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LETTER TO THE EDITOR

Study on the magnetic structure in lightly doped manganese oxidesMao-Zhi Li[†], Liang-Jian Zou^{†‡} and Q Q Zheng^{†§}[†] Institute of Solid State Physics, Academia Sinica, PO Box 1129, Hefei 230031, People's Republic of China[‡] CCAST (World Laboratory), PO Box 8730, Beijing 100083, People's Republic of China[§] Hefei Institute for Advanced Study, University of Science and Technology of China, Hefei 230031, People's Republic of China

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Abstract. Based on the double exchange model, together with superexchange interaction and Coulomb interaction, the ground state of a lightly doped manganese system is studied in the semi-classical approximation of spins. It is shown that for a lightly doped system, the ground state energy of a canted state is lower than that of a spiral state; a canted state is therefore deduced to be more stable than a spiral state. This result is in agreement with experiments.

Rare-earth manganite perovskites exhibit many interesting properties associated with the connection between magnetic structure and charge transport, and have been studied for more than four decades [1–8]. Recently interest has been revived following the observation of colossal magnetoresistance (CMR) in hole-doped manganese oxides $R_{1-x}A_xMnO_3$ ($R=La, Pr, Nd, \dots$ and $A=Ca, Sr, Ba, Pb, \dots$). Much theoretical and experimental research has been carried out on the CMR effect and related phenomena. The theoretical basis for understanding the properties of Mn oxides is usually the double exchange model proposed by Zener in 1950 [4], in which the presence of $Mn^{3+}-Mn^{4+}$ mixed valence ions is responsible for both ferromagnetic coupling and charge transport. At present, however, some questions such as the spin state in lightly doped manganese oxides, are still under investigation. It is essential to clarify the spin arrangement for understanding the ground state, magnetic phase diagram and microscopic mechanism of CMR. So far some efforts have been devoted to this question, but two distinct conclusions have been obtained [6, 9, 10].

In 1960, de Gennes [6] predicted that for lightly doped manganese compounds, the double exchange suggests a canted state. By considering the ferromagnetic coupling between the localized spins mediated via the hopping of the conduction electrons, and the superexchange interaction between the localized spins mediated by anions, he showed that the competition between the kinetic and exchange energies leads to the existence of a canted magnetic structure for $0 < x < 0.2$. Experimentally, the ferromagnetic moment increasing with carrier concentration has been considered as evidence for canted spin order [7]. However, Inoue and Maekawa [9], by using a local spin quantization axis transformation and a mean field approximation, proposed that a spiral state is more favourable energetically than a canted state for a small doping region, and the canted state is favoured in highly doped Mn oxides. The same result was also obtained by Jiang *et al* [10] by using the slave-fermion method and local spin quantization axis transformation. To examine the possible existence of a spiral state, neutron-scattering experiments have been carried out. It has been shown [11] that the magnetic ordering of an insulating, lightly doped $La_{1-x}Sr_xMnO_3$ with $x \leq 0.17$

has a canted antiferromagnetic order rather than a spiral one. Recently, the existence of the canted spin order in the double-exchange magnet has again been theoretically examined by using a combination of the Hartree–Fock approximation and an exact diagonalization scheme using the Lanczos method [12]. It has been shown that the existence of a canted state depends significantly on the relative magnitudes of the electronic parameters, and that the double-exchange mechanism does not always lead to a canted magnetic state, even for small carrier concentration. Thus the issue of the magnetic structure in low-doped manganites is still under debate. In particular, the theoretical result is not consistent with the experimental one. Further study is therefore necessary to clarify this question.

In this letter, considering the double exchange interaction together with the superexchange interaction and Coulomb interaction, we study the ground state energy and show that a canted state is more stable than a spiral state for a small doping region. In addition, it is pointed out that the superexchange interaction considered in [9] and [10] is not suitable for lightly doped manganese oxides.

