Origin of Jahn-Teller Distortion and Orbital Order in $LaMnO_3$

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The origin of the cooperative Jahn-Teller distortion and orbital order in $LaMnO_3$ is central to the physics of the manganites. The question is complicated by the simultaneous presence of tetragonal and $GdFeO_3$-type distortions and the strong Hund's rule coupling between e_g and t_{2g} electrons. To clarify the situation we calculate the transition temperature for the Kugel-Khomskii superexchange mechanism by using the local density approximation + dynamical mean-field method, and disentangle the effects of superexchange from those of lattice distortions. We find that superexchange alone would yield $T_{KK} \sim$ 650 K. The tetragonal and $GdFeO_3$-type distortions, however, reduce T_{KK} to $\sim$550 K. Thus electron-phonon coupling is essential to explain the persistence of local Jahn-Teller distortions to $\gtrsim$1150 K and to reproduce the occupied orbital deduced from neutron scattering.

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The insulating perovskite $LaMnO_3$ is the parent compound of the colossal magnetoresistance manganites [1] and it is considered a textbook example of a cooperative Jahn-Teller (JT) orbitally ordered material [2]. Two distinct mechanism have been proposed to explain the cooperative distortion: many-body Kugel-Khomskii (KK) superexchange (SE) [3] and one-electron electron-phonon (EP) coupling [4]. Determining the relative strength of these mechanisms will provide a measure of the importance of strong correlation effects for the orbital physics in the manganites. Unfortunately, the situation is complicated by the simultaneous presence of tetragonal and $GdFeO_3$-type distortions as well as a strong Hund's rule coupling between the Mn e_g and t_{2g} electrons.

In $LaMnO_3$ the Mn^{3+} ions are in a $t_{2g}^3 e_g^1$ configuration. Because of strong Hund's rule coupling the spin of the e_g electron is parallel to the spin of the t_{2g} electrons on the same site. Above $T_N = 140$ K the spins on neighboring sites are disordered [5]. The crystal structure is orthorhombic (Fig. 1). It can be understood by starting from an ideal cubic perovskite structure with axes **x**, **y**, and **z**: first, a tetragonal distortion reduces the Mn-O bond along **z** by 2%. The La-O and La-Mn covalencies induce a $GdFeO_3$-type distortion [6,7] resulting in an orthorhombic lattice with axes **a**, **b**, and **c**, with the oxygen-octahedra tilted about **b** and rotated around **c** in alternating directions. Finally, the octahedra distort, with long (l) and short (s) bonds alternating along **x** and **y**, and repeating along **z** [8–11]. This is measured by $\delta_{JT} = (l - s)/((l + s)/2)$. The degeneracy of the e_g orbitals is lifted and the occupied orbital, $|\theta\rangle = \cos\frac{\theta}{2}|3z^2 - 1\rangle + \sin\frac{\theta}{2}|x^2 - y^2\rangle$, is $\sim|3l^2 - 1\rangle$, i.e., it points in the direction of the long axis. Thus orbital order (OO) is d-type with the sign of θ alternating along **x** and **y** and repeating along **z**. At 300 K the JT distortion is substantial, $\delta_{JT} = 11\%$, and $\theta \sim 108°$ was estimated from neutron scattering data [8]. Above $T_{OO} \sim 750$ K a strong reduction to $\delta_{JT} = 2.4\%$ was reported [8,12], accompanied by a change in θ to $\sim$90° [8]. Recently this was, however, identified as an order-to-disorder transition [10,11]: because of orientational disorder, the crystal appears cubic on average, while, within nanoclusters, the MnO_6 octahedra remain fully JT distorted up to $T_{JT} \gtrsim 1150$ K [11].

Model calculations based on superexchange alone can account for d-type order, but yield, for the classical ground state, $\theta \sim 90°$ [13]. Models of electron-phonon coupling in simple cubic perovskites instead give $\sim$120° [4]. To explain the observed $\sim$108°, one might thus conclude that both mechanisms are of similar importance [3]. Such models are lacking, however, a realistic description of the crystal and the calculated θ is sensitive to the choice of parameters [4,14]. LDA + U calculations yield $\theta = 109°$

