Dimerization versus Orbital-Moment Ordering in a Mott Insulator YVO_3

Peter Horsch,[1] Giniyat Khaliullin,[1,2] and Andrzej M. Oleś[1,3]

[1]*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*
[2]*E. K. Zavoisky Physical-Technical Institute of the Russian Academy of Sciences, 420029 Kazan, Russia*
[3]*M. Smoluchowski Institute of Physics, Jagellonian University, Reymonta 4, PL-30059 Kraków, Poland*

(Received 31 December 2002; published 16 December 2003)

We use exact diagonalization combined with mean-field theory to investigate the phase diagram of the spin-orbital model for cubic vanadates. The spin-orbit coupling competes with Hund's exchange and triggers a novel phase, with the ordering of t_{2g} orbital magnetic moments stabilized by the tilting of VO_6 octahedra. It explains qualitatively spin canting and reduction of magnetization observed in YVO_3. At finite temperature, an orbital instability in the C-type antiferromagnetic phase induces modulation of magnetic exchange constants *even in the absence of lattice distortions*. The calculated spin structure factor shows a magnon splitting at $\vec{q} = (0, 0, \frac{\pi}{2})$ due to the orbital dimerization.

DOI: 10.1103/PhysRevLett.91.257203 PACS numbers: 75.10.Jm, 71.27.+a, 71.70.Ej, 75.30.Et

Many transition metal oxides are Mott-Hubbard insulators, in which local Coulomb interaction $\propto U$ suppresses charge fluctuations and leads to strongly correlated $3d$ electrons at transition metal ions [1]. When degenerate d orbitals are partly filled, the *orbital degrees of freedom* have to be considered on equal footing with electron spins and the magnetic properties of undoped compounds are described by spin-orbital superexchange (SE) models [2,3]. Such SE interactions are typically strongly frustrated on a perovskite lattice, leading to enhanced quantum effects [4]. In systems with e_g orbital degeneracy (manganites, cuprates), this frustration is usually removed by a structural transition that occurs well above the magnetic ordering temperature and lifts the orbital degeneracy via the cooperative Jahn-Teller (JT) effect.

A different situation arises when t_{2g} orbitals are partly filled such as in titanium and vanadium oxides. As the JT coupling is much weaker, the intrinsic frustration between spin and orbital degrees of freedom may show up in this case. Unusual magnetic properties of titanates have recently been discussed in terms of coupled spin-orbital SE dynamics [5]. In addition to SE, spin $\vec{S}_i$ and orbital $\vec{l}_i$ variables are coupled also via atomic spin-orbit interaction, $H_{\rm so} \propto \Lambda(\vec{S}_i \cdot \vec{l}_i)$. Interplay between *intersite* SE and *on-site* $H_{\rm so}$ should lead to rich physics which has not been explored until now. $H_{\rm so}$ is particularly relevant for vanadates with a triplet ${}^3T_2$ ground state of V^{3+} ions, as observed in the canonical spin-orbital system V_2O_3 [6].

The magnetic properties of cubic vanadate YVO_3 are particularly puzzling [7], and indicate dimerization along the ferromagnetic (FM) direction within the C-type antiferromagnetic (AF) phase [8]. In this Letter, we argue that such an exotic C-AF phase follows from the realistic spin-orbital model for vanadates that emphasizes the competition between SE bond physics and intra-atomic spin-orbit coupling $\propto \Lambda$. We investigate the phase diagram of this model and show that *orbital moments* are induced in the C-AF phase by finite Λ, and form at larger Λ a novel orbital moment (OM) phase.

