

Orbital ordering and superexchange in manganite oxides

A. J. Millis*

*Lucent Technologies Bell Laboratories, 700 Mountain Avenue, Murray Hill, New Jersey 07974
and Institute for Theoretical Physics, University of California, Santa Barbara, California 93106*

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The magnetic couplings in insulating LaMnO_3 , CaMnO_3 , and the planar analogs $\text{La}_{n+1}\text{Mn}_n\text{O}_{3n+1}$ are estimated using standard superexchange arguments. The orbital ordering observed in LaMnO_3 is found to lead to the observed magnetic exchange constants if the effective Mn on-site interaction U_{Mn} is larger than the charge transfer energy. Differences between the pseudocubic and the planar materials are accounted for. The effect of doping is discussed. [S0163-1829(97)05410-6]

This paper presents estimates of the magnetic exchange constants of LaMnO_3 and CaMnO_3 , the two end members of the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ series and also of the planar analogs $\text{La}_{n+1}\text{Mn}_n\text{O}_{3n+1}$. These rare-earth manganite perovskites have been studied for more than four decades¹ and interest has recently revived following the observation of ‘‘colossal’’ magnetoresistance in the related material $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$.² The magnetic couplings have an interesting and complicated dependence on crystal structure and doping. CaMnO_3 has a cubic symmetry and is a simple two-sublattice antiferromagnet.¹ LaMnO_3 is substantially distorted from the ideal ABO_3 perovskite structure because of a frozen-in Jahn-Teller distortion (sometimes referred to as ‘‘orbital ordering’’).^{3,4} Magnetically it is a $(0,0,\pi)$ antiferromagnet¹ apparently well described by a nearest-neighbor Heisenberg model with an antiferromagnetic coupling along the c axis and a ferromagnetic in-plane coupling.⁵ The planar compounds such as La_2MnO_4 are apparently quasi-two-dimensional antiferromagnets, at least when undoped or lightly doped. In $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ and related three-dimensional compounds the antiferromagnetic tendency apparently vanishes rapidly upon doping away from $x=0$. By $x\sim 0.2$ only purely ferromagnetic phases are observed¹ and in samples with $x\sim 0.3\text{--}0.4$ only ferromagnetic fluctuations are observed at all T .^{6,7} However, in the planar compounds, correspondingly doped samples exhibit antiferromagnetic fluctuations at high T ,⁸ although the ground state is ferromagnetic as expected from Zener double-exchange.

In this paper it is shown that all of these facts follow naturally from simple superexchange argument, i.e., from a perturbation expansion in the hopping about a well-defined insulating state. The basic result—that orbital ordering can affect the sign of the superexchange interactions—has been known for decades³ and has recently been discussed.^{9,10} However, an explicit estimate demonstrating the interplay of orbital ordering and on-site and charge transfer energies has apparently not before now been presented in the literature.

For a model, take a Mn-O-Mn bond, and focus on the Mn e_g and $O_{2p\sigma}$ orbitals. For evidence that these are the relevant orbitals see Refs. 1 and 11. Each Mn atom also has three t_{2g} ‘‘core’’ electrons which are assumed to form a ‘‘core spin’’ of magnitude $S_c=3/2$. In the main body of this paper the t_{2g} electrons will be assumed to be electrically inert, and

transitions involving them will be neglected. Their effect will be qualitatively discussed in the conclusion.

