Electronic origin of magnetic and orbital ordering in insulating $LaMnO_3$

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We derive a spin-orbital model for insulating $LaMnO_3$ which fulfills the SU(2) symmetry of $S=2$ spins at Mn^{3+} ions. It includes the complete e_g and t_{2g} superexchange which follows from a realistic Mn^{2+} multiplet structure in cubic site symmetry, and the Jahn-Teller-induced orbital interactions. We show that the magnetic ordering observed in $LaMnO_3$ is stabilized by a purely electronic mechanism due to the e_g superexchange alone, and provides a unique and quantitatively correct explanation of the observed transition temperature and the anisotropic exchange interactions. [S0163-1829(99)14901-4]

The fascinating properties of doped manganites $R_{1-x}A_xMnO_3$, where R is a rare-earth element, and A is a divalent element, were discovered almost half a century ago,[1] but the various phase transitions occurring under doping and in particular the phenomenon of ''colossal magnetoresistance'' (CMR) are still not fully understood. The phase diagrams of $La_{1-x}(Ca,Sr)_xMnO_3$ (Ref. 2) show a complex interplay between magnetic, charge, and structural order, so that all these ordering phenomena may affect CMR at least indirectly. It is therefore important to obtain first of all a full understanding of the mechanism(s) stabilizing the observed order in the *undoped* insulating parent compound $LaMnO_3$. This will be an essential element in putting together a satisfactory description of the more complicated *doped* compounds, and recognizing which mechanism(s) other than or in addition to double exchange[3] might be responsible for CMR.[4]

In this paper we therefore reconsider the problem of the microscopic origin of the experimentally observed type of antiferromagnetic (AF) order in $LaMnO_3$,[5] which consists of ferromagnetic (FM) planes ordered antiferromagnetically in the third direction (A-AF phase). As the magnetic order in $LaMnO_3$ couples to orbital order,[6] one possible explanation might be the occurrence of a cooperative Jahn-Teller (JT) effect[7] which induces a particular order of the singly occupied e_g orbitals.[8] However, while the JT effect plays a crucial role in charge transport,[9] we show here that a purely *electronic mechanism* drives orbital and magnetic ordering in the manganites near the Mott-Hubbard transition.[10]

The local Coulomb interaction U is the dominating energy scale in late transition-metal oxides. If partly filled orbitals are degenerate, as in $KCuF_3$ or in $LaMnO_3$, this leads to an effective low-energy Hamiltonian, where *spin and orbital* degrees of freedom are interrelated.[8,11] In the simplest case of d^9 ions in $KCuF_3$, such a model describes spins $S=1/2$ of e_g holes coupled to the discrete orbital variables. Finite Hund's rule exchange J_H removes the classical degeneracy of magnetically ordered phases,[8,12] and stabilizes the A-AF phase in conjunction with the particular orbital order observed in $KCuF_3$. Here we show that a similar state follows from a *realistic* $S=2$ *spin-orbital model* for the d^4 ions in $LaMnO_3$. We include also the t_{2g} superexchange and the JT interaction and show that these, while unessential qualitatively, are important for a quantitative understanding.

The *superexchange between total spins* $S=2$ at the d^4 Mn^{3+} ions originates in the large-U regime from virtual (e_g or t_{2g}) excitations, $d_i^4d_j^4 \rightleftharpoons d_i^3d_j^5$. A simplified approach proposed recently by Ishihara *et al.*[13] emphasizes the role of orbitals but violates the SU(2) spin symmetry, and involves a Kondo coupling between e_g and t_{2g} spins, which by itself is not a faithful approximation to the multiplet structure. The latter objection applies also to the model proposed by Shiina *et al.*[14] In contrast, the spin-orbital model presented below follows from the full multiplet structure of the Mn ions in octahedral symmetry, both in the d^4 $(t_{2g}^3e_g)$ configuration of the Mn^{3+} ground state and in the d^3 and d^5 virtually excited states.

