MAGNETIC ORDER IN TRANSITION METAL OXIDES WITH ORBITAL DEGREES OF FREEDOM*

Andrzej M. Oleś

Institute of Physics, Jagellonian University,
Reymonta 4, 30-059 Kraków, Poland
e-mail: amoles@if.uj.edu.pl

(Received June 21, 2001)

We investigate the frustrated magnetic interactions in cubic transition metal oxides with orbital degeneracy. The e_g orbitals order easier and their ordering explains the A-type antiferromagnetic phase in $KCuF_3$ and $LaMnO_3$. In t_{2g} systems the magnetic order changes at a transition from an orbital liquid to orbital ordered states. The fluctuations of t_{2g} orbitals play a prominent role in $LaVO_3$ and YVO_3, where they compete with the Jahn-Teller effect and trigger the C-type antiferromagnetic order.

PACS numbers: 75.10.Jm, 71.27.+a, 75.30.Et, 75.30.Vn

1. Spin-orbital physics in transition metal oxides

Large on-site Coulomb interactions $\propto U$ in transition metal oxides suppress charge fluctuations and lead to the (partial) localization of d electrons which consequently interact by effective superexchange interactions. When such localized electrons occupy degenerate orbital states, one has to consider orbital degrees of freedom at equal footing with electron spins [1]. The importance of the orbital degrees of freedom in such systems has been emphasized long ago for cuprates [2] and for V_2O_3 [3], when it was also realized that FerroMagnetic (FM) superexchange could be induced by the Hund's exchange interaction $\propto J_{\rm H}$ [4], but only recently it has been fully appreciated that *orbital physics* leads to several novel and interesting phenomena.

The superexchange which involves the orbital degrees of freedom is described by the so-called spin-orbital models [5], and is typically *highly frustrated* even on a cubic lattice [6]. Although this frustration might even lead to the collapse of magnetic (or orbital) long-range order in the limit of weak

* Presented at the XII School of Modern Physics on Phase Transitions and Critical Phenomena, Lądek Zdrój, Poland, June 21–24, 2001.

$J_{\rm H}$, in real e_g systems it is largely suppressed by $J_{\rm H}/U \simeq 0.12$ [7], where U is the intraorbital interaction, and structural phase transitions stabilize a particular ordering of occupied orbitals, supporting the A-type AntiFerromagnetic (AF) order. Here we show that this happens even in the absence of the Jahn-Teller (JT) effect in the e_g systems with degenerate orbitals filled either by one hole ($KCuF_3$) [8], or by one electron ($LaMnO_3$) [9].

The transition metal oxides with partly filled t_{2g} orbitals are even more fascinating. The quantum phenomena are here more important and stabilize the *coherent orbital liquid* ground state in the spin $S = 1/2$ Mott-insulator $LaTiO_3$ [10], which preserves the cubic symmetry and explains the observed isotropic G-type AF order [11]. In vanadium compounds rather involved spin–orbital models, which describe coexisting AF and FM interaction, were recently introduced for $LiVO_2$ [12] and V_2O_3 [13]. The superexchange is again frustrated in cubic systems, and C-type AF order, observed both in $LaVO_3$ at $T = 0$ [14] and in YVO_3 for $77 < T < 114$ K [15], can be explained as supported by quantum one-dimensional (Q1D) orbital fluctuations [16].

2. Magnetic and orbital order in cuprates and manganites

Conceptually the simplest realistic spin-orbital model can be derived for d^9 ions interacting on a cubic lattice, as in $KCuF_3$. The charge excitations $d_i^9 d_j^9 \rightleftharpoons d_i^8 d_j^{10}$ lead to: one high spin $^3A_2$ state, and two low-spin ^1E and $^1A_1$ states [8]. The energy spectrum in Fig. 1(a) is obtained from the model Hamiltonian which includes the on-site U and $J_{\rm H}$ interactions for degenerate d orbitals [17], and reproduces the exact spectrum [18]. The superexchange

