MAGNETIC ORDER IN TRANSITION METAL OXIDES WITH ORBITAL DEGREES OF FREEDOM

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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.

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 interact by the 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$_2$O$_3$ [3], when it was also realized that ferromagnetic (FM) superexchange could be induced by the Hund’s exchange interaction $\propto J_H$ [4], but only recently it has been fully appreciated that the 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 $\propto J_H$, in real $e_g$ systems it is largely suppressed by $J_H/U \simeq 0.12$ [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

(1)
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$_2$O$_3$ [13]. The superexchange is again frustrated in cubic systems, and C-type of AF order, observed both in LaVO$_3$ and $T = 0$ [14] and in YVO$_3$ $77 < T < 114$ 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 $d^9_{i}d^9_{j} \rightarrow d^8_{i}d^{10}_{j}$ 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 $J_H$ interactions for degenerate $d$ orbitals [17], and reproduces the exact spectrum [18]. The superexchange is $\propto J_e = t_\sigma^2/U$, where $t_\sigma$ 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

$$\mathcal{H}(d^9) = J \sum_{\gamma} \sum_{\langle ij \rangle |\gamma|} \left[ (\vec{S}_i \cdot \vec{S}_j + S^2) \hat{J}_{ij}^{(\gamma)}(d^9) + \hat{K}_{ij}^{(\gamma)}(d^9) \right], \quad (1)$$

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

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

$$\hat{K}_{ij}^{(\gamma)}(d^9) = -[1 + \eta(3p_1 + p_2)/2] P^{\zeta\zeta}_{ij} - [1 + \eta(p_2 - p_3)/2] P^{\zeta\zeta}_{ij}, \quad (3)$$

describe spins and orbital superexchange, with $\eta = J_H/U$, $p_1 = 1/(1 - 3\eta)$, $p_2 = 1/(1 - \eta)$, and $p_3 = 1/(1 + \eta)$. They depend on orbital operators:

$$P^{\zeta\xi}_{ij} = (1/2 + \tau^\gamma_i)(1/2 - \tau^\gamma_j) + (1/2 - \tau^\gamma_i)(1/2 + \tau^\gamma_j), \quad (4)$$

$$P^{\zeta\zeta}_{ij} = 2(1/2 - \tau^\gamma_i)(1/2 - \tau^\gamma_j), \quad (5)$$

which project on the orbital states, being either parallel to the bond $\langle ij \rangle$ direction on one site ($P_{ij\zeta} = 1/2 - \tau^\gamma_i$) and perpendicular on the other ($P_{ij\xi} = 1/2 + \tau^\gamma_i$).
\[\tau_i^{a(b)} = (-\sigma_i^z \pm \sqrt{3}\sigma_i^x)/4, \quad \tau_i^c = \sigma_i^z/2,\]

where the \(\sigma_i^s\)'s are Pauli matrices acting on: \(|x\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |z\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix},\)

which transform as \(|x\rangle \propto x^2 - y^2\) and \(|z\rangle \propto (3z^2 - r^2)/\sqrt{3}\).

The superexchange in LaMnO\(_3\) couples total spins \(S = 2\) at the \(d^4\) Mn\(^{3+}\) ions and originates from the charge excitations, \(d_i^4d_j^4 \rightleftharpoons d_i^3d_j^5\) [9]. The \(e_g\) part, following from \(d_i^4d_j^3 \rightleftharpoons d_i^3(t_{2g}^3)d_j^5(t_{2g}^3e_g^2)\) 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)], is orbital dependent. By contrast, the \(t_{2g}\) part \(\propto j_t \simeq 0.09\), which follows from \(d_i^4d_j^1 \rightleftharpoons d_i^3(t_{2g}^3d_j^5(t_{2g}e_g)\) excitations, is purely AF and orbital independent. Both terms give

