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ORBITAL PHASES IN $Pr_{1-x}Ca_x MnO_3$ MANGANITE

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Introduction

In order to consider the properties of real systems with strongly correlated electrons, such as transition metal (TM) oxides, one often has to take into account, the charge and spin degrees of freedom and also the orbital structure of corresponding TM ions. The orbital degrees of freedom are especially important in the cases of orbital degeneracy - the situation when the orbital state of the TM ions in a regular oxygen octahedron turns out to be degenerate. This is the situation with the Mn^{3+} ions in manganites. These ions have double orbital degeneracy and are strong Jahn-Teller ions, causing structural distortions and orbital ordering.

Orbital ordering is known to exist in most manganites at half-doping. Together with charge and spin degrees of freedom, the orbital ordering determines all the rich variety of the properties of manganites in different doping regions. The ordering mechanisms and the consequences of orbital order are discussed in Ref. [1].

The structure of orbital ordering can be determined by synchrotron X-ray diffraction study [2]. However, the interpretation of the results obtained by this method may be ambiguous [3] and that is why the basic information on the orbital state of manganese ion is usually extracted from data on the exact structure of the MnO_6 octahedron. New srtuctural data on the phase transition (PT) in $Pr_{0.6}Ca_{0.4}MnO_3$ manganite to a state with both charge and orbital ordering was reported in Ref. [4]. These experimental results are interpreted as an observation of ordered Zener polarons in the low temperature phase. It was concluded also that this electronic state of the manganese ion may be its ground state in manganites, in which the PT with charge and orbital ordering is observed at the doping level $x = 0.5$. The main feature of this electronic state is that manganese ions have the

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same valence throughout the crystal, whereas in the other state [5, 6] the manganese ions have different valence and the Mn^{3+} and Mn^{4+} ions are spatially ordered.

The phenomenological theory of the phase transition (PT) in $Pr_{0.6}Ca_{0.4}MnO_3$ manganite is developed in Ref. [7] on the basis of symmetry analysis. It is shown that this PT is the orbital PT. The two states reported in [4] and [5, 6] correspond to the two types of orbital ordering of a single orbital order parameter.

The aim of this study is to investigate the low symmetry orbital phases in $Pr_{1-x}Ca_xMnO_3$ ($0.3 \leq x \leq 0.5$).

Free energy expansion

Using two invariants, $I_1 = \varphi_1^2 + \varphi_2^2$ and $I_2 = \varphi_1^2 \varphi_2^2$, the free energy expansion describing the orbital PT takes the form

$$F = F_\varphi + F_{\varphi,\psi} + F_\psi + F_{\varphi,\xi} + F_\xi + F_{\varphi,\eta} + F_\eta + F_{\varphi,e} + F_e, \tag{1}$$

where

$$F_\varphi = \frac{1}{2} r \left(\varphi_1^2 + \varphi_2^2 \right) + \frac{1}{4} u \left(\varphi_1^2 + \varphi_2^2 \right)^2 + \frac{1}{6} u_1 \left(\varphi_1^2 + \varphi_2^2 \right)^3 +$$

$$+ \frac{1}{8} u_2 \left(\varphi_1^2 + \varphi_2^2 \right)^4 + \frac{1}{4} v \varphi_1^2 \varphi_2^2 + \frac{1}{8} v_1 \varphi_1^4 \varphi_2^4,$$

$$F_{\varphi,\psi} = \beta_1 \left(\varphi_1^2 - \varphi_2^2 \right) \psi, \qquad F_\psi = \frac{1}{2} r_1 \psi^2,$$

$$F_{\varphi,\xi} = \beta_2 \varphi_1 \varphi_2 \xi, \qquad F_\xi = \frac{1}{2} r_2 \xi^2,$$

$$F_{\varphi,\eta} = \beta_3 \left(\varphi_1 \eta_1 + \varphi_2 \eta_2 \right), \qquad F_\eta = \frac{1}{2} r_3 \left(\eta_1^2 + \eta_2^2 \right),$$

$$F_{\varphi,e} = \left(\alpha_1 e_1 + \alpha_2 e_2 + \alpha_3 e_3 \right) \left(\varphi_1^2 + \varphi_2^2 \right) + \alpha_5 e_5 \left(\varphi_1^2 - \varphi_2^2 \right),$$

$$F_e = \frac{1}{2} \sum_{i=1}^{6} C_{ii} e_i^2 + C_{12} e_1 e_2 + C_{13} e_1 e_3 + C_{23} e_2 e_3. \tag{2}$$