So we consider a spin-orbital model for the manganites,

$$H=H_e+H_t+H_{\rm JT}+H_\tau, \tag{1}$$

which includes superexchange terms due to e_g (H_e) and t_{2g} (H_t) excitations, JT interaction $(H_{\rm JT})$, and a low-symmetry crystal field (H_τ). Our starting point is that each Mn^{3+} (d^4) ion is in the strong-field $(t_{2g}^3e_g)$ Hund's rule ground state, i.e., the high-spin $(S=2)$ orbital doublet ^5E. First, we analyze the strongest channel of superexchange, which originates in the hopping of an e_g electron from site i to its neighbor j. When we consider a bond oriented along the cubic c axis, only a $3z^2-r^2$ electron can hop and four d^5 states may be reached: the high-spin $^6A_1$ state $(S=5/2)$, and the lower-spin $(S=3/2)$ $^4A_1$,^4E, and $^4A_2$ states (Fig. 1). The $d_i^4d_j^4 \rightleftharpoons d_i^3(t_{2g}^3)d_j^5(t_{2g}^3e_g^2)$ excitation energies require for their description in principle *all three* Racah parameters, A, B, and C:[15] $\varepsilon(^6A_1)=A-8B$, $\varepsilon(^4A_1)=A+2B+5C$, $\varepsilon(^4E)\simeq A+6B+5C$,[16] $\varepsilon(^4A_2)=A+14B+7C$. In view of the realistic values of $B=0.107$ and $C=0.477$ eV for Mn^{2+} (d^5) ions,[17] one may use an approximate relation $C\simeq 4B$, and

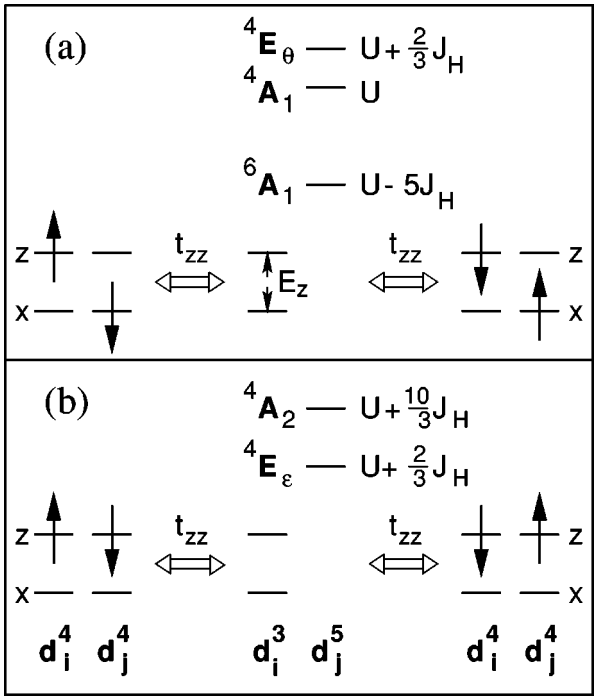

FIG. 1. Virtual $d_i^4 d_j^4 \rightarrow d_i^3 d_j^5$ excitations which generate effective interactions for a bond $(ij)\|c$ axis: (a) for one $|x\rangle$ and one $|z\rangle$ electron, and (b) for two $|z\rangle$ electrons.

write the excitation energies in terms of Coulomb, $U \equiv A + 2B + 5C$, and Hund's exchange, $J_H \equiv 2B + C$, parameters: $\varepsilon(^6A_1) = U - 5J_H$, $\varepsilon(^4A_1) = U$, $\varepsilon(^4E) = U + \frac{2}{3}J_H$, $\varepsilon(^4A_2) = U + \frac{10}{3}J_H$. Using the spin algebra (Clebsch-Gordon coefficients) and the reduction of product representations in cubic site symmetry[15] for the intermediate states, and making a rotation of the terms derived for a bond $\langle ij \rangle \| c$ with respect to the cubic axes, one finds a compact expression

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

where t is the hopping element along the c axis, and $\mathcal{P}^{\alpha\beta}_{\langle ij \rangle}$ are projection operators for each bond $\langle ij \rangle$,

$$\mathcal{P}^{\zeta\xi}_{\langle ij \rangle} = P_{i\zeta}P_{j\xi} + P_{i\xi}P_{j\zeta}, \quad \mathcal{P}^{\zeta\zeta}_{\langle ij \rangle} = 2P_{i\zeta}P_{j\zeta}, \qquad (3)$$

projecting on the orbital states, being either parallel to the bond direction on one site ($P_{i\zeta} = \frac{1}{2} - \tau_i^\alpha$) and perpendicular on the other ($P_{j\xi} = \frac{1}{2} + \tau_j^\alpha$), or parallel on both sites. They are represented by the orbital operators τ_i^α associated with the three cubic axes ($\alpha = a$, b, or c),

$$\tau_i^{a(b)} = \frac{1}{4}(-\sigma_i^z \pm \sqrt{3}\sigma_i^x), \quad \tau_i^c = \frac{1}{2}\sigma_i^z, \qquad (4)$$

where the σ's are Pauli matrices acting on the orbital pseudospins $|x\rangle = \binom{1}{0}$, $|z\rangle = \binom{0}{1}$, and the orbitals transform as $|x\rangle \propto x^2 - y^2$ and $|z\rangle \propto (3z^2 - r^2)/\sqrt{3}$.

