Spin Order due to Orbital Fluctuations: Cubic Vanadates

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We investigate the highly frustrated spin and orbital superexchange interactions in cubic vanadates. The fluctuations of t_{2g} orbitals trigger a novel mechanism of ferromagnetic interactions between spins $S = 1$ of V^{3+} ions along one of the cubic directions which operates already in the absence of Hund's rule exchange J_H, and leads to the C-type antiferromagnetic phase in $LaVO_3$. The Jahn-Teller effect can stabilize the orbital ordering and the G-type antiferromagnetic phase at low temperatures, but large entropy due to orbital fluctuations favors again the C phase at higher temperatures, as observed in YVO_3.

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Large Coulomb interactions play a crucial role in transition metal oxides, and are responsible for the collective behavior of strongly correlated d electrons which localize in Mott-Hubbard (or charge-transfer) insulators [1]. Such localized electrons may occupy degenerate orbital states which make it necessary to consider orbital degrees of freedom on equal footing with electron spins, and leads to the effective (superexchange) spin-orbital models to describe the low-energy physics [2–4]. A remarkable feature of these models is that the superexchange interaction is *highly frustrated* on a cubic lattice, which was recognized as the origin of novel quantum effects in transition metal oxides [5]. In case of e_g orbital systems this frustration is likely removed by orbital order due to the order-out-of-disorder mechanism, which maximizes the energy gain from quantum spin fluctuations [6]. Moreover, quantum effects among e_g orbitals are largely suppressed by the Jahn-Teller (JT) effect in real systems, which together with superexchange often leads to structural phase transitions accompanied by a certain ordering of occupied orbitals, supporting particular magnetic structures. Some well-known examples are systems with degenerate e_g orbitals filled either by one hole ($KCuF_3$), or by one electron ($LaMnO_3$), which order antiferromagnetically well below the structural transition.

The transition metal oxides with partly filled t_{2g} orbitals exhibit different and more interesting phenomena. This occurs due to the relative weakness of the JT coupling in this case, and due to the higher degeneracy and additional symmetry of t_{2g} orbitals [7]. As a result, the orbitals may form the *coherent orbital-liquid* ground state stabilized by quantum effects, as observed in the spin $s = 1/2$ Mott insulator $LaTiO_3$ [8]. It is puzzling what happens when the t_{2g} orbitals are filled by two electrons, as in vanadium oxides. On one hand, the occupied t_{2g} orbitals are known to order in noncubic vanadium compounds, such as $LiVO_2$ [9] and V_2O_3 [10]. In fact, the first spin-orbital model for V_2O_3 with spins $s = 1/2$ was proposed over twenty years ago [11], but later it was realized that the Hund's exchange J_H is large [12], and the relevant model has to involve $S = 1$ spins [10]. On the other hand, the situation in cubic systems might be very different as all the bonds are *a priori* magnetically equivalent, and quantum fluctuations among orbitals are expected to play an important role in this case.

In this Letter we derive and investigate the spin-orbital model for cubic vanadates: $LaVO_3$ and YVO_3. The magnetic order in $LaVO_3$ is C type [ferromagnetic chains along the c axis which stagger within (a, b) planes], with the Néel temperature $T_N \simeq 140$ K [13,14], while it is staggered in all three directions (G type) in YVO_3 at $T < 77$ K and C type at higher temperatures $77 < T < 114$ K [14–16]. The C phase is particularly surprising as arising from a practically undistorted structure of $LaVO_3$ at $T > T_N$ [14]. Recent Hartree-Fock studies have shown that indeed C and G phases are energetically close [17]. In order to understand the microscopic origin of their competition we consider the regime of large U, and address the following questions: (i) can the superexchange interactions *alone* explain why the ferromagnetic (FM) and antiferromagnetic (AF) interactions coexist in $LaVO_3$ in spite of a practically ideal cubic structure at $T > T_N$ with almost equal V–V bonds; (ii) why the structural transition in $LaVO_3$ occurs only *below* the magnetic transition; and (iii) why is the G-type AF order stable in the low-temperature phase of YVO_3, while the C-type order *wins* at higher temperatures?

