Symmetry Origin of the Phase Transitions and Phase Separation in Manganites at Low Doping

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We analyze the symmetry changes of the paramagnetic to the A-type antiferromagnetic and to the ferromagnetic phase transitions in undoped and moderately doped LaMnO₃, respectively. We show that in the orthorhombic–distorted perovskite manganites the phase separation at low doping is associated with the noncollinear nature of the magnetic orders permitted by symmetry. A simple model for the competition between the two phase transitions is put forward within the framework of Landau theory of phase transitions.

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The discovery of “colossal” magnetoresistance (CMR) has stimulated a renaissance of interest in doped rare-earth manganese oxides because of their promising practical applications and their similarity to the cuprate superconductor. Although great efforts have been devoted to this system, the various phase transitions occurring under doping is still not fully understood as a result of the complex interplay among magnetic, charge, orbital and structural orders. Present lack of precise command of strong correlations makes difficult discriminating models based on, for example, pure double exchange, Jahn–Teller and doping variants. Therefore, it is desirable to investigate such general properties as symmetry of the system that are feasible and meanwhile informative enough both to impose rigorous general restrictions and to shed light to microscopic theories.

The perovskite–structured LaMnO₃ is believed to be a Jahn–Teller distorted orthorhombic structure with a crystallographic space group Pnma(D₁₆h) at room temperatures. Below T_N ≈ 140K, it undergoes a magnetic transition from a paramagnetic (PM) to an A-type antiferromagnetic (AFM) phase in which ferromagnetic (FM) layers are coupled antiferromagnetically, different from the usual AFM couplings along all nearest neighbors (G-type), while its lattice remains unaltered. The Mn⁴⁺(d⁵) ion is believed to be in the t₂g⁴e_g high-spin state; and strong on-site correlations render the compound insulating in both magnetic phases. Upon doping of divalent ions, some Mn ions lose their Jahn-Teller active e_g electrons leaving much smaller Mn³⁺ ions with mobile holes, a sufficient amount of which may make the low–temperature phase metallic and ferromagnetic via a double exchange, a superexchange interaction between localized t₂g spins which is facilitated by an external magnetic field and hence follows the so-called colossal magnetoresistance. In addition to this magneto-transport behavior, many unusual phenomena show up such as the magneto–structural transition, charge and orbital orders and their stability to external influences such as magnetic field, pressure, x–ray, electric field and light irradiations. A particular issue that pose a great challenge to theorists besides the mechanism of CMR itself, is the tendency of the system to phase separation not only at high doping through a first order FM to charge–ordered AFM transition, but also at low doping. We shall show below by symmetry analysis that both the PM to AFM and the PM to FM transition are induced by the same irreducible corepresentation, which, among others, permits a common FM component for both the AFM and FM phase. The competition between these two phases upon doping leads to the electronic phase separation at low doping when combined with the microscopic mechanism of double exchange.

First we analyze the symmetry change of the PM to AFM phase transition in undoped LaMnO₃. Since the crystallographic space group remains unaltered during the magnetic phase transition, this transition must associate with a one–dimensional irreducible corepresentation of the magnetic group at the center (k = 0) of the orthorhombic Brillouin zone. As a result, the PM to AFM transition is governed by a single order parameter that acquires a nonzero value representing the staggered magnetization below T_N.

The magnetic group of the PM phase contains the time–reversal operation R itself as one of its elements and so is the grey group Pnma1', a direct product group of Pnma and the group \{E,R\} with E being the identity operation. All its irreducible corepresentations are (ICR) thus multiplied into a doubled set of even and odd groups. Only the odd representations are relevant as \( R \) reverse the direction of a spin; and so the transition from a PM state can be described simply by the axial vector basis functions of the irreducible representations of the space group Pnma. Designate a space group element by \( \{ R(t_R + t) \} \), where \( R \) represents a proper or improper rotation, \( t_R \) a nonprimitive (fractional) translation associated with \( R \), and \( t \) a primitive translation, the eight coset representatives of Pnma with respect to the subgroup of pure translations \( \{ E[t] \} \) are...
where \( I \) denotes an inversion, \( U_z \) a rotation by \( \pi \) about \( x \)-axis and \( \sigma_x \) a reflexion about the plane perpendicular to \( x \), etc, and \( h_i \)'s are Kovalev’s symbols. Then according to the character table of the point group \( D_{2h} \), Table I, the magnetic symmetries of the phases that arise from the corresponding irreducible representations can be determined as follows:

\[
\begin{array}{cccccccc}
\tau^1 & \tau^2 & \tau^3 & \tau^4 & \tau^5 & \tau^6 & \tau^7 & \tau^8 \\
Pnma & Pn'm'a' & Pn'm'a' & Pn'm'a' & Pn'm'a' & Pn'm'a' & Pn'm'a' & Pn'm'a' \\
\end{array}
\]  

(1)

Here the primes indicate the symmetry elements that are associated with \( \mathcal{R} \) in the respective magnetic groups, for example, all the reflexion planes of \( \tau^2 \) must combine with \( \mathcal{R} \) to give \( Pn'm'a' \) since all their corresponding characters are \(-1\).

### Table I. Characters of the irreducible representations of \( Pnma \) at \( k = 0 \)

| \( \tau^1 \) | \( \tau^2 \) | \( \tau^3 \) | \( \tau^4 \) | \( \tau^5 \) | \( \tau^6 \) | \( \tau^7 \) | \( \tau^8 \) |
|---|---|---|---|---|---|---|---|
| \( h_1 \) | \( h_2 \) | \( h_3 \) | \( h_4 \) | \( h_{25} \) | \( h_{26} \) | \( h_{27} \) | \( h_{28} \) |
| 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 1 | 1 | 1 | -1 | -1 | -1 | -1 | -1 |
| 1 | 1 | -1 | -1 | 1 | 1 | 1 | 1 |
| 1 | 1 | -1 | -1 | -1 | 1 | 1 | 1 |
| 1 | -1 | 1 | 1 | -1 | -1 | 1 | 1 |
| 1 | -1 | 1 | 1 | -1 | -1 | 1 | 1 |
| 1 | -1 | -1 | 1 | 1 | 1 | 1 | 1 |
| 1 | -1 | -1 | 1 | 1 | 1 | 1 | 1 |

### Table II. Transformation table of the magnetic moments

| \( \mu_1 \) | \( \mu_2 \) | \( \mu_3 \) | \( \mu_4 \) | \( \mu_5 \) | \( \mu_6 \) | \( \mu_7 \) | \( \mu_8 \) |
|---|---|---|---|---|---|---|---|
| \( h_1 \) | \( h_2 \) | \( h_3 \) | \( h_4 \) | \( h_{25} \) | \( h_{26} \) | \( h_{27} \) | \( h_{28} \) |
| \( \mu_1 \) | \( \mu_2 \) | \( \mu_3 \) | \( \mu_4 \) | \( \mu_5 \) | \( \mu_6 \) | \( \mu_7 \) | \( \mu_8 \) |
| \( \mu_3 \) | \( \mu_1 \) | \( \mu_2 \) | \( \mu_4 \) | \( \mu_5 \) | \( \mu_6 \) | \( \mu_7 \) | \( \mu_8 \) |
| \( \mu_4 \) | \( \mu_2 \) | \( \mu_3 \) | \( \mu_5 \) | \( \mu_6 \) | \( \mu_7 \) | \( \mu_8 \) | \( \mu_8 \) |

Next we determine the nature of the magnetic order below \( T_N \). The elementary unit–cell of LaMnO\(_3\) contains four formula units with Mn\(^{3+}\) ions located at the 4a sites \( 1(000), 2(0\frac{1}{2}0), 3(0\frac{1}{2}0), \) and \( 4(\frac{1}{2}\frac{1}{2}\frac{1}{2}) \) (see Fig. 1). Associating each ion with a magnetic moment \( \mu \), one can find their transformations by \( h_i \)'s as shown in Table I. Let