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

where the exchange interactions depend on the multiplet structure,

\[\mathcal{J}_{ij}^{(\gamma)}(d^4) = 2\left[1 - 4/3\eta(q_3 + 2q_4)\right] \mathcal{P}_{ij}^{(\gamma)} - 2/15\eta(36q_1 + 9q_2 + 20q_3) \mathcal{P}_{ij}^{(\gamma)} + j_t,\]

with \(q_1 = 1/(1 - 3\eta), \quad q_2 = 1/(1 + 2\eta), \quad q_3 \simeq 1/(1 + 8\eta/3),^3\) and \(q_4 \simeq 1/(1 + 16\eta/3)\) [18]. The orbital part \(\hat{\mathcal{K}}_{ij}^{(\gamma)}(d^4)\) 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 \(J_H \rightarrow 0\), which takes a universal form,

\[\mathcal{H}_e^{(0)} = J_e \sum_{\gamma} \sum_{\langle ij \rangle |\gamma|} \left[ (\vec{S}_i \cdot \vec{S}_j/S^2 + 1)(1/2 - \tau_i^\gamma)(1/2 - \tau_j^\gamma) - 1 \right].\]

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 \(\langle (1/2 - \tau_i^\gamma)(1/2 - \tau_j^\gamma) \rangle = 0\), as obtained for staggered planar orbitals, e.g. for \(x^2 - y^2/g^2 - z^2\). The model (9) is qualitatively different from the idealized SU(4)-symmetric case [19] due to the directionality of \(e_g\) orbitals.

At finite \(J_H\) 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, \(|i\mu\sigma\rangle = \cos \theta_i |i\sigma\rangle \pm \sin \theta_i |ix\sigma\rangle\), 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 decrease with
increasing $J_H/U$ [Fig. 2(a)], but still dominate at realistic $J_H/U \simeq 0.12$ [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 $J_H/U = 0$ 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 $J_H/U$ [Fig. 2(b)], and have similar values in LaMnO$_3$ ($J_H/U \simeq 0.117$ [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 $J_H/U < 0.05$ ($J_H/U > 0.05$). 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 $|\langle x \rangle + |z \rangle/|\langle x \rangle - |z \rangle|$ 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 $d^5$ 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 $J_H$, with $J_H$ standing now for the Hund’s element between two $t_{2g}$ orbitals. As usually, the excitation energy to high-spin ($^3A_2$ and $^4A_2$) states is $U - 3J_H$, while the energy of the next (low-spin) excited states is either $U - J_H$ for $d^2$ ions ($^1T_2$, $^1E$), or $U$ for $d^3$ ions ($^2T_1$, $^2E$), respectively. The highest excitation energy of $U + 2J_H$ 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 $\gamma$, for instance between the pairs of $a$ and $b$ orbitals along the $c$ axis. Therefore, it is convenient to define pseudospin operators, $\tilde{\tau} = \{\tilde{\tau}^x, \tilde{\tau}^y, \tilde{\tau}^z\}$, which act in the subspace spanned by two active orbital flavors [10, 16]. For instance, for a bond $\langle ij \rangle || c$, these operators are: $\tilde{\tau}^x = a_i^\dag b_i$, $\tilde{\tau}^y = b_i^\dag a_i$, $\tilde{\tau}^z = \frac{1}{2}(n_{ia} - n_{ib})$, and $n_i^{(c)} = n_{ia} + n_{ib}$, where $\{a_i, b_i\}$ are Schwinger bosons for $a$ and $b$ orbitals.

The model for titanates follows from the $d_i^\dag d_j^\dag \equiv d_i^0 d_j^0$ processes,

$$\mathcal{H}(d^1) = J \sum_{\gamma} \sum_{\langle ij \rangle \parallel \gamma} \left[ (\vec{S}_i \cdot \vec{S}_j + S^2) \tilde{J}_{ij}^{(\gamma)}(d^1) + \tilde{K}_{ij}^{(\gamma)}(d^1) \right], \quad (10)$$
with the exchange constants between $S = 1/2$ spins,

\[
\hat{J}_{ij}^{(\gamma)} = 2(\vec{\tau}_i \cdot \vec{\tau}_j + n_i n_j / 4) + \eta((-3r_1 + r_2)(n_{ja}n_{jb} + n_{ib}n_{ja} + n_{ic} + n_{jc} - n_{ic}n_{jc})
+ 3r_1 + r_2)(\tau_1^+ \tau_2^- + \tau_1^- \tau_2^+)) + 4(r_2 - r_3)(n_{ia}n_{ja} + n_{ib}n_{jb})/3)/2,
\]

