = \varphi_2 \neq 0$, which corresponds to the $Pmn2_1(C_{2v}^7)$ phase, and

$$F_{1,eff.} = f(\rho) + \alpha(\rho) + \beta(\rho); \quad (4)$$

(b) at $\varphi = 0$ we have $\varphi_1 \neq 0$, $\varphi_2 = 0$ (or in the other domain $\varphi_1 = 0$, $\varphi_2 \neq 0$), which corresponds to the $P2_1/m(C_{2h}^2)$ phase, and

$$F_{2,eff.} = f(\rho); \quad (5)$$

(c) at $\varphi \in \left(0; \frac{\pi}{4}\right)$ we have $\varphi_1 \neq \varphi_2 \neq 0$, which corresponds to the $Pm(C_s^1)$ phase, and

$$F_{3,eff.} = f(\rho) + \alpha(\rho) \sin^2(2\varphi) + \beta(\rho) \sin^4(2\varphi). \quad (6)$$

Here, $F_{j,eff.}$ is an effective free energy of the j^{th} phase.

The boundaries between different phases are determined from the conditions: $F_{1,eff.} = F_{2,eff.}$, $F_{1,eff.} = F_{3,eff.}$, $F_{2,eff.} = F_{3,eff.}$.

The temperature dependence of the main OP is defined from the system of equations $\partial F_{j,eff.}/\partial \varphi_i = 0$, $i=1,2$. Using the relations $\partial F_{j,eff.}/\partial \varphi = 0$, $\partial F_{j,eff.}/\partial \rho = 0$, and a positive definition of the matrix of the second derivatives, one can obtain equilibrium values of ρ ($\rho \neq 0$ in the low-symmetry phases) and φ corresponding to a minimum of the potential (2).

The matrix of second derivatives of the potential is equal to the inverse susceptibility matrix

$$\frac{\partial^2 F}{\partial \varphi_i \partial \varphi_j} = (\chi^{-1})_{ij}, \quad (i, j = 1, 2). \quad (7)$$

One should distinguish two kinds of susceptibilities: (a) free order parameter (low-frequency) susceptibilities $\chi^{(fr)}$, when the secondary order parameters are able to follow the fluctuations of the main orbital OP, and (b) elastically clamped (high-frequency) susceptibilities $\chi^{(cl)}$, when the secondary order parameters cannot follow the fluctuations of the main orbital OP. Following the calculation approach in [6] for obtaining the free order parameter susceptibilities, one must use the potential minimized in secondary order parameters (2), while for obtaining the elastically clamped ones one should differentiate Eq. (1) in polar representation, and only after that substitute the equilibrium values of the secondary order parameters.

Using equilibrium conditions, for the low-temperature phases in the case of free angle susceptibility $\chi_{\varphi\varphi}^{(fr)-1}$, we obtain

$$\chi_{\varphi\varphi}^{(fr)-1} = \frac{\partial^2 F^{(fr)}}{\partial \varphi^2} = \begin{cases} 8\alpha(\rho), \\ 8\alpha(\rho) \left(-2 - \frac{\alpha(\rho)}{\beta(\rho)} \right), \\ 8\alpha(\rho) \left(-1 - 2 \frac{\beta(\rho)}{\alpha(\rho)} \right), \end{cases} \quad (8)$$

for the phases with symmetries $P2_1/m(C_{2h}^2)$, $Pm(C_s^1)$ and $Pmn2_1(C_{2v}^7)$, respectively.