Any e_g electrons present are assumed to be aligned to the core spins by a Hund coupling J_H which is taken to be very large. Configurations in which e_g electrons are antiparallel to the core spin are excluded. The magnetic exchange constants will be defined in terms of the difference between the ground-state energy with core spins parallel and the state with core spins antiparallel; this will be calculated by a perturbation expansion in the Mn-O hopping t about an idealized ground state. For LaMnO_3 this ground state has one e_g electron on each Mn atom (so the Mn valence is d^4) and two electrons on the oxygen atom; for CaMnO_3 this ground state has no e_g electrons on the Mn atom (so the Mn valence is d^3) and two electrons on the oxygen atom. The leading spin-dependent term is $\mathcal{O}(t^4)$; to obtain this we need all states which can be reached from the ground state by two hops. These are listed in Table I, along with the on-site energies. The states L1–L6 pertain to LaMnO_3 and the states C1–C4 to CaMnO_3 . For CaMnO_3 the on-site energies involve the $d^3\rightarrow d^4L$ charge transfer energy Δ' ; for LaMnO_3 they involve the $\bar{d}^4\rightarrow d^5L$ charge transfer energy Δ and the Mn and O on-site energies $U_{\text{Mn}}=E[d^5d^3]-2E[d^4]$ and $U_{\text{Oxy}}=E[2L]-2E[L]$. Here L denotes a hole on the O ion, and in the definition of U_{Mn} all d electrons on the same site are assumed to be in the same spin state. Note that in the

TABLE I. States, distinguished by Mn and O occupancy, along with energies.

Label	Mn	-O	-Mn	Energy
L1	1	2	1	0
L2	2	1	1	Δ
L3	1	1	2	Δ
L4	2	0	2	$2\Delta + U_{\text{Oxy}}$
L5	2	2	0	U_{Mn}
L6	0	2	2	U_{Mn}
C1	0	2	0	0
C2	1	1	0	Δ'
C3	0	1	1	Δ'
C4	1	0	1	$2\Delta' + U_{\text{Oxy}}$

literature the on-site energies are often defined in a much more complicated fashion, with a variety of interaction parameters. In the simple situation considered here, these many parameters are not needed; the definitions adopted here involve the quantities directly appearing in the calculations below, and have a transparent physical meaning, but the notation is unfortunately nonstandard.

The superexchange for CaMnO_3 may now be calculated. The simplest method is to write and diagonalize the Hamiltonian matrix in the basis listed in Table I and then obtain the leading spin-dependent term. This is of order t^4/Δ'^3 ; calculation of higher-order terms would require expanding the basis. If the two core spins are parallel, the relevant states are $C1$, $C2$, and $C3$ from Table I and the Hamiltonian matrix is

$$H_{\uparrow\uparrow} = \begin{bmatrix} 0 & t & t \\ t & \Delta' & 0 \\ t & 0 & \Delta' \end{bmatrix}. \quad (1)$$

If the two core spins are antiparallel, all of $C1$ - $C4$ are relevant and the Hamiltonian matrix is

$$H_{\uparrow\downarrow} = \begin{bmatrix} 0 & t & t & 0 \\ t & \Delta' & 0 & t \\ t & 0 & \Delta' & t \\ 0 & t & t & 2\Delta' + U_{\text{oxy}} \end{bmatrix}. \quad (2)$$

The difference of leading eigenvalues is

$$E_{\uparrow\uparrow} - E_{\uparrow\downarrow} = \frac{6t^4}{\Delta'^2(\Delta' + U_{\text{oxy}}/2)}. \quad (3)$$

Thus the coupling is antiferromagnetic, as observed. Interpreting this as the classical Heisenberg energy $2J(S^z)^2$ with $S=3/2$ gives

$$J_{\text{CaMnO}_3} = \frac{3t^4}{4\Delta'^2(\Delta' + U_{\text{oxy}}/2)}. \quad (4)$$

Use of the cubic-lattice Heisenberg model result¹² $T_N = 2.9(S+1)SJ$ and $S=3/2$, along with the observed $T_N \approx 110$ K,¹ yields $J_{\text{CaMnO}_3} \approx 10$ K. Note that although this J couples the t_{2g} electrons on adjacent Mn sites, the t_{2g} electrons are not directly involved in the superexchange process.