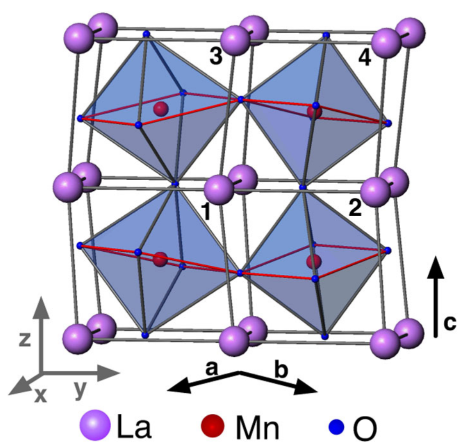

FIG. 1 (color online). Structure of $LaMnO_3$ at 300 K [8]. The conventional cell is orthorhombic with axes **a**, **b**, and **c**, and contains 4 formula units. The pseudocubic axes (left corner) are defined via $\mathbf{a} = (\mathbf{x} - \mathbf{y})(1 + \alpha)$, $\mathbf{b} = (\mathbf{x} + \mathbf{y})(1 + \beta)$, and $\mathbf{c} = 2\mathbf{z}(1 + \gamma)$, with α, β, γ small numbers. For sites 1 and 3 the long (short) bond l (s) is $\sim$ along **y** (**x**), vice versa for sites 2 and 4 (d-type pattern). All Mn sites are equivalent. The symmetries that transform them into a site of type 1 are $x \leftrightarrow y$ (site 2) $z \to -z$ (site 3), $x \leftrightarrow y$, $z \to -z$ (site 4).

and show that Coulomb repulsion is fundamental to stabilize the Jahn-Teller distortions in the ground state [15]. This might be taken as evidence that Kugel-Khomskii superexchange is the dominant mechanism, and electron-phonon coupling, enhanced by electron localization [15,16], merely helps. On the other hand, recent semiclassical many-body calculations for model cubic perovskites indicate that electron-phonon coupling is essential to explain orbital ordering above 300 K [17].

While it is not obvious how well LDA + U or semiclassical approaches capture the many-body nature of the KK superexchange, it seems clear that the inclusion of the real crystal structure is crucial [3,6,18,19]. The tetragonal and $GdFeO_3$-type distortions result in a sizable narrowing of the e_g bands [6,7,20], likely changing the relative strength of superexchange and electron-phonon coupling. Since, in the presence of a crystal field, Coulomb repulsion suppresses orbital fluctuations [6,21], they may even compete with SE and EP coupling. To identify the driving mechanism for orbital order in $LaMnO_3$, it is thus mandatory to account for both the realistic electronic structure and many-body effects. To understand the mechanism one has to disentangle the contribution of KK superexchange from that of the JT or the $GdFeO_3$-type and tetragonal distortions.

In this Letter, we do this by calculating directly the Kugel-Khomskii superexchange transition temperature $T_{\rm KK}$ with and without tetragonal and $GdFeO_3$-type distortions. We adopt the method used successfully for $KCuF_3$ [21], based on local-density approximation (LDA) + dynamical mean-field theory (DMFT) [22].

First, we calculate the electronic structure *ab initio* using the Nth order muffin-tin orbital method. Since the Hund's rule energy gain is larger that the e_g-t_{2g} crystal-field splitting, the t_{2g} bands are $\frac{1}{2}$ filled and the e_g bands $\frac{1}{4}$ filled; the three t_{2g} electrons behave as a spin $\mathbf{S}_{t_{2g}}$ and couple to the e_g electron via an effective magnetic field $h = JS_{t_{2g}}$. In the paramagnetic phase ($T > T_N = 140$ K) the t_{2g} spins are spatially disordered. The minimal model to study the KK mechanism in $LaMnO_3$ is thus [23]

$$H = \sum_{im\sigma, jm'\sigma'} t^{i,i'}_{m,m'} u^{i,i'}_{\sigma,\sigma'} c^\dagger_{im\sigma} c_{i'm'\sigma'} - h\sum_{im}(n_{im\Uparrow} - n_{im\Downarrow}) + U\sum_{im} n_{im\Uparrow} n_{im\Downarrow} + \frac{1}{2}\sum_{im(\neq m')\sigma\sigma'} (U - 2J - J\delta_{\sigma,\sigma'}) n_{im\sigma} n_{im'\sigma'}. \quad (1)$$

