Joint superexchange–Jahn-Teller mechanism for A-type antiferromagnetism in LaMnO$_3$

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We propose a mechanism for A-type antiferromagnetism in orthorhombic LaMnO$_3$, compatible with the large Jahn-Teller splitting inferred from structural data. Orbital ordering resulting from Jahn-Teller distortions effectively leads to A-type ordering (antiferromagnetic in the $c$ axis and ferromagnetic in the $ab$ plane) provided the in-plane distortion $Q_2$ is large enough, a condition generally fulfilled in existing data.

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Stoichiometric LaMnO$_3$ (LMO) is known to be an A-type antiferromagnetic insulator (AFM), where ferromagnetically ordered MnO$_2$ planes (in the $xy$ direction) have staggered magnetization along the $z$ axis. Upon increasing the temperature a paramagnetic insulating phase (PMI) is reached. On the other hand sufficient hole doping (e.g. by substituting La with Sr or Ca) gives rise via the so-called double-exchange hopping mechanism to a low-temperature ferromagnetic metallic phase (FMM) turning into a PMI phase at higher temperature. Not only magnetism determines the main physical properties, in fact both theoretical and experimental evidences emphasize the relevance of electron-lattice coupling. Charge and orbital ordering also occur, further showing the competition between various physical mechanisms. Notice that the crucial role of spin and lattice coupling was repeatedly emphasized to account for the properties of the FMM phase and the FMM-PMI transition at finite doping, as well as charge-ordering phenomena. However, this liaison regarded the double-exchange mechanism for charge transport, being dynamically dressed by lattice degrees of freedom. No emphasis was put on the role of static cooperative Jahn-Teller (JT) deformations in stabilizing specific magnetic structures in the AFMI phase.

Here we investigate an approach to the stoichiometric phase of LMO showing that the layered antiferromagnetic structure may result from the interplay between superexchange and JT couplings. Our analysis is alternative to the more qualitative one based on the semicovariant exchange mechanism and is complementary to the superexchange mechanism investigated by Kugel and Khomskii (KK) for perovskites with JT ions. This latter analysis focused on the interplay between magnetic and orbital ordering within the two $e_g$ orbital manifold, assumed degenerate. In particular, basic ingredients were a strong local electron-electron repulsion $U$, the Hund coupling $J_H$ between electrons on the two $e_g$ orbitals, and the orbital mixing (described by a mixing angle $\theta$) due to JT distortion. In the approach of Ref. 8, only $e_g$ (spin and orbital) degrees of freedom were considered, and the spin and orbital order were self-consistently determined to lowest order in $J_H/U$. The $e_g$ level degeneracy was lifted by superexchange but the JT splitting resulting from the lattice distortions induced by orbital ordering was not explicitly considered. Only a correction due to a small local JT anharmonicity was introduced. This point of view, considering magnetic exchange to be the main cause of orbital mixing/ordering, but neglecting the orbital splitting resulting from JT effect, might be questioned in LMO where strong JT distortions arise. Moreover, magnetic exchange interactions are somewhat modest, e.g. $J_{AF} \approx 0.58$ meV and $J_F \approx 0.83$ meV $> J_{AF}$ from inelastic neutron scattering experiments, while the KK theory results in $J_F \approx (J_H/U)J_{AF}$, that is $J_F$ much smaller than $J_{AF}$. Moreover, as pointed out by KK, the observed orthorhombic distortion with $c < a$ is not expected from considering solely orbital ordering. Therefore, it is not obvious, considering the actual distortion, that the magnetic A-phase is still the most stable.