The model Hamiltonian of the electronic interaction for manganese oxides can be written as a summation of two parts, the double exchange interaction H_{DE} , and the superexchange interaction H_m ,

$$H = H_{DE} + H_m$$

$$H_{DE} = \sum_{\langle ij \rangle > \sigma} t_{ij} d_{i\sigma}^\dagger d_{j\sigma} - J_H \sum_{i\mu\nu} \mathbf{S}_i \cdot d_{i\mu}^\dagger \boldsymbol{\sigma}_{\mu\nu} d_{i\nu} + \frac{U}{2} \sum_{i\sigma} n_{i\sigma} n_{i\bar{\sigma}} \quad (1)$$

$$H_m = \sum_{\langle ij \rangle} A_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (2)$$

where $d_{i\sigma}^\dagger$ creates an itinerant electron with spin σ in the e_g orbital at site R_i , and t_{ij} denotes the effective transfer integral of itinerant electrons between i and j Mn sites. Only the transfer integral between nearest neighbour Mn sites is considered here and is denoted as t . $J_H (> 0)$ represents the Hund's coupling between the local spins and the itinerant electrons, U is the on-site Coulomb repulsion between itinerant electrons and $n_{i\sigma} = d_{i\sigma}^\dagger d_{i\sigma}$. Equation (2) describes the superexchange interaction between localized spins. A_{ij} denotes the superexchange coupling constant between the nearest neighbour spins. For the low-doped system, the superexchange coupling gives rise to an A-type antiferromagnetism [3, 11], alternating ferromagnetic layers coupled antiferromagnetically along the [001] direction. That is, in the xy plane, ferromagnetic coupling constant $A = A_{\parallel} (< 0)$ and antiferromagnetic coupling constant $A = A_{\perp} (> 0)$ along the z axis. $\langle \dots \rangle$ indicates that only the nearest neighbour interaction is considered.

In the semi-classical approximation, the spin operator at the i th site can be replaced with

$$S_i^z = S \cos \theta_i \quad S_i^{\pm} = S e^{\pm i\phi_i} \sin \theta_i \quad (3)$$

where θ_i is the angle between spin and the z axis, ϕ_i is the angle between the x axis and the projection of spin in the xy plane. For symmetry, we assume that for all spins, the angles θ_i are equal and denoted as θ . Along the z axis, for the nearest neighbour spins between the two nearest interlayers, the difference between the two projection angles, $\phi_i - \phi_{i-1}$, is considered to be the same as ϕ . Obviously, if $\phi = \pi$, the corresponding magnetic structure is a canted order, but if $0 < \phi < \pi$, the corresponding magnetic structure is a spiral one. The values of θ and ϕ can be obtained by minimizing the ground state energy, and finally the magnetic structure can be determined. We must therefore derive the ground state energy.

For a small doped system, the carrier is hole. Transforming the electron representation into a hole representation, the Hamiltonian can be expressed in the momentum space as:

$$\begin{aligned}
 H = \sum_k [4A_{\parallel}S^2 + 2A_{\perp}S^2(\cos^2\theta + \sin^2\theta\cos\phi)] \\
 + \sum_{k\sigma} [(-\epsilon_k + U \langle n_{\bar{\sigma}} \rangle + \sigma J_H S \cos\theta) d_{k\sigma}^{\dagger} d_{k\sigma} \\
 + J_H S \sin\theta (e^{i\phi} d_{k+Q\uparrow}^{\dagger} d_{k\downarrow} + e^{-i\phi} d_{k\downarrow}^{\dagger} d_{k+Q\uparrow})] \quad (4)
 \end{aligned}$$

where $\epsilon_k = 2zt\gamma_k$ denotes the dispersion of holes, $\gamma_k = z^{-1} \sum_{\delta} \exp(i\mathbf{k} \cdot \delta)$, z is the coordination number and δ 's are the nearest neighbour vectors. The Coulomb interaction is treated with the Hartree–Fock approximation. Diagonalizing the carrier part of the Hamiltonian, two subbands are obtained:

$$\begin{aligned}
 E_{k\sigma} = U \langle n_{\bar{\sigma}} \rangle + \frac{1}{2} \left[-\epsilon_k(1 + \cos\phi) \right. \\
 \left. \pm \sqrt{\epsilon_k^2(1 - \cos\phi)^2 + 4(J_H S)^2 + 4J_H S \epsilon_k \cos\theta(1 - \cos\phi)} \right] \quad (5)
 \end{aligned}$$

which involves θ and ϕ , therefore the dependence of the energy spectrum on the angles can be used to determine the magnetic structure for small doping.