$c^\dagger_{im\sigma}$ creates an electron with spin $\sigma = \Uparrow, \Downarrow$ in a Wannier orbital $|m\rangle = |x^2 - y^2\rangle$ or $|3z^2 - 1\rangle$ at site i, and $n_{im\sigma} = c^\dagger_{im\sigma} c_{im\sigma}$. $\Uparrow$ ($\Downarrow$) indicates the e_g spin parallel (antiparallel) to the t_{2g} spins (on that site). The matrix u ($u^{i,i'}_{\sigma,\sigma'} = 2/3$ for $i \neq i'$, $u^{i,i}_{\sigma,\sigma'} = \delta_{\sigma,\sigma'}$) accounts for the orientational disorder of the t_{2g} spins [23]; $t^{i,i'}_{m,m'}$ is the LDA hopping integral from orbital m on site i to orbital m' on site i', obtained *ab initio* by downfolding the LDA bands and constructing a localized e_g Wannier basis. The on-site terms $i = i'$ give the crystal-field splitting. U and J are the direct and exchange screened on-site Coulomb interaction [24]. We use the theoretical estimate $J = 0.75$ eV [25] and vary U between 4 and 7 eV. The Hund's rule splitting was estimated *ab initio* to $2JS_{t_{2g}} \sim 2.7$ eV [7]. We solve (1) using DMFT [26] or cellular DMFT (CDMFT) and a quantum Monte Carlo [27] solver, working with the full self-energy matrix $\Sigma_{mm'}$ in orbital space [6]. The spectral matrix on the real axis is obtained by analytic continuation [28].

We consider several structures: (i) the room temperature structure R_{11} with $\delta_{\rm JT} = 11\%$, and a series of hypothetical structures $R_{\delta_{\rm JT}}$ with reduced JT distortion $\delta_{\rm JT}$, (ii) the (average) structure found at 800 K, $R^{800\,{\rm K}}_{2.4}$, which has a slightly larger volume than R_{11} and a smaller $GdFeO_3$-type distortion, and (iii) the ideal cubic structure I_0 with the same volume as R_{11}. For all structures we find that at each site the e_g spins align to $\mathbf{S}_{t_{2g}}$. We calculate the orbital polarization p as a function of temperature [29] by diagonalizing the DMFT (or CDMFT) occupation matrix and taking the difference between the occupation of the most ($|\theta\rangle$) and least ($|\theta + \pi\rangle$) filled orbital. To test the t_{2g} spins picture we perform calculations for the 5-band ($e_g + t_{2g}$) Hubbard model [30]. We find that it holds even at high temperatures.

For the 300 K structure (R_{11}) the bandwidths are $W_{t_{2g}} \sim 1.6$ eV and $W_{e_g} \sim 3.0$ eV. The e_g states split by $\sim$840 meV, in good agreement with experimental estimates [31]. The lower crystal-field state at site 1 is $|1\rangle = 0.574|3z^2 - 1\rangle + 0.818|x^2 - y^2\rangle$. We find an insulating solution in the full range $U = 4$–7 eV (Fig. 2). The Mott gap E_g is $\sim$0.6 eV for $U = 4$ eV, and increases almost linearly with increasing U. For $U = 5$ eV, suggested by recent estimates [7,32], the Hubbard bands are at ~ -1.5 and 2 eV. In addition there is a broad feature around 5 eV due to e_g states with spin antiparallel to the randomly oriented t_{2g} spins. These spectra are in line with experiments [31–34]. We find that even at 1150 K the system is fully orbitally polarized ($p \sim 1$). On sites 1 and 3, the

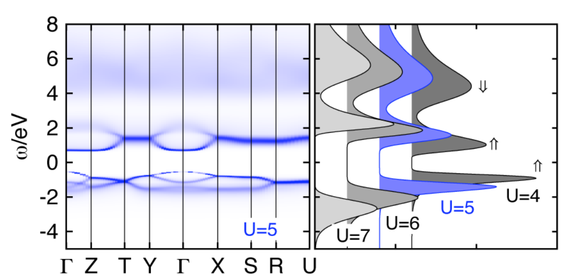

FIG. 2 (color online). Right: LDA + DMFT spectral function for the room temperature structure R_{11} for different U. $\Uparrow$ ($\Downarrow$) indicates states with e_g spins parallel (antiparallel) to $\mathbf{S}_{t_{2g}}$. Left: $\mathbf{k}$-resolved spectral function for $U = 5$ eV.