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Here $\{\varphi_1, \varphi_2\}$ is the main orbital two-component order parameter (OP) with the wave vector $\mathbf{k}_1 = (1/2,0,0)$; $\{\eta_1, \eta_2\}$ is an OP characterized by the wave vector $\mathbf{k}_1 = (1/2,0,0)$ and the symmetry of the main OP, it may be the phonon Jahn-Teller OP; ξ and ψ are the secondary OPs with the wave vector $\mathbf{k}_2 = (0,0,0)$; C_{ij}, e_i are the elastic coefficients and the strain tensor components, respectively, in the Voight's notation; $r = \alpha(T - T_c)$, T_c- is the bare PT temperature; $\alpha > 0$, α_i, β_i, $r_i > 0$, u_i, v_i are the phenomenological parameters independent on temperature.

The free energy expansion (1)-(2) describes the PTs from the $Pnma(D_{2h}^{16})$ high temperature phase to any 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.

From the equilibrium conditions, $\dfrac{\partial F}{\partial \psi} = 0$, $\dfrac{\partial F}{\partial \xi} = 0$, $\dfrac{\partial F}{\partial \eta_i} = 0$, $i = 1,2$ and $\dfrac{\partial F}{\partial e_j} = 0$, $j = 1,2,3,5$, one obtains the following dependancies of secondary OPs:

$$\psi = -\frac{\beta_1}{r_1}\left(\varphi_1^2 - \varphi_2^2\right), \quad \xi = -\frac{\beta_2}{r_2}\varphi_1\varphi_2, \quad \eta_1 = -\frac{\beta_3}{r_3}\varphi_1, \quad \eta_2 = -\frac{\beta_3}{r_3}\varphi_2,$$

$$e_1 = A_1\left(\varphi_1^2 + \varphi_2^2\right), \quad e_2 = A_2\left(\varphi_1^2 + \varphi_2^2\right),$$

$$e_3 = A_3\left(\varphi_1^2 + \varphi_2^2\right) \text{ and } e_5 = -\frac{\alpha_5}{C_{55}}\left(\varphi_1^2 - \varphi_2^2\right), \quad C_{55} \neq 0. \tag{3}$$

Here

$$A_1 = \frac{-\left(\alpha_1 C_{23} - \alpha_2 C_{13}\right)\left(C_{12}C_{33} - C_{23}C_{13}\right) + \left(\alpha_1 C_{33} - \alpha_3 C_{13}\right)\left(C_{12}C_{23} - C_{22}C_{13}\right)}{\left(C_{11}C_{23} - C_{12}C_{13}\right)\left(C_{12}C_{33} - C_{23}C_{13}\right) - \left(C_{11}C_{33} - C_{13}C_{13}\right)\left(C_{12}C_{23} - C_{22}C_{13}\right)},$$

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$$\left(C_{11}C_{23} - C_{12}C_{13}\right)\left(C_{12}C_{33} - C_{23}C_{13}\right) \neq \left(C_{11}C_{33} - C_{13}C_{13}\right)\left(C_{12}C_{23} - C_{22}C_{13}\right),$$

$$A_2 = \frac{-\left(\alpha_1 C_{23} - \alpha_2 C_{13}\right)\left(C_{11}C_{33} - C_{13}C_{13}\right) + \left(\alpha_1 C_{33} - \alpha_3 C_{13}\right)\left(C_{11}C_{23} - C_{12}C_{13}\right)}{\left(C_{11}C_{33} - C_{13}C_{13}\right)\left(C_{12}C_{23} - C_{22}C_{13}\right) - \left(C_{11}C_{23} - C_{12}C_{13}\right)\left(C_{12}C_{33} - C_{23}C_{13}\right)},$$