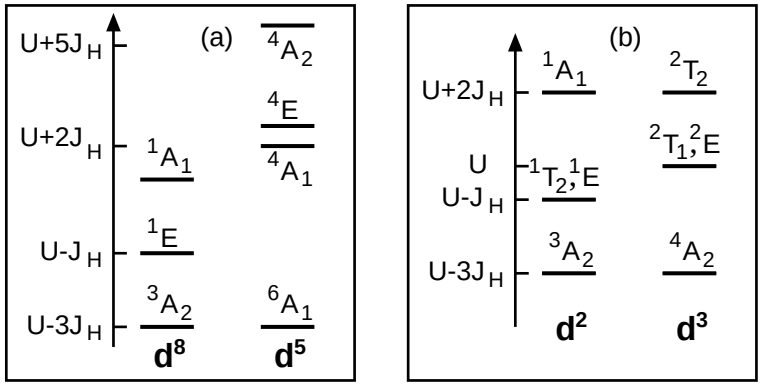

Fig. 1. Excitation spectra in cubic transition metal oxides for: (a) e_g systems: Cu^{3+} (d^8) and Mn^{2+} (d^5) ions; (b) t_{2g} systems: Ti^{2+} (d^2) and V^{2+} (d^3) ions.

is $\propto J_e = t_\sigma^2/U$, where t_σ is the largest hopping element between two $3z^2-r^2$ orbitals along the c axis (note that this is a natural unit for the anisotropic hopping between e_g orbitals [5]), and is given by

$$\mathcal{H}(d^9) = J_e \sum_\gamma \sum_{\langle ij\rangle \| \gamma} \Big[\Big(\vec{S}_i \cdot \vec{S}_j + \tfrac{1}{4} \Big) \hat{J}_{ij}^{(\gamma)}(d^9) + \hat{K}_{ij}^{(\gamma)}(d^9) \Big] , \tag{1}$$

where $\vec{S}_i$ are spin $S=1/2$ operators. The operator expressions:

$$\hat{J}_{ij}^{(\gamma)}(d^9) \;=\; (2+\eta p_2 - \eta p_3)\mathcal{P}_{\langle ij\rangle}^{\zeta\zeta} - \eta(3p_1-p_2)\mathcal{P}_{\langle ij\rangle}^{\zeta\xi} , \tag{2}$$

$$\hat{K}_{ij}^{(\gamma)}(d^9) \;=\; -\Big[1+\frac{\eta}{2}(3p_1+p_2)\Big]\,\mathcal{P}_{\langle ij\rangle}^{\zeta\xi} - \Big[1+\frac{\eta}{2}(p_2-p_3)\Big]\,\mathcal{P}_{\langle ij\rangle}^{\zeta\zeta} , \tag{3}$$

describe spin and orbital superexchange, with $\eta = J_{\rm H}/U$, $p_1 = 1/(1-3\eta)$, $p_2 = 1/(1-\eta)$, and $p_3 = 1/(1+\eta)$. It depends on orbital operators:

$$\mathcal{P}_{\langle ij\rangle}^{\zeta\xi} \;=\; (\tfrac{1}{2}+\tau_i^\gamma)(\tfrac{1}{2}-\tau_j^\gamma) + (\tfrac{1}{2}-\tau_i^\gamma)(\tfrac{1}{2}+\tau_j^\gamma) , \tag{4}$$

$$\mathcal{P}_{\langle ij\rangle}^{\zeta\zeta} \;=\; 2(\tfrac{1}{2}-\tau_i^\gamma)(\tfrac{1}{2}-\tau_j^\gamma) , \tag{5}$$

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

$$\tau_i^{a(b)} = -\frac{1}{4}\sigma_i^z \pm \frac{\sqrt{3}}{4}\sigma_i^x , \qquad \tau_i^c = \frac{1}{2}\sigma_i^z , \tag{6}$$

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

In $LaMnO_3$ the superexchange couples *total spins* $S=2$ at the d^4 Mn^{3+} ions and originates from the charge excitations, $d_i^4 d_j^4 \rightleftharpoons d_i^3 d_j^5$ [9]. The e_g part, following from $d_i^4 d_j^4 \rightleftharpoons d_i^3(t_{2g}^3) d_j^5(t_{2g}^3 e_g^2)$ processes, involves FM terms due to the high-spin ${}^6A_1$ state, and AF terms due to the low-spin states: ${}^4A_1$, ${}^4E$, and ${}^4A_2$ [Fig. 1(a)], and is orbital dependent. By contrast, the t_{2g} part $\propto j_t \simeq 0.09$, which follows from $d_i^4 d_j^4 \rightleftharpoons d_i^3(t_{2g}^3) d_j^5(t_{2g}^4 e_g)$ excitations, is purely AF and nearly orbital independent. Both terms together give

$$\mathcal{H}(d^4) = J_e \sum_\gamma \sum_{\langle ij\rangle \| \gamma} \Big[(\vec{S}_i \cdot \vec{S}_j + 4)\hat{J}_{ij}^{(\gamma)}(d^4) + \hat{K}_{ij}^{(\gamma)}(d^4) \Big] , \tag{7}$$

where the exchange interactions depend on the multiplet structure,

$$\hat{J}_{ij}^{(\gamma)}(d^4) = \frac{1}{8}\Big[1-\frac{4}{3}\eta(q_3+2q_4)\Big]\mathcal{P}_{\langle ij\rangle}^{\zeta\zeta} - \frac{1}{30}\eta\Big(9q_1+\frac{9}{4}q_2+5q_3\Big)\mathcal{P}_{\langle ij\rangle}^{\zeta\xi} + j_t, \quad (8)$$

with $q_1 = 1/(1-3\eta)$, $q_2 = 1/(1+2\eta)$, $q_3 \simeq 1/(1+8\eta/3)$, and $q_4 \simeq 1/(1+16\eta/3)$ [18]. The orbital part $\hat{K}_{ij}^{(\gamma)}(d^4)$ is given in Ref. [9].

Both d^9 model and d^4 model at $j_t = 0$ describe strongly frustrated superexchange in the limit of $J_{\rm H} \to 0$, which takes a universal form,

$$\mathcal{H}_e^{(0)} = J_e \sum_{\gamma} \sum_{\langle ij\rangle\|\gamma} \Big[\Big(\frac{1}{S^2}\vec{S}_i\cdot\vec{S}_j+1\Big)(\tfrac{1}{2}-\tau_i^{\gamma})(\tfrac{1}{2}-\tau_j^{\gamma})-1\Big]. \quad (9)$$

Several classical phases have the same energy of $-3J_e$ per site at this point [6]: the G-AF phases with arbitrary occupation of orbitals, and A-AF phases with $\langle(\frac{1}{2}-\tau_i^{\gamma})(\frac{1}{2}-\tau_j^{\gamma})\rangle = 0$, as obtained for staggered planar orbitals along two cubic directions, *e.g.* for x^2-y^2/y^2-z^2 along a and b axes. The model (9) is qualitatively different from the idealized SU(4)-symmetric case [19] due to the directionality of e_g orbitals.

At finite $J_{\rm H}$ the degeneracy of classical phases is removed, and the A-AF phase is stable, with two-sublattice alternating orbital order in both cuprate (1) and manganite (7) model, $|i\mu\sigma\rangle = \cos\theta_i|iz\sigma\rangle \pm \sin\theta_i|ix\sigma\rangle$, where $\pm$ refers to $i \in A(B)$ sublattice. In the cuprates the orbital order, given by $\cos 2\theta = (1-\eta/2)/(2+3\eta)$, induces FM interactions J_{ab} within the (a,b) planes, and AF interactions J_c between them [5]. The AF interactions

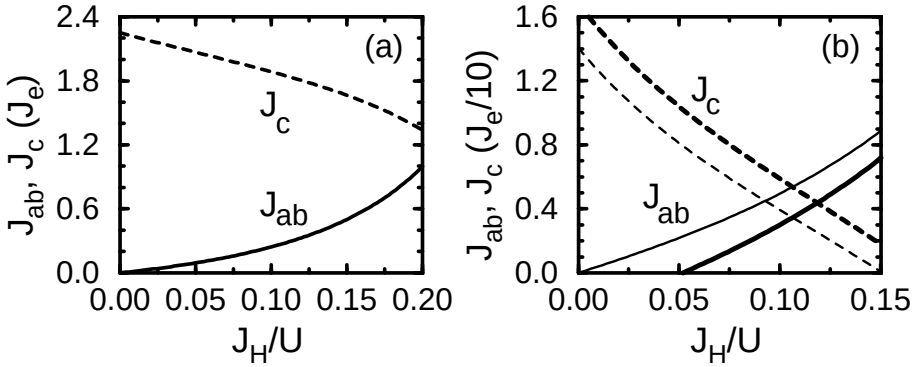

Fig. 2. Exchange constants FM J_{ab} (solid lines) and AF J_c (dashed lines) in A-AF phase of e_g systems as functions of $J_{\rm H}/U$ for: (a) cuprates ($KCuF_3$); (b) manganites ($LaMnO_3$), for: $j_t = 0$ (thin lines) and $j_t = 0.09$ (heavy lines).

determined in mean field decrease with increasing $J_{\rm H}/U$ [Fig. 2(a)], but still dominate at realistic $J_{\rm H}/U \simeq 0.12$ [7], explaining why the excitation spectra of $KCuF_3$ are dominated by Q1D spin excitations of $S = 1/2$ spin chains [20].

Although the orbital order found in the manganite model (7) at $J_{\rm H}/U = 0$ is again $x^2 - z^2/y^2 - z^2$, and the A-AF phase is stable, the situation is here *qualitatively* different as J_{ab} and J_c change much faster with increasing $J_{\rm H}/U$ [Fig. 2(b)], and have similar values in $LaMnO_3$ ($J_{\rm H}/U \simeq 0.117$ [7]), demonstrating the proximity to ferromagnetism which is indeed observed in doped manganites [1,5]. Including the (smaller) t_{2g} interactions one finds a somewhat enhanced tendency towards antiferromagnetism, with the G-AF (A-AF) phase stable for $J_{\rm H}/U < 0.05$ ($J_{\rm H}/U > 0.05$). In order to explain quantitatively the experimental ratio $J_c/J_{ab} \simeq 0.7$ in $LaMnO_3$, one has to include also the JT effect which stabilizes the orbital order closer to $(|x\rangle+|z\rangle)/(|x\rangle-|z\rangle)$ alternation [9]. This modification of the orbital ordering changes not only the effective magnetic interactions, but also considerably reduces the scattering of a hole on spin excitations in $LaMnO_3$ [21].

3. Orbital fluctuations in t_{2g} systems

As in the d^9 case, the excitation spectra of d^2 and d^3 ions in the t_{2g} subspace [18], shown in Fig. 1(b), may be faithfully reproduced with a model Hamiltonian [17] containing only two parameters: U and $J_{\rm H}$, with $J_{\rm H}$ standing now for the Hund's element between two t_{2g} orbitals (which is somewhat smaller than that between two e_g orbitals [18]). As usually, the excitation energy to high-spin ($^3A_2$ and $^4A_2$) states is $U - 3J_{\rm H}$, while the energy of the next (low-spin) excited states is either $U - J_{\rm H}$ for d^2 ions ($^1T_2$, ^1E), or U for d^3 ions ($^2T_1$, ^2E), respectively. The highest excitation energy of $U + 2J_{\rm H}$ is the same for d^2 ($^1T_1$) and d^3 ($^2T_2$) ions.

Each t_{2g} orbital is orthogonal to one of the cubic axes, so we label them as a, b , and c (for instance, xy orbitals are labelled as c). The superexchange interactions $\propto J = 4t^2/U$ follow from the hopping between two orbitals *active along a given direction* γ, for instance between the pairs of a and b orbitals along the c axis. Therefore, it is convenient to define pseudospin operators, $\vec{\tau}_i = \{\tau_i^x, \tau_i^y, \tau_i^z\}$, which act in the subspace spanned by two active orbital flavors [10,16]. For instance, for a bond $\langle ij\rangle \parallel c$, these operators are: $\tau_i^+ = a_i^\dagger b_i$, $\tau_i^- = b_i^\dagger a_i$, $\tau_i^z = \frac{1}{2}(n_{ia} - n_{ib})$, and $n_i^{(c)} = n_{ia} + n_{ib}$, where $\{a_i^\dagger, b_i^\dagger\}$ are Schwinger bosons for a and b orbitals, respectively.

The model for titanates follows from the $d_i^1 d_j^1 \rightleftharpoons d_i^0 d_j^2$ processes,

$$\mathcal{H}(d^1) = J \sum_\gamma \sum_{\langle ij\rangle \parallel \gamma} \Big[\left(\vec{S}_i \cdot \vec{S}_j + \tfrac{1}{4} \right) \hat{J}_{ij}^{(\gamma)}(d^1) + \hat{K}_{ij}^{(\gamma)}(d^1) \Big], \qquad (10)$$

with the exchange constants between $S=1/2$ spins,

$$\begin{aligned}\hat{J}_{ij}^{(\gamma)}(d^1) &= 2\left(\vec{\tau}_i\cdot\vec{\tau}_j+\tfrac{1}{4}n_in_j\right)^{(\gamma)}\\ &+\tfrac{1}{2}\eta\Big[(-3r_1+r_2)(n_{ia}n_{jb}+n_{ib}n_{ja}+n_{ic}+n_{jc}-n_{ic}n_{jc})\\ &+(3r_1+r_2)(\tau_i^+\tau_j^-+\tau_i^-\tau_j^+)+\tfrac{8}{3}(r_2-r_3)\left(\tau_i^z\tau_j^z+\tfrac{1}{4}n_in_j\right)\Big]^{(\gamma)},\end{aligned}\tag{11}$$

depending on: $r_1=1-3\eta$, $r_2=1-\eta$, $r_3=1+2\eta$, while $\hat{K}_{ij}^{(\gamma)}(d^1)$ stands for purely orbital interactions. *A priori,* the magnetic interactions are anisotropic, and may be either AF or FM, depending on the orbital correlations. In the limit of $J_{\rm H}/U=0$ the Hamiltonian (10) takes the form,

$$\mathcal{H}^{(0)}=\tfrac{1}{2}J\sum_{\gamma}\sum_{\langle ij\rangle\|\gamma}\left[\left(\frac{1}{S^2}\vec{S}_i\cdot\vec{S}_j+1\right)\left(\vec{\tau}_i\cdot\vec{\tau}_j+\tfrac{1}{4}n_in_j\right)^{(\gamma)}-\frac{4}{3}S\right],\tag{12}$$

and shows again a strong frustration of superexchange interactions [10]. Although formally it resembles the SU(4)-symmetric spin-orbital models [19] even more than Eq. (9), the pseudospin operators $\vec{\tau}_i$ have here a different meaning and refer to different orbital flavors for each cubic direction γ. One may also notice a certain analogy with the models of valence bond solids [22], but this analogy is again only partial, as the formation of orbital singlets in all directions simultaneously is impossible.

In the Mean Field Approach (MFA) the G-AF phase is degenerate with FM phases, if $\langle\vec{\tau}_i\cdot\vec{\tau}_j+\frac{1}{4}n_in_j\rangle^{(\gamma)}=0$, as realized for alternating orbitals (*e.g.* for staggered a/b orbitals). Such FM states, with anisotropic exchange constants: J_{Fa} and J_{Fc} along a (b) and c axis [Fig. 3(a)], respectively, would be favored classically at finite $J_{\rm H}$. However, the quantum fluctuations take over, remove the anisotropy, and stabilize the *orbital liquid* state, if the JT interactions are weak [10]. Indeed, the spin-wave spectrum of $LaTiO_3$ is nearly isotropic [11], showing that the orbital moments of t_{2g} ions are fully quenched [10]. Increasing $J_{\rm H}$ almost does not change the exchange constants J_{AF} evaluated using the MFA in this state [Fig. 3(a)].

The superexchange interactions between $S=1$ spins in $LaVO_3$ [16],

$$\mathcal{H}\left(d^2\right)=J\sum_{\gamma}\sum_{\langle ij\rangle\|\gamma}\left[\left(\vec{S}_i\cdot\vec{S}_j+1\right)\hat{J}_{ij}^{(\gamma)}\left(d^2\right)+\hat{K}_{ij}^{(\gamma)}\left(d^2\right)\right],\tag{13}$$

follow from the $d_i^2d_j^2\rightleftharpoons d_i^1d_j^3$ processes active on the bonds, with

$$\begin{aligned}\hat{J}_{ij}^{(\gamma)}(d^2) &= \frac{1}{2}\Big[(1+2\eta R)\Big(\vec{\tau}_i\cdot\vec{\tau}_j+\frac{1}{4}n_in_j\Big)\\ &-\eta r\Big(\tau_i^z\tau_j^z+\frac{1}{4}n_in_j\Big)-\frac{1}{2}\eta R(n_i+n_j)\Big]^{(\gamma)},\end{aligned}\tag{14}$$

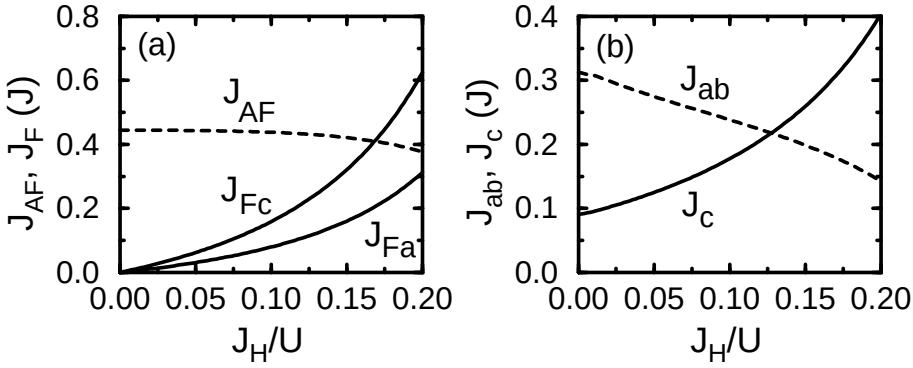

Fig. 3. Exchange constants as functions of $J_{\rm H}/U$ for t_{2g} systems: (a) G-AF ($J_{\rm AF}$, dashed line) and FM (J_{Fa} and J_{Fc}, solid lines) phase in titanates; (b) AF J_{ab} (dashed line) and FM J_c (solid line) for C-AF phase in vanadates ($LaVO_3$).

and the orbital term $\hat{K}_{ij}^{(\gamma)}(d^2)$ given in Ref. [16]. The coefficients $R = 1/(1-3\eta)$ and $r = 1/(1+2\eta)$ follow from the multiplet structure of d^3 ions [Fig. 1(b)]. In the limit of $J_{\rm H} \to 0$ one finds again the frustrated superexchange (12). While the orbital liquid cannot stabilize in this case, orbital singlets may form along the c direction when c orbitals have condensed ($n_{ic} = 1$) and the a and b orbitals fluctuate. This gives a *novel mechanism of ferromagnetic interactions* which operates already in the limit of $J_{\rm H} = 0$ and gets amplified at finite $J_{\rm H}$ [16].

The exchange constants within the (a,b) planes and along the c axis:

$$J_{ab} = \tfrac{1}{4}J\left[1-\eta(R+r)+(1+2\eta R-\eta r)\langle n_{ia}n_{ja}\rangle^{(b)}\right], \quad (15)$$

$$J_c = \tfrac{1}{2}J\left[(1+2\eta R)\left\langle \vec{\tau}_i\cdot\vec{\tau}_j+\tfrac{1}{4}\right\rangle^{(c)} - \eta r\left\langle \tau_i^z\tau_j^z+\tfrac{1}{4}\right\rangle^{(c)} - \eta R\right], \quad (16)$$

are given by orbital correlations. Their values at $\eta = 0$ were obtained from the Bethe Ansatz for a Q1D Heisenberg chain, while the orbital wave spectrum, $\omega_k^{\rm C} = [\Delta^2 + R^2(1-\cos^2 k)]^{1/2}$, with a gap

$$\Delta = \{\eta(R+r)[2R+\eta(R+r)]\}^{1/2}, \quad (17)$$

was used at finite $J_{\rm H}$ [16]. As a result, one finds increasing FM (J_c) and decreasing AF (J_{ab}) exchange constants with increasing $J_{\rm H}$ [Fig. 3(b)], and both interactions have similar values in $LaVO_3$ at $J_{\rm H}/U \simeq 0.15$ [7].

While the cubic structure of $LaVO_3$ is almost undistorted [14], YVO_3 has a distorted structure, and a and b orbitals stagger in the (a,b) planes and repeat themselves along the c axis [15]. Such ordering can be promoted by the JT effect term which lowers the energy by $-2V$ on the bonds along

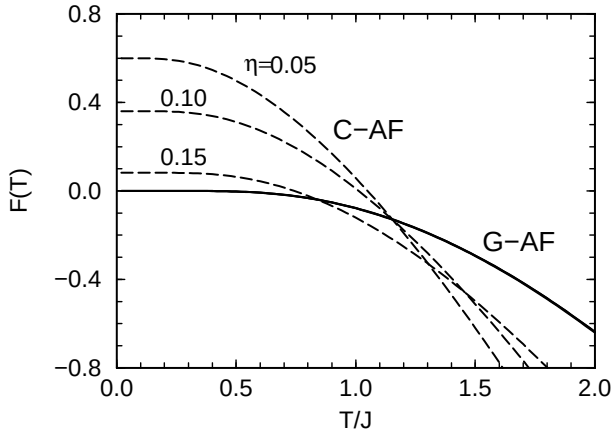

Fig. 4. Free energies $F(T) = \langle \mathcal{H}(d^2) \rangle - T\mathcal{S}$ (in units of J) of: G-AF phase obtained with the JT interaction $V = 0.65J$ (solid line), and C-AF phase for $\eta = 0.05$, 0.10 and 0.15 (dashed lines), as functions of temperature T/J (after Ref. [16]).

the c axis when a (b) orbitals are repeated in the C-type orbital ordered state [16]. Finite $V > 0$ lowers the energy of the G-phase, but the entropy $\mathcal{S}$ determined by orbital excitations increases faster in the C-phase, and thus induces a transition from G-AF to C-AF order around $T^* \simeq 0.8J$ (Fig. 4), reproducing qualitatively the first order transition observed in YVO_3 [15].

4. Summary and open problems

In summary, the transition metal oxides with orbital degrees of freedom show a very fascinating behavior, with various types of magnetic and *orbital order*. While e_g orbitals usually order and explain A-AF phases, further stabilized by the JT effect, the t_{2g} orbitals have a generic tendency towards disorder, which leads to the orbital liquid in the isotropic G-AF phase in $LaTiO_3$. In cubic vanadates the JT interactions compete with the *orbital disorder*, and the Q1D orbital fluctuations stabilize the C-AF phase in $LaVO_3$, and also in YVO_3 at finite temperatures. A better understanding of these fluctuations is required to explain quantitatively the observed phase transitions and the strong reduction of the magnetic order parameter in $LaVO_3$ and YVO_3. This problem is as urgent as the theoretical understanding of the colossal magnetoresistance in the manganites.

It is a pleasure to thank Lou-Fe' Feiner, Peter Horsch, Giniyat Khaliullin, and Jan Zaanen for a friendly collaboration on this subject and for numerous stimulating discussions. This work was supported by the Polish State Committee for Scientific Research (KBN), Project no. 5 P03B 055 20.

REFERENCES

[1] Y. Tokura, N. Nagaosa, *Science* **288**, 462 (2000).

[2] K.I. Kugel, D.I. Khomskii, *Usp. Fiz. Nauk* **136**, 621 (1982) [*Sov. Phys. Usp.* **25**, 231 (1982)].

[3] C. Castellani, C.R. Natoli, J. Ranninger, *Phys. Rev.* **B18**, 4945, 4967, 5001 (1978).

[4] M. Cyrot, C. Lyon-Caen, *J. Phys.* **36**, 253 (1975); S. Inagaki, *J. Phys. Soc. Jpn.* **39**, 596 (1975); J. Spałek, K.A. Chao, *J. Phys. C* **13**, 5241 (1980).

[5] A.M. Oleś, M. Cuoco, N.B. Perkins, in: *Lectures on the Physics of Highly Correlated Electron Systems IV*, ed. F. Mancini, AIP Conference Proceedings Vol. 527, New York 2000.

[6] L.F. Feiner, A.M. Oleś, J. Zaanen, *Phys. Rev. Lett.* **78**, 2799 (1997).

[7] T. Mizokawa, A. Fujimori, *Phys. Rev.* **B54**, 5368 (1996).

[8] A.M. Oleś, L.F. Feiner, J. Zaanen, *Phys. Rev.* **B61**, 6257 (2000).

[9] L.F. Feiner, A.M. Oleś, *Phys. Rev.* **B59**, 3295 (1999).

[10] G. Khaliullin, S. Maekawa, *Phys. Rev. Lett.* **85**, 3950 (2000).

[11] B. Keimer, D. Casa, A. Ivanov, J.W. Lynn, M.v. Zimmermann, J.P. Hill, D. Gibbs, Y. Taguchi, Y. Tokura, *Phys. Rev. Lett.* **85**, 3946 (2000).

[12] H.F. Pen, J. van den Brink, D.I. Khomskii, G.A. Sawatzky, *Phys. Rev. Lett.* **78**, 1323 (1997).

[13] F. Mila, R. Shiina, F.-C. Zhang, A. Joshi, M. Ma, V.I. Anisimov, T.M. Rice, *Phys. Rev. Lett.* **85**, 1714 (2000); R. Shiina, F. Mila, F.-C. Zhang, T.M. Rice, *Phys. Rev.* **B63**, 144422 (2001); S. Di Matteo, N.B. Perkins, C.R. Natoli, `cond-mat/0107026` (unpublished).

[14] S. Miyasaka, T. Okuda, Y. Tokura, *Phys. Rev. Lett.* **85**, 5388 (2000).

[15] Y. Ren, T.T.M. Palstra, D.I. Khomskii, A.A. Nugroho, A.A. Menovsky, G.A. Sawatzky, *Phys. Rev.* **B62**, 6577 (2000); M. Noguchi, A. Nakazawa, S. Oka, T. Arima, Y. Wakabayashi, H. Nakao, Y. Murakami, *Phys. Rev.* **B62**, R9271 (2000).

[16] G. Khaliullin, P. Horsch, A.M. Oleś, *Phys. Rev. Lett.* **86**, 3879 (2001).

[17] A.M. Oleś, *Phys. Rev.* **B28**, 327 (1983).

[18] J.S. Griffith, *The Theory of Transition Metal Ions*, Cambridge University Press, Cambridge 1971.

[19] Y.Q. Li, M. Ma, D.N. Shi, F.-C. Zhang, *Phys. Rev. Lett.* **81**, 3527 (1998); B. Frischmuth, F. Mila, M. Troyer, *Phys. Rev. Lett.* **82**, 835 (1999); F. Mila, B. Frischmuth, A. Deppeler, M. Troyer, *Phys. Rev. Lett.* **82**, 3697 (1999); G.-M. Zhang, S.-Q. Shen, *Phys. Rev. Lett.* **87**, 157201 (2001).

[20] B. Lake, D.A. Tennant, S.E. Nagler, *Phys. Rev. Lett.* **85**, 832 (2000).

[21] J. Bała, G.A. Sawatzky, A.M. Oleś, A. Macridin, *Phys. Rev. Lett.* **87**, 067204 (2001).

[22] I. Affleck, T. Kennedy, E.H. Lieb, H. Tasaki, *Phys. Rev. Lett.* **59**, 799 (1987).