\[
\begin{align*}
M &= \mu_1 + \mu_2 + \mu_3 + \mu_4 \\
L_1 &= \mu_1 - \mu_2 + \mu_3 - \mu_4 \\
L_2 &= \mu_1 + \mu_2 - \mu_3 - \mu_4 \\
L_3 &= \mu_1 - \mu_2 - \mu_3 + \mu_4,
\end{align*}
\]

which represent, respectively, the total magnetization and three possible AFM collinear orders of \( C \), \( A \) and \( G \) types \( [3,4,12] \) then according to Table II, the transformation properties of \( M \) and \( L_i \)'s can be derived. Noting that both \( U_z \) and \( \sigma_x \) change the sign of the \( y \) and \( z \) components of an axial vector, one deduces further the transformation properties of their respective components, from which those components that form bases of the irreducible corepresentations (ICR) of \( Pnma \) at \( k = 0 \) can be found to be

\[
\begin{array}{c|c}
\text{ICR} & \text{BASES} \\
\tau^1 & L_{3x}, L_{1y}, L_{2z} \\
\tau^3 & M_x, L_{2y}, L_{1z} \\
\tau^5 & L_{2x}, M_y, L_{3z} \\
\tau^7 & L_{1x}, L_{3y}, M_z \\
\end{array}
\]  

(3)
that is, \( L_{2x} \), for instance, transforms according to the representation \( \tau^5 \), so do \( M_y \) and \( L_{1z} \). Accordingly, it is straightforward to construct the magnetic Landau free-energy that is an invariant:

\[
F = \sum_{i=1}^{3} \frac{a_i}{2} L_i^2 + \frac{c}{2} M^2 + \frac{3}{2} \sum_{i=1}^{3} \frac{b_i}{4} L_i^4 + \frac{d}{4} M^4 + \frac{1}{2} \sum_{\alpha=x,y,z} \sum_{i=1}^{3} \nu_{\alpha i} L^\alpha_{\alpha i} + \beta_{\alpha} M^2_{\alpha} + \gamma_1 L_{3z} L_{1y} + \gamma_2 L_{3z} L_{2z} + \gamma_3 L_{1y} L_{2z} + \\
\gamma_4 M_x L_{2y} + \gamma_5 M_x L_{1z} + \gamma_6 M_y L_{1z} + \gamma_7 L_{2x} M_y + \gamma_8 L_{2x} L_{3z} + \gamma_9 M_y L_{3z} + \gamma_{10} L_{1z} L_{3y} + \gamma_{11} L_{1z} M_z + \gamma_{12} L_{3y} M_z.
\]  

We have expanded the exchange contributions (first four terms) to the fourth order and the magnetic anisotropic energies (the remaining terms) to the second order because of their relatively smaller magnitude. Among all the coefficients, \( b_i \) and \( d \) are positive for stability, and \( \gamma_i, \nu_{\alpha i}, \) and \( \beta_\alpha \) are small constants from relativistic effects.\(^3\)\(^4\) By ignoring the anisotropic contributions, it is readily seen that Eq.

\[
\begin{align*}
\text{Eq. (4)}
\end{align*}
\]

may yield FM or AFM phase of \( G, A \) or \( C \) type depending on the coefficients \( a_i \) and \( c \).

Experimentally, it has been observed that the magnetic structure of LaMnO\(_3\) is \( A \)-type AFM order with the magnetic moments directing primarily along \( x \) axis.\(^3\)\(^4\) As a result, the magnetic transition is described by a non–zero \( L_{2x} \) below \( T_N \). So \( a_2 \) should become negative first among \( a_i \) and \( c \) upon cooling. Retaining only those terms in Eq.