The superexchange in cubic vanadates originates from virtual charge excitations, $d_i^2 d_j^2 \rightarrow d_i^3 d_j^1$, by the hopping t which couples pairs of identical orbitals. When such processes are analyzed on individual bonds $\langle ij \rangle \parallel \gamma$ along each cubic axis $\gamma = a, b, c$, one finds the spin-orbital Hamiltonian with $S = 1$ spins ($J = 4t^2/U$) [9],

$$\mathcal{H} = J \sum_{\gamma} \sum_{\langle ij \rangle \parallel \gamma} [\tfrac{1}{2}(\vec{S}_i \cdot \vec{S}_j + 1)\hat{J}_{ij}^{(\gamma)} + \hat{K}_{ij}^{(\gamma)}] + H_{\rm so}, \quad (1)$$

where the orbital operators $\hat{J}_{ij}^{(\gamma)}$ and $\hat{K}_{ij}^{(\gamma)}$ depend on the pseudospin $\tau = 1/2$ operators $\vec{\tau}_i = \{\tau_i^x, \tau_i^y, \tau_i^z\}$, given by two orbital flavors active along a given direction γ. For instance, yz and zx orbitals are active along the c axis, and we label them as a and b, as they lie in the planes orthogonal to these axes. The general form of the SE (1) was discussed before, and we have shown that strong quantum fluctuations in the orbital sector provide a mechanism for the C-AF phase [9]. When c (xy) orbitals are occupied ($n_{ic} = 1$), as suggested by the electronic structure [10] and by the lattice distortions in YVO_3 [7,11], the electron densities in a and b orbitals satisfy the local constraint $n_{ia} + n_{ib} = 1$. The interactions along the c axis simplify then to

$$\hat{J}_{ij}^{(c)} = (1 + 2R)(\vec{\tau}_i \cdot \vec{\tau}_j + \tfrac{1}{4}) - r(\vec{\tau}_i \otimes \vec{\tau}_j + \tfrac{1}{4}) - R, \quad (2)$$

$$\hat{K}_{ij}^{(c)} = R(\vec{\tau}_i \cdot \vec{\tau}_j + \tfrac{1}{4}) + r(\vec{\tau}_i \otimes \vec{\tau}_j + \tfrac{1}{4}). \quad (3)$$

They involve the fluctuations of a and b orbitals $\propto \vec{\tau}_i \cdot \vec{\tau}_j$, and $\vec{\tau}_i \otimes \vec{\tau}_j = \tau_i^x \tau_j^x - \tau_i^y \tau_j^y + \tau_i^z \tau_j^z$, while the interactions along the $\gamma = a(b)$ axis depend on the static correlations $\propto n_{ib} n_{jb}$ ($n_{ia} n_{ja}$) only; for instance,

$$\hat{J}_{ij}^{(a)} = \tfrac{1}{2}[(1 - r)(1 + n_{ib} n_{jb}) - R(n_{ib} - n_{jb})^2], \quad (4)$$

$$\hat{K}_{ij}^{(a)} = \tfrac{1}{2}(R + r)(1 + n_{ib} n_{jb}). \quad (5)$$

Hund's exchange $\eta = J_H/U$ determines the multiplet structure of d^3 excited states which enter via the

coefficients $R = \eta/(1-3\eta)$ and $r = \eta/(1+2\eta)$. The pseudospin operators in Eqs. (2) and (3) may be represented by Schwinger bosons: $\tau_i^x = \frac{1}{2}(a_i^\dagger b_i + b_i^\dagger a_i)$, $\tau_i^y = \frac{1}{2}i(a_i^\dagger b_i - b_i^\dagger a_i)$, $\tau_i^z = \frac{1}{2}(n_{ia} - n_{ib})$.

The individual VO_6 octahedra are tilted by angle $\phi_i = \pm\phi$, which alternate along the c axis [11]. As the xy orbital is inactive, two components of the orbital moment $\vec{l}_i$ are quenched, while the third one ($2\tau_i^y$), parallel to the local axis of a VO_6 octahedron, couples to the spin projection. Because of AF correlations of τ_i^y moments, spin-orbit coupling induces a staggered spin component. As the spin interactions are FM, weak spin-orbit coupling would give no energy gain, if the spins were oriented along the c axis. Thus, finite Λ breaks the SU(2) symmetry and favors easy magnetization axis within the (a, b) plane. As a quantization axis for $\vec{l}_i$ and $\vec{S}_i$, we use the octahedral axis and its projection on the (a, b) plane, respectively. The spin-orbit term is

$$H_{\rm so} = 2\Lambda\sum_i (S_i^x \cos\phi_i + S_i^z \sin\phi_i)\tau_i^y, \qquad (6)$$

and we use $\lambda = \Lambda/J$ as a free parameter. In order to understand the important consequences of the tilting for the interplay between spin and orbital degrees of freedom, we consider first the idealized structure with $\phi = 0$. The coherent spin-and-orbital fluctuations lower then the energy due to on-site correlations $\langle S_i^x \tau_i^y\rangle < 0$. Since these fluctuations do not couple to the spin order, no orbital moments can be induced at small λ as long as $\phi = 0$.