$$\left(C_{11}C_{33} - C_{13}C_{13}\right)\left(C_{12}C_{23} - C_{22}C_{13}\right) \neq \left(C_{11}C_{23} - C_{12}C_{13}\right)\left(C_{12}C_{33} - C_{23}C_{13}\right)$$

and $A_3 = -\dfrac{\left(\alpha_1 + A_1 C_{11} + A_2 C_{12}\right)}{C_{13}}$, $C_{13} \neq 0$.

The temperature dependence of the main OP is defined from the system of equations $\dfrac{\partial F_{j,\mathit{eff}}}{\partial \varphi_i} = 0$, $i = 1,2$, here $F_{j,\mathit{eff}}$ is an effective free energy of the jth phase. Using the polar representation, $\varphi_1 = \rho\cos(\varphi)$ and $\varphi_2 = \rho\sin(\varphi)$, for the $Pmn2_1(C_{2v}^7)$ phase (where $\varphi_1 = \varphi_2 \neq 0$) one obtains

$$F_{1.\mathit{eff}} = \frac{1}{2}\tilde{r}\rho^2 + \frac{1}{4}\tilde{u}\rho^4 + \frac{1}{6}u_1\rho^6 + \frac{1}{8}u_2\rho^8 + \frac{1}{4}\tilde{v}\rho^4 + \frac{1}{8}\tilde{v_1}\rho^8. \tag{4}$$

The temperature dependence of the main OP in this phase is defined by the equation

$$\tilde{r} + \tilde{u}\rho^2 + u_1\rho^4 + u_2\rho^6 + \tilde{v}\rho^2 + \tilde{v_1}\rho^6 = 0. \tag{5}$$

The phase of the $P2_1 / m(C_{2h}^2)$ symmetry is described by the following nonzero components of main OP $\varphi_1 \neq 0$ (or $\varphi_2 \neq 0$). In this case $F_{2.\mathit{eff}}$ is written as

$$F_{2.\mathit{eff}} = \frac{1}{2}\tilde{r}\rho^2 + \frac{1}{4}\tilde{u}\rho^4 + \frac{1}{6}u_1\rho^6 + \frac{1}{8}u_2\rho^8, \tag{6}$$

and the temperature dependence of the main OP is determined by the equation

$$\tilde{r} + \tilde{u}\rho^2 + u_1\rho^4 + u_2\rho^6 = 0. \tag{7}$$

For the $Pmn2_1(C_{2v}^7)$ phase ($\varphi_1 \neq \varphi_2 \neq 0$) we obtain

$$F_{3.\mathit{eff}} = \frac{1}{2}\tilde{r}\rho^2 + \frac{1}{4}\tilde{u}\rho^4 + \frac{1}{6}u_1\rho^6 + \frac{1}{8}u_2\rho^8 + \frac{1}{4}\tilde{v}\rho^4\sin^2(2\varphi) + \frac{1}{8}\tilde{v_1}\rho^8\sin^4(2\varphi). \tag{8}$$

The temperature dependence of the main OP is determined by the system of equations

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$$\begin{cases} \widetilde{r} + \widetilde{u}\rho^2 + u_1\rho^4 + u_2\rho^6 + \widetilde{v}\rho^4 \sin^2(2\varphi) + \widetilde{v_1}\rho^6 \sin^4(2\varphi) = 0 \\ \qquad\qquad \sin^2(2\varphi) = -\dfrac{\widetilde{v}}{\widetilde{v_1}\rho^4} \end{cases}, \qquad (9)$$

here $\widetilde{v_1} \neq 0$, $\rho \neq 0$ and $\varphi \in (0, \pi / 4)$.