The spin operators $\vec{S}_i$ in Eq. (2) are $S = 2$ spins, but otherwise H_e resembles the spin-orbital model for d^9 ions in the cuprates.[12] Both models contain superexchangelike couplings between spin and orbital degrees of freedom. The orbital sector carries a discrete cubic symmetry, and is *identical* in both cases, while the *spin problem fulfills the* SU(2) *symmetry*, and different representations apply for the manganites ($S = 2$) and for the cuprates ($S = 1/2$). We emphasize that the Hamiltonian H_e *is not equivalent* to that of Ref. 13 in any nontrivial limit. A common feature is that FM interactions are enhanced due to the lowest excited $^6A_1$ state, but the dependence of the magnetic interactions on J_H is quite different, and it gives a different answer concerning the stability of the A-AF phase. The balance between AF and FM interactions is also different from that in Ref. 14 due to the multiplet structure of Mn^{2+}.

A similar derivation gives the t_{2g} superexchange[18]

$$H_t = \frac{1}{4}J_t \sum_{\langle ij \rangle} (\vec{S}_i \cdot \vec{S}_j - 4), \qquad (5)$$

where $J_t = (J_{11} + J_{22} + J_{12} + J_{21})/4$. The exchange elements, $J_{mn} = t_\pi^2/\varepsilon(^4T_m, ^4T_n)$, where $t_\pi = t/3$ is the hopping between the t_{2g} orbitals, result from local $d_i^4 d_j^4 \rightleftharpoons d_i^5(t_{2g}^4 e_g) d_j^3(t_{2g}^2 e_g)$ excitations within a $\langle ij \rangle$ bond, with energies $\varepsilon(^4T_1, ^4T_1) \simeq U + 8J_H/3$, $\varepsilon(^4T_1, ^4T_2) \simeq U + 2J_H/3$, $\varepsilon(^4T_2, ^4T_1) \simeq U + 4J_H$, $\varepsilon(^4T_2, ^4T_2) \simeq U + 2J_H$, where ^4T_m (^4T_n) stands for the symmetry of d_i^5 (d_j^3) excited configurations, respectively.

The manganite model (1) is completed by the JT term which leads to static distortions and mixes e_g orbitals,[7]

$$H_{\rm JT} = \kappa \sum_{\langle ij \rangle} (\mathcal{P}^{\zeta\zeta}_{\langle ij \rangle} - 2\mathcal{P}^{\zeta\xi}_{\langle ij \rangle} + \mathcal{P}^{\xi\xi}_{\langle ij \rangle}), \qquad (6)$$

with $\mathcal{P}^{\xi\xi}_{\langle ij \rangle} = 2P_{i\xi}P_{j\xi}$, and by the tetragonal crystal field,

$$H_\tau = -E_z \sum_i \tau_i^c. \qquad (7)$$

The strength of e_g and t_g superexchange can be estimated fairly accurately from the basic electronic parameters for the Mn ion as determined from spectroscopy[17,19] with an estimated accuracy of $\sim 10\%$. We thus use $U = 7.3$ eV and $J_H = 0.69$ eV, and taking into account that the Mn-Mn hopping occurs via the bridging oxygen, $t = 0.41$ eV as follows from $t = t_{pd}^2/\Delta$ with Mn-O hopping $t_{pd} = 1.5$ eV and charge-transfer energy $\Delta = 5.5$ eV.[20] This yields $J = t^2/U = 23$ meV and $J_t = 2.1$ meV. The accuracy of these parameters may be appreciated from the resulting prediction for the Néel temperature of $CaMnO_3$, where a similar derivation gives $\hat{H}_t \sim 2\hat{J}_t(\frac{4}{9}\vec{S}_i \cdot \vec{S}_j - 1)$ in terms of Mn^{4+} spins $S = 3/2$ and $\hat{J}_t \approx J_t(1 + J_H/U)$. With our present estimates we obtain $\hat{J}_t = 2.3$ meV and thus $T_N = 124$ K, in excellent agreement with the experimental value $T_N = 110$ K.[5]