Even in the absence of the spin-orbit term ($\lambda = 0$), the vanadate spin-orbital model (1) poses a highly nontrivial quantum problem. We obtained first qualitative insight into the possible types of magnetic and orbital ordering by investigating the stability of different phases within the mean-field approximation (MFA), but including the leading orbital fluctuations on FM bonds along the c axis. In the absence of Hund's exchange ($\eta = 0$), two orbital flavors experience an antiferro-orbital (AO) coupling on these bonds due to $\hat{J}_{ij}^{(c)}$ [Eq. (2)], but are decoupled within the (a, b) planes ($\hat{K}_{ij}^{(a,b)} = 0$ [12]). This one-dimensional (1D) system is unstable towards *dimerization* with orbital singlets and FM interactions at every second bond along the c axis [13], stabilizing the orbital valence bond (OVB) phase. The spin interactions $\hat{J}_{ij}^{(a,b)}$ [Eq. (4)] and the intersinglet interactions along the c axis are AF. In contrast, for large η more energy is gained when the orbital singlets resonate along the c direction, giving uniform FM interactions in the C-AF phase [9]. We determined the quantum energy due to orbital fluctuations using the orbital waves found in the Schulz approximation, known to be accurate for weakly coupled AF chains [14]. Using this approach, the transition from the OVB to C-AF phase [$\langle S_i^z\rangle = S^z e^{i\vec{R}_i\vec{Q}_C}$ with $\vec{Q}_C = (\pi, \pi, 0)$] takes place at $\eta_c \simeq 0.09$ (Fig. 1), and the orbital ordering, $\langle \tau_i^z\rangle = \tau^z e^{i\vec{R}_i\vec{Q}_G}$ with $\vec{Q}_G = (\pi, \pi, \pi)$, sets in, promoted by the AO interactions $\hat{K}_{ij}^{(a,b)}$ [Eq. (5)].

The ground state changes qualitatively at finite λ and $\phi > 0$. The magnetic moments $\langle S_i^z\rangle$ induce then the *orbital moments*, $2\langle \tau_i^y\rangle = l^z e^{i\vec{R}_i\vec{Q}_A}$, which stagger along the c axis with $\vec{Q}_A = (0, 0, \pi)$. This novel type of ordering with $l_i^z \neq 0$ can be described as a staggered ordering of complex orbitals $a \pm ib$ (corresponding to $l_i^z = \mp 1$ eigenstates) that competes at $\eta > \eta_c$ with the staggered (a/b) ordering of real orbitals with $\tau^z \neq 0$ in the C-AF phase. Already at small λ, the orbital moments induce in turn opposite to them weak $\langle S_i^x\rangle \neq 0$ moments, lowering the energy by $\langle S_i^x \tau_i^y\rangle < 0$. In the OM phase favored at large λ (Fig. 1), the spin order has therefore two components: $\langle S_i^z\rangle = S^z e^{i\vec{R}_i\vec{Q}_C}$, and $\langle S_i^x\rangle = S^x e^{i\vec{R}_i\vec{Q}_G}$.

Unbiased information about the spin and orbital degrees of freedom was obtained by the accurate treatment of quantum effects within the exact diagonalization (ED) method. Thereby the coupled spin-orbital excitations, terms $\propto S_i^\alpha S_j^\alpha \tau_i^\beta \tau_j^\beta$ in Eq. (1), are now fully included. We performed ED of four-site chains along the c axis, both for free and periodic boundary conditions (PBC).

