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Symmetry analysis of the magnetic structures of bilayered manganites \( \text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7 \) near \( x=0.3 \): Phase separations and percolation

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We analyze the symmetry of the magnetic structures of tetragonal bilayered manganites \( \text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7 \) with doping near \( x=0.3 \) and formulate a corresponding Landau theory of the phase transitions involved. It is shown that a phase with a single magnetic order cannot be canting though with a mixture of different magnetic orders can, as is possibly the case near \( x=0.4 \). Accordingly, a schematic magnetic phase diagram near \( x=0.3 \) is constructed which may consistently account for the controversial experimental observations. Possible phase separations and a percolation mechanism of the colossal magnetoresistance are discussed.

Recent extensive investigation of the so-called colossal magnetoresistance (CMR) Ref. 1 in doped perovskite manganites has stimulated considerable interest in relative bilayered compound \( \text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7 \) in an attempt to understand and to improve the sensitivity of the magnetoresistive response.2–4 The material of interest is comprised of perovskite (La, Sr)MnO₃ bilayers separating by (La, Sr)O blocking layers, namely, the \( n=2 \) member of the Ruddlesden-Popper series of manganites (La, Sr)O[(La, Sr)MnO₃]ₙ. 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, whose Jahn-Teller distortion was argued to be responsible for the CMR of the perovskite manganites,5 observation of antiferromagnetic (AFM) correlations above \( T_e \) of a paramagnetic (PM) to ferromagnetic (FM) transition in \( \text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7 \) was suggestive as an alternative origin to \( T_c \). Accordingly, the AFM correlations and more generally the magnetic structure seem to play an important role in the bilayered manganites.

Although the bilayered manganites exhibit an FM order below \( T_c \), with an easy axis at the layer for \( 0.32 \leq x \leq 0.4 \), the magnetic structure at \( x=0.3 \) is somewhat complicated and so there exists no consensus. Perring et al.10 proposed a bilayered AFM order of an intrabilayer FM and interbilayer AFM structure (denoted as AFM-B) with the easy axis along \( z \) below about 90 K from magnetic neutron diffraction. However, a substantial component within the layers rises up and then falls between 60 and 90 K 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) shows canting in a similar AFM-B structure with substantial components both in the plane and 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 60 K either. Still another scenario at the 30% doping is this: The magnetic structure changes from PM to AFM-B at about 100 K and then to FM at 70 K or so. The easy axis rotates correspondingly from in-plane in the AFM-B to \( z \) direction in the FM state.4,13,14 From these experiments, whether there exists canting of spins at \( x=0.3 \) is still ambiguous. Noticing the importance of the magnetic correlations in the \( x \approx 0.4 \) doping, clarification of the magnetic structure of the \( x=0.3 \) doping is a key to understand its characteristic transport behavior.3,15

In this paper, we show from symmetry analysis and a corresponding Landau theory that a single magnetic structure like AFM-B or FM order cannot be canting, though competition between them can. This result allows us to construct a
hypothetic phase diagram. Fig. 1, for the bilayered manganites doped near \( x = 0.3 \). The unexpectedly complicated phase diagram contains five phases among which the two pairs of AFM-B and FM phases differ only by their orientation of the magnetic moments as indicated by the subscripts. It can explain all the three contradictory observed scenarios above, provided that the reported doping level has a slight difference. Moreover, it is predicted that there are phase separations, which lead to coexistence of different phases as shown in Fig. 1.b by the dashed lines. Furthermore, CMR of percolation origin may be envisioned since the AFM-B phase is insulating.

First we identify the order parameters and their symmetry responsible for the possible magnetic structures. The Mn ions with magnetic moments \( \vec{\mu}_i \) in the \( 14/mmm \) structure occupy four positions at \( i = 1(0,0,z) \), \( 2(0,0,1-z) \) (\( z \approx 0.1 \)) and their translation by \( \vec{t}_0 = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \), i.e., \( (\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \pm z) \) (see Fig. 2).\(^{16}\) Following the representation analysis of magnetic structures,\(^{17-19}\) we define two magnetic vectors

\[
\vec{M} = \vec{\mu}_1 + \vec{\mu}_2, \\
\vec{L} = \vec{\mu}_3 - \vec{\mu}_2.
\]