When considering the manganite (d^4) model (1), it is instructive to treat J_H and E_z as freely variable parameters in

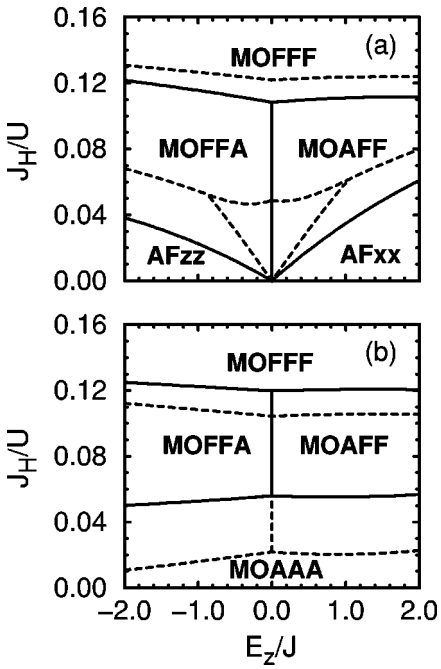

FIG. 2. Classical phase diagram of the manganite model (1): (a) no JT effect ($\kappa=0$), $J_t=0$ (full lines), and $J_t=0.092J$ (dashed lines), with the AFxx and AFzz phases separated by a MOAAA phase; (b) including the JT effect ($\kappa=0.5J$), $J_t=0$ (dashed lines), and $J_t=0.092J$ (full lines).

order to appreciate the physical consequences of Hund's rule multiplet splitting and orbital degeneracy. The cuprate (d^9) model exhibits symmetry breaking into classical states with simultaneous spin and orbital order,[8,12] and similar behavior is expected here.[21] We have considered classical phases with two and four sublattices, and mixed orbitals (MO), $|i\mu\sigma\rangle = \cos\theta_i|ix\sigma\rangle + \sin\theta_i|iz\sigma\rangle$. The mean-field (MF) phase diagram of the e_g part of model (1), $H=H_e+H_\tau$, at $T=0$ is similar to that of the cuprate spin-orbital model:[12] at large positive (negative) E_z, one finds AF phases with either $|x\rangle$ (AFxx) or $|z\rangle$ (AFzz) orbitals occupied, while MO phases with orbitals alternating between the sublattices ($\theta_i = \pm\theta$, with $\cos 2\theta<0$) are favored by increasing J_H. If $E_z<0$ the spin order is FM (AF) in the (a,b) planes (along the c axis) in the MOFFA phase, while at $E_z>0$ two similar phases, MOAFF and MOFAF, are degenerate. For the parameters appropriate for $LaMnO_3$ ($J_H/U\simeq 0.095$) one finds a MOFFA/MOAFF ground state, i.e., A-AF *magnetic order*, while a FM (MOFFF) phase is found only at $J_H/U>0.12$. The region of stability of the A-AF phase is modified by t_{2g} superexchange [Fig. 2(a)], but this change is small as $J_t \ll J$. Thus, the observed A-AF magnetic order in $LaMnO_3$ is caused by the *orbital dependence* of the e_g superexchange and not by competition between FM e_g and AF t_{2g} superexchange as proposed in Ref. 13 (where an unrealistically large J_t was used), supporting the qualitative results of Ref. 14.

Although the MF phase diagrams are modified significantly by JT coupling [Fig. 2(b)], the A-AF phase survives around $J_H/U=0.095$. In fact, the JT interaction (6) by itself enforces alternating orbitals with $\cos 2\theta=0$, which favors AF spin order, thus stabilizing at small J_H/U the MOAAA phase, promoted further by finite J_t. But at larger J_H/U, even though the JT interaction sets the stage by inducing

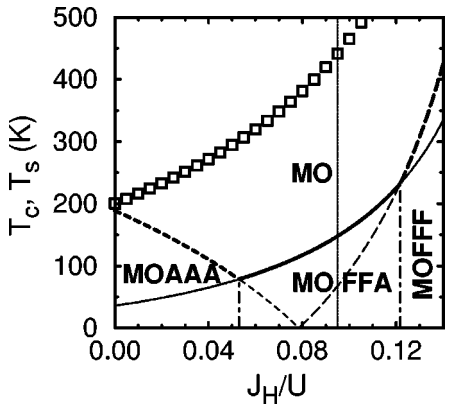

FIG. 3. Magnetic transition temperatures T_c ($J=23$ meV, $E_z=0$, $J_t=0.092J$, $\kappa=0.5J$) for: MOAAA (dashed line), MOFFF (long-dashed line), and MOFFA (full line) phases, and T_s for the structural (MO) phase transition at $\kappa=0$ (squares). The dotted line indicates realistic $J_H/U=0.095$.