Now turn to LaMnO_3 . The situation is more complicated because the starting Mn valence is d^4 , and so one of the two e_g orbitals is occupied on each site. It is convenient to take the z axis to be along the Mn-O-Mn bond and to choose the e_g orbitals to be $|3z^2 - r^2\rangle$ and $|x^2 - y^2\rangle$. It will be assumed that only the $|3z^2 - r^2\rangle$ orbital hybridizes with the O_{2p} . In LaMnO_3 there is a long-range Jahn-Teller order which selects a preferred d state, and the d splitting induced by the Jahn-Teller gap contributes to the energies Δ and U_{Mn} . The preferred d state on a given site i , $|\text{occ}, i\rangle$ may be written

$$|\text{occ}, i\rangle = \cos\theta_i |3z^2 - r^2\rangle + \sin\theta_i |x^2 - y^2\rangle. \quad (5)$$

The empty state is then

$$|\text{unocc}, i\rangle = \sin\theta_i |3z^2 - r^2\rangle - \cos\theta_i |x^2 - y^2\rangle \quad (6)$$

(phase factors do not enter the superexchange calculation, and so have been omitted).

Hopping between an occupied level and an oxygen involves the factor $\cos\theta_i$; for hopping between an unoccupied state and an oxygen the factor is $\sin\theta_i$. Denote the angle describing the left-hand Mn atom as θ_1 and the right-hand Mn atom as θ_2 . Then for parallel spins the relevant states are $L1$, $L2$, $L3$, $L5$, and $L6$ and the Hamiltonian matrix is

$$H_{\uparrow\uparrow} = \begin{bmatrix} 0 & t\sin\theta_1 & t\sin\theta_2 & 0 & 0 \\ t\sin\theta_1 & \Delta & 0 & t\cos\theta_2 & 0 \\ t\sin\theta_2 & 0 & \Delta & 0 & t\cos\theta_1 \\ 0 & t\cos\theta_2 & 0 & U_{\text{Mn}} & 0 \\ 0 & 0 & t\cos\theta_1 & 0 & U_{\text{Mn}} \end{bmatrix}. \quad (7)$$

For antiparallel spins the relevant states are $L1$, $L2$, $L3$, $L4$, and

$$H_{\uparrow\downarrow} = \begin{bmatrix} 0 & t\sin\theta_1 & t\sin\theta_2 & 0 \\ t\sin\theta_1 & \Delta & 0 & t\sin\theta_2 \\ t\sin\theta_2 & 0 & \Delta & t\sin\theta_1 \\ 0 & t\sin\theta_2 & t\sin\theta_1 & 2\Delta + U_{\text{oxy}} \end{bmatrix}. \quad (8)$$

A general solution, valid to order t^4 , may be obtained analytically. One finds

$$E_{\uparrow\uparrow} - E_{\uparrow\downarrow} = \frac{2t^4}{\Delta^2(\Delta + U_{\text{oxy}}/2)} \sin^2\theta_1 \sin^2\theta_2 - \frac{t^4}{U_{\text{Mn}}\Delta^2} (\sin^2\theta_1 \cos^2\theta_2 + \cos^2\theta_1 \sin^2\theta_2). \quad (9)$$

From this equation one sees explicitly that there is a strong dependence both on orbital ordering and the ratio Δ/U_{Mn} . In the ‘‘Hubbard limit’’ $\Delta/U_{\text{Mn}} \rightarrow \infty$ at fixed t^2/Δ , the coupling is always ferromagnetic, as found by other workers.¹⁰ In the ‘‘charge transfer’’ limit $\Delta/U_{\text{Mn}} \rightarrow 0$ the coupling is generally antiferromagnetic, but may change sign if one of θ_1, θ_2 is near 0 or π and the other is not near $\pi/2$. Optical data¹³ suggest that the charge transfer limit is the most appropriate.

The angles θ_1 and θ_2 appropriate to LaMnO_3 have been estimated.¹⁴ Unfortunately, the angles θ_1 given in Table I of Ref. 14 pertain to the *unoccupied* orbitals (although they are stated to pertain to the occupied orbitals). To conform to the conventions of this paper the θ_1 must be replaced by $\bar{\theta}_1 = \theta_1 + \pi/2$. The angles listed in Ref. 14 are calculated in coordinates tied to the crystal c axis. The values $\bar{\theta}_2 = -\bar{\theta}_1 + \pi$ and $2\pi/3 < \bar{\theta}_1 < 3\pi/4$ were found from an analysis of the structure. Using $E_{\uparrow\uparrow} - E_{\uparrow\downarrow} = 2JS^2$ and $S=2$ gives

$$\frac{t^4}{16\Delta^3} \left(1 - \frac{\Delta + U_{\text{oxy}}/2}{U_{\text{Mn}}} \right) < J_{\text{caxis}}^{\text{LaMnO}_3} < \frac{9t^4}{64\Delta^3} \left(1 - \frac{\Delta + U_{\text{oxy}}/2}{U_{\text{Mn}}} \right). \quad (10)$$