Then an FM state corresponds to \( \vec{M} \) propagating with a wave vectors \( \vec{k}_f = (000) \), a bilayered-type AFM-B and an \( A \)-type AFM (intrabilayer AFM but interbilayer FM) state to \( \vec{M} \) and \( \vec{L} \) propagating, respectively, with \( \vec{k}_M = (00\frac{1}{2}) \) of the first Brillouin zone. Denoting the latter two vectors as \( \vec{L}_B \) and \( \vec{L}_A \), respectively, and noticing that \( \vec{k}_f \) and \( \vec{k}_M \) share the same irreducible representations (IR’s) of the \( 14/mmm \) group,\(^{20}\) 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 \( \tau^2 \) and \( \tau^3 \) are both two dimensional, and so \( M_z \) and \( M_y \) form a basis vector of \( \tau^2 \), so do \( L_{B_x}, \) and \( L_{B_y} \). From Table I and the possible experimental magnetic structures,\(^{9,11,14}\) we identify \( \vec{L}_B \) with the order parameter for the major phase, \( M_z \) and \( (L_{B_x}, L_{B_y}) \) for the minor phase of \( x = 0.3 \), \( (M_z, M_y) \) with the order parameter for \( 0.3 < x \leq 0.38 \), \( (M_z, M_x) \) and \( (L_{A_x}, L_{A_y}) \) for \( 0.38 < x < 0.48 \), and \( (L_{A_x}, L_{A_y}) \) for \( 0.48 \leq x < 0.5 \), which are \( A \)-type AFM’s.

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

\[
F = \frac{c}{2} \vec{M}^2 + \sum_w \frac{a_w}{2} \vec{L}_w^2 + \sum_w b_w \frac{1}{4} \vec{L}_w^4 + \frac{d}{4} \vec{M}^4 + \frac{1}{2} \beta_z M_z^2 \\
+ \frac{1}{2} \beta_{xy} (M_x^2 + M_y^2) + \sum_w \left[ \frac{1}{2} \alpha_{wx} (L_{w_x}^2 + L_{w_y}^2) \right] \\
+ \left[ \frac{1}{2} \alpha_{wz} L_{w_z}^2 \right].
\]

where \( w \) represents the summation over \( L, L_A, \) and \( L_B \). Note that the latter two vectors will carrier a factor \( \exp[-i \vec{k}_M \cdot \vec{t}_0] = -1 \) when they are translated by \( \vec{t}_0 \) and hence 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 \( O(v_e^2/c_0^3) \), ordinarily about \( 10^{-2} - 10^{-3} \), 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 \( v_0/c_0 \).\(^{21}\) Hence \( \alpha \) and \( \beta \) are small constants due to their relativistic origin, \( b_w \) and \( d \) are positive for stability.

We now consider the AFM-B order \( \vec{L}_B \) at \( x = 0.3 \). Minimizing Eq. (2), one obtains, besides the PM phase with \( \vec{L}_B = \vec{0} \), two additional ordered phases, one, denoted by AFM-B, with \( L_z \) magnetic moments point to the \( z \) axis, with \( L_{B_z}^2 = -(d_{B_z} + a_{B_z})/b \), and the other AFM-B \( \vec{xy} \) with \( L_{B_x}^2 + L_{B_y}^2 = -(d_{B_x} + a_{B_{xy}})/b \) since the moments lie in the \( xy \) plane. As higher-order anisotropic terms like \( L_z^2 L_{xy}^2 \) have not been included, we shall let the direction of the moments in the \( xy \) plane be undetermined. Note that the transition points at \( a_{Bz} \)

![Image](Image.png)

FIG. 2. Elementary unit cell of \( 14/mmm \) with four Mn ions and their numbering.
+ \alpha_B = 0 \) of the two phases differ only by the small quantities \( \alpha_B \). Moreover, the difference between their free energies, 
\(- \alpha_B (\alpha_{Bz} - \alpha_{Bxy}) / D_B \), to first order in \( \alpha_B \), is also small. As a result, \( \text{AFM-}B_{xy} \) is a stable phase if \( \alpha_{Bz} > \alpha_{Bxy} \) and vice versa, assuming \( \alpha > 0 \) without loss of generality. The two phases have respectively crystallographic space groups \( P4/mnc \) and \( Cmca \), which cannot be related by an active IR and so the transition between them is necessarily discontinuous.\(^2\) Another reason is that the two directions are not connected continuously.