occupied state is $|\theta\rangle \sim |106°\rangle$, on sites 2 and 4 it is $|-\theta\rangle \sim |-106°\rangle$ (d-type OO); $|\theta\rangle$ is close to the lower crystal-field state obtained from LDA (Table I) and in excellent agreement with neutron diffraction experiments [8]. We find that things hardly change when the JT distortion is halved (R_6 structure in Fig. 3). Even for the average 800 K structure ($R_{2.4}^{800\ \mathrm{K}}$) OO does not disappear: Although the Jahn-Teller distortion is strongly reduced to $\delta_{\mathrm{JT}} = 2.4\%$, the crystal-field splitting is $\sim$168 meV and the orbital polarization at 1150 K is as large as $p \sim 0.65$, while θ is now close to 90°. For all these structures, orbital order is already determined by the distortions via the crystal-field splitting.

To find the temperature T_{KK} at which Kugel-Khomskii superexchange drives orbital order we consider the zero crystal-field limit, i.e., the ideal cubic structure I_0. The e_g bandwidth increases to $W_{e_g} \sim 3.7$ eV and for $U = 5$ eV the system is a Mott insulator with a tiny gap only below $T \sim 650$ K. We find $T_{\mathrm{KK}} \sim 650$ K, very close to the metal-insulator transition (Fig. 3). To check how strongly T_{KK} changes when the gap opens, we increase U. For $U = 5.5$ eV we find an insulating solution with a small gap of $\sim$0.5 eV and T_{KK} still close to $\sim$650 K. For $U = 6$ eV, $E_g \sim 0.9$ eV and $T_{\mathrm{KK}} \sim 550$ K. Even with an unrealistically large $U = 7$ eV, giving $E_g \sim 1.8$ eV, T_{KK} is still as large as $\sim$470 K. Thus, despite the small gap, T_{KK} decreases as $\sim 1/U$, as expected for superexchange. For a realistic $U \sim 5$ eV, the calculated $T_{\mathrm{KK}} \sim 650$ K is surprisingly close to the order-disorder transition temperature, $T_{\mathrm{OO}} \sim 750$ K, though still much smaller than $T_{\mathrm{JT}} \gtrsim 1150$ K. The occupied state at site 1 is $|\theta\rangle \sim |90°\rangle$ for all U.

Such a large T_{KK} is all the more surprising when compared with the value obtained for $KCuF_3$, $T_{\mathrm{KK}} \sim 350$ K [21]. For the ideal cubic structure the hopping matrix (Table I) is $t_{m,m'}^{i,i\pm\mathbf{z}} \sim -t\delta_{m,m'}\delta_{m,3z^2-1}$, $t_{m,m}^{i,i\pm\mathbf{x}} = t_{m,m}^{i,i\pm\mathbf{y}} \sim -t/4(1+2\delta_{m,x^2-y^2})$, and for $m \neq m'$ $t_{m,m'}^{i,i\pm\mathbf{x}} = -t_{m,m'}^{i,i\pm\mathbf{y}} \sim \sqrt{3}t/4$. Since the effective (after averaging over the directions of $\mathbf{S}_{t_{2g}}$) hopping integral in $LaMnO_3$, $2t/3 \sim 345$ meV is $\sim$10% smaller than $t \sim 376$ meV in $KCuF_3$ [21], one may expect a slightly smaller T_{KK} in $LaMnO_3$, opposite to what we find. Our result can, however, be understood in superexchange theory. The KK SE part of the Hamiltonian, obtained by second-order perturbation theory in t from Eq. (1), may be written as

$$H_{\mathrm{SE}}^{i,i'} \sim \frac{J_{\mathrm{SE}}}{2}\sum_{\langle ii'\rangle_{\mathbf{x},\mathbf{y}}}[3T_i^xT_{i'}^x \mp \sqrt{3}(T_i^zT_{i'}^x + T_i^xT_{i'}^z)] + \frac{J_{\mathrm{SE}}}{2}\sum_{\langle ii'\rangle_{\mathbf{x},\mathbf{y}}}T_i^zT_{i'}^z + 2J_{\mathrm{SE}}\sum_{\langle ii'\rangle_{\mathbf{z}}}T_i^zT_{i'}^z, \quad (2)$$