According to the experimental evidences for the relevance of the $t_{2g}$ (spin) degrees of freedom, e.g. in the double-exchange hopping processes, and for a strong JT coupling, we propose to reconsider the problem. We take properly into account the Hund coupling between $e_g$ and $t_{2g}$ electrons, and assume, contrarily to KK, that the JT splitting is much larger than the exchange energy. This makes the JT effect the driving mechanism for orbital ordering, which in turn controls the magnetic interactions. Hereafter we assume some staggered orbital order (i.e. we fix $\theta$ on the two sublattices) as determined by strong JT distortions, without attempting to calculate them, since they can be extracted from crystallographic data. Given the orbital order and the related (relatively large) $e_g$ orbital splitting $\epsilon$, we calculate at any order in $\epsilon$ and $J_H/U$ the superexchange interactions. Finally, we determine the parameter ranges which are compatible with the observed A-type AF phase.

For the sake of simplicity we disregard the oxygen sites in the perovskite structure, thus focusing on a single-site model. On each site two Manganese orbitals, the $d_{x^2-y^2}$ $(x)$ and the $d_{z^2-r^2}$ $(z)$, are available. The real lattice structure is effectively taken into account via the sign and the magnitude of the intersite hopping along the
$x - y - z$ directions. Specifically, we notice that, for a standard choice of phases, the hopping between the $d_x$ and the $d_z$ orbitals on Mn are given by

$$t_{xz} = 3t; \quad t_{xz} = -\sqrt{3}t$$
along $\hat{x}$

$$t_{zz} = -t; \quad t_{zz} = \sqrt{3}t,$$
along $\hat{y}$

$$t'_{xz} = -4t; \quad t'_{zz} = t''_{zz} = 0. \quad (1)$$

Throughout this paper the apex indicates hoppings in the $z$ direction. The (static) JT distortions mix the $x$ and $z$ orbitals into a (lower) and b (upper) orbitals with $e_g$ symmetry split by an energy $\epsilon = 2g\sqrt{Q_1^2 + Q_2^2}$ where $g$ is an electron-lattice coupling constant. Specifically, using the same notations of Ref. 3 the uniform distortion $Q_1$ (corresponding to a uniform variation of the lattice parameter along the $z$ direction) couples to the $x - z$ density difference $n_x - n_z$. In systems like LMO, where the lattice spacing in the $z$ direction is shorter than the (average) spacing in the $xy$ plane, the $d_z$ orbitals overlap more and are pushed at higher energy by the Coulomb interaction. Then $Q_1$ is negative. As pointed out by KK, this disfavors hopping in the $z$-direction, thus making the JT effect compete with the A-type superexchange which alone would imply the opposite distortion. The reverse is true in systems like KCuF$_3$, where the lattice parameter along $z$ is larger than in the $xy$ plane and $Q_1$ is positive.

On the other hand, the distortion $Q_2$ (opposite on the two sublattices of the $xy$-planes) corresponds to an alternate contraction and dilation of the Mn-O bonds on the $xy$ plane and mixes the $x$ and $z$ components of the $a, b$ orbitals

$$|a\rangle = \cos(\theta/2)|x\rangle \pm \sin(\theta/2)|z\rangle$$

$$|b\rangle = \sin(\theta/2)|x\rangle \mp \cos(\theta/2)|z\rangle \quad (2)$$

where $\tan(\theta) = Q_2/Q_1$ and the upper (lower) sign is for sites on sublattice 1 (2) of the $xy$-planes. Accordingly the hoppings between the $a$ and $b$ orbitals of neighbouring sites can straightforwardly be obtained via Eqs. (2).

$$t_{aa} = -t \left(1 + 2\cos\theta\right);$$

$$t_{ab} = -t \left(\pm \sqrt{3} + 2\sin\theta\right); \quad t_{ba} = -t \left(\mp \sqrt{3} + 2\sin\theta\right); \quad (3)$$

$$t'_{aa} = 2t \left(1 - \cos\theta\right); \quad t'_{ab} = t'_{ba} = -2t \sin\theta \quad (4)$$

the upper (lower) sign is for planar hopping in the $x$ ($y$) direction.

As customarily done, we assume that the Hund coupling between $\sigma = 1/2 e_g$ electrons and the $S = 3/2$ spin of the $t_{2g}$ electrons is so large that the initial and final states always have maximal total spin $S_T = 2$. Moreover, and most importantly, we also consider a large local repulsion ($\sim U$) between electrons on Mn sites forbidding to two electrons to reside on the two $e_g$ levels of the same site. Then we work on a reduced Hilbert space with only Mn$^{3+}$ initial and final states.

We then carry out a perturbative calculation of both FM and AFM magnetic couplings between sites 1 and 2 by considering second order hopping processes from and to the ground state configuration with one electron per Mn site occupying the lower $a$ orbital. We thus neglect the exchange-induced mixing of $e_g$ orbitals, considered by KK. Notice that this last assumption relies on the JT splitting $\epsilon$ being substantially larger than both the temperature and the superexchange scale $\sim t^2/U$. Due to the condition $S_T = 2$, each site $i = 1, 2$ is five times degenerate, $|2, m\rangle_i$ with $m = -2, -1, ..., 2$. The first step consists in forming two-site states with given total spin $J = 0, ..., 4$ from the 25 basis states $|2, m\rangle_1 \otimes |2, m\rangle_2$. The suitable Clebsch-Gordan coefficient are easily obtained. Within each $J$ subspace (the hopping processes conserve the total spin), the hopping perturbation

$$H_t = - \sum_{\sigma_\alpha, \sigma'_\alpha = 0, \pm} t_{aa'} \left(c_{\sigma_\alpha 2\sigma_\alpha}^\dagger c_{2\sigma_\alpha 1\sigma_\alpha} + \text{h.c.}\right)$$

is applied twice to obtain the $\langle J, M | H_t^2 | J, M \rangle$ matrix elements. The double-hopping processes are of two types: $aa$ and $ab$ depending on whether the initial $a$ electron hops on the neighboring $a$ or $b$ orbitals. Accordingly there are two superexchange channels, leading to couplings constants $J_{aa}$ and $J_{ab}$. The easiest to be calculated is $J_{aa}$ since the Pauli principle forces the two initial $a$ electrons to have opposite spins. As a consequence only one intermediate virtual state per $J$ channel is allowed, with one empty and one doubly occupied $a$ orbital. Both the empty and the doubly occupied orbitals cost an energy $3J'_H/4$, where $J'_H$ is the Hund coupling between $e_g$ and $t_{2g}$ orbitals (the Hund energy is set to zero in the Mn$^{3+}$ ground state configuration). The doubly occupied $a$ orbital has an additional energy cost $U$. All the intermediate states have then an energy $E_V = U + (3/2)J'_H$ above the ground state energy $E_0 = 0$. As it is standard, the perturbative energy gain can be compared with the energies of $\langle J, M \rangle$ states as given by the effective Heisenberg model for the $aa$ channel

$$H_{aa} = J_{aa} (S_1 \cdot S_2 + C)$$

with $C$ being a constant energy shift to be determined. The direct comparison provides, besides $C = -4$,

$$J_{aa} = \frac{1}{4} \frac{t_{aa}^2}{U + (3/2)J'_H} \quad (6)$$

This is an effective AFM coupling between electrons on the $xy$-plane. A similar expression is obtained for the interplane coupling (i.e., in the $z$ direction) $J'_{aa'}$, provided $t_{aa}$ is replaced by $t'_{aa}$ in Eq. (6).

The calculation for $J_{ab}$ is slightly more complicated, since the hopping electron can now give rise on the doubly occupied site to both a $S_T = 5/2$ or a $S_T = 3/2$
state, thus increasing the number of virtual states. However, the same procedure illustrated above yields

\[
J_{ab} = \frac{-t_{ab}^2}{40} \left( \frac{8}{U' + \epsilon - J_H/2} - \frac{3}{U' + \epsilon - J_H/2 + 5J_H'/2} - \frac{5}{U' + \epsilon + J_H/2 + 3J_H'/2} \right)
\]  

(7)

where \( U' \) is the local Coulomb repulsion between electrons on the \( a \) and \( b \) orbitals and

\[
t_{ab}^2 = \frac{(t_{ab}^2 + t_{ba}^2)}{2} = t^2 (3 + 4 \sin^2(\theta)).
\]  

(8)

Again the analogous coupling in the \( z \) direction can be obtained by replacing \( t_{ab} \) and \( t_{ba} \) with the corresponding primed quantities of Eq. (6). It can easily be seen that this coupling is ferromagnetic and vanishes when \( J_H \) and \( J_H' \) are both zero. Notice also that, since \( J_{ab} \) arises from virtual hopping \( i \rightarrow j \rightarrow i \) and \( j \rightarrow i \rightarrow j \) and since the \( a \) and \( b \) orbital combinations are reversed on neighboring sites, the \( t_{ab}^2 \) combination appears, which is the same in the \( x \) and \( y \) directions [cf. instead (4)]. Thus for each crystalline direction one can write the effective Heisenberg couplings \( J = J_{aa} + J_{ab} \) and \( J' = J'_{aa} + J'_{ab} \) in the \( xy \) planes and \( z \) direction respectively. Then the question arises concerning the parameter ranges such that the observed A-type AF is realized. In this case the coupling must be dominantly ferromagnetic in the \( xy \) planes and dominantly AF in the \( z \) direction. To this purpose we rewrite the \( J \)'s in the following more compact way

\[
J_{aa} = t_{aa}^2/D_{aa}, \quad J_{ab} = \frac{-t_{ab}^2}{2D_{ab}}
\]  

(9)

The condition that the \( xy \) planes are ferromagnetically coupled is written as \( |J_{ab}| > |J_{aa}| \), i.e.

\[
\alpha^2 \equiv \frac{t_{ab}^2}{t_{aa}^2} > D.
\]  

(10)

where \( D = \frac{D_{ab}}{D_{aa}} \). At the same time, the condition for AF coupling in the \( z \) direction is expressed by \( |J'_{ab}| < |J'_{aa}| \), that is

\[
\alpha'^2 \equiv \frac{t'_{ab}^2}{t'_{aa}^2} < D.
\]  

(11)

Now, both \( \alpha \) and \( \alpha' \) (i.e. \( t_{aa}, t_{ab}, t'_{aa}, \) and \( t'_{ab} \)) are functions of \( \theta \), or of the JT ratio \( Q_2/Q_1 \). Plotting \( \alpha^2 \) and \( \alpha'^2 \) as a function of \( Q_2/Q_1 \) for \( Q_1 < 0 \) (the relevant case for LMO), one obtains the curves in Fig. 1. Since from the inequalities (10) and (11), one can deduce the condition

\[
\alpha^2 > D > \alpha'^2,
\]  

(12)

the value of \( D \) should be below the solid curve and above the dashed ones. The assumed orbital order becomes compatible with A-AFMI order for \( Q_2/Q_1 \gtrsim 2.6 \), where the relation (12) can be satisfied. Notice instead that for \( Q_1 > 0 \) the curve \( \alpha'^2 \) is always smaller than \( \alpha^2 \), so that no restriction on the \( Q_2/Q_1 \) ratio is needed to fulfill the condition (12). This is in agreement with the cooperation between superexchange and JT effect, found in this case, see for example the case of KCuF\(_3\).
range \[^{[12]}\]. To this purpose we consider typical values of \(U = 10\) eV, \(U' = U - 2J_H = 6 - 10\) eV, and \(\epsilon = 0.1 - 0.5\) eV, and we obtain the ratio \(D\) as a function of \(J_H/U\). For simplicity the ratio \(J_H/J_H'\) is taken equal to 1. Then, from Fig. 1, we consider typical ranges for \(D\) between, e.g., \(\alpha^2 \approx 1.4\) and \(\alpha^2 \approx 4\), roughly corresponding to \(Q_2/|Q_1| \approx 6.69\), and \(\alpha^2 \approx 2\) and \(\alpha^2 \approx 2.4\), roughly corresponding to \(Q_2/|Q_1| \approx 2.84\). Then we look for what range of \(J_H/U\) the conditions \(4 > D > 1.4\) or \(2.4 > D > 2\) are realized. In the first case the quite reasonable range \(0.1 \lesssim J_H/U \lesssim 0.35\) is found, while in the second case \(0.1 \lesssim J_H/U \lesssim 0.15\). The observed values \[^{[10]}\] \(J = 0.83\) meV (ferro) and \(J' = 0.58\) meV (antiferro) are obtained with \(J_H = J_H' = 1.25\) eV and \(t = 0.34\) eV in the case of \(Q_2/|Q_1| = 2.84\). This value of \(t\) is fairly large, but it can be substantially decreased by taking larger values of \(Q_2/|Q_1|\). Notice that, contrary to the calculations of KK, the planar ferromagnetic coupling can easily be larger than the \(z\)-axis antiferromagnetic one. This comes from the ratio \(t_{2g}/t'_{uu} \approx 2\) in \[^{[13]}\] where, due to the orbital order stabilized by the JT distortion, hopping in the plane directions is enhanced with respect to the \(z\)-axis. In conclusion, we have illustrated the possibility of an alternative mechanism for the layered antiferromagnetism of the stoichiometric LMO compound. In particular, we showed that the superexchange mechanism, together with strong JT planar distortions, can be responsible for the specific A-type magnetic structure. Like in the analysis of Ref. \[^{[3]}\], the sinergetic effect of both magnetic superexchange and orbital ordering is a crucial ingredient. However, contrary to the assumption of Ref. \[^{[3]}\], in the present scenario, we assumed a given orbital ordering strongly lifting the degeneracy of the \(e_g\) orbitals \((\epsilon \gg J_{ab}, J_{aa})\). A relevant role here is also played by the \(t_{2g}\) spin degrees of freedom, as seen from the expressions \[^{[8]}\] and \[^{[13]}\], which depend rather strongly on \(J_H'\). Despite the basic differences between our scheme and the proposal of Ref. \[^{[3]}\], we find some similarities in the overall result. Specifically we find that for systems with positive \(Q_1\), like, e.g., KCuF\(_3\), no restriction is needed on the \(Q_2/|Q_1|\) ratio to make the orbital ordering compatible with A-AFMI magnetic structure. This is not the case for negative \(Q_1\), where the above discussed conditions have to be imposed on \(Q_1/|Q_2|\) and, consequently on the values of \(J_H/U\). Similar values of the \(J_H/U\) were found in \[^{[3]}\]. Within the present model, to be more realistic one should also take into account the existence of tilt distortions and consider the effects of non vanishing transfer integrals \(t_{xx}'\) and \(t_{xz}'\). In fact these hopping constants are strictly zero only for lattices without tilting of the MnO\(_6\) octaedra around axes on the \(xy\) plane. We have found that positive \(t_{xy}'\) and negative \(t_{xz}'\) favour A-type ordering. Another contribution to the problem is the antiferromagnetic exchange originating from \(t_{2g}\) electrons. Finally, a full calculation involving all superexchange processes should be feasible. We stress again that the mechanism proposed here is based on the tight interplay of lattice and electronic degrees of freedom existing even in the undoped LMO system, and that it is aimed to correlate the magnetic ordering with the JT distortions. Justifying the values of \(Q_1\) and \(Q_2\) from microscopic grounds is beyond the scope of the present paper. Some mixing between lattice and spin dynamics and isotopic or pressure dependence of the spin-wave velocity are expected to be rather natural consequences of the proposed scenario.

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