orbital order as such, the actual magnetic (A-AF) and orbital ($\cos 2\theta\neq 0$) order are *entirely due* to the e_g-superexchange interactions (2).

Finite-temperature behavior was investigated in MF approximation, with $\langle\vec{\sigma}\rangle$, $\langle\vec{S}\rangle$, and $\langle\vec{\sigma}\vec{S}\rangle$ constituting independent order parameters.[22] As the largest interaction is in the pure orbital ($\vec{\sigma}$) channel, one may estimate the JT coupling κ from the temperature of the structural transition, $T_s^{\rm exp} \approx 750$ K. The electronic interactions contribute $\simeq 440$ K (Fig. 3), and the rest, $6\kappa\simeq 760$ K, comes from the JT term.[23] Thus $\kappa\simeq 11$ meV, and we have adopted the representative value $\kappa/J=0.5$. We then calculated the temperatures T_c for the possible magnetic transitions (Fig. 3), taking into account that orbital order with $\cos 2\theta=0$ already exists below T_s, and calculating self-consistently the corresponding order parameter $\langle\vec{\sigma}\rangle$ at finite T. The spin order sets in simultaneously with a modification of orbital ordering towards $\cos 2\theta\neq 0$. We find that the preexisting structural transition plays an important role at finite T and reduces the magnetic transition temperature, being otherwise $T_c\simeq J$.[14] The results are consistent with the phase diagrams at $T=0$

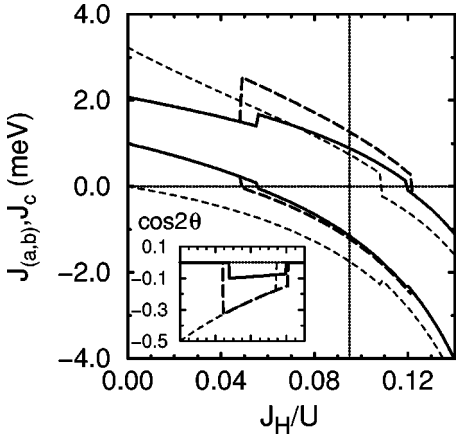

FIG. 4. Exchange interactions J_{ab} and J_c in the ground state for increasing J_H/U, for $J=23$ meV and: $J_t=0$, $\kappa=0$ (dashed lines), $J_t=0.092J$, $\kappa=0$ (long-dashed lines), and $J_t=0.092J$, $\kappa=0.5J$ (full lines). The inset shows $\cos 2\theta$.

(Fig. 2), as the magnetic transition corresponds to the same order as found at $T=0$. For the A-AF (MOFFA) phase we find $T_c \simeq 106$ K,[23] in reasonable agreement with the experimental value of 136 K.[24]

The magnetic interactions in the A-AF (MOFFA) phase may be found using averages $\langle \mathcal{P}^{\alpha\beta}_{\langle ij\rangle}\rangle$ of the orbital projection operators (3) at $E_z=0$. They are FM in the (a,b) planes $(J_{(a,b)})$, and AF in the c direction (J_c) (Fig. 4). Both large J_H/U and $\kappa=0.5J$ play a decisive role in determining the actual composition of the orbitals, and we find $J_{(a,b)} = -1.15$ and $J_c=0.88$ meV, somewhat higher than the experimental -0.83 and 0.58 meV.[25] However, their ratio, $J_c/|J_{(a,b)}|=0.77$, agrees very well with the experimental value of 0.7–0.72;[25] in contrast, it would amount to 1.04 for $\kappa=0$, and to 2.25 if in addition the orbitals were chosen to satisfy $\cos 2\theta=-0.5$, as in the Kugel-Khomskii version[8] of the d^9 model, which results in a much weaker dependence on Hund's exchange J_H.