More importantly, there is no phase with both the \( z \) and \( xy \) components finite. This is because for a tetragonal lattice, the \( z \) and \( xy \) components decouple, each carrying an IR of different dimensions (see Table I). Consequently, they are not related to each other, and so both cannot generally acquire nonzero values in a phase transition. Indeed, it can be shown that inclusion of next higher-order mixing terms such as \( L_{Bz}^2 (L_{Bz}^2 + L_{Bxy}^2) \) and \( L_{Bz} L_{Bxy} \), as well as \( L_{Bz}^2 (L_{Bz}^2 + L_{Bxy}^2) \) can only yield real solutions directing along either \( z \) axis or \( xy \) plane, but not both. Therefore, for a single \( L_B \) order, symmetry does not allow the spins to cant. These results also apply to a single FM order. Thus there are two possible FM phases with different easy axes but close transition temperatures, canting is, however, not allowed.

Nevertheless, canting containing different magnetic vectors is still possible. This may arise from the competition between them, as for example, the competition between double exchange and AFM superexchange, which may be the origin of spin canting around \( x = 0.4 \). Near \( x = 0.3 \), coupling of the type \( M^F L^S \) of either an exchange or a relativistic origin may lead to a canting of the minor phase. However, as such canting involves two different IR’s as seen in Table I, a transition from a disordered PM phase should be first order in compliance with Landau’s criterion.\(^2\)

We now turn to the experiments to see whether our results help to clarify the controversy near \( x = 0.3 \). We first argue that there is an independent \( \text{AFM-}B_{xy} \) phase. Consider the detailed analysis by Argyriou et al. which gives rise to canting.\(^1\) It is found\(^1\) by high-resolution synchrotron x-ray diffraction that the nominal \( x = 0.3 \) single crystals used in the experiments separate into two naturally distinct phases, the minor phase possessing a slightly higher \( x \) value than the major one. For the neutron diffractions, when the planar \( \text{AFM-}B \) component is negligible at temperature \( T = 5 \) K, the results agree with a mixture of a major \( \text{AFM-}B_z \) and a minor \( \text{FM}_z \) phase, whereas at 80 K near which it peaks, if it was exclusively associated with only one phase to produce canting, the resultant total magnetic moment was too large. This is the reason for the assignment of two canting phases with their canting angles varying with temperature.\(^1\) Now noting that a canting \( \text{AFM-}B \) phase is prohibited, the same reason also excludes the possibility of a canting minor phase and a pure \( \text{AFM-}B_z \) phase. Accordingly, the planar \( L_{Bxy} \) reflections should arise at least partly from an independent \( \text{AFM-}B_{xy} \) phase.

If this is accepted, the controversial observations near \( x = 0.3 \) may be resolved. According to Argyriou et al.,\(^1\) as the temperature is lowered, the reflections from the \( \text{AFM-}B_{xy} \) phase decline accompanying the emergence of those from the \( \text{FM}_z \) one. This may be viewed as a transition from the former phase to the latter one, in accordance with the results reported by Kubota and co-workers,\(^3,4\) though canting may still be possible, but the peak from the \( \text{AFM-}B_{xy} \) reflections should be properly accounted for. On the other hand, although Perring et al. proposed an \( \text{AFM-}B_z \) phase,\(^5\) their neutron-diffraction measurements also contain reflections from \( L_{Bxy} \) which also peak near 80 K similar to Argyriou’s. There are two possibilities as the temperature is further lowered. One is that there is an \( \text{FM}_z \) phase upon closer inspection of the diffraction data as was done by Argyriou et al. Another is that the low-temperature phase is simply \( \text{AFM-}B_z \) as they reported. The \( \text{AFM-}B_{xy} \) phase only shows up at intermediate temperatures. The former might be compatible with a possible “spin flop” mechanism in which the FM tendency due to double exchange acts as a magnetic field that drive the transition from \( \text{AFM-}B_{xy} \) to \( \text{AFM-}B_z \). At lower temperatures, the double exchange may then be strong enough to align all the spins along the \( z \) axis. For the latter possibility, although there is not yet a direct experimental determination of the magnetic structure below \( x = 0.3 \), it has been shown that substitution of a smaller lanthanide ion Nd with La at fixed \( x = 0.3 \) suppresses the FM order.\(^6\) This seems to imply an \( \text{AFM-}B_z \) phase below \( x = 0.3 \). In this case, the peak may be accounted for by a proper dependence of \( \alpha_{Bxy} \) on temperature, leading to a reorientation transition to the other phase.