We start with a Mott-insulator picture of cubic vanadites, consistent with the large value of an on-site intraorbital Coulomb element $U \simeq 4.5$ eV [12], and with the results of electronic-structure calculations [18]. Because of the Hund's coupling $J_H \simeq 0.68$ eV [12] the V^{3+} ions are in triplet configuration ${}^3T_2$. Each t_{2g} orbital is orthogonal to one cubic axis. For instance, yz is orthogonal to the a axis and will be labeled as a, while zx and xy will be labeled as b and c, respectively. The electron densities at V^{3+} ions satisfy a local constraint, $n_{ia} + n_{ib} + n_{ic} = 2$.

The superexchange interactions between $S = 1$ spins arise from the virtual excitations $d_i^2 d_j^2 \rightarrow d_i^3 d_j^1$ on a given bond $\langle ij \rangle$, with the hopping t allowed only between *two out of three* t_{2g} orbitals. The d_i^3 excited state may be either a high-spin ${}^4A_2$ state, or one of three low-spin states: ${}^2E$, ${}^2T_1$, or ${}^2T_2$ [19]. When the second order processes

$d_i^2 d_j^2 \rightarrow d_i^3 d_j^1 \rightarrow d_i^2 d_j^2$ are analyzed, one has to project the d_i^3 (d_i^2) configuration generated after an individual hopping process on the above d_i^3 eigenstates ($^3T_2$ ground state). This leads to the spin-orbital Hamiltonian,

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

where the orbital operators $\hat{J}_{ij}^{(\gamma)}$ and $\hat{K}_{ij}^{(\gamma)}$ follow from the processes active on the bond $\langle ij \rangle \parallel \gamma$, where $\gamma = a, b, c$:

$$\begin{aligned} \hat{J}_{ij}^{(\gamma)} &= \tfrac{1}{2}[(1 + 2\eta R)(\vec{\tau}_i \cdot \vec{\tau}_j + \tfrac{1}{4} n_i n_j) \\ &\quad - \eta r(\tau_i^z \tau_j^z + \tfrac{1}{4} n_i n_j) - \tfrac{1}{2}\eta R(n_i + n_j)]^{(\gamma)}, \qquad (2) \\ \hat{K}_{ij}^{(\gamma)} &= [\eta R(\vec{\tau}_i \cdot \vec{\tau}_j + \tfrac{1}{4} n_i n_j) + \eta r(\tau_i^z \tau_j^z + \tfrac{1}{4} n_i n_j) \\ &\quad - \tfrac{1}{4}(1 + \eta R)(n_i + n_j)]^{(\gamma)}, \qquad (3) \end{aligned}$$

and $J = 4t^2/U$. The coefficients $R = 1/(1 - 3\eta)$ and $r = 1/(1 + 2\eta)$ originate from the multiplet structure of the t_{2g}^3 excited states via $\eta = J_H/U$ [19]. The operators $\vec{\tau}_i = \{\tau_i^x, \tau_i^y, \tau_i^z\}$ are defined in the orbital pseudospin subspace spanned by two orbital flavors which are *active along a given direction* γ. For instance, for a bond $\langle ij \rangle \parallel c$, the interactions follow from the electron hopping between the pairs of a and b orbitals, and may be expressed by Schwinger bosons: $\tau_i^+ = a_i^\dagger b_i$, $\tau_i^- = b_i^\dagger a_i$, $\tau_i^z = \frac{1}{2}(n_{ia} - n_{ib})$, and $n_i^{(c)} = n_{ia} + n_{ib}$, and therefore

$$\begin{aligned} 2(\vec{\tau}_i \cdot \vec{\tau}_j + \tfrac{1}{4} n_i n_j)^{(c)} &= (n_{ia} n_{ja} + a_i^\dagger b_i b_j^\dagger a_j) \\ &\quad + (a \leftrightarrow b), \qquad (4) \\ 2(\tau_i^z \tau_j^z + \tfrac{1}{4} n_i n_j)^{(c)} &= n_{ia} n_{ja} + n_{ib} n_{jb}. \end{aligned}$$

Consider first the interactions in the $J_H \rightarrow 0$ limit:

$$\mathcal{H}_0 = \tfrac{1}{2} J \sum_{\gamma} \sum_{\langle ij \rangle \parallel \gamma} (\vec{S}_i \cdot \vec{S}_j + 1)(\vec{\tau}_i \cdot \vec{\tau}_j + \tfrac{1}{4} n_i n_j)^{(\gamma)}, \qquad (5)$$

where a constant energy of $-2J$ per V^{3+} ion is neglected. It is straightforward to understand why the interactions in this limit turn out to have the same structure as in $LaTiO_3$ [7], where for $s = 1/2$ spins of Ti^{3+} ions one finds instead $(\vec{s}_i \cdot \vec{s}_j + \frac{1}{4})$. In fact, the spin interactions follow entirely from the *Pauli principle,* as the terms $\propto \vec{S}_i \cdot \vec{S}_j$ due to the high-spin $^4A_2$ and low-spin ^2E states, which involve $d^3\{abc\}$ configurations, cancel each other.

A remarkable feature of the t_{2g} superexchange in Eq. (5) is that every bond is represented by two equivalent orbitals giving a SU(2) symmetric $\propto (\vec{\tau}_i \cdot \vec{\tau}_j + \frac{1}{4} n_i n_j)^{(\gamma)}$ structure of the orbital part. Depending on the type of orbital correlations this may result in a spin coupling constant of either sign. This important property resembles that of one-dimensional (1D) SU(4) model [20]. The present problem is however more involved since there are *three t_{2g} flavors* in a cubic crystal, and SU(2) orbital correlations among two of them along a particular direction will necessarily frustrate those correlations in other directions. One may also notice a certain analogy with the models of valence bond solids [21]: Actually, a large orbital moment $L = 1$ of t_{2g} states is formally decomposed in Eq. (5) onto pseudospins one-half, active on different bonds. The analogy is again only partial since independent rotations within orbital doublets active on different bonds are not allowed here by construction, and thus the formation of orbital singlets in all directions simultaneously is impossible.

Another key observation is the difference between the interactions derived for the pairs of Ti^{3+} and V^{3+} ions: In the d^1 configuration spin $s = 1/2$ is small, and the idea of composite spin-orbital resonance, in analogy to SU(4) excitations [20], helped to resolve the orbital frustration problem [7]. In that case the superexchange is best optimized by the spin-orbital resonance in all three directions, and the orbitals form a three-dimensional quantum liquid which coexists with weak spin order of the G type. This mechanism is however suppressed in the present case of large spin $S = 1$ at d^2 ions, and the quantum energy can be gained mainly from the orbital sector. This suggests that a particular *classical spin configuration* may be picked up which maximizes the energy gain from *orbital fluctuations.* Indeed, orbital singlets (with $n_{ia} + n_{ib} = 1$) may form on the bonds parallel to the c axis, exploiting fully the SU(2) symmetry of the orbital interactions in one direction, while the second electron occupies the third t_{2g} orbital ($n_{ic} = 1$), controlling spin interactions in the (a, b) planes.

In order to understand why orbital fluctuations support the C-AF–type spin order, it is instructive to start with a single bond along the c axis. A crucial observation is that the lowest energy of $-J/2$ is obtained when the spins are *ferromagnetic,* and the orbitals a and b form a singlet, with $\langle \vec{\tau}_i \cdot \vec{\tau}_j \rangle^{(c)} = -\frac{3}{4}$ [22]. Thus, one finds a *novel mechanism of ferromagnetic interactions* which operates due to local fluctuations of a and b orbitals. At the same time, the orbital resonance on the bonds in (a, b) planes is blocked, as $n_{ic} = n_{jc} = 1$, and the superexchange is AF due to the excitations to $^2T_1$ and $^2T_2$ states with doubly occupied c orbitals. Such an electron distribution and the formation of quasi-1D orbital pseudospin chains support FM spin order along the c axis in the C phase, and could be stable only at low temperature when a coherent spin state breaking the cubic symmetry is formed as well. The onset of the magnetic order which coexists with such orbital fluctuations explains also why a structural transition is here *induced* by this coherent electronic state.