At zero temperature, only the lower energy band of equation (5) is considered for the ground state properties of lanthanum manganites. In the double exchange model $2zt/J_H S$ is a small quantity, and equation (5) can be approximated as

$$E_{k\sigma} = U \langle n_{\bar{\sigma}} \rangle + \frac{1}{2} [-\epsilon_k(1 + \cos\phi) - 2J_H S - \epsilon_k \cos\theta(1 - \cos\phi)]. \quad (6)$$

The ground state energy of the system with uniform doping x is therefore

$$\begin{aligned}
 E_G = N[4A_{\parallel}S^2 + 2A_{\perp}S^2(\cos^2\theta + \sin^2\theta\cos\phi)] \\
 + \sum_{k\sigma}^{k_F} \{U \langle n_{\bar{\sigma}} \rangle + \frac{1}{2} [-\epsilon_k(1 + \cos\phi) - 2J_H S - \epsilon_k \cos\theta(1 - \cos\phi)]\} \quad (7)
 \end{aligned}$$

where k_F is the Fermi wavevector.

By minimizing the total energy E_G with respect to θ and ϕ , we can obtain the following two equations

$$\cos\theta = \frac{\alpha}{8A_{\perp}S^2} \quad (8)$$

$$[4A_{\perp}S^2 \sin^2\theta + \alpha(\cos\theta - 1)] \sin\phi = 0 \quad (9)$$

where $\alpha = N^{-1} \sum_k^{k_F} \epsilon_k$. Obviously only $\phi = 0$ or π and the two equations are satisfied simultaneously. It is easy to find that when $\phi = \pi$, the total ground state energy in equation (7) is at its lowest, so we can obtain that $\phi = \pi$. As mentioned above, when $\phi = \pi$, the corresponding magnetic structure of doped manganites is a canted order.

Through the above derivation and analysis, it is shown that the energy of a canted state is lower than that of a spiral state. Therefore, a canted state is more stable than a spiral state, which is in agreement with experiment [11]. The canted angle is given by equation (8), which is the same as that obtained in [13]. For small doping, $\alpha \approx 2zt x$ [13], x is the doping concentration. Apparently, the angle between the nearest neighbour spins along the z axis decreases with increasing doping concentration x , which is consistent with experiments [3, 7, 14–17].

It is obvious that our result is contrary to that obtained by Inoue *et al* [9] and by Jiang *et al* [10]. In these two papers, the nearest neighbour localized spins are all considered to

couple antiferromagnetically with each other. However, this kind of exchange interaction between localized spins is not consistent with the real situation in low-doped manganese oxides as in a low doped system not all the nearest neighbour localized spins couple antiferromagnetically with each other. As mentioned above, the coupling between the nearest neighbour spins should be an A-type antiferromagnetic, rather than G-type, which is antiferromagnetic coupling for all the nearest neighbour localized spins.

It is well known that pure LaMnO_3 is an A-type antiferromagnetic insulator [3, 7]. With the increase in doping concentration, the magnetic structure gradually evolves from an A-type antiferromagnet into a ferromagnet. Because the double exchange interaction arising from the itinerant electrons makes the localized spins tend to parallel each other, not to antiparallel. Experimentally, Kawano *et al* [11] has also demonstrated by the neutron scattering technique that the magnetic structure of a $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ sample with $x = 0.04$ is commensurate with layer-type (A-type) antiferromagnetism, and the $x = 0.125$ sample still exhibits a small A-type antiferromagnetic component. Therefore, in the low-doping region, the coupling between the nearest neighbour localized spins is A-type antiferromagnetic coupling, not G-type. The model considered in [9] and [10], where nearest neighbour spins couple antiferromagnetically with each other, is not suitable for the low-doped system of manganese oxides.

In order to further demonstrate our result, we consider a general case which only involves the xy plane—a two-dimensional situation—the relative angle between the nearest neighbour localized spins denoted as β can be changed from 0 to π , and the nearest neighbour superexchange coupling constant is A . If the coupling between the nearest neighbour localized spins is ferromagnetic, the coupling constant $A < 0$ and β is close to or equal to zero; but when the coupling between the nearest neighbour localized spins is antiferromagnetic, $A > 0$ and β is equal to π or a little smaller than π .

Thus the dependence of the free energies on the spiral and the canted states on the relative angle β is studied, and the two cases, coupling constants $A < 0$ and $A > 0$, are compared. By using a local spin quantization axis transformation,

$$\begin{pmatrix} a_{i\uparrow} \\ a_{i\downarrow} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\beta/2} & e^{-i\beta/2} \\ e^{i\beta/2} & -e^{i\beta/2} \end{pmatrix} \begin{pmatrix} d_{i\uparrow} \\ d_{i\downarrow} \end{pmatrix}$$

the expressions of the free energies of the double exchange model for the spiral and the canted states can easily be derived, and for $A < 0$ and $A > 0$, the dependence of the free energies for the spiral and the canted states on the relative angle is calculated at doping concentration $x = 0.1$ as shown in figures 1(a) and (b), respectively. It is shown in figure 1(a), that when the relative angle β is very small, the free energy of a canted state is lower than that of a spiral state. In contrast, figure 1(b) shows that when β is close to or equal to π , the free energy of a spiral state is lower than that of a canted state. Therefore, if the nearest neighbour localized spins couple antiferromagnetically with each other, a spiral state is more stable than a canted state, which corresponds to the case in [9] and [10]. On the other hand, if the nearest neighbour localized spins couple ferromagnetically with each other, a canted state is more stable than a spiral state. For the lightly doped system of manganese oxides, the coupling between the nearest neighbour localized spins in the xy plane is ferromagnetic and the relative angle is close to zero; a canted state is therefore more favourable than a spiral state.

To summarize, we can draw the conclusion that a canted state is more stable than a spiral state in lightly doped regions of manganites, which is in agreement with the experimental phase diagram.

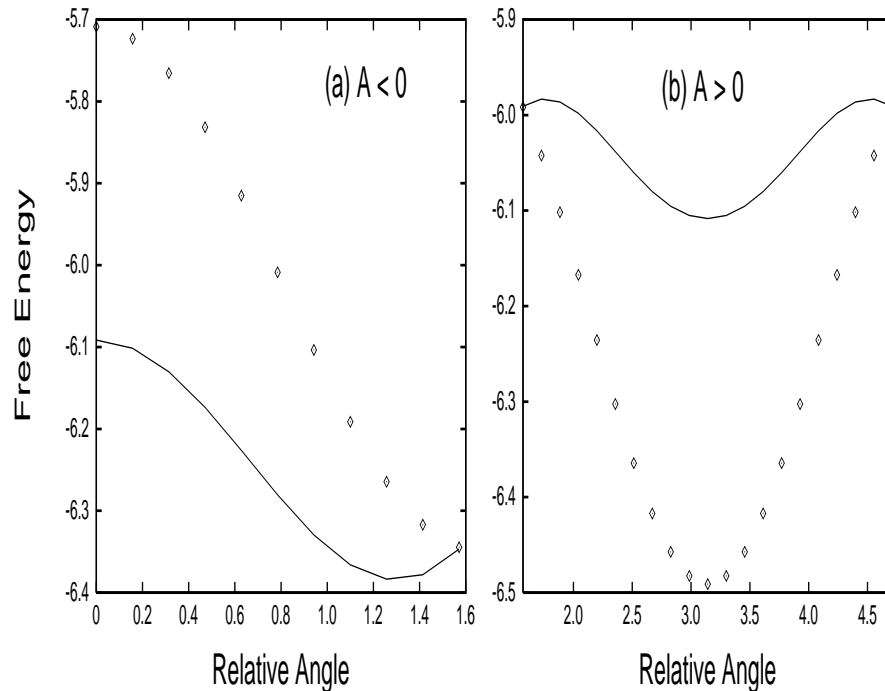


Figure 1. The dependence of the free energies of the canted and spiral states on the relative angle β for (a) $A < 0$ and (b) $A > 0$. The diamonds denote the free energy of spiral state, and the solid line denotes that of canted state. The hole concentration $x = 0.1$.

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