In (4)-(9) $\quad \widetilde{r} \equiv r - \dfrac{\beta_3^2}{r_3}, \quad \dfrac{\widetilde{v}}{4} \equiv v - 2\dfrac{\beta_2^2}{r_2} + 8\dfrac{\beta_1^2}{r_1} + 8\dfrac{\alpha_5^2}{C_{55}}, \quad \widetilde{v_1} \equiv \dfrac{v_1}{16},$

$\widetilde{u} \equiv u - 2\dfrac{\beta_1^2}{r_1} - 2\dfrac{\alpha_5^2}{C_{55}} + 2\sum\limits_{i=1}^{3}\left(C_{ii}A_i^2 + 2\alpha_i A_i\right) + 4\sum\limits_{i<j;i,j=1}^{3} C_{ij}A_i A_j$.

The boundaries between different phases are defined from the following conditions

$$F_{1,eff} = F_{2,eff}, \ F_{1,eff} = F_{3,eff} \text{ and } F_{2,eff} = F_{3,eff}. \qquad (10)$$

The temperature dependencies of elastic coefficients are determined from the equation $C_{ij}(T) = \dfrac{dX_i}{de_j}$, where $X_i = \dfrac{\partial F}{\partial e_i}$ is the external field conjugated to the strain tensor component e_i. Thus one obtains

$$C_{ij}(T < T_c) = C_{ij} - \dfrac{2\alpha_i \alpha_j}{B}, \ \ B \neq 0. \qquad (11)$$

Here $B = u - 2\dfrac{\beta_1^2}{r_1} + 2u_1\rho^2 + 3u_2\rho^4 + \dfrac{v}{4} - \dfrac{\beta_2^2}{8r_2} + 3\widetilde{v_1}\rho^4$, $i \leq j$, $i,j = 1,2,3$ for the

$Pmn2_1(C_{2v}^7)$ phase and $B = u - 2\dfrac{\beta_2^2}{r_2} + 2u_1\rho^2 + 3u_2\rho^4$, $i \leq j$, $i,j = 1,2,3$ and

$i = j = 5$ for the $P2_1 / m(C_{2h}^2)$ phase.

Discussion of the results and conclusions

The free energy decomposition (1) describes all PTs from the high temperature phase of the $Pnma(D_{2h}^{16})$ symmetry with the wave vector $\mathbf{k}_1 = (1 / 2, 0, 0)$. The PT with the $Pnma(D_{2h}^{16}) \rightarrow P2_1 / m(C_{2h}^2)$ symmetry change is described by the following nonzero components of the main OP $\varphi_1 \neq 0$ (or

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$\varphi_2 \neq 0$), the $Pnma(D_{2h}^{16}) \rightarrow Pmn2_1(C_{2v}^7)$ symmetry change- by $\varphi_1 = \varphi_2 \neq 0$ and $Pnma(D_{2h}^{16}) \rightarrow Pm(C_s^1) - \varphi_1 \neq \varphi_2 \neq 0$.

The effective free energies for these phases have the forms (4), (6) and (8). The boundaries between different phases are defined by equations (10). In the low-symmetry phase the secondary OPs are described by the formulas (3) and the temperature dependence of main OP for each of the phases is defined by equations (5), (7) and (9), respectively. Note that similar free energy expansion was used to describe the structural phase transitions in La₂CuO₄ [8].
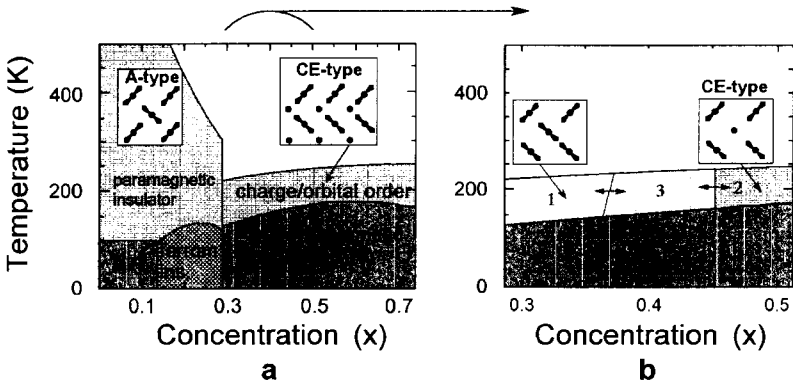
Fig.1. a). Phase diagram of Pr₁₋ₓCaₓMnO₃ [6,9]. In the insets the orbital structures are shown. b). Possible phase diagram of Pr₁₋ₓCaₓMnO₃ ($0.3 < x \leq 0.5$). The phase 1 has the $Pmn2_1(C_{2v}^7)$ symmetry, the phase 2 has the $P2_1/m(C_{2h}^2)$ symmetry and the intermediate phase 3 - the $Pm(C_s^1)$ symmetry. The boundaries between different orbital phases are schematically indicated.