Thus, if Δ is sufficiently small (basically $\Delta < U_{\text{Mn}}$), the sign is antiferromagnetic; the magnitude depends sensitively on the angle and is smallest for $\theta_1 = 3\pi/4$ and largest for $\theta_1 = 2\pi/3$. The latter value corresponds to pure ‘‘ $d_{3x^2-r^2}/d_{3y^2-r^2}$ ’’ order. As discussed in Refs. 3 and 14 the actually occurring order is distorted away from this to some degree.

Now consider the in-plane bond. To transform to the coordinates appropriate to an in-plane bond one must rotate θ_1 and θ_2 by $-\pi/3$; the result is $\bar{\theta}_2^{\text{in plane}} = -\bar{\theta}_1^{\text{in plane}} - \pi/3$ and $\pi/3 < \bar{\theta}_1^{\text{in plane}} < 5\pi/12$. One finds

$$\frac{-3t^4}{32\Delta^2 U_{\text{Mn}}} < J_{\text{in plane}}^{\text{LaMnO}_3} < -7t^4/64\Delta^2 U_{\text{Mn}} \left(1 - \frac{U_{\text{Mn}}}{7(\Delta + U_{\text{oxy}}/2)} \right). \quad (11)$$

Here the left-hand inequality (most ferromagnetic coupling) corresponds to $\theta_1 = 2\pi/3$ and the right-hand inequality to $\theta_1 = 3\pi/4$.

The exchange couplings in LaMnO_3 were recently determined from a neutron scattering measurement of the spin-wave spectrum;⁵ a ferromagnetic $J_{\text{in plane}}$ and antiferromagnetic J_c were found, with $-J_c/J_{\text{in plane}} \approx 0.7$ and $J_{\text{in plane}} \approx 10$ K. If the material is assumed to be in the charge transfer ($\Delta < U_{\text{Mn}}$) limit, then this experimental finding can be explained if θ_1 is not too far from $3\pi/4$ (i.e., the structure is substantially distorted from the $d_{3x^2-r^2}/d_{3y^2-r^2}$ one) and $U_{\text{Mn}}/(\Delta + U_{\text{oxy}}/2) \approx 2$. The conventional wisdom is $U_{\text{Mn}} \sim 6$ eV and $\Delta \sim 1-2$ eV; it is not clear what a reasonable value of U_{oxy} is. If $\Delta = 1.5$ eV is assumed then the observed J implies $t \approx 0.6$ eV so the effective Mn-Mn hopping $t_{\text{Mn-Mn}} \sim t^2/\Delta \approx 0.2$ eV, which is a very reasonable value.

Within the charge transfer approach presented here the evolution of the magnetism with doping may be understood. The antiferromagnetic nature of the c axis exchange depends crucially upon orbital ordering which is suppressed rapidly with doping.^{15,14} Also coupling between a d^4 and a d^3 site is ferromagnetic for the usual double-exchange reasons. Thus with doping the antiferromagnetism weakens rapidly and the ferromagnetism strengthens.