We compared the ground state energies of the C and G phases using the spin-wave theory for the spin part, while either the exact Bethe ansatz result or the Gaussian fluctuations around the ordered state were used for the orbital part. The exchange constants within (a, b) planes ($J_{ab} > 0$) and along the c axis ($J_c < 0$) determine the spin waves. They follow from Eqs. (1)–(3) (in units of J):

$$\begin{aligned} J_c &= \tfrac{1}{2}[(1 + 2\eta R)\langle \vec{\tau}_i \cdot \vec{\tau}_j + \tfrac{1}{4} \rangle^{(c)} \\ &\quad - \eta r \langle \tau_i^z \tau_j^z + \tfrac{1}{4} \rangle^{(c)} - \eta R], \\ J_{ab} &= \tfrac{1}{4}[1 - \eta(R + r) + (1 + 2\eta R - \eta r) \\ &\quad \times \langle n_{ia} n_{ja} \rangle^{(b)}], \end{aligned} \qquad (6)$$

and are given by orbital correlations. Their values at $\eta = 0$ are easily obtained from the Bethe ansatz result for a 1D Heisenberg chain of disordered a and b orbitals (in this case $\langle n_{ia} n_{ja} \rangle^{(b)} = \frac{1}{4}$): $J_{ab} = 0.313$ and $J_c = -0.097$. Although the FM interaction along c axis J_c is weaker in this limit, it gives a considerable energy gain of $\sim 0.2J$ over the G-AF order. It is further enhanced at $J_H > 0$ by a mechanism similar to that known from cuprates and manganites [2,4], as the high-spin ${}^4A_2$ state lies by $3J_H \simeq 2.0$ eV below its low-spin ${}^2E$ counterpart. This splitting modifies the 1D orbital-wave (OW) spectrum,

$$\omega_k^C = \sqrt{\Delta^2 + R^2(1 - \cos^2 k)}, \tag{7}$$

and the gap $\Delta = \{\eta(R + r)[2R + \eta(R + r)]\}^{1/2}$ opens. Using the spin-wave theory we determined the orbital correlations in Eqs. (6). As a result, one finds increasing (decreasing) FM (AF) exchange constants with increasing J_H (Fig. 1). Taking a representative value of the hopping integral $t = 0.2$ eV gives $J = 35.6$ meV which leads to the exchange constants in the C phase obtained for a realistic ratio $J_H/U = 0.15$: $J_{ab} \simeq 7.1$ and $J_c \simeq -9.3$ meV. These values are in the expected range, taking the Néel temperature $T_N \simeq 140$ K of the C phase in LaVO$_3$ [14]. We emphasize that the orbital quantum fluctuations play here a dominating role, and the well-known Hund's mechanism due to J_H alone *would not suffice* to obtain $|J_c| > J_{ab}$, giving instead $J_c \simeq -4.4$ meV.

Next we consider the reasons for the stability of the G phase in YVO$_3$. Unlike LaVO$_3$ with almost equal V–V bonds [14], this compound crystallizes in the distorted structure [14,15], indicating that the JT effect plays a significant role. It was suggested that energy may be gained due to C-type *orbital ordering,* with a and b orbitals staggered in (a, b) planes and repeated along the c axis, while $n_{ic} = 1$ [16–18]. Such ordering can be promoted by

$$H_{\mathrm{JT}} = -2V \sum_{\langle ij \rangle \parallel c} \tau_i^z \tau_j^z + V \sum_{\langle ij \rangle \parallel (a,b)} \tau_i^z \tau_j^z, \tag{8}$$