For the clamped susceptibilities, all second derivatives are renormalized:

$$\begin{aligned} \chi_{\rho\rho}^{(cl)-1} &= \chi_{\rho\rho}^{(fr)-1} + \frac{\beta_3^2}{r_3} + 2 \left[\frac{2\beta_1^2}{r_1} - \sum_{i=1}^3 (3C_{ii}A_i^2 + 5\alpha_i A_i) - 6 \sum_{i<j, i, j=1}^3 C_{ij}A_i A_j + \frac{4\alpha_5^2}{C_{55}} \right] \rho^2 + \\ &+ \left[\frac{\beta_2^2}{r_2} - \frac{4\beta_1^2}{r_1} - \frac{4\alpha_5^2}{C_{55}} \right] \rho^2 \sin^2(2\varphi), \\ \chi_{\rho\varphi}^{(cl)-1} &= \chi_{\rho\varphi}^{(fr)-1} + 2 \left[\frac{\beta_2^2}{2r_2} - \frac{2\beta_1^2}{r_1} - \frac{2\alpha_5^2}{C_{55}} \right] \rho^3 \sin(2\varphi) \cos(2\varphi), \\ \chi_{\varphi\varphi}^{(cl)-1} &= \chi_{\varphi\varphi}^{(fr)-1} + \frac{\beta_3^2}{r_3} \rho^2 + \left[\frac{4\beta_1^2}{r_1} - \frac{\beta_2^2}{r_2} + \frac{4\alpha_5^2}{C_{55}} \right] \rho^4 \sin^2(2\varphi) + \frac{\beta_2^2}{r_2} \rho^4, \end{aligned} \quad (9)$$

where for the phase with $P2_1/m(C_{2h}^2)$ symmetry, $\sin^2(2\varphi)=0$; for the phase with $Pm(C_s^1)$ symmetry, $\sin^2(2\varphi)=-\alpha(\rho)/2\beta(\rho)$; and for the phase with $Pmn2_1(C_{2v}^7)$ symmetry, $\sin^2(2\varphi)=1$.

3. Conclusions

The free energy (1) describes all phase transitions from the high-temperature phase of the $Pnma(D_{2h}^{16})$ symmetry with wave vector $\mathbf{k}_1=(1/2,0,0)$. The PT with the symmetry change:

(a) $Pnma(D_{2h}^{16}) \rightarrow P2_1/m(C_{2h}^2)$ - is described by $\varphi_1 \neq 0, \varphi_2 = 0$ (or $\varphi_1 = 0, \varphi_2 \neq 0$), which corresponds to $\varphi = 0$;

(b) $Pnma(D_{2h}^{16}) \rightarrow Pmn2_1(C_{2v}^7)$ - is described by $\varphi_1 = \varphi_2 \neq 0$, which corresponds to $\varphi = \pi/4$;

(c) $Pnma(D_{2h}^{16}) \rightarrow Pm(C_s^1)$ - is described by $\varphi_1 \neq \varphi_2 \neq 0$, which corresponds to $\varphi \in (0; \pi/4)$.

The effective free energies in Eqs. (4), (5) and (6) for the low-temperature phases are obtained from the free energy expansion in Eq. (2), at different values of the polar angle $\varphi \in [0; \pi/4]$. A similar free energy expansion was used to describe the structural phase transitions in La_2CuO_4 [6]. It is concluded from the experimental data [3, 5] that the phases with $P2_1/m(C_{2h}^2)$ and $Pm(C_s^1)$ symmetries take place in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ at $x \approx 0.5$. The phase diagram of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ manganite for $0.3 \leq x \leq 0.5$ [5, 7] (see Fig. 1a in Ref. [2]) should be verified in further experiments. In this concentration range, the phase diagram can be presented as shown in Fig. 1b of ref. [2].

For the low-temperature orbital phases in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.3 < x \leq 0.5$), the free order parameter susceptibilities and elastically clamped ones have been calculated (see Eqs. (8), (9)). One notes that, here, in contrast to ref. [6], for the high-temperature phase ($\rho = 0$) the free order parameter susceptibilities are not the same as the clamped ones (see the first of Eqs. (9)). In the general case, however, the free order parameter susceptibilities should not be the same as the clamped ones (e.g. high-frequency phonons are different from low-frequency ones).

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