One may also extend the calculations presented here to the planar manganites such as La_2MnO_4 and $\text{La}_3\text{Mn}_2\text{O}_7$. In these materials the crystal structure is such that the Jahn-Teller splitting is locked into the value $\bar{\theta} = 0$ on each site (in c axis coordinates). The in-plane exchange is then given by $\bar{\theta}_1 = \pi/3, \bar{\theta}_2 = 2\pi/3$, i.e., by

$$J^{\text{planar}} = \frac{9t^4}{64\Delta^2(\Delta + U_{\text{oxy}}/2)} \left(1 - \frac{\Delta + U_{\text{oxy}}/2}{3U_{\text{Mn}}} \right). \quad (12)$$

In other words, in the charge transfer limit the in-plane superexchange is antiferromagnetic and of large magnitude (if the estimates presented above for LaMnO_3 are applicable to the planar materials, $J^{\text{planar}}/J_{c\text{axis}}^{\text{LaMnO}_3} \approx 4$). Further, if this Jahn-Teller order is not changed by doping, the antiferromagnetic nature of the interaction should survive upon doping, although of course a ferromagnetic double-exchange contribution from mobile carriers will be added to it. These conclusions appear to be at least qualitatively consistent with present data.⁸

The interplay between superexchange and orbital ordering in LaMnO_3 has recently been studied by other workers. Solov'yev, Hamada, and Terakura⁹ have used a band-theory-based formalism within which the contribution to the exchange from the e_g orbitals is found to be positive for all bonds (the distortion simply changed the magnitude of J). An additional negative contribution arising from t_{2g} orbitals was also calculated, and found in some circumstances to change the sign of J_c as observed. The results of Ref. 9 seem consistent with the results presented here because the formalism of Ref. 9 involves a weak-interaction approximation; U_{Mn} is therefore small, while Δ , which has a large contribution from band effects, is not. The calculation is thus effectively in the ‘‘Hubbard’’ limit.

Ishihara *et al.* have performed superexchange calculations based on the Hubbard limit,¹⁰ finding that all e_g processes are ferromagnetic (as found here also, in the Hubbard limit). These authors invoked a phenomenological t_{2g} exchange to explain the sign change.

Within the present approach the t_{2g} processes may be estimated. The Mn t_{2g} electrons hybridize mainly with the $O_{p\pi}$ orbitals, which do not hybridize with the e_g ; this therefore leads to an independent channel for superexchange. The unoccupied t_{2g} states lie farther from the Fermi energy than the e_g states, and the hybridization to the oxygen is weaker, as may be seen from the roughly factor-of-2 ratio¹⁶⁻¹⁸ of the bandtheory e_g and t_{2g} band-widths. In addition, the Coulomb repulsion may be stronger.¹⁹ These processes, however, gain a factor of 2 from the twofold degeneracy of the $O_{p\pi}$ orbitals. The basic process involves occupying an unoccupied t_{2g} orbital, and so the result is an antiferromagnetic exchange as found for J^{CaMnO_3} . The net result of these considerations is to suggest that the t_{2g} processes make up at most 1/3–1/2 of the observed J^{CaMnO_3} and have a weak doping dependence. Numerically, I estimate $J_{t_{2g}} \leq 5$ K; thus it does not have a crucial effect on the considerations presented above, but does increase somewhat the range of structural angles which can explain the data. Note that this estimate is smaller than the value $J_{t_{2g}} \approx 15$ K found in Ref. 9. Presumably the difference is that the formalism of Ref. 9 assumes weak interactions while here strong interactions are assumed. The estimate is also rather smaller than the value estimated from the T_c of CaMnO_3 in Ref. 10, because those authors assumed that *only* the t_{2g} processes contribute to J^{CaMnO_3} ; they neglected the e_g processes which were argued above to be dominant.

To summarize, superexchange estimates of magnetic couplings in insulating manganites have been presented. The combination of the strong Hund's coupling, the charge transfer nature of the insulating phase of LaMnO_3 , and the orbital ordering seems to account for the observed sign, magnitude and doping dependences. The calculations presented here are based on a simple insulating limit; the small (~ 1 eV) charge transfer gap observed in LaMnO_3 (Ref. 13) renders the quantitative validity of the results questionable, but the qualitative trends including the extreme sensitivity of the exchange constants to the orbital ordering and the relative sizes of the e_g and t_{2g} may be more generally valid.

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- *Present address: Department of Physics and Astronomy, The Johns Hopkins University, 3400 North Charles Street, Baltimore, Maryland 21218.
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