\[
\text{Eq. (4)}
\]

that contain the components pertinent to \( L_{2x} \), we have

\[
F' = \frac{a_2}{2} L_{2x}^2 + \frac{a_3}{2} L_{3z}^2 + \frac{b_2}{4} L_{2x}^4 + \frac{\nu_2 x}{2} L_{2x}^2 + \frac{c}{2} M_y^2 + \frac{1}{2} \beta_3 y M_y^2 + \gamma_7 L_{2x} M_y + \gamma_8 L_{2x} L_{3z},
\]

with a solution

\[
\begin{align*}
L_{2x}^2 &= -\frac{1}{b_2}(a_2 + \nu_2 x) - \frac{\gamma_7}{c + \beta_3} \frac{a_2}{a_3} \approx -\frac{a_2}{b_2}, \\
M_y &= -\frac{\gamma_7}{c + \beta_3} L_{2x} \approx -\frac{\gamma_7}{c} \sqrt{-\frac{a_2}{b_2}}, \\
L_{3z} &= -\frac{\gamma_8}{a_3} L_{2x} \approx -\frac{\gamma_8}{a_3} \sqrt{-\frac{a_2}{b_2}},
\end{align*}
\]

that minimizes \( F' \), where the last approximate equalities in each line neglect those terms that are orders of magnitude smaller.

Equations \( \text{Eq. (4)} \) corresponds to an \( A \)-type AFM order with the magnetic moments directing primarily along \( \pm x \)–axis in alternative Mn–O layers perpendicular to \( y \)–axis. Meanwhile, all the moments tilt slightly along both \( y \)–axis and \( z \)–axis giving rise to a weak FM and a weak \( G \)-type AFM order respectively in these two directions. The solution associates with the irreducible corepresentations \( \tau^5 \), and the magnetic group of the asymmetry phase is thus \( Pn''ma' \). The orientation of the magnetic moments can also be obtained directly from the irreducible representation except their relative magnitude. In other words, all these three types of order along their respective directions are simultaneously allowed by the symmetry. So in the symmetry point of view, canted phase is allowed. A weak ferromagnetic component along \( y \) has been inferred and observed in experiments.\(^3\)\(^4\) The magnetic structure obtained also agrees with the results of the local–spin–density–approximation calculations.

We now move on to the effect of doping. An important feature of Eqs.

\[
\text{Eq. (4)}
\]

is the global ferromagnetism along \( y \) axis. Weak as it is, the partial FM order in alternative \( xz \) planes indicates that upon doping this weak FM component should be so enhanced that the FM phase arising at sufficient doping rates should also direct along this \( y \) axis as observed experimentally.\(^3\)\(^4\) In other words, the PM to FM phase transition should also associate with \( \tau^5 \). Formally, this is induced by the coupling of \( L_{2x} \) with \( M_y \) in Eq.

\[
\text{Eq. (4)}
\]

. Microscopically, the doped holes promote the mobility of the \( e_g \) electrons that mediate FM coupling. Accordingly, as doping increases, the FM coupling is enhanced and hence \( T_c \), the FM transition temperature increases. On the other hand, doping suppresses the antiferromagnetism. Therefore, when the doping level \( \delta \) (we use here \( \delta \) instead of \( x \) to avoid confusion) is not too large, we may assume that

\[
\begin{align*}
a_2(\delta) &= a_0(T - T_N + a'_0 \delta), \\
c(\delta) &= c_0(T - T_c - c'_0 \delta),
\end{align*}
\]

where \( T_N \) and \( T_c \) denote the AFM and the FM transition temperatures at \( \delta = 0 \), respectively, and \( a_0, a'_0, c_0, \) and \( c'_0 \) are positive constants. Then, once \( \delta > \delta_c \equiv (T_N - T_c)/(a'_0 - c'_0) \), the coefficient \( c \) will become negative first upon
cooling; and so the system exhibits a PM to FM instead of AFM transition. In this case, similar analysis yields a dominant magnetization $M \approx \sqrt{-c/d}$ with now weak canting of $L_{2x} \approx -\gamma_1 M/a_2$ and $L_{3z} \approx -\gamma_3 M/a_3$ in contrast to the AFM state. This simple approximation is in qualitative agreement with the magnetic phase diagram at low doping as in Refs. [21,22], namely, the AFM transition temperature decreases but the FM one increases with increasing doping.

More importantly, this simple model for the competition between the two phase transitions exhibits phase separations at low doping. It is possible to extend the present theory to a generalized Ginzburg–Landau theory by including Coulomb repulsion and Boltzmann entropy terms for the holes as well as gradient contributions from spatial inhomogeneities to give a quantitative account. Here to illustrate the essential point, it is instructive to compare the bulk free–energy of a doped uniform AFM state with that of a state composed of a hole–depleted AFM and a hole–rich FM phase. To this end, note that a uniform ordered AFM state at a doping level $\delta_0$ has a bulk free-energy $-a_2^2/4b_2$, neglecting the small relativistic contribution. Accordingly, when it is separated into, for instance, a pure AFM state with $\delta_L = 0$ and another weaker AFM state of a number fraction $n$ ($\delta_0 \leq n < 1$) with a higher doping $\delta_H = \delta_0/n$ due to the conservation of holes, its bulk free–energy alone is lowered by $(1-n)a_2^2a_0^2\delta_0^2/4bn > 0$. Meanwhile, the FM component also gains a bulk free–energy $nc^2(\delta_H)/4d$ or $(1-n)c_0^2c_1^2\delta_0^2/4dn$ for the separation at high temperatures when $c(\delta_0) > 0$ but $c(\delta_H) < 0$ or at low temperatures when $c(\delta_L) < 0$, respectively. While as intermediate temperatures, whether or not the FM component alone favors a separation depends on the system (via the parameters). These gained energies may possibly overtake those cost for hole aggregation particularly for low doping levels at which the aggregated holes can still be distant enough to reduce their Coulomb repulsion. As a result, a doped system tends to separate into hole–rich regions with the FM order and hole-depleted region with the AFM order. In reality, these electronically separated regions may be broken into microscopic pieces by the long range Coulomb interaction in order to spread the charge uniformly. Furthermore, the FM and AFM orders may possess a certain variable strength depending on the concentration of the doped holes owing to their common FM component. This accounts qualitatively for the coexistence of FM and AFM features and the liquid–like distribution of FM droplets observed in neutron scattering experiments at low doping.

Note that the symmetry relationship between the two phases plays an essential role in the above analysis. The tendency to favor separation is caused by an instability in the inverse compressibility $\sim \partial^2 F/\partial \delta^2 = -(\partial a_2/\partial \delta)^2/2b_2 - a_2(\partial^2 a_2/\partial \delta^2)/2b_2 < 0$ for an AFM state since doped holes always raise its energy by frustrating the AFM order. Similarly, the FM state favors more holes to a certain extent in order to lower kinetic energies through the double exchange. Nevertheless, for a single AFM or FM state, a phase separation is hardly possible because of the Coulomb repulsion for charged particles. In general, this fact is taken into account within the Landau–Ginzburg theory by including quadratic terms to assure stability. In the present case, however, both the hole–depleted AFM phase and the hole–rich FM phase are energetically favored relative to a uniform state. An underlying mechanism that makes this separation feasible is the close symmetry correlation that facilitates the transition from the AFM state to the FM state by the itinerant holes. Thus, as the doped holes hop, they enhance the weak FM component of the AFM state via the double–exchange interactions. Such enhanced FM regions can catch more holes which in turn can further strengthen the PM order. This avalanche effect due to a common FM component could trigger the separation of the holes into hole–depleted and hole–rich regions.

In conclusion, we have shown that both the PM to $A$–type AFM and the PM to FM transition in undoped and moderately doped LaMnO$_3$, respectively, correspond to the transition from a magnetic group $Pnma$ to $Pn'^ma'$, and associate with the irreducible corepresentation $\delta^5$ of the parent phase. This irreducible representation allows an $A$ mode AFM, a $G$ mode AFM and an FM order along the respective $a$, $c$ and $b$ axis in the $Pnma$ setting. Accordingly, the $A$–type AFM phase of undoped LaMnO$_3$ also possesses an FM component, albeit weak, which is identical in direction with the FM phase present at moderate doping. This symmetry relation may lead to a phase separation into hole–depleted AFM regions and hole–rich FM regions in order to take energetic advantage of both phases. Such a competition of the two relevant phases may also work in other systems like La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ where phase separation was also observed although their symmetry may be different. Nevertheless, further investigation is awaited.

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