where $\langle i,i'\rangle_{\mathbf{x},\mathbf{y}}$ and $\langle i,i'\rangle_{\mathbf{z}}$ indicate near neighboring sites along $\mathbf{x}$, $\mathbf{y}$, or $\mathbf{z}$; $-(+)$ refers to the $\mathbf{x}$ ($\mathbf{y}$) direction, T_i^x and T_i^z are pseudospin operators [3], with $T^z|3z^2-1\rangle = 1/2|3z^2-1\rangle$, $T^z|x^2-y^2\rangle = -1/2|x^2-y^2\rangle$. The superexchange coupling is $J_{\mathrm{SE}} = (\bar{t}^2/U)(w/2)$, where $\bar{t}$ is the effective hopping integral. In the large U limit (negligible J/U and h/U), $w \sim 1 + 4\langle S_i^z\rangle\langle S_{i'}^z\rangle + (1 - 4\langle S_i^z\rangle \times \langle S_{i'}^z\rangle)u_{\Uparrow,\Downarrow}^{i,i'}/u_{\Uparrow,\Uparrow}^{i,i'}$, where S_i^z are the e_g spin operators. In $LaMnO_3$ the e_g spins align with the randomly oriented t_{2g} spins, thus $\bar{t} = 2t/3$, $w \sim 2$, and $J_{\mathrm{SE}} \sim 2(2t/3)^2/U$. For d-type order, the classical ground state is $|\theta\rangle \sim |90°\rangle$, in agreement with our DMFT results. In $KCuF_3$, with configuration $t_{2g}^6e_g^3$, the Hund's rule coupling between e_g and t_{2g} plays no role, i.e., $\langle S_i^z\rangle = 0$. The hopping integral $\bar{t} = t$ is indeed slightly larger than in $LaMnO_3$, but $w \sim 1$, a reduction of 50%. Consequently, J_{SE} is reduced by $\sim$0.6 in $KCuF_3$. For finite J/U and h/U, w is a more complicated function, but the conclusions stay the same. We verified solving (1) with LDA + DMFT that also for $LaMnO_3$ T_{KK} drops drastically if $u_{\sigma,-\sigma}^{i,i'} = 0$ and $h = 0$.

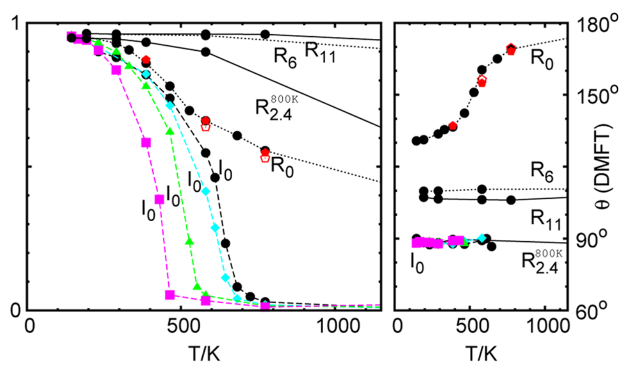

FIG. 3 (color online). Orbital polarization p (left) and (right) occupied state $|\theta\rangle$ ($|-\theta\rangle$) for sites 1 and 3 (2 and 4) as a function of temperature. Solid line: 300 K (R_{11}) and 800 K ($R_{2.4}^{800\ \mathrm{K}}$) structures. Dots: orthorhombic structures with half (R_6) or no (R_0) Jahn-Teller distortion. Pentagons: 2 (full) and 4 (empty) sites CDMFT. Dashes: ideal cubic structure (I_0). Circles: $U = 5$ eV. Diamonds: $U = 5.5$ eV. Triangles: $U = 6$ eV. Squares: $U = 7$ eV. Crystal-field splitting (meV): 840 (R_{11}), 495 (R_6), 219 (R_0), 168 ($R_{2.4}^{800\ \mathrm{K}}$), and 0 ($I_0$).

TABLE I. Hopping integrals $t_{m,m'}^{i,i'}$/meV from a site i of type 1 to a neighboring site i' of type 2 in direction $l\mathbf{x} + n\mathbf{y} + m\mathbf{z}$ for structures R_{11}, $R_{2.4}^{800\ \mathrm{K}}$, R_0, and I_0. The states m, m' are $|\pi\rangle = |x^2-y^2\rangle$ and $|0\rangle = |3z^2-1\rangle$. The crystal-field states are the eigenvectors of the on-site matrix ($l = m = n = 0$).