(11)

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

\[
\mathcal{H}^{(0)} = (J/2) \sum_{\gamma} \sum_{(ij)\|\gamma} [(\vec{S}_i \cdot \vec{S}_j / S^2 + 1)(\vec{\tau}_i \cdot \vec{\tau}_j + n_i n_j / 4) - 4S/3],
\]

(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 $\gamma$. 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 $\langle \vec{\tau}_i \cdot \vec{\tau}_j + 4n_i n_j \rangle = 0$, 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 $J_H$. On the contrary, the quantum fluctuations take over, remove the anisotropy, and stabilize the \textit{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 $J_H$ 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],

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

(13)

follow from the $d_i^dd_j^d \rightleftharpoons d_i^ad_j^a$ processes active on the bonds, with

\[
\hat{J}_{ij}^{(\gamma)} = \frac{1}{2} \left[(1 + 2\eta R)(\vec{\tau}_i \cdot \vec{\tau}_j + 1/4 n_i n_j) - \eta (\tau_1^+ \tau_2^- + \tau_1^- \tau_2^+) - \frac{1}{2} \eta R(n_i + n_j)\right]^{(\gamma)},
\]

(14)

and the orbital term $\hat{K}_{ij}^{(\gamma)}$ 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 $J_H \rightarrow 0$ 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 $J_H = 0$ [16].

The exchange constants within $(a, b)$ planes ($J_{ab}$) and along $c$ axis ($J_c$):

$$J_{ab} = [1 - \eta(R+r) + (1 + 2\eta R - \eta r)\langle n_{ia} n_{ja}\rangle^{(b)}]/4,$$

$$J_c = [(1 + 2\eta R)(\vec{\tau}_i \cdot \vec{\tau}_j + 1/4)^{(c)} - \eta r(\tau^z_i \tau^z_j + 1/4)^{(c)} - \eta R]/2,$$

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, $\omega_k^C = [\Delta^2 + R^2(1 - \cos^2 k)]^{1/2}$, with a gap $\Delta = \{\eta(R + r)[2R + \eta(R + r)]\}^{1/2}$, was used at finite $J_H$. As a result, one finds increasing FM ($J_c$) and decreasing AF ($J_{ab}$) exchange constants with increasing $J_H$ [Fig. 3(b)], and both interactions have similar values at $J_H/U \simeq 0.15$ [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 $(a, b)$ planes and
repeated themselves along $c$ axis [15]. Such ordering can be promoted by
the JT effect term which lowers the energy by $-2V$ on the bonds along
the $c$ axis when $a$ ($b$) orbitals are repeated in $C$-type orbital ordered state
[16]. Finite $V > 0$ lowers the energy of the $G$-phase, but the entropy $S$
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.

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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 (1978); B18, 4967 (1978); B18, 5001 (1978).

[4] M. Cyrot, C. Lyon-Caen, J. Phys. 36, 253 (1975); S. Inagaki, J. Phys. Soc. Jpn. 39, 596 (1975); J. Spalek, 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, edited by F. Mancini, AIP Conference Proceedings Vol. 527 (New York, 2000), p. 226.

[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] 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).

[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).

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

[21] J. Bala, 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).
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.

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 $J_H/U$ for: (a) cuprates (KCuF$_3$); (b) manganites (LaMnO$_3$), for: $j_t = 0$ (thin lines) and $j_t = 0.09$ (heavy lines).

Fig. 3. Exchange constants as functions of $J_H/U$ for $t_{2g}$ systems: (a) G-AF ($J_{AF}$, 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) C-AF phase in vanadates (LaVO$_3$).

Fig. 4. Free energies $F(T) = \langle H(d^2) \rangle - TS$ (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]).
$F(T)$ vs $T/J$ for different values of $\eta$ and $\text{C-AF}$ and $\text{G-AF}$.