Summarizing, a coherent overall picture has been obtained for $LaMnO_3$, which is even quantitatively satisfactory.[26] It includes simultaneously the full (e_g and t_{2g}) superexchange and the JT effect, and shows that the orbital dependence of the e_g superexchange, a *purely electronic mechanism*, is responsible for the observed A-AF order. We emphasize that no fitting of parameters was needed, and the used values of J_H, U, and t, known with an accuracy of $\sim 10\%$, allowed to deduce the value of the JT coupling κ, and gave T_c, $J_{(a,b)}$, and J_c within 30% from the experimental values. We thus believe that Hamiltonian (1) provides a realistic starting point for understanding how the delicate balance of magnetic and orbital interactions in $LaMnO_3$ is affected by doping, leading to a change of magnetic order and to the possible onset of an orbital liquid state.[27]

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[1] G. Jonker and J. van Santen, Physica (Amsterdam) **16**, 337 (1950).
[2] A. P. Ramirez, J. Phys.: Condens. Matter **9**, 8171 (1997).
[3] P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955); P.-G. de Gennes, *ibid.* **118**, 141 (1960).
[4] A. J. Millis *et al.*, Phys. Rev. Lett. **74**, 5144 (1995).
[5] E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).
[6] J. B. Goodenough, Phys. Rev. **100**, 564 (1955).
[7] B. Halperin and R. Englman, Phys. Rev. B **3**, 1698 (1971); A. J. Millis, *ibid.* **53**, 8434 (1996).
[8] K. I. Kugel and D. I. Khomskii, Sov. Phys. JETP **37**, 725 (1973).
[9] A. J. Millis *et al.*, Phys. Rev. B **54**, 5389 (1996); **54**, 5405 (1996).
[10] C. M. Varma, Phys. Rev. B **54**, 7328 (1996).
[11] C. Castellani, C. R. Natoli, and J. Ranninger, Phys. Rev. B **18**, 4945 (1978); **18**, 4967 (1978); T. M. Rice, in *Spectroscopy of Mott Insulators and Correlated Metals*, edited by A. Fujimori and Y. Tokura (Springer-Verlag, Berlin, 1995).
[12] L. F. Feiner, A. M. Oleś, and J. Zaanen, Phys. Rev. Lett. **78**, 2799 (1997).
[13] S. Ishihara, J. Inoue, and S. Maekawa, Physica C **263**, 130 (1996); Phys. Rev. B **55**, 8280 (1997).
[14] R. Shiina, T. Nishitani, and H. Shiba, J. Phys. Soc. Jpn. **66**, 3159 (1997).
[15] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, Cambridge, 1971).
[16] Only a particular linear combination of two ^4E states can be reached by hopping which has average energy $\varepsilon(^4E)$.
[17] A. E. Bocquet *et al.*, Phys. Rev. B **46**, 3771 (1992); J. Zaanen and G. A. Sawatzky, J. Solid State Chem. **88**, 8 (1990).
[18] We neglected here smaller anisotropic orbital-dependent terms $\sim J_H/U$ that cannot affect the results.
[19] T. Mizokawa and A. Fujimori, Phys. Rev. B **51**, 12 880 (1995); **54**, 5368 (1996).
[20] Note that U and Δ are defined with respect to the Mn^{2+} $^4A_1$ state, in contrast to other conventions (Refs. 17 and 19).
[21] Different symmetry-broken states are degenerate at $J_H=E_z=0$, as in the d^9 model (Ref. 12), revealing a high frustration of magnetic interactions which might lead to a spin liquid with strong orbital correlations. Such quantum behavior is suppressed for the parameters of $LaMnO_3$ with sizable J_H/U, and because of the large $S=2$ spins.
[22] R. G. Ditzian *et al.*, Phys. Rev. B **22**, 2542 (1980).
[23] The MF values typically overestimate transition temperatures by a factor close to 1.6; it reduces the used MF value of $T_s = 1200$ K to the observed $T_s^{\rm exp} \simeq 750$ K.
[24] H. Kawano *et al.*, Phys. Rev. B **53**, R14 709 (1996).
[25] K. Hirota *et al.*, J. Phys. Soc. Jpn. **65**, 3736 (1996); F. Moussa *et al.*, Phys. Rev. B **54**, 15 149 (1996).
[26] It is plausible that a further extension of the present model by including lattice distortions would allow to explain the easy magnetization axis in $LaMnO_3$.
[27] S. Ishihara, M. Yamanaka, and N. Nagaosa, Phys. Rev. B **56**, 686 (1997).