lmn	$t_{\pi,\pi}^{i,i'}$	$t_{\pi,0}^{i,i'}$	$t_{0,\pi}^{i,i'}$	$t_{0,0}^{i,i'}$	$t_{\pi,\pi}^{i,i'}$	$t_{\pi,0}^{i,i'}$	$t_{0,\pi}^{i,i'}$	$t_{0,0}^{i,i'}$
		R_{11}				$R_{2.4}^{800\ \mathrm{K}}$		
000	0	409	409	305	0	84	84	−2
001	−8	−47	−47	−445	−2	−13	−13	−439
010	−322	233	174	−129	−328	196	190	−105
100	−322	−174	−236	−129	−328	−190	−196	−105
		R_0				I_0		
000	0	5	5	218	0	0	0	0
001	−1	−2	−2	−433	−10	0	0	−518
010	−333	206	207	−121	−391	220	220	−137
100	−333	−207	−206	−121	−391	−220	−220	−137

It remains to evaluate the effect of the orthorhombic distortion on the transition. For this we perform calculations for the system R_0 with no Jahn-Teller distortion, but keeping the tetragonal and $GdFeO_3$-type distortion of the 300 K structure. This structure is metallic for $U = 4$ eV; for $U = 5$ eV it has a gap of $\sim$0.5 eV. We find a large polarization already at 1150 K ($p \sim 0.45$). Such polarization is due to the crystal-field splitting of about 219 meV, with lower crystal-field states at site 1 given by $|1\rangle \sim |x^2 - y^2\rangle$. Surprisingly, the most occupied state $|\theta\rangle$ is close to $|1\rangle$ ($\theta \sim 180$) only at high temperature ($\sim$1000 K). The orthorhombic crystal field thus competes with superexchange, analogous to an external field with a component perpendicular to an easy axis. On cooling the occupied orbitals rotate to $|\theta\rangle \sim |132°\rangle$ (see Fig. 3). This effect of superexchange occurs around a characteristic temperature $T_{\rm KK}^R \sim 550$ K, still surprisingly large, but reduced compared to $T_{\rm KK}$ for the ideal cubic system I_0 and much smaller than the experimental $T_{\rm JT} \gtrsim 1150$ K. Short-range correlations could reduce $T_{\rm KK}^R$ or modify θ. To estimate this effect we perform CDMFT calculations; our results (Fig. 3) remain basically unchanged. Thus, electron-phonon coupling is necessary to explain both the transition temperature and the correct occupied orbital $|\theta\rangle \sim |108°\rangle$.

In conclusion, we find that $T_{\rm KK}^R$ in orthorhombic $LaMnO_3$ is $\sim$550 K. We have shown that two elements are crucial: the superexchange mechanism, which yields a transition temperature as high as 650 K, and the tetragonal plus $GdFeO_3$-type distortion, which, due to the reduced hopping integrals and the competing orthorhombic crystal field, reduces $T_{\rm KK}$ to 550 K. Experimentally, an order-to-disorder transition occurs around $T_{\rm OO} \sim 750$ K, but a local Jahn-Teller distortion persists in the disordered phase up to $T_{\rm JT} \gtrsim 1150$ K. The Kugel-Khomskii mechanism alone cannot account for the presence of such Jahn-Teller distortions above 550 K ($T_{\rm KK}^R \ll T_{\rm JT}$). It also cannot justify the neutron scattering estimate $\theta = 108°$. Thus electron-phonon coupling is a crucial ingredient, both for making the Jahn-Teller distortions energetically favorable at such high temperatures and in determining the occupied orbital.