It is concluded from experimental data [4,6] that two phases of the $P2_1/m(C_{2h}^2)$ and $Pm(C_s^1)$ symmetry take place in Pr₁₋ₓCaₓMnO₃ (x ∼ 0.5) manganite. In our analysis these phases are described by the nonzero components of OP $\varphi_1 \neq \varphi_2 \neq 0$ and $\varphi_1 \neq 0$, respectively. Thus, the phase diagram of Pr₁₋ₓCaₓMnO₃ for $0.3 \leq x \leq 0.5$ [6,9] (see Fig.1a) should be verified in further experiments. In this concentration range the phase diagram can be presented, as it

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shown in Fig.1b (or the boundary between the phases 1 and 3 goes out the value x ~0.3 and in such case only two phases, 2 and 3, can be observed).

To describe the phase diagram shown in Fig.1b, one can use a linear dependence of the phenomenological constant $\tilde{v}$, $\tilde{v} = a(x - x_0)$, where x_0 ~0.45 and $a > 0$. Further experimental mesurements are needed to understand the phase diagram of $Pr_{1-x}Ca_xMnO_3$ (x ~ 0.5).

References

1. J. van den Brink, G. Khaliullin and D. Khomskii, cond-mat/0206053 (2002).

2. Y. Murakami, H. Kawada, H. Kawata, et al., *Phys. Rev. Lett.*, **80**, 1932 (1998).

3. J. Garcia, M.S. Sanchez, J.Blasco, et al., *J. Phys.*, **C13**, 3243 (2001).

4. A. Daoud - Aladine, J. Rodriguez-Carvajal, L. Pinsard-Gaudart, et al., *Phys. Rev. Lett.*, **89**, 097205 (2002).

5. P.G. Radaelli, D.E. Cox, M. Marezio, and S.-W. Cheong, *Phys. Rev.*, **B55**, 3015 (1997).

6. Z. Jirak, F. Damay, M. Hervieu, et al., *Phys. Rev.*, **B61**, 1181 (2000).

7. V.S. Shakhmatov, N.M. Plakida and N.S. Tonchev, *JETP Letters*, **77**, 15 (2003).

8. A.Yu. Cherny, *Physica*, **C244** , 129 (1995).

9. M.v. Zimmermann, C.S. Nelson, J.P. Hill et al., *Phys. Rev.*, **B64**, 195133-1 (2001).

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Орбитальные фазы в манганите $Pr_{1-x}Ca_xMnO_3$

Развита феноменологическая теория орбитальных фазовых переходов в манганите $Pr_{1-x}Ca_xMnO_3$. Исследованы фазовые переходы между различными орбитальными фазами. Рассчитаны температурные зависимости упругих коэффициентов в этих фазах. Обсуждена фазовая диаграмма $Pr_{1-x}Ca_xMnO_3$ $(x \sim 0{,}5)$.

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Orbital Phases in $Pr_{1-x}Ca_xMnO_3$ Manganite

The phenomenological theory of the orbital phase transitions in the $Pr_{1-x}Ca_xMnO_3$ manganite is developed. The phase transitions between different orbital phases are studied. The temperature dependences of elastic coefficients in these phases are calculated. The phase diagram of $Pr_{1-x}Ca_xMnO_3$ $(x \sim 0.5)$ is discussed.

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