Symmetry Does Not Allow Canting of Spins in La$_{1.4}$Sr$_{1.6}$Mn$_2$O$_7$

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(October 28, 1999)

We analyze the symmetry of all possible magnetic structures of bilayered manganites La$_{2-x}$Sr$_{1+2x}$Mn$_2$O$_7$ with doping $0.3 \leq x < 0.5$ and formulate a corresponding Landau theory of the phase transitions involved. It is shown that canting of spins is not allowed at $x = 0.3$ though is at $x = 0.4$. The observed magnetic reflections from the sample with $x = 0.3$ may be described as arising from two spatially distributed phases with close transition temperatures but different easy axes and ranges of stability. Experimental results are revisited on the basis of the theoretical findings.

PACS number(s): 75.25.+z, 75.30.-m, 75.40.Cx, 75.30.Kz

Recent extensive investigation of the so-called colossal magnetoresistance (CMR) in doped perovskite manganites has stimulated considerable interest in relative magnetoresistive response [2–4]. The material of interest is to understand and to improve the sensitivity of the magnetic field for the huge magnetoresistance. As the tetragonal $I4/mmm$ symmetry of the material a priori lifts the degeneracy of the $e_g$ orbitals of the Mn$^{3+}$ ions, the Jahn-Teller distortion of which was argued to be responsible for the CMR of the perovskite manganites [5], observation of antiferromagnetic (AFM) correlations above $T_c$ of a para- (PM) to ferromagnetic (FM) transition in La$_{1.2}$Sr$_{1.3}$Mn$_2$O$_7$ was suggestive as an alternative origin to assist localization of carriers above $T_c$ [6].

We analyze the symmetry of all possible magnetic structures of bilayered manganites. This quasi two-dimensional nature promotes fluctuations that lower the critical temperature $T_c$ of the magnetic transition and hence the relevant scale of a magnetic field for the huge magnetoresistance. As the tetragonal $I4/mmm$ symmetry of the material a priori lifts the degeneracy of the $e_g$ orbitals of the Mn$^{3+}$ ions, the Jahn-Teller distortion of which was argued to be responsible for the CMR of the perovskite manganites [5], observation of antiferromagnetic (AFM) correlations above $T_c$ of a para- (PM) to ferromagnetic (FM) transition in La$_{1.2}$Sr$_{1.3}$Mn$_2$O$_7$ was suggestive as an alternative origin to assist localization of carriers above $T_c$ [6].

Importance of the AFM superexchange interaction shows up at the same doping level as canting of the ordered moments in neighboring layers within each bilayer as inferred from the sign reversal of the Mn-O bond compressibility below $T_c$. Further neutron scattering investigation of PM correlations provided evidence for the strong canting of the spins with an average angle that depends on both the magnetic field and the temperature above $T_c$ owing to the weaker FM correlation within the bilayers [8]. The canting angle, in particular, changes from 86° at zero field to 74° at an external magnetic field of 1 Tesla to 53° at 2 Teslas at 125K. Comprehensive neutron diffraction studies on the other hand found that the canting angle increases from 6.3° at $x = 0.4$ to 180° (A-type AFM) at $x = 0.48$ at 10K, while $T_c$ decreases from 120 K to 0 K correspondingly. Moreover, the AFM correlations above $T_c$ were identified as an intermediate phase whose order parameter decreases in an anomalous exponential manner upon increasing temperature to about 200K [9]. Accordingly, the AFM correlations and more generally the magnetic structure seem to play an important role in the bilayered manganites.

For $0.32 \lesssim x \lesssim 0.4$, the bilayered manganites exhibit a FM order below $T_c$ with an easy axis at the layer. The magnetic structure at $x = 0.3$, however, is somewhat complicated and so there exists no consensus. Perring et al [10] proposed an AFM order of an intra-bilayer FM and inter-bilayer AFM structure (denoted as AFM-B) with the easy axis along $z$ below about 90K from magnetic neutron diffraction. However, a substantial component within the layers rises up and then falls down between 60 and 90K or so. Argyriou et al [11] by neutron diffractions and Heffner et al [12] by muon spin rotation measurements reported, on the other hand, that their sample with the same doping involves two structurally similar phases: The major phase (hole poor) arranges itself in a similar AFM-B structure with a substantial canting in the plane as well as out of it. The minor phase (hole rich but $x < 0.32$) differs from the major one only by its FM arrangement along $z$ axis and its lower ordering temperature. However, as they pointed out, the assignment of the in-plane component is not so unambiguous.

Also their in-plane AFM reflections become vanishingly small below about 60K either. Still another scenario at the 30 percent doping is this: The magnetic structure changes from PM to AFM-B at about 100K and then to FM at 70K or so. The easy axis rotates correspondingly from in-plane in the AFM-B to $z$ direction in the FM state [13,14]. From these experiments, whether there exists canting of spins at $x = 0.3$ is still ambiguous. So, noticing the importance of the magnetic structure in the $x \gtrsim 0.4$ doping, clarification of the magnetic structure of the $x = 0.3$ doping is a key to understand its characteristic transport behavior [14]. In this Letter, we show that there is a qualitative difference between doping at $x = 0.3$ and $x = 0.4$ by analyzing the symmetry of the magnetic structures. It is found that the symmetry of the magnetic order parameters cannot allow canting at $x = 0.3$ in contrast to $x = 0.4$. This result sheds new light to the mechanism of the CMR behavior.

First we identify the order parameters and their sym-
TABLE I. Components of the magnetic vectors that form a basis of the IR’s of \(I4/mmm\) at \(k_F\) and \(k_M\).

| IR | BASES |
|----|--------|
| \(\tau^4\) | \(L_z, L_{Ax}\) |
| \(\tau^3\) | \(M_z, L_{Bz}\) |
| \(\tau^9\) | \((M_x, M_y); (L_{Bx}, L_{By})\) |
| \(\tau^{10}\) | \((L_z, L_y); (L_{Ax}, L_{Ay})\) |

metry responsible for the possible magnetic structures. The Mn ions with magnetic moments \(\mu_i\) in the \(I4/mmm\) structure occupy four positions at \(i = 1(0, 0, z), 2(0, 0, 1-z) (z \sim 0.1)\) and their translation by \(\epsilon_0 = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\), i.e., \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \pm z)\) (see Fig. 1). Following the representation analysis of magnetic structures [9,11,14], we identify the possible experimental magnetic structures [9], so do \(k_F\) and \(k_M\) share the same irreducible representations (IR’s) of the \(I4/mmm\) group [21], one can find the components of the four vectors that form bases of the IR’s shown in Table I. Note that the IR’s \(\tau^9\) and \(\tau^{10}\) are both two-dimensional, and so \(M_z\) and \(M_y\) together form a basis vector of \(\tau^9\), so do \(L_{Bx}\) and \(L_{By}\). From Table I, we identify \(L_B\) with the order parameter for the major phase, \(M_z\) and \((L_{Bx}, L_{By})\) for the minor phase of \(x = 0.3\), \((M_x, M_y)\) with the order parameter for \(0.3 < x \lesssim 0.38\), \((M_x, M_y)\) and \((L_{Ax}, L_{Ay})\) for \(0.38 < x < 0.48\), and \((L_{Ax}, L_{Ay})\) for \(0.48 \lesssim x < 0.5\) which is A-type AFM.

From Table I, the relevant lowest order magnetic part of the Landau free-energy can be written as

\[
F = \frac{c}{2} M^2 + \sum_w \frac{a_w}{2} L_w^2 + \sum_w \frac{b_w}{4} L_w^4 + \frac{d}{4} M^4 \\
+ \frac{1}{2} \beta_z M_z^2 + \frac{1}{2} \beta_{xy} (M_x^2 + M_y^2) \\
+ \sum_w \left( \frac{1}{2} \alpha_{wx} M_w^2 + \frac{1}{2} \alpha_{wxw} L_{wxw}^2 \right),
\]

where \(w\) represents the summation over \(L, L_A, \) and \(L_B\).

Then a FM state corresponds to \(M\) propagating with a wave vectors \(k_F = (000)\), a bilayered-type AFM-B and an A-type AFM (inter-bilayer AFM but inter-bilayer FM) state to \(M\) and \(L\), respectively, with \(k_M = (00\frac{1}{2})\) of the first Brillouin zone. Denoting the latter two order parameters as \(L_B\) and \(L_A\) respectively, and noticing that \(k_F\) and \(k_M\) share the same irreducible representations (IR’s) of the \(I4/mmm\) group [21], one can find the components of the four vectors that form bases of the IR’s shown in Table I. Note that the IR’s \(\tau^9\) and \(\tau^{10}\) are both two-dimensional, and so \(M_z\) and \(M_y\) together form a basis vector of \(\tau^9\), so do \(L_{Bx}\) and \(L_{By}\). From Table I, we identify \(L_B\) with the order parameter for the major phase, \(M_z\) and \((L_{Bx}, L_{By})\) for the minor phase of \(x = 0.3\), \((M_x, M_y)\) with the order parameter for \(0.3 < x \lesssim 0.38\), \((M_x, M_y)\) and \((L_{Ax}, L_{Ay})\) for \(0.38 < x < 0.48\), and \((L_{Ax}, L_{Ay})\) for \(0.48 \lesssim x < 0.5\) which is A-type AFM.

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where \(w\) represents the summation over \(L, L_A, \) and \(L_B\).

Note that the latter two vectors will carry a factor \(\exp(-i k_M \cdot \epsilon_0) = -1\) when they are translated by \(\epsilon_0\), and so cannot appear in odd powers. In Eq. (2), we have separated the exchange contributions (first four terms), which depend only on the relative orientation of the spins, from the magnetic anisotropic energies (remaining terms), which depend on the relative direction of the magnetic moments to the lattice and arise from the relativistic spin-spin and spin-orbit interactions and so are effects of the order of \(O(v_0^2/c_0^4)\), ordinarily about \(10^{-2}\) to \(10^{-5}\), where \(v_0\) is the speed of electrons in the crystal and \(c_0\) that of light, since the magnetic moments themselves contain a factor \(v_0/c_0\) [22]. Hence \(\alpha\) and \(\beta\) are small constants due to their relativistic origin. \(b_w\) and \(d\) are positive for stability.

We now focus on the \(x = 0.3\) doping. The relevant magnetic vectors in this case is \(L_B\) and \(M\). Minimizing Eq. (2) with the components of these vectors, one obtains five solutions

\[
M = L_B = 0, \quad (3a)
\]

\[
M = 0, L_{Bx} = L_{By} = 0, L_{Bz}^2 = -\frac{a_B + \alpha_{Bz}}{b}, \quad (3b)
\]

\[
M = 0, L_{Bz} = 0, L_{Bx}^2 + L_{By}^2 = -\frac{a_B + \alpha_{Bxy}}{b}, \quad (3c)
\]

\[
L_B = 0, M_z = M_y = 0, M_x^2 = -\frac{c + \beta_x}{d}, \quad (3d)
\]

\[
L_B = 0, M_z = 0, M_x^2 + M_y^2 = -\frac{c + \beta_{xy}}{d}. \quad (3e)
\]

Since anisotropic terms like \(M_x^2 M_y^2\) have not been included, the direction in the \(xy\)-plane cannot yet be determined. Note that the exchange term of \((L_B \cdot M)^2\) type is irrelevant, since \(M \cdot L_B = 0\) due to the incompatibility of \(M\) and \(L_B\) along a single direction. Eq. (3a) represents the PM phase, Eqs. (3b) and (3c) pure AFM-B phases with the moments directing respectively along the \(z\)-axis and the \(xy\)-plane, and Eqs. (3d) and (3e) pure FM phases. An remarkable feature of Eqs. (3) is that there is no mixed order such as \(L_{Bz}\) with \(L_{By}\) or \(L_{Bx}\), \(M_z\) with \(M_x\) or \(M_y\) and \(L_B\) with \(M\). In other words, no canting state exists. The reason is that there is no symmetry relation between \(\alpha_{Bz}(\beta_z)\) and \(\alpha_{Bxy}(\beta_{xy})\), so that both \(L_{Bz}\) (\(M_z\)) and \(L_{Bx}\) (\(M_x\)) or \(L_{By}\) (\(M_y\)) cannot simultaneously acquire nonzero values in general. This can also been seen from Table II that the \(z\) and the \(xy\) components transform according to different IR’s.

In order to determine the range of stability of the phases, one substitutes the solutions Eqs. (3) into the
the case for the change of the FM magnetization direction to be either along the $z$-axis, whereas, if $\beta_z > \beta_{xy} > 0$, they will lie on the $xy$-plane. This may be the case for the change of the FM magnetization direction with increasing doping observed experimentally.\cite{4}

Accordingly, if $0 < \beta < \beta_{xy}$, for instance, then $F_{Mz} < F_{Mxy}$ and so the moments will point to $z$-axis, whereas, if $\beta_z > \beta_{xy} > 0$, they will lie on the $xy$-plane. This may be the case for the change of the FM magnetization direction with increasing doping observed experimentally.\cite{4}

Similarly, when $\alpha_Bz$ becomes bigger than $\alpha_Bxy$ (both are assumed to be positive without loss of generality), the system changes from the phase $L_{Bz}$ [Eq. (3)] to $L_{Bxy}$ [Eq. (4)]. The two phases have respectively crystallographic space groups $P4/mnc$ and $Cmc2a$, which cannot be related by an active IR and so the transition between them is necessarily discontinuous.\cite{22}

Another reason is that the two directions are not connected continuously. In practice, the two phases may appear almost simultaneously within of a single sample at different places where there is, for example, a small variation of doping or inhomogeneity since the two phases differ in their transition points $[\alpha_{Bz} + \alpha_B = 0$, Eqs. (3)] and free energies by only values of the order of $O(\delta^2/c_0^2)$, and so which will appear depend rather sensitively on detailed conditions. This same reason also implies that the separation might be mesoscopic. Moreover, the two phases may have different temperature windows of stability due to different variations of $\alpha_Bz$ and $\alpha_Bxy$ with the temperature. Occurrence of AFM-B or FM order relies on the other hand on whether $\alpha_B$ or $c$ becomes negative first, respectively.

There exists possible mixing of $L_{Bz}$ and its $xy$-plane counterparts at higher order terms, but it cannot produce canting either. As the transition points of the two phases differ by only small quantities of order of $O(\delta^2/c_0^2)$, we use the expansion in $L_B$ itself. Thus, besides those pure $L_B$ terms in the free energy Eq. (3), we add terms

$$
\frac{1}{4} \lambda_1 L_{Bz}^2, \quad \frac{1}{4} \lambda_2 (L_{Bz}^2 + L_{Bxy}^2)^2,
$$

$$
\frac{1}{2} \lambda_3 L_{Bz}^2 (L_{Bz}^2 + L_{Bxy}^2), \quad \frac{1}{2} \lambda_4 L_{Bz}^2 L_{Bxy}^2,
$$

with the coefficients $\lambda$’s of order $O(\delta^2/c_0^2)$ relative to the exchange ones $\lambda_i$.\cite{17}

Then one can obtain new solutions that determine the direction of the moments in the $xy$-plane to be either along the $x$ or $y$ axis or along its diagonal depending respectively on whether $\lambda_4$ is positive or negative. In addition, there appear solutions such as

$$
L_{Bz} = 0,
$$

and a similar one in the diagonal plane perpendicular to the $xy$-plane, where we have kept terms of order $\lambda$ in both the numerators and denominators. However, it is readily seen that the left hand sides of Eqs. (3) and (4) possess just opposite signs in general, so that only one of them can have a real solution. Similar result can also be proved by expanding the free energy in the unit vector along $L_B$ valid at low temperatures. Further, there is no external or demagnetizing field to tilt the moments. Therefore, canting is not allowed for the bilayered-type AFM order of the major phase with $x = 0.3$ doping. The observation of both the $z$ and the $xy$ components of the AFM-B order should thus arise from the two phases each with one kind of the AFM-B components.

Nevertheless, mixing of different magnetic vectors is still possible by coupling of the type $M^2L_{Bz}^2$ for instance. This can exist due to either an exchange or a relativistic origin. Adding such a term with a coefficient $\delta/2$ for the coupling of, say, $M_z$ and $L_{Bz}$ and $L_{Bxy}$ for the minor phase of $x = 0.3$, one obtains, besides Eqs. (6b) and (6c), a new phase with mixing

$$
M_z^2 \simeq \frac{\delta a_B - c b_B}{db_B - \delta^2},
$$

$$
L_{Bz}^2 + L_{Bxy}^2 \simeq \frac{\delta c - da_B}{db_B - \delta^2},
$$

where we have neglected $\alpha_B$ and $\beta$. A system with such a coupling may exhibit several scenarios depending on the strength of the coupling and the nature of the pure phases.\cite{22, 19} It may appear in a pure phase, which may transform continuously or discontinuously to the mixed phase, or discontinuously to another pure phase at lower temperatures, the latter can only take place in the strong coupling of $\delta^2 > db_B$. It may even change directly to the mixed phase when the transition temperatures of the two pure phases get identical. Reentrant phase transitions from a pure phase to a mixed one and then back to the pure phase are also possible.

We now compare our results with experiments. The experimental assignment of both a canting major phase and a canting minor phase is based on the result that if canting is exclusively associated with only one phase, the resultant total magnetic moment is too large at 80K, near the peak temperature of the plane AFM reflections.\cite{11} This excludes the possibility of a canting minor phase and a pure $L_{Bz}$ phase and appears to suggest instead that the plane AFM reflections arise at least partly from an independent $L_{Bxy}$ phase. The fact that the reflections from $L_{Bz}$ and $L_{Bxy}$ start appearing at almost the same temperature seems to support the theoretical results that both phases emerge almost simultaneously at different places where there is a small variation of doping.
or inhomogeneity, which balances the small quantities $\alpha_{Bz}$ and $\alpha_{Bxy}$ in their transition temperatures. With the two phases rather than a single canting major phase, the too large magnetic moment may be remedied. The peak structure of the reflection intensities from the $L_{Bxy}$ phase $[1][2]$ may then arise from the different temperature dependence of $\alpha_{Bxy}$ and $\alpha_{Bz}$ in such a way that below about 60K, $\alpha_{Bxy} > \alpha_{Bz}$, and so the $L_{Bxy}$ phase transforms to the $L_B$ phase by a reorientation transition. The small remaining reflections may originate from the remnant $L_{Bxy}$ phase due to possible inhomogeneity or supercooling.

For higher doping, noting that the reflections from the $M_z$ component emerge separately and accompany with the decline of the $L_{Bxy}$ reflections $[1][2]$, it seems that the minor phase may be a pure FM phase with the $z$-axis as its easy orientation. Its significantly lower $T_c$ of about 80K than those of slightly higher doping $[1][2]$ might result from its competition with the $L_{Bxy}$ phase, which suppresses its occurrence via a positive $\delta$. Nevertheless, a canting minor phase may still be possible, but its lower $T_c$ and the peak feature of the $L_{Bxy}$ reflections should be properly accounted for. When doping increases, $T_c$ increases but $\beta_{xy}$ becomes smaller than $\beta_z$, and so the moment aligns ferromagnetically in the $xy$-plane. At high doping near 0.5, the A-type AFM is the most stable state. In between these two cases, the two types of states compete with each other via mixing terms similar to Eqs. $[\delta]$, leading possibly to the lowering of their respective transition temperatures $[\delta]$ and a $(M_x, M_y)$ and $(L_{Ax}, L_{Ay})$ tilt as observed experimentally. The exponential-like growth of the A-type AFM with cooling might be due to two-dimensional FM fluctuations.

In conclusion, noticing the importance of magnetic correlations to magnetoresistive response, we have analyzed the symmetry of all possible magnetic structures of bilayered manganites with doping $0.3 < x < 0.5$ on the basis of experimental results. A corresponding Landau theory of the phase transitions involved is formulated. A prominent result is that the ordered magnetic moments of the $x = 0.3$ doping (the major phase $[13]$) cannot be canting though $x = 0.4$ can, since the former is characterized by a single magnetic vector $L_B$ whereas the latter by two different magnetic vectors, which may be mixed by an exchange or relativistic mechanism. Such a result indicates that the magnetic structure of the $x = 0.3$ doping is far more complex than what has been proposed and demands further experimental clarifications. Instead of a canting major phase, there exist two spatially distributed phases with close transition temperatures but different easy axes and ranges of stability, to which the observed magnetic reflections from the $x = 0.3$ sample may be attributed. Such a picture can account for the peak of the plane AFM reflections. Furthermore, it seems to accord with the two-step variation of lattice parameters with temperatures through an assumption that the $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbital states correspond to magnetic orientations along $z$ and $xy$ respectively, namely, an increase in the $L_{Bxy}$ phase elongates the in-plane scale but shortens the $z$ scale, and then a decrease gives rise to a reverse effect $[1][2]$. As both the $z$ and the $xy$ components possess a bilayered-type AFM structure, the material should be expected to display an insulating behavior in the whole temperature range. So the metal-insulator transition should mostly be attributed to the percolation of the minor FM phase, whose transition temperature, however, seems to be too low $[1]$. Further work is desirable to clarify this.

This work was supported by a URC fund at HKU.

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