Combining the above results, and noticing that for \( x > 0.32 \) the FM moments lie in the \( xy \) plane,\(^1\) we propose Fig. 1 as a schematic phase diagram near \( x = 0.3 \). There are five phases showing up around that doping, much more complicated than one might expect. The boundaries between the phases are only hypothetic, their exact position rests on further experiments. The gross feature of the phase diagram can be accounted for by a proper assumption on the temperature and doping dependences of quadratic coefficients in Eq. (2). In the following we discuss possible phase separations and percolation implied in Fig. 1.

The dashed lines in Fig. 1 indicate regions of coexistence. There is likely a phase separation between the \( \text{AFM-}B_z \) and the \( \text{AFM-}B_{xy} \) phase. It was reported experimentally that coexistence of the \( \text{AFM-}B_z \) and the \( \text{FM}_z \) phases arises from a single crystal that is biphasic.\(^1\) Whether different signals come from a monophase or a biphase is controversial.\(^2\) Our theory shows that the transition temperatures of the \( \text{AFM-}B_z \) and the \( \text{AFM-}B_{xy} \) phase differ only by the small quantities \( \alpha_{Bz} \) and \( \alpha_{Bxy} \). This seems to be borne out by the experiments that the reflections from the two phases start appearing at almost the same temperature.\(^10,11\) Furthermore, from the theory, the two phases then possess close free energies. Accordingly, a small spatial variation of doping or inhomogeneity may make the two phases emerge almost simultaneously at different places. This is the phase separation between the two \( \text{AFM-}B \) phases, which may possibly be the reason that the \( L_{Bxy} \) signals cannot be exclusively associated with the minor FM phase, since at least part of the signals come from the phase separated phase. Reversely, this in turn provides an indirect evidence for the phase separation. At lower temperatures, it is not yet clear whether coexistence of the \( \text{AFM-}B_z \) phase and the \( \text{FM} \) phase arises from a phase separation similar to the perovskite manganites\(^19\) or from the
reported biphasic behavior, which should still exist at high enough temperatures where phase separation cannot occur.

There should be another coexistence due to a different mechanism between the AFM-\(B_{xy}\) phase and the FM\(_z\) phase, and is related to percolation mechanism of CMR at this region. It should be noted that a phase with AFM-B structures must be insulating, at least along z axis. So it is surprising that a familiar CMR peak is observed at the temperature where the AFM-B orders emerge, but not below the \(L_{Bxy}\) reflection peak, i.e., at the temperature where the FM order becomes detectable. Tunneling as suggested by Kimura et al.\(^3\) appears unlikely to produce the peak. Instead, percolation of FM regions seems possible. By adopting a strong-coupling picture between \(M_z\) and \(L_{Bxy}\), the transition between them is of first order.\(^{24}\) Accordingly, regions of FM\(_z\) may exist far in the AFM-\(B_{xy}\) phase. In the present quasi-two-dimensional system, because of a stronger FM correlation in the layers, percolation through these FM regions is easier to occur, leading to the CMR peak at higher temperatures. So there is a subtle balance among the AFM-\(B_{xy}\), the AFM-\(B_{xy}\) and the FM\(_z\) phase. Also due to the first-order nature, a remnant AFM-\(B_{xy}\) phase resulting from inhomogeneities or supercooling is reasonable, giving rise to the negligible reflections at low temperatures.\(^{11}\) Further, the strong competition between \(L_{Bxy}\) and \(M_z\) suppresses the occurrence of the FM\(_z\) phase, leading to its substantially lower transition temperature of about 80 K than those of slightly higher doping.\(^{11}\)

In conclusion, we have analyzed the magnetic structures of the tetragonal bilayered manganites with doping near \(x = 0.3\) on the basis of experimental results, as these are basic for understanding the related transport behavior. A prominent result from the symmetry analysis is that the AFM-B order near the \(x = 0.3\) doping (the major phase\(^{11}\)) cannot be canting, since it is characterized by a single magnetic vector \(L_B\). From this, a detailed analysis of the controversial experimental results leads to a complicated phase diagram, which contains five magnetic phases near \(x = 0.3\). It can consistently account for the observations near this doping. The experimental results also provides an indirect evidence for a phase separation between the AFM-\(B_{xy}\) and the AFM-\(B_{xy}\) phase, a phase separation between the latter phase and the FM\(_z\) phase via a first-order transition between them, and thereby a percolation mechanism for the CMR behavior near \(x = 0.3\). Further experimental and theoretical work is highly desirable.

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