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[1] Y. Tokura and N. Nagaosa, Science **288**, 462 (2000).
[2] P. Fazekas, *Lecture Notes on Electron Correlation and Magnetism* (World Scientific, Singapore, 1999).
[3] K. I. Kugel and D. I. Khomskii, Zh. Eksp. Teor. Fiz. **64**, 1429 (1973) [Sov. Phys. JETP **37**, 725 (1973)].
[4] J. Kanamori, J. Appl. Phys. **31**, S14 (1960).
[5] E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).
[6] E. Pavarini *et al.*, Phys. Rev. Lett. **92**, 176403 (2004); M. De Raychaudhury, E. Pavarini, and O. K. Andersen, *ibid.* **99**, 126402 (2007); E. Pavarini, A. Yamasaki, J. Nuss, and O. K. Andersen, New J. Phys. **7**, 188 (2005).
[7] A. Yamasaki *et al.*, Phys. Rev. Lett. **96**, 166401 (2006).
[8] J. Rodríguez-Carvajal *et al.*, Phys. Rev. B **57**, R3189 (1998).
[9] T. Chatterji *et al.*, Phys. Rev. B **68**, 052406 (2003).
[10] M. C. Sánchez, G. Subías, J. García, and J. Blasco, Phys. Rev. Lett. **90**, 045503 (2003).
[11] X. Qiu, Th. Proffen, J. F. Mitchell, and S. J. L. Billinge, Phys. Rev. Lett. **94**, 177203 (2005); A. Sartbaeva *et al.*, *ibid.* **99**, 155503 (2007).
[12] Y. Murakami *et al.*, Phys. Rev. Lett. **81**, 582 (1998).
[13] J. Bała and A. M. Oleś, Phys. Rev. B **62**, R6085 (2000).
[14] R. Maezono, S. Ishihara, and N. Nagaosa, Phys. Rev. B **58**, 11583 (1998).
[15] W. G. Yin, D. Volja, and W. Ku, Phys. Rev. Lett. **96**, 116405 (2006).
[16] E. Koch and E. Pavarini (to be published).
[17] C. Lin and A. J. Millis, Phys. Rev. B **78**, 174419 (2008).
[18] T. Hotta, S. Yunoki, M. Mayr, and E. Dagotto, Phys. Rev. B **60**, R15009 (1999).
[19] L. E. Gonchar' and A. E. Nikiforov, Fiz. Tverd. Tela **42**, 1038 (2000) [Phys. Solid State **42**, 1070 (2000)].
[20] C. Ederer, C. Lin, and A. J. Millis, Phys. Rev. B **76**, 155105 (2007).
[21] E. Pavarini, E. Koch, and A. I. Lichtenstein, Phys. Rev. Lett. **101**, 266405 (2008).
[22] V. I. Anisimov *et al.*, J. Phys. Condens. Matter **9**, 7359 (1997); A. I. Lichtenstein and M. I. Katsnelson, Phys. Rev. B **57**, 6884 (1998).
[23] K. H. Ahn and A. J. Millis, Phys. Rev. B **61**, 13545 (2000).
[24] J. Kanamori, Prog. Theor. Phys. **30**, 275 (1963).
[25] T. Mizokawa and A. Fujimori, Phys. Rev. B **54**, 5368 (1996).
[26] A. Georges, G. Kotliar, W. Kraut, and M. J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).
[27] J. E. Hirsch and R. M. Fye, Phys. Rev. Lett. **56**, 2521 (1986).
[28] J. E. Gubernatis, M. Jarrell, R. N. Silver, and D. S. Sivia, Phys. Rev. B **44**, 6011 (1991).
[29] With e_g spins aligned to the t_{2g} spins, the SE coupling [see discussion after Eq. (2)] is $J_{\rm SE} \sim 2\tilde{t}^2(1/(U-3J) + (u_{\Uparrow,\Downarrow}/u_{\Uparrow,\Uparrow})(1/(U+2h-2J) - 1/(U+2h))$, i.e., depends weakly on the $u^{ii'}_{\sigma-\sigma}$ terms in (1); thus we neglect them.
[30] Structure R_{11}, parameters $1/k_BT = 5$ eV, $U = 5$ eV, $J = 0.75$ eV. We find $\sim t_{2g}^3 e_g^1$ and Hubbard bands in line with $S_{t_{2g}} = 3/2$; the e_g orbital polarization, p and the gap are close to the results for Hamiltonian (1).
[31] N. N. Kovaleva *et al.*, Phys. Rev. Lett. **93**, 147204 (2004).
[32] J.-H. Park *et al.*, Phys. Rev. Lett. **76**, 4215 (1996).
[33] K. Takenaka *et al.*, J. Phys. Soc. Jpn. **68**, 1828 (1999); J. H. Jung *et al.*, Phys. Rev. B **57**, R11 043 (1998); M. A. Quijada *et al.*, *ibid.* **64**, 224426 (2001); K. Tobe *et al.*, *ibid.* **64**, 184421 (2001).
[34] A. Chainani, M. Mathew, and D. D. Sarma, Phys. Rev. B **47**, 15 397 (1993); T. Saitoh *et al.*, *ibid.* **51**, 13 942 (1995); T. Saitoh *et al.*, *ibid.* **56**, 8836 (1997).