and *competes with the orbital disorder*. This behavior is remarkably different from the e_g systems, where the JT effect and superexchange support each other, inducing orbital ordering [2–4]. While $V > 0$ causes orbital splitting by $4V$ and thus lowers the energy of the G phase (E_G), it has little effect on the energy of the C phase (E_C). The energy difference is given by

$$\Delta E = E_C - E_G \simeq V - \tfrac{1}{2}\eta(3R + r) - \delta E_{\mathrm{OW}}, \tag{9}$$

where $\delta E_{\mathrm{OW}} > 0$ is the energy contribution due to quantum fluctuations of t_{2g} orbitals. Large spins $S = 1$ are almost classical and their fluctuations could be neglected.

Orbital excitations are quite different in both AF phases: while the gap Δ is small and grows $\propto \sqrt{\eta}$ in the C phase (7), a large gap $\sim 4V$ opens in the OW spectrum of the G phase, $\omega_k^{\mathrm{G}} = 4V + \eta R \cos k$. Thus, both the larger quantum fluctuations and additional (classical) energy gain due to finite J_H in the C phase have to be overbalanced by the JT energy $\propto V$ in order to stabilize the G-AF order at $T \to 0$. However, the G phase may be destabilized at finite T by larger orbital entropy of the C phase. Indeed, taking $V = 0.65J$ and $\eta = 0.15$, the free energy, $\mathcal{F} = \langle \mathcal{H} \rangle - TS$, with the entropy S determined by orbital excitations, gives a transition from the G to the C phase around $T^* \simeq 0.8J$ (Fig. 2). While this behavior reproduces qualitatively the first order transition observed in YVO$_3$ [15,16], its quantitative description requires a careful consideration of lattice and spin entropy contributions to the free energy $\mathcal{F}$. These effects are expected to reduce the transition temperature T^* down to experimental values.

The exchange constants in the G phase are anisotropic which can be understood by analyzing the superexchange

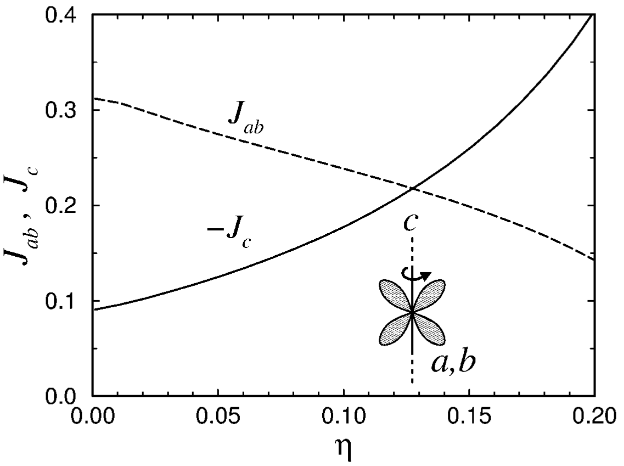

FIG. 1. Exchange interactions J_c and J_{ab} (6) in the C phase (in units of J) as functions of $\eta = J_H/U$. The inset indicates the local fluctuation between $a(= yz)$ and $b(= zx)$ orbitals due to singlet formation along the c axis.

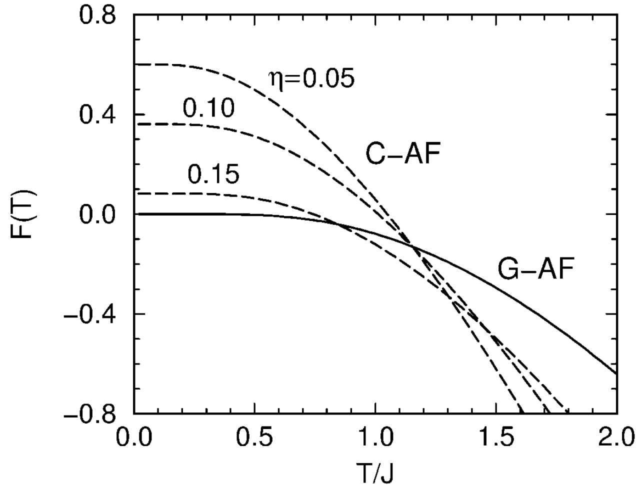

FIG. 2. Free energies $\mathcal{F}(T)$ (in units of J) of the G phase obtained with $V = 0.65J$ (full line), and the C phase for $\eta = 0.05$, 0.10, and 0.15 (dashed lines), as functions of temperature T/J.

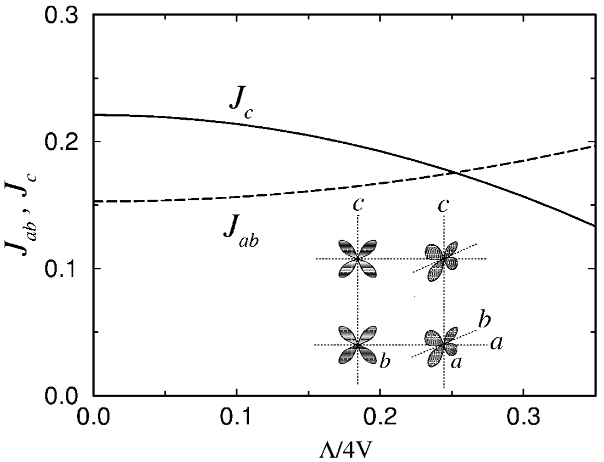

FIG. 3. Exchange interactions J_c and J_{ab} (10) in the G phase (in units of J) as functions of spin-orbit coupling $\Lambda/4V$, for $\eta = 0.15$. The inset shows a and b orbitals, which are staggered in (a, b) planes, and repeat themselves along the c axis.

expressions (6). The transitions to the low-spin $^2T_1$ and $^2T_2$ states occur in all three directions between pairs of occupied orbitals of the same kind, and give the leading AF contribution $\propto (1 - \eta r)$. The excitations of $d^3\{abc\}$ configurations occur in addition on the bonds in the (a, b) planes, and reduce the AF coupling J_{ab} by ηR, giving $J_{ab} < J_c$. Including in addition a relativistic spin-orbit coupling $\propto \Lambda$ ($\simeq$ 18 meV [12]), we find for the G phase:

$$\begin{aligned} J_c &= \tfrac{1}{4}(1 - \eta r) - \tfrac{1}{2}(1 + 2\eta R - \eta r)\bar{\Lambda}^2, \\ J_{ab} &= \tfrac{1}{4}(1 - \eta R - \eta r) + \tfrac{1}{4}(1 + 2\eta R - \eta r)\bar{\Lambda}^2, \end{aligned} \tag{10}$$

where $\bar{\Lambda} = \Lambda/4V$. The spin-orbit coupling enhances (reduces) the effective superexchange in (a, b) planes (along the c axis), as shown in Fig. 3. For example, taking a value of $\Lambda/4V = 0.2$ which is believed to be close to realistic for YVO$_3$, we find $J_{ab} \simeq 5.9$ and $J_c \simeq 6.9$ meV. These values lie in the expected range for the G phase of YVO$_3$. This also demonstrates that the magnetic structure and the spin-wave spectrum are completely different depending on the orbital state—the exchange constant J_c which is FM in LaVO$_3$ may become even the *strongest* AF bond when the orbitals have ordered, as in YVO$_3$, and the JT splitting (8) dominates over the spin-orbit coupling.

Summarizing, strong t_{2g} orbital fluctuations in a half-filled system of yz and zx orbitals in cubic vanadites lead to a new mechanism of ferromagnetic superexchange which stabilizes the C phase in first undistorted LaVO$_3$, and the structural transition follows. The JT effect opposes the superexchange and can stabilize the G phase with orbital ordering but only at low temperatures, as the fluctuations of t_{2g} orbitals release high entropy, and are thus responsible for the transition from the orbital ordered G phase to the C phase with 1D orbital disorder, as observed in YVO$_3$.

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