We were surprised to see that the exact ground state of a *free chain* at $\eta = \lambda = 0$ consists indeed in a very good approximation of two orbital singlets on the external (12) and (34) FM bonds ($\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1}\rangle = -0.729$), connected by an AF bond (23) with decoupled orbitals ($\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1}\rangle = -0.038$). The spin correlations are FM/AF on the external/central bond, $\langle \vec{S}_i \cdot \vec{S}_{i+1}\rangle = 0.95$ and -1.56. With increasing η the AF interaction weakens, the sequence of spin multiplets labelled by the total spin S_t is inverted at $\eta_c \simeq 0.12$, and the ground state changes from a singlet ($S_t = 0$) to a high-spin ($S_t = 4$) state. At finite λ no level crossing occurs, but the nondegenerate ground state

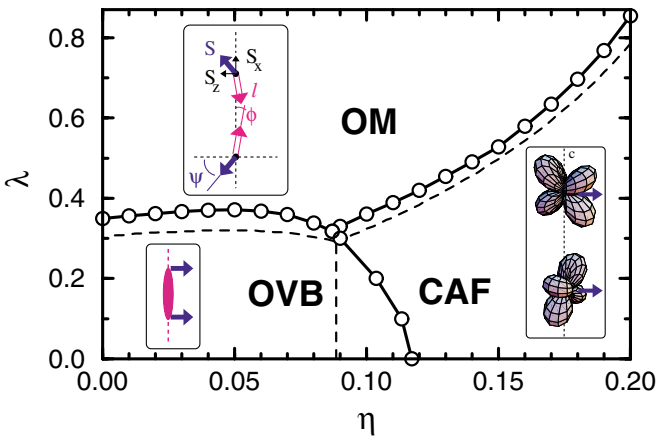

FIG. 1 (color online). Phase diagram of the spin-orbital model at $T = 0$, reflecting the competition between orbital valence bond (OVB), staggered orbitals (C-AF), and orbital moment ordering (OM), as obtained by the ED of a four-site embedded chain for $\phi = 11°$ (circles), and in the MFA (dashed lines). Orbital moments in the OM phase (open arrows) induce spin canting (solid arrows) with angle ψ. (Estimated parameters for YVO_3 are $\eta \simeq 0.12$, $\lambda \sim 0.3$–0.4 [15]).

describes a smooth crossover in the spin and orbital correlations with increasing η. We verified that several excited states lie within $0.1J$ away from the ground state—all of them would contribute to thermal fluctuations already at temperatures $T \simeq 30$ K.

We simulate a *cubic system* by including infinitesimal symmetry-breaking dimerization field which favors the orbital singlets on the bonds (12) and (34) in a cluster with the PBC, embedded within one of three phases stable in the MFA (Fig. 1), with mean fields determined self-consistently in each phase. All phases are characterized by finite magnetic moments $\langle S_i^z \rangle$, either staggered pairwise (OVB phase), or aligned (C-AF phase) along the c axis, and weak $\langle S_i^x \rangle$ moments. In addition, the orbital ordering ($l^z \neq 0$) appears in the OM phase, while the orbitals stagger ($\tau^z \neq 0$) in the C-AF phase.

By computing the energies of different phases, we obtained the phase diagram that confirms the qualitative picture extracted from the MFA (Fig. 1). All transitions are accompanied by reorientation of spins (Figs. 2 and 3). The orbital and spin fluctuations change only weakly at small values of λ, weak $\langle S_i^x \rangle$ moments are ordered pairwise on the bonds (12) and (34), and the spin correlations on the intersinglet bonds are almost classical (Fig. 2). These features show that the spins and orbitals are almost decoupled and the OVB phase is robust. At $\lambda > \lambda_c$ the on-site correlations $\langle S_i^x \tau_i^y \rangle < 0$ dominate, while the orbital fluctuations are suppressed, and the correlation functions $\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1} \rangle$ approach the classical value $-\frac{1}{4}$. As the staggered spin moments $\langle S_i^x \rangle$ are induced, the spin correlations $\langle \vec{S}_i \cdot \vec{S}_{i+1} \rangle$ become soon AF within the OM phase. In this regime the spins follow the spin-orbit coupling λ, and the FM interaction J_c is frustrated.

At the transition from the C-AF to the OM phase the orbital ordering changes from staggered *real orbitals* ($\tau^z \neq 0$) to staggered *orbital moments* ($l^z \neq 0$), as shown in Fig. 3(a). As a precursor effect of the forthcoming OM phase, the orbital moments l_i^z are induced already in the C-AF phase by increasing λ. The transition to the OM phase is accelerated by the increasing tilting angle ϕ [Fig. 3(b)]. Also the spin correlations change here discontinuously at the transition (not shown), similar to the OVB/OM transition [Fig. 2(b)]. The staggered spin components in the OM phase $\langle S_i^x \rangle$ are similarly large to those shown in Fig. 2(c) for smaller η, and the spin canting angle ψ approaches $\frac{\pi}{2} - \phi$ in the regime $\lambda \gg 1$. For realistic parameters for YVO_3: $J \sim 30$ meV [9], $\eta \sim 0.12$ (estimated with $J_H = 0.64$ eV and intraorbital element $U = 5.5$ eV for V^{2+} ions [16]), and $\lambda \sim 0.3$–0.4 (considering $\Lambda \simeq 13$ meV for free V^{3+} ions [17]), one finds a competition between the staggered a/b orbital order parameter ($\tau^z \sim 0.25$) and the orbital magnetic moments ($l^z \sim 0.30$–0.35). This reflects the interplay between intersite SE and on-site spin-orbit couplings, and, hence, orbital and spin moments are not collinear (except for large λ values)—in contrast to the conventional picture where orbital moments induced by λ coupling are antiparallel to spin, as suggested, e.g., for V_2O_3 [18].

Finally, although the C-AF phase cannot dimerize at $T = 0$, we show that it dimerizes at finite temperatures due to the intrinsic instability towards alternating orbital singlets [19]. The spin correlations $\langle \vec{S}_i \cdot \vec{S}_{i+1} \rangle$ [Fig. 4(a)], found using open boundary conditions, alternate between strong and weak FM bonds due to the *orbital Peierls dimerization*, $2\delta_\tau = |\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1} \rangle - \langle \vec{\tau}_i \cdot \vec{\tau}_{i-1} \rangle|$, which has a distinct maximum at $T \simeq 0.24J$ for $\eta = 0.12$.

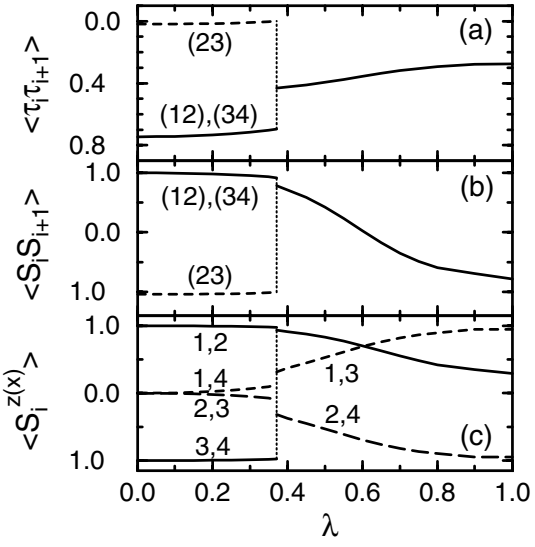

FIG. 2. Pair correlation functions along the c axis: (a) orbital $\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1} \rangle$, (b) spin $\langle \vec{S}_i \cdot \vec{S}_{i+1} \rangle$, and (c) spin components $\langle S_i^z \rangle$ (full lines) and $\langle S_i^x \rangle$ (dashed, long-dashed lines), as functions of λ for the OVB ($\lambda < \lambda_c \simeq 0.37$) and the OM ($\lambda > \lambda_c$) phase, found by the ED at $\eta = 0.07$. FM/AF bonds (ij) in the OVB phase are shown by solid/dashed lines in (a) and (b).

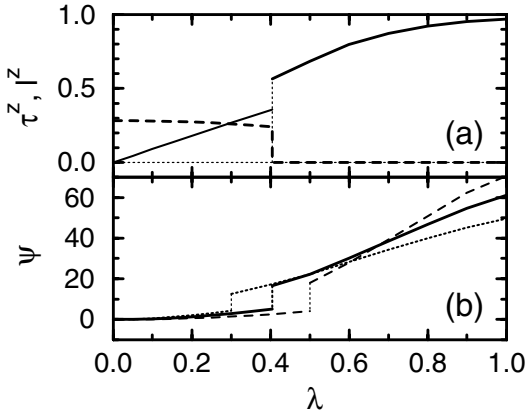

FIG. 3. Crossover from the C-AF to the OM phase for increasing λ at $\eta = 0.12$: (a) orbital order parameters: τ^z (dashed line), and l^z (solid lines) at $\phi = 11°$; (b) spin canting angle $\psi = \arctan(S^x/S^z)$ (see Fig. 1), as obtained for the tilting angle: $\phi = 5°$, $11°$, and $20°$ (dashed, solid, and dotted lines).

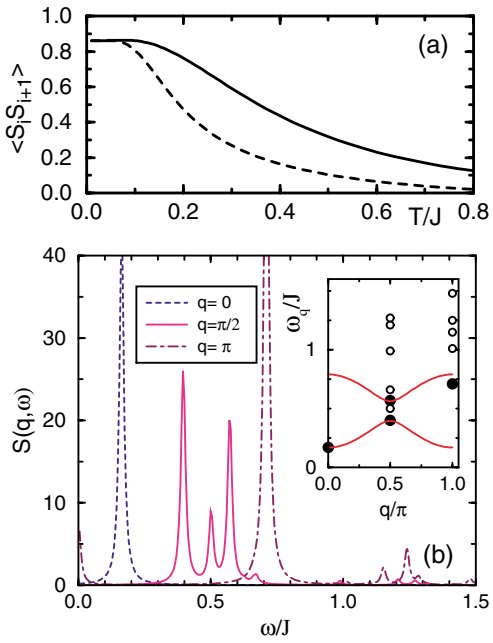

FIG. 4 (color online). Orbital Peierls dimerization in the C-AF phase at $T > 0$: (a) spin-spin correlations $\langle \vec{S}_i \cdot \vec{S}_{i+1} \rangle$ on strong/weak FM bonds (solid/dashed lines); (b) spin response $S(\vec{q}, \omega)$ in the dimerized C-AF phase for $\vec{q} = (0, 0, q)$ with $q = 0, \frac{\pi}{2}, \pi$. Inset: filled (open) circles indicate strong (weak) features in $S(\vec{q}, \omega)$; lines show the fitted spin-wave dispersion for $\eta = 0.12$ and $\lambda = 0.4$.

Consistent with our discussion above, the modulation of $\langle \vec{S}_i \cdot \vec{S}_{i+1} \rangle$ vanishes in the C phase at low T.

Until now, the sole experimental evidence for dimerization of the C phase is the splitting of FM spin waves in the neutron scattering study of Ulrich *et al.* [8]. Figure 4(b) shows the dynamical spin structure factor $S(\vec{q}, \omega)$ [20] obtained by exact diagonalization of a four-site cluster with PBC at $T = 0$, assuming the same orbital dimerization, $\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1} \rangle$, as found above for $T/J = 0.25$. At $\vec{q} = (0, 0, \frac{\pi}{2})$, we observe a splitting of the spin-wave similar to experiment. The finite energy of the $\vec{q} = (0, 0, 0)$ mode results from the Λ term [Eq. (6)] and the mean-field coupling to neighbor chains. Additional features seen in $S(\vec{q}, \omega)$, e.g., for $\vec{q} = (0, 0, \pi)$ at $\omega \sim 1.25J$, we attribute to the coupling to orbital excitations. The spin-wave energies can be fitted by a simple Heisenberg model with two FM coupling constants: $J_{c1} = 5.7$, $J_{c2} = 3.3$ meV, and a small anisotropy term, as shown in the inset (solid lines). Although these values are strongly reduced by spin-orbit coupling [Eq. (6)], they are still larger than those extracted from the spin waves in YVO_3: $J_{c1}^{\rm exp} = 4.0$ and $J_{c2}^{\rm exp} = 2.2$ meV at $T = 85$ K [8]. We attribute this overestimate of exchange interactions to quantum fluctuations involving the occupancy of xy orbitals ($n_{ic} < 1$); this will be treated elsewhere.

In summary, we have shown that the spin-orbit coupling Λ competes with Hund's exchange in the spin-orbital model for cubic vanadates. It leads to a new orbital moment ordered phase at large Λ and can explain qualitatively the spin canting and large reduction of magnetization in the C phase. We argue that transition to the C-AF phase observed in YVO_3 at $T_{N1} \simeq 77$ K [7] emerges from a competition of *quantum effects* due to orbital moment formation at $\Lambda > 0$ and *thermal fluctuations*, which opens the way towards dimerized orbital and spin correlations triggered by the superexchange.

We thank B. Keimer and C. Ulrich for stimulating discussions. This work was supported by the Committee of Scientific Research (KBN), Project No. 5 P03B 055 20.

[1] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998).
[2] K. I. Kugel and D. I. Khomskii, Sov. Phys. Usp. **25**, 231 (1982).
[3] Y. Tokura and N. Nagaosa, Science **288**, 462 (2000).
[4] L. F. Feiner, A. M. Oleś, and J. Zaanen, Phys. Rev. Lett. **78**, 2799 (1997).
[5] B. Keimer *et al.*, Phys. Rev. Lett. **85**, 3946 (2000); G. Khaliullin and S. Maekawa, *ibid.* **85**, 3950 (2000); G. Khaliullin and S. Okamoto, *ibid.* **89**, 167201 (2002).
[6] W. Bao *et al.*, Phys. Rev. Lett. **78**, 507 (1997); Phys. Rev. B **58**, 12727 (1998); L. Paolasini *et al.*, Phys. Rev. Lett. **82**, 4719 (1999).
[7] Y. Ren *et al.*, Phys. Rev. B **62**, 6577 (2000); M. Noguchi *et al.*, *ibid.* **62**, R9271 (2000).
[8] C. Ulrich *et al.*, preceding Letter, Phys. Rev. Lett. **91**, 257202 (2003).
[9] G. Khaliullin, P. Horsch, and A. M. Oleś, Phys. Rev. Lett. **86**, 3879 (2001).
[10] H. Sawada, N. Hamada, K. Terakura, and T. Asada, Phys. Rev. B **53**, 12 742 (1996); H. Sawada and K. Terakura, *ibid.* **58**, 6831 (1998).
[11] G. R. Blake *et al.*, Phys. Rev. Lett. **87**, 245501 (2001).
[12] Spins are AF, so $\hat{J}_{ij}^{(a,b)}$ do not contribute either.
[13] S. Q. Shen, X. C. Xie, and F. C. Zhang, Phys. Rev. Lett. **88**, 027201 (2002).
[14] H. Schulz, Phys. Rev. Lett. **77**, 2790 (1996).
[15] Below $T_{N1} = 77$ K, the C-AF phase of YVO_3 changes to the G-type AF spin structure [7]. As we have argued [9], the G-AF phase is stabilized at low temperature by the JT effect, and the phase transition at T_{N1} is promoted by the larger (spin and orbital) entropy of the C-AF phase.
[16] J. Zaanen and G. A. Sawatzky, J. Solid State Chem. **88**, 8 (1990).
[17] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Oxford University Press, New York, 1970).
[18] A. Tanaka, J. Phys. Soc. Jpn. **71**, 1091 (2002).
[19] Similar to the 1D spin-orbital chain [J. Sirker and G. Khaliullin, Phys. Rev. B **67**, 100408(R) (2003)].
[20] See, e.g., A. Auerbach, *Interacting Electrons and Quantum Magnetism* (Springer, New York, 1994).