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DIMER STATES IN THE SPIN–ORBITAL MODEL FOR CUBIC VANADATES *

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We investigate the ground state of the spin-orbital superexchange model for cubic vanadates. For small Hund's coupling $J_{\rm H}$ strong fluctuations of t_{2g} orbitals stabilize a dimerized state with orbital valence bond correlations, while for realistic values of $J_{\rm H}$ either a C-type or G-type antiferromagnetic phase is found, depending on the strength of the Jahn-Teller interaction.

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1. Spin-orbital model and orbital fluctuations

The superexchange interactions in the strongly correlated transition metal oxides involve both spin and orbital degrees of freedom, leading to the so-called spin-orbital models [1, 2]. A remarkable feature of these systems is that the superexchange interactions are *highly frustrated*, which was recognized as the origin of novel quantum effects [3]. Recently we derived the spin-orbital model for cubic vanadates: LaVO$_3$ and YVO$_3$, and investigated the stability of C-type antiferromagnetic (AF) phase [4].

Cubic vanadates are Mott insulators due to large on-site intraorbital Coulomb element $U \simeq 5.5$ eV [5]. The Hund's coupling $J_{\rm H} = 0.64$ eV [5] stabilizes the triplet configuration $^3T_2$ at V^{3+} ions. Unlike for e_g orbitals, the hopping t conserves the orbital flavor, and the Jahn–Teller (JT) coupling to the lattice is much weaker. Each t_{2g} orbital is orthogonal to one cubic axis, so we label it by this axis index, *e.g.*, xy is labelled as c. The superexchange

$$\mathcal{H} = J\sum_{\gamma}\sum_{\langle ij\rangle\|\gamma}\left[(\vec{S}_i\cdot\vec{S}_j+1)\hat{J}_{ij}^{(\gamma)}+\hat{K}_{ij}^{(\gamma)}\right], \qquad J = 4t^2/U, \tag{1}$$

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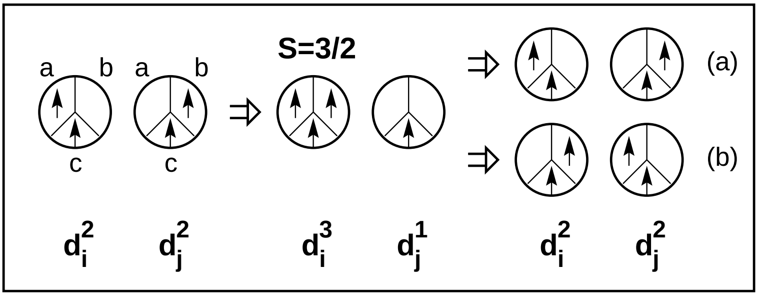

Fig. 1. Schematic picture of the virtual processes $d_i^2 d_j^2 \rightarrow d_i^3 d_j^1 \rightarrow d_i^2 d_j^2$ contributing to the superexchange on the bond $\langle ij \rangle$ along c axis, for the high-spin ($S = 3/2$) state. Next to the (usual) retraceable transitions (a), the orbital fluctuations (b) happen and trigger the FM interaction even at $J_{\rm H} = 0$ [4].

follows from the virtual charge excitations which lead either to high-spin ($S = 3/2$) (Fig. 1), or to low-spin ($S = 1/2$) V^{2+} states [4]. The orbital operators in Eq. (1) are summed over bonds $\langle ij \rangle \parallel \gamma = a, b, c$:

$$\hat{J}_{ij}^{(\gamma)} = \tfrac{1}{2}\left[(1+2\eta R)\left(\vec{\tau}_i \cdot \vec{\tau}_j + \tfrac{1}{4} n_i n_j\right) - \eta r\left(\tau_i^z \tau_j^z + \tfrac{1}{4} n_i n_j\right) - \tfrac{1}{2}\eta R n_{ij}\right]^{(\gamma)}, \quad (2)$$

$$\hat{K}_{ij}^{(\gamma)} = \left[\eta R\left(\vec{\tau}_i \cdot \vec{\tau}_j + \tfrac{1}{4} n_i n_j\right) + \eta r\left(\tau_i^z \tau_j^z + \tfrac{1}{4} n_i n_j\right) - \tfrac{1}{4}(1+\eta R) n_{ij}\right]^{(\gamma)}, \quad (3)$$

where $R = 1/(1-3\eta)$, $r = 1/(1+2\eta)$, $\eta = J_{\rm H}/U$, and $n_{ij}^{(\gamma)} = (n_i + n_j)^{(\gamma)}$. For a given direction, for instance for $\gamma = c$, $n_i^{(c)} = n_{ia} + n_{ib}$, and the operators $\vec{\tau}_i = \{\tau_i^x, \tau_i^y, \tau_i^z\}$ are defined in the orbital pseudospin subspace spanned by two active orbital flavors represented by Schwinger bosons $\{a_i^\dagger, b_i^\dagger\}$: $2\left(\vec{\tau}_i \cdot \vec{\tau}_j + \frac{1}{4} n_i n_j\right)^{(c)} = (n_{ia} n_{ja} + a_i^\dagger b_i b_j^\dagger a_j) + (a \leftrightarrow b)$. The orbital fluctuations $\propto \tau_i^+ \tau_j^- = a_i^\dagger b_i b_j^\dagger a_j$ are shown in Fig. 1(b).

2. Results and discussion

The ground state of the spin-orbital model (1) follows from a compromise between more classical spin ($S = 1$) and quantum orbital ($\tau = 1/2$) interactions. The study below is based on the suggestion that xy orbitals are occupied in $\mathrm{LaVO_3}$ [6] and $\mathrm{YVO_3}$ [7], so we consider the V^{3+} ions with local constraints: $n_{ic} = 1$, $n_{ia} + n_{ib} = 1$. We have analyzed three different types of magnetic and orbital ordering using the mean-field approximation for the spins, and including the quantum effects in the orbital subspace

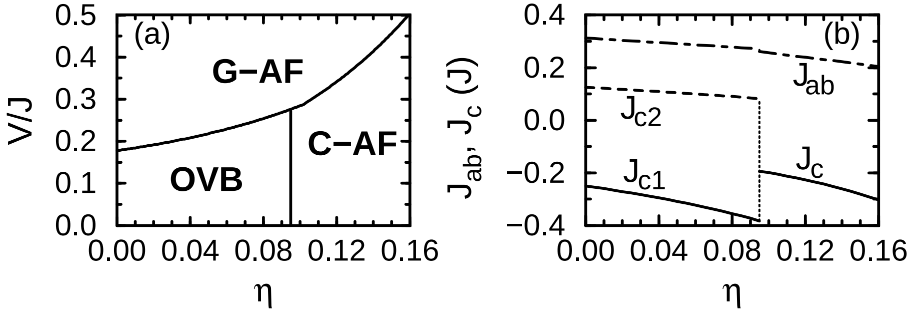

Fig. 2. The mean-field phase diagram (a) of the vanadate spin-orbital model in $(\eta, V/J)$ plane with three phases stable at $T = 0$: OVB, C-AF, and G-AF. The superexchange interactions (b) in the OVB (J_{c1}, J_{c2} and J_{ab}) and in the C-AF phase (J_c and J_{ab}), as functions of η for $V = 0$.

(Fig. 2): (*i*) C-AF phase [ferromagnetic (FM) chains along c-axