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# Phase Separation and Phase Diagram in Lightly Doped Manganites: Temperature and Magnetic Field Effects\*

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## Abstract

The effects of magnetic field and temperature on the phase separation and phase diagram of lightly doped manganites are studied. Based on the double exchange model with on-site Coulomb interaction, we show that in the case of a homogeneous charge distribution, the canting angle of localised core spins and the critical doping concentration of the system from canted phase to ferromagnetic (FM) phase become large because the effective FM coupling between localised core spins is weakened when the temperature increases. The boundary of the canted phase and FM phase shifts to a high doping concentration regime at high temperatures. In comparison with the zero-temperature result, the phase separation can take place more easily in lightly doped manganites at finite temperatures. The application of a magnetic field decreases the energy of the FM cluster in the system, favours the separation of the hole-rich FM phase from the antiferromagnetic (AFM) background, and shifts the cant-FM border to the low doping regime. The effect of the Jahn–Teller electron–phonon coupling on the phase diagram and phase separation is also discussed.

## 1. Introduction

Perovskite transition-metal oxides offer a rich and fruitful phase diagram and exhibit many novel properties near the border of different phases; one example is the high- $T_c$  superconducting materials. Recently the colossal magnetoresistance (CMR) effect in doped lanthanum manganese oxides was found near the edges of ferromagnetic to paramagnetic phases and the metal–insulator-like transition. The  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  series compounds exhibit rich phases with chemical composition (Wollan and Koeller 1955; Schiffer *et al.* 1995; Martin *et al.* 1996; Yoshizawa *et al.* 1995). Studies on the phase diagram of manganese oxides over doping concentration, temperature and magnetic field may provide us with insights into the nature of the variation of electronic states with physical parameters and conditions. These studies are also helpful for understanding the microscopic mechanism of the CMR effect.

Although the earliest phase diagram for  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  was drawn by Wollan and Koeller in 1955, detailed studies on the full phase diagram for  $\text{La}_{1-x}\text{B}_x\text{MnO}_3$  compounds ( $B = \text{Ca}, \text{Sr}, \text{Ba}, \text{etc.}$ ) were not carried out until a few years

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ago. Experimentally, it is known that at low temperatures undoped  $\text{LaMnO}_3$  is a layered A-type antiferromagnetic insulator, whereas at high temperatures it is paramagnetic (Schiffer *et al.* 1995). At low doping  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  is a spin-canted insulator (Martin *et al.* 1996; Yoshizawa *et al.* 1995). When the doping concentration is larger than a critical concentration, ferromagnetism becomes dominant for there exists enough double exchange components, and the system enters the ferromagnetic insulating or metallic phase. At high temperature, the magnetic long-range order disappears and the paramagnetic state emerges. Theoretically, Goodenough (1955, 1957) and De Gennes (1960) first addressed the A-type antiferromagnetic phase in undoped  $\text{LaMnO}_3$  and the spin canted phase for lightly doped manganese oxides. A few authors (Inoue and Maekawa 1995; Jie Jiang *et al.* 1997) argued that the double exchange model gives rise to the spin spiral ground state; however our work (Zou *et al.* 1997*a*, 1997*b*; Li *et al.* 1998) has shown that the lightly doped manganites should be in the spin canted ground state if the correct superexchange interaction between local spins is taken into account, and we further pointed out (Zou *et al.* 1997*a*, 1997*b*) that phase separation can take place in lightly doped manganites. These results were all restricted to the temperature region near absolute zero.

In this paper we generalise our studies to the finite temperature case. Taking the semiclassical approximation for the spin degrees of freedom, in Section 2 we use the functional integral approach to integrate out the degree of freedom of the electrons and obtained the saddle point partial partition function, the free energy and the ground state energy. From there we show how the phase evolves with increasing temperature in Section 3. We then discuss the effects of finite temperature and magnetic field on the phase separation in lightly doped manganites in Sections 4 and 5. Finally, we draw some conclusions in Section 6.

## 2. Model and Formalism

The first theoretical attempt to address the basic physics in manganites was given by Zener's (1951) double exchange model. In this model three 3d electrons in Mn ions filling the lower  $t_{2g}$  orbitals form a localised spin through Hund's rule coupling  $J_H$ . The extra electron filling the  $e_g$  orbit in  $\text{Mn}^{3+}$  ions is mobile and interacts with the local spin through strong Hund's rule coupling, which contributes the electric conduction and ferromagnetic coupling between Mn ions in manganese oxides. The corresponding model Hamiltonian is

$$H = \sum_{i\sigma} \epsilon_d d_{i\sigma}^\dagger d_{i\sigma} - t \sum_{\langle ij \rangle \sigma} (d_{i\sigma}^\dagger d_{j\sigma} + h.c.) + \frac{U}{2} \sum_{i\sigma} n_{i\sigma} n_{i\bar{\sigma}} - J_H \sum_{i\mu\nu} \mathbf{S}_i \cdot d_{i\mu}^\dagger \sigma_{\mu\nu} d_{i\nu} + \sum_{\langle ij \rangle} A_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - \sum_i g\mu_B B S_i^z. \quad (1)$$

Here  $d_{i\sigma}^\dagger$  creates an  $e_g$  electron at site  $\mathbf{R}_i$  with spin  $\sigma$ ,  $t$  denotes the hopping energy of the  $e_g$  electron from one site to its nearest-neighbour, and  $\epsilon_d$  is the site energy of the mobile electron with respect to the chemical potential  $\mu$ . The term  $-g\mu_B B$  represents the Zeeman energy in the magnetic field  $\mathbf{B}$ . The mobile electron couples with the localised spin  $\mathbf{S}_i$  through Hund's rule  $J_H$ , and in the limit of double exchange,  $J_H S \gg t$ . Here  $U$  denotes the on-site Coulomb interaction

strength, while  $A_{ij}$  denotes the super-exchange interaction between local spins, which is ferromagnetic in the  $xy$  plane,  $A_{ij} = -A' < 0$ , and antiferromagnetic along the  $z$ -axis,  $A_{ij} = A > 0$ . To account for the dynamic Jahn–Teller (JT) effect, one can add the following terms to equation (1):

$$\sqrt{\alpha\hbar\omega} \sum_i n_i [b_i^\dagger + b_i] + \sum_i \hbar\omega b_i^\dagger b_i. \quad (2)$$

In our previous work (Zou *et al.* 1997a, 1997b), we have shown that the JT effect results in a renormalisation of the hopping integral  $t$  by a factor of  $\exp(-S_T)$ ,  $\tilde{t} = t \exp(-S_T)$  with  $S_T = \alpha/\hbar\omega(\langle n_B \rangle + \frac{1}{2})$ , where  $\alpha$  is the dynamic electron–phonon coupling strength,  $\hbar\omega$  is the phonon frequency and  $\langle n_B \rangle$  is the average phonon number with energy  $\hbar\omega$  per site at temperature  $T$ .

For the ground state, the spin operator can be treated by the semiclassical approximation:

$$S_l^\pm = S e^{\pm i\phi_l} \sin(\theta_l), \quad S_l^z = S \cos(\theta_l), \quad (3)$$

where  $\theta_l$  represents the angle between the local spin at site  $R_l$  and the  $z$ -axis (direction of the external magnetic field), and  $\phi_l$  denotes the angle of the projection of spin  $\mathbf{S}_l$  in the  $xy$  plane relative to the  $x$ -axis. For the homogeneous system, it is assumed that the difference  $\phi_{l+1} - \phi_l$  and  $\theta_l$  are independent of the site  $R_l$ , or  $\phi_{l+1} - \phi_l = \phi$  and  $\theta_l = \theta$ . Different parameters  $(\phi, \theta)$  describe different spin structures in doped manganites. Through a variational method we have shown (Li *et al.* 1998; Zou *et al.* 1997a, 1997b) that the ground state has  $\phi = \pi$ . In the following we take  $\phi_l = l\pi = \mathbf{Q} \cdot \mathbf{R}_l$ , where  $\mathbf{Q}$  is half the reciprocal lattice vector  $(0, \pi/a, 0)$ , and  $a$  is the lattice constant. Here  $\theta$  is the so-called canted angle and  $2\theta$  is the angle between two nearest-neighbour spins. In this paper we adopt the Hartree–Fock approximation to decouple the on-site Coulomb interaction.

The partition function of the system is

$$Z = \int D\theta Dd Dd^\dagger \exp \left[ - \int_0^\beta d\tau \hat{L}(\tau) \right], \quad (4)$$

where the Lagrangian is expressed as

$$\begin{aligned} \hat{L}(\tau) = & NS[-g\mu_B B \cos\theta - 4A'S + 2AS \cos(2\theta)] + \sum_{k\sigma} d_{k\sigma}^\dagger (\partial_\tau + \epsilon_k + U\langle n_{\bar{\sigma}} \rangle) d_{k\sigma} \\ & - J_H S \sum_k [\cos\theta (d_{k\uparrow}^\dagger d_{k\uparrow} - d_{k\downarrow}^\dagger d_{k\downarrow}) + \sin\theta (d_{k+Q\downarrow}^\dagger d_{k\uparrow} - d_{k\uparrow}^\dagger d_{k+Q\downarrow})], \end{aligned} \quad (5)$$

with  $\epsilon_k = 2z\tilde{t}\gamma_k - \epsilon_d$  in the hole representation. After performing the integration, the partition function of the system becomes

$$Z = \int D\theta \exp[-S(\theta)], \quad (6)$$

where the action  $S(\theta)$  is

$$\begin{aligned}
S(\theta) = & \beta NS[-g\mu_B B \cos\theta - 4A'S + 2AS \cos(2\theta)] \\
& - \sum_k \text{Tr} \ln[(\partial_\tau + \epsilon_k + U < n_\downarrow > - J_H S \cos\theta) \\
& \times (\partial_\tau - \epsilon_k + U \langle n_\downarrow \rangle + J_H S \cos\theta) - (J_H S \sin\theta)^2]. \quad (7)
\end{aligned}$$

After making the saddle point approximation to the above action, one obtains the free energy of the system:

$$\begin{aligned}
F(T, \theta) = & NS[-g\mu_B B \cos\theta - 4A'S + 2AS \cos(2\theta)] \\
& - \frac{1}{\beta} \sum_k \ln(1 + e^{\beta E_k^1})(1 + e^{\beta E_k^2}), \quad (8)
\end{aligned}$$

with

$$E_k^{1,2} = \frac{U \langle n \rangle}{2} \pm \sqrt{(\epsilon_k + J_H S \cos\theta)^2 + (J_H S \sin\theta)^2}, \quad (9)$$

where  $E_k^{1,2}$  denotes the positive and negative subbands of the  $e_g$  electrons. Thus one can discuss the ground state properties of manganese oxides with doping concentration, temperature, and applied magnetic field based on the free energy  $F(T, \theta)$  in equation (8).

### 3. Finite-temperature Phase Diagram

We first examine the effect of increasing temperature on the canted angle and the phase diagram. In the ground state, the free energy as a function of angle  $\theta$  is at its minimum. Taking the derivative of  $F(T, \theta)$  with respect to  $\theta$  gives

$$\cos\theta = \frac{g\mu_B B}{8AS} + \frac{1}{8AS^2} \frac{1}{N} \sum_k \epsilon_k \left( \frac{1}{e^{\beta E_k^1} + 1} - \frac{1}{e^{\beta E_k^2} + 1} \right). \quad (10)$$

In the limit of strong Hund coupling,  $J_H S \sim U \gg \tilde{t}$ , and the low doping density  $x \ll 1$ , one gets the canted angle in the absence of a magnetic field:

$$\cos\theta = \frac{z\tilde{t}x}{4AS^2} \tanh\left(\frac{\beta J_H S}{2}\right), \quad (11)$$

and therefore the critical doping concentration for the system entering ferromagnetic long-range order phase is

$$x_c(T) = \frac{4AS^2}{z\tilde{t}} C \tanh\left(\frac{\beta J_H S}{2}\right). \quad (12)$$

Compared with the zero-temperature result (Zou *et al.* 1997a, 1997b),  $x_c(T) > x_c(0)$ , the thermal excitation at finite temperature weakens the interaction of the double exchange, and therefore more doping is needed to overcome

the antiferromagnetic super-exchange interaction for the system to enter the ferromagnetic phase. Therefore, the increasing thermal fluctuation effect will shift the canted antiferromagnetic (CAFM) phase–ferromagnetic (FM) phase border in the phase diagram to the high doping regime. In the temperature–concentration phase diagram, the CAFM–FM borderline will bend to the high doping regime at high temperatures, rather than being a straight line as sketched by Schiffer *et al.* (1995) and Martin *et al.* (1996). At high temperatures, the value of  $x_c(T)$  is very large compared with  $x_c(0)$  due to the  $e_g$  electron polaron effect, since in this case the effective ferromagnetic DE coupling becomes weak.

It is noteworthy that the above results are based on the assumption that the length of the local spin  $S$  is rigid. In fact, at sufficiently high temperatures, this assumption is no longer valid. Therefore, we cannot apply the above results to the case where the temperature is sufficiently high due to magnetic excitations. One improvement is to consider the correction of the spin wave excitation with the spin length  $S$  being replaced by an effective value  $S_{\text{eff}} = S - n_B$ , where  $n_B$  is the average occupation of the spin wave excitation in the presence of super-exchange and double-exchange interactions.

#### 4. Finite Temperature Effect on Phase Separation

In previous work (Zou *et al.* 1997a, 1997b) we found that at absolute zero temperature, a phase separation may take place in lightly doped manganites where holes form charge-rich FM droplets or clusters in the AFM background. Some recent work (Yunoki *et al.* 1998; Hennion *et al.* 1998) also discussed the possibility of phase separation in doped manganites. In this section we consider the effect of finite temperature on phase separation.

Based on the free energy  $F(T, \theta)$ , once the phase separation takes place, the two-phase state energy density of the systems at temperature  $T$  is then

$$e(x, T) = \begin{cases} 4AS^2 \cos^2 \theta + \frac{1}{N} \sum_{k,i=1,2} E_k^i / (e^{\beta E_k^i} + 1) & x < x_c \\ 4AS^2 + \frac{1}{N} \sum_{k,i=1,2} E_k^i / (e^{\beta E_k^i} + 1) & x \geq x_c, \cos \theta = 1. \end{cases} \quad (13)$$

To establish a stable two-phase state, the on-site Coulomb interaction should be smaller than the critical value

$$U_c = \frac{(z\tilde{t})^2}{2AS^2} \left[ \tanh\left(\frac{\beta J_H S}{2}\right) \right]^2, \quad (14)$$

since the Coulomb interaction opposes a phase separation in general. The two-phase state has an energy minimum at concentration

$$x_0 = \sqrt{\frac{8AS^2}{U}}. \quad (15)$$

We also find that the critical value of the Coulomb interaction is reduced by a factor of  $\tanh^2/(\beta J_H S/2)$ , but the charge density in separated phase  $x_0$  is not affected by increasing temperature. It is interesting to note that the ratio

$$\frac{x_0}{x_c} = \sqrt{\frac{U_c}{U}} \quad (16)$$

is invariant under change of temperature.

The physical reason for the above results lies in the fact that with an increase in temperature, the random thermal fluctuation of the  $e_g$  electron results in a weakening of the double exchange interaction. Since the thermal motion of the  $e_g$  electron becomes stronger when  $T$  increases, so the screening effect is enhanced and the effective Coulomb interaction between the  $e_g$  electrons decreases, and therefore phase separation can take place more easily.

### 5. Magnetic Field Effect on Phase Separation

The application of a magnetic field will affect the state of the local spins and tend to align all the spins parallel. In this section we discuss the effect of the applied magnetic field on the phase separation. For clarity, we consider only the zero-temperature situation.

At a temperature of absolute zero most of the electrons fill in the spin-up (lower) subband:

$$E_k = \frac{1}{2}U\langle n \rangle - \sqrt{\epsilon_k^2 + (J_H S)^2 + 2\epsilon_k J_H S \cos\theta}. \quad (17)$$

After minimising the ground state energy, one finds that

$$\cos\theta = \begin{cases} g\mu_B S B + 2z\tilde{t}x/8AS^2 & B \text{ and } x \text{ are small} \\ 1 & B \text{ or } x \text{ are large.} \end{cases} \quad (18)$$

Therefore the critical concentration for a system from a canted phase to an FM phase is

$$x_c = \frac{4AS^2}{zt} \left( 1 - \frac{g\mu_B B}{8AS} \right).$$

Once the density of charge is fixed and only the magnetic field is allowed to vary, one finds that at a critical magnetic field,

$$B_{c1} = \frac{8AS^2 - 2z\tilde{t}x}{g\mu_B S}, \quad (19)$$

the system begins to exhibit ferromagnetic long-range order. Therefore the presence of a magnetic field will move the CAFM–FM borderline to the low doping density regime.

Similar to Section 3 we can obtain the field-dependent two-phase state energy density:

$$e(x, B) = \begin{cases} \frac{2z\tilde{t}\mu_B B x}{8A} [-g + x] & B < B_{c1} \\ g\mu_B S \left[ -B + \frac{g\mu_B}{16AS} B^2 \right] & B \geq B_{c1}. \end{cases} \quad (20)$$

We consider the case of  $x \ll 1$  and find that, when the external field is smaller than the critical field  $B_{c1}$ , the increase in magnetic field strength will always lead to a decrease in the total energy. Therefore, the application of an external magnetic field favours the phase separation. We also find that in the ferromagnetic droplet the internal magnetic field is

$$B_0 = 8AS/g\mu_B, \quad (21)$$

which is just the strength needed to overcome the super-exchange interaction.

If we consider both the doping effect and magnetic field effect together, we find that the critical value of the Coulomb interaction for phase separation to occur is almost fixed:

$$U_c = \frac{(z\tilde{t})^2}{2AS^2}, \quad (22)$$

and the stable charge density in the ferromagnetic droplet of the two-phase state is

$$x_0 = \sqrt{\frac{8AS^2}{U}} \left( 1 - \frac{g\mu_B B}{8AS} \right). \quad (23)$$

Therefore the charge density for a magnetic field in equilibrium becomes smaller and the phase separation occurs more easily in a magnetic field. Again we find that the ratio:

$$\frac{x_0}{x_c} = \sqrt{\frac{U_c}{U}} \quad (24)$$

is invariant under variation of an external magnetic field. Therefore, this relation is universal for all manganite compounds.

Physically, the effect of a magnetic field on the phase separation can be understood as follows: for certain doping concentrations, the system tends to form small ferromagnetic clusters (droplets) due to the double-exchange interaction; after the external magnetic field is applied along the direction of the ferromagnetic cluster, the nearby local spins are pulled to align parallel to the FM cluster and hence the cluster grows bigger; the growth of small clusters may result in the fusion of many small clusters and hence lead to the formation of large ferromagnetic clusters; therefore, the application of a magnetic field leads to the further occurrence of phase separation. The phenomenon of a magnetic field leading to the growth of small ferromagnetic clusters has been observed by De Teresa *et al.* (1997) in a small angle neutron scattering experiment.

With regard to the Jahn–Teller effect, we found that it does not affect the phase separation state qualitatively but decreases the threshold value of the Coulomb interaction for phase separation, as can be seen from equations (13) and (21). Phase separation results from the competition among double exchange, the AFM interaction, and the Coulomb interaction. Once phase separation takes place, the equilibrium charge density is determined by the super-exchange coupling strength and the Coulomb interaction, and it is independent of the Jahn–Teller coupling.



## 6. Conclusion

In summary, we found that the cant-FM borderline in the phase diagram of lightly doped manganites slightly shifts to the high doping regime with an increase in temperature, while the magnetic field tends to shift the borderline to the low doping regime. The phase separation becomes easier in the high temperature region and it is favoured by an external magnetic field.

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## References

- De Gennes, P. G. (1960). *Phys. Rev.* **118**, 141.
- De Teresa, J. M., Ibarra, M. R., Algarabel, P. A., Ritter, C., Marquina, C., Blasco, J., Garcia, J., del Moral, A., and Arnorld, Z. (1997). *Nature* **386**, 256.
- Goodenough, J. B. (1955). *Phys. Rev.* **100**, 564.
- Goodenough, J. B. (1957). *Phys. Rev.* **129**, 111.
- Hennion, M., Moussa, F., Biotteau, G., Rodriguez-Carvajal, J., Pinsard, L., and Revcolevschi, A. (1998). Los Alamos Preprint, Cond-mat/9806272.
- Inoue, J., and Maekawa, S. (1995). *Phys. Rev. Lett.* **74**, 3407.
- Jiang, J., Dong, J., and Xing, D. Y. (1997). *Phys. Rev. B* **55**, 8973.
- Li, M. Z., Zou, L.-J., and Zheng, Q.-Q. (1998). *J. Phys. Condens. Mat.* **10**, L5211.
- Martin, M. C., Shirane, G., Endoh, Y., Hirota, K., Moritomo, Y., and Tokura, Y. (1996). *Phys. Rev. B* **53**, 14285.
- Schiffer, P., Ramirez, A. P., Bao, W., and Cheong, S.-W. (1995). *Phys. Rev. Lett.* **75**, 3336.
- Wollan, E. O., and Koeller, W. C. (1955). *Phys. Rev.* **100**, 545.
- Yoshizawa, H., Kawano, H., Tomioka, Y., and Tokura, Y. (1995). *Phys. Rev. B* **52**, 13145.
- Yunoki, S., Hu, J., Malvezzi, A. L., Moreo, A., Furukawa, N., and Dagotto, E. (1998). *Phys. Rev. Lett.* **80**, 845.
- Zener, C. (1951). *Phys. Rev.* **81**, 440; **82**, 403.
- Zou, L.-J., Zheng, Q.-Q., and Lin, H. Q. (1997a). *Phys. Rev. B* **56**, 13669.
- Zou, L.-J., Lin, H. Q., and Zheng, Q.-Q. (1997b). *J. Phys. Condens. Mat.* **9**, 8623.