

ORIGIN OF THE ORBITAL ORDERING IN LaMnO_3 *

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We use the temperature of the structural phase transition to determine the Jahn-Teller (JT) coupling constant in the model derived for LaMnO_3 which includes both the superexchange between $S = 2$ spins and the JT effect. We also investigate the dependence of the exchange constants on the value of the on-site Coulomb element U , and on the orbital ordering.

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For degenerate e_g orbitals the superexchange (SE) interactions involve both spin and orbital degrees of freedom. Therefore, these interactions alone could stabilize the orbital ordering, either in cuprates [1], or in manganites [2]. However, large lattice distortions observed in LaMnO_3 suggest that the Jahn-Teller (JT) effect also plays an important role in inducing the staggered orbital ordering. In particular, if the SE interactions are ignored, the observed temperature of the structural transition $T_s = 780$ K leads to a large JT coupling constant [3]. We show that the orbital interactions which originate either from the SE or from the JT effect support each other, so one can deduce the JT coupling constant only by analyzing all the terms responsible for the orbital ordering [4].

We consider a model Hamiltonian for LaMnO_3 [2]:

$$H = H_e + H_t + H_{\text{JT}}, \quad (1)$$

which includes the SE due to e_g (H_e) and t_{2g} (H_t) electrons, and the JT term (H_{JT}). The term H_e originates from the virtual hopping to four $t_{2g}^3 e_g^2$ excited states: one high-spin 6A_1 state and three low-spin 4A_1 , 4E , 4A_2 states, with the excitation energies: $\varepsilon({}^6A_1) = U - 3J_{\text{H}}$, $\varepsilon({}^4A_1) = U + 2J_{\text{H}}$, $\varepsilon({}^4E) = U + \frac{8}{3}J_{\text{H}}$,

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$\varepsilon(4A_2) = U + \frac{16}{3}J_H$ [2]. The Coulomb and exchange elements are: $U \simeq 5.9$ eV and $J_H = 0.69$ eV [5]. One finds

$$H_e = \frac{1}{16} \sum_{\langle ij \rangle} \left\{ -\frac{8}{5} \frac{t^2}{\varepsilon(6A_1)} (\vec{S}_i \cdot \vec{S}_j + 6) \mathcal{P}_{\langle ij \rangle}^{\zeta\xi} + (\vec{S}_i \cdot \vec{S}_j - 4) \times \left[\left(\frac{t^2}{\varepsilon(4E)} + \frac{3}{5} \frac{t^2}{\varepsilon(4A_1)} \right) \mathcal{P}_{\langle ij \rangle}^{\zeta\xi} + \left(\frac{t^2}{\varepsilon(4E)} + \frac{t^2}{\varepsilon(4A_2)} \right) \mathcal{P}_{\langle ij \rangle}^{\zeta\zeta} \right] \right\}, \quad (2)$$

for the SE between $S = 2$ spins, where t is the hopping element between two directional $3z^2 - r^2$ orbitals along the c -axis (here we take $t = 0.48$ eV which is consistent with the experimental exchange constants [6]), and the operators $\mathcal{P}_{\langle ij \rangle}^{\alpha\beta} = P_i^\alpha P_j^\beta + P_i^\beta P_j^\alpha$ consist of the orbital projections at both sites, P_i^α and P_j^β [2]. Virtual hopping of t_{2g} electrons gives the second SE contribution, $H_t = \frac{1}{4}J_t \sum_{\langle ij \rangle} (\vec{S}_i \cdot \vec{S}_j - 4)$, with an average exchange constant $J_t \simeq 2.9$ meV. The JT term induced by the oxygen distortions [3]:

$$H_{JT} = \kappa \sum_{\langle ij \rangle} \left(\mathcal{P}_{\langle ij \rangle}^{\zeta\zeta} - 2\mathcal{P}_{\langle ij \rangle}^{\zeta\xi} + \mathcal{P}_{\langle ij \rangle}^{\xi\xi} \right), \quad (3)$$

favors alternating ordering of orbitals parallel ($|\zeta\rangle$) and perpendicular ($|\xi\rangle$) to the bond direction, such as $|z\rangle = 3z^2 - r^2$ and $|x\rangle = x^2 - y^2$ along c -axis.

We assume the A -AF spin structure [spins parallel in (a, b) plane and staggered along c axis], and C -type orbital ordering, with the orbital state

$$|\theta\rangle = \cos \frac{\theta}{2} |z\rangle + \sin \frac{\theta}{2} |x\rangle, \quad (4)$$

alternating ($|\pm\theta\rangle$) in (a, b) plane and repeating itself along c direction. By averaging the orbital operators one can derive an effective Heisenberg model with intraplanar (J_{ab}) and interplanar (J_c) exchange constants, which give the Néel temperature T_N in the mean-field approximation (MFA).

The exchange constants J_{ab} and J_c depend strongly on the orbital ordering (4), and the A -AF phase is stable for $\theta/\pi < 0.65$, while G -AF order occurs for $\theta/\pi > 0.65$ [Fig. 1(a)]. The values obtained for the optimal orbital state $|\theta_{\text{opt}}|$ which gives the lowest energy at $T = 0$, agree well with the experimental data [6] (Table I). From the dependence of J_{ab} and J_c on the value of U we conclude that only values of $U \leq 6$ eV are able to explain the experimental result $|J_{ab}| > J_c$ [Fig. 1(b)]. Moreover, J_{ab} and J_c obtained for $\theta = 2\pi/3$, often assumed for LaMnO_3 , are never close to experiment.

Now we turn to the structural transition. Using realistic parameters one finds that $T_s \simeq 380$ K, calculated in the MFA with only the SE terms considered, is much lower than observed (the MFA value was reduced by a factor

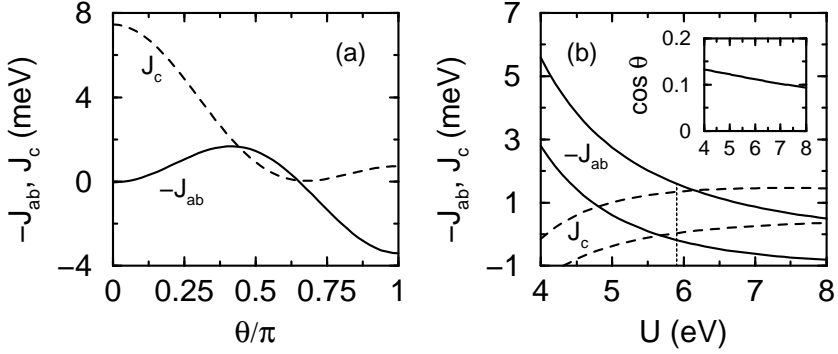


Fig. 1. Exchange constants J_{ab} (solid lines) and J_c (dashed lines) as functions of: (a) orbital angle θ/π for $U = 5.9$ eV, (b) U for the optimal orbital angle θ_{opt} (higher lines) shown in the inset, and for a fixed ordering with $\theta = 2\pi/3$ (lower lines).

TABLE I
Exchange constants J_{ab} and J_c and e_g contributions $J_{ab}(e_g)$ and $J_c(e_g)$ (all in meV) obtained with $U = 5.9$ eV, compared with experimental values.

θ	orbital state	$J_{ab}(e_g)$	$J_c(e_g)$	J_{ab}	J_c
$\pi/3$	$ y^2 - z^2\rangle/ x^2 - z^2\rangle$	-2.23	2.67	-1.50	3.40
$\pi/2$	$(x\rangle + z\rangle)/(x\rangle - z\rangle)$	-2.18	0.20	-1.45	0.92
$2\pi/3$	$ 3x^2 - r^2\rangle/ 3y^2 - r^2\rangle$	-0.54	-0.69	0.18	0.03
$\sim 83^\circ$	$ +\theta_{\text{opt}}\rangle/ -\theta_{\text{opt}}\rangle$	-2.33	0.62	-1.60	1.34
—	exp [6]	—	—	-1.66	1.16

$f_s = 0.629$ adequate for pseudospins 1/2). This proves that the JT term (3) cannot be ignored. Considering the full Hamiltonian (1) we obtained the JT coupling constant $\kappa \simeq 9.1$ meV. We verified that 12κ corresponds to g_{JT}^2/K in the JT Hamiltonian derived by Okamoto *et al.* [4]. This allows us to determine $E_{\text{JT}} \simeq 320$ meV which turns out to be significantly higher than the value $50 < E_{\text{JT}} < 100$ meV estimated before. Note however that a different reduction factor $f'_s = 0.75$ used in Ref. [4] would result in a somewhat lower value $E_{\text{JT}} \simeq 270$ meV also in our model [Fig. 2(a)].

The values of κ depend strongly on U as the energies of excited states which contribute to the SE (2) become higher, and the JT term has to compensate for the reduced SE contribution [see Fig. 2(a)]. Although we did not perform a self-consistent calculation of the orbital ordering as a function of T , we emphasize that the values of T_N obtained for the orbital ordering given either by θ_{opt} (at $T = 0$), or by $\theta = \pi/2$ (at $T = T_N$), agree well with the experimental $T_N^{\text{exp}} = 136$ K [6] for $U \simeq 5.9$ eV [Fig. 2(b)].

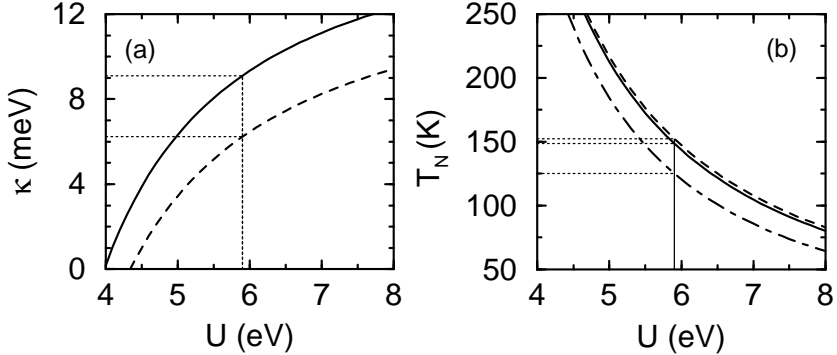


Fig. 2. Values of: (a) JT interaction κ , and (b) the Néel temperature T_N (obtained by reducing the value found in the MFA by a factor $f_N = 0.705$), for increasing U , and for $f_s = 0.629$ (solid lines) and $f'_s = 0.75$ (dashed lines). The values of T_N for the orbital ordering given by $\theta = \pi/2$ are shown in (b) by dot-dashed lines.

Summarizing, we have found that the SE and the JT terms *contribute about equally* to the structural transition, and the JT coupling constant in LaMnO_3 , $E_{\text{JT}} \simeq 300$ meV, is at least three times larger than found using a simplified model of the SE [4]. In addition, we argue that the orbital state in LaMnO_3 has to be *significantly different* from $\theta = 2\pi/3$, an angle which would give almost vanishing and AF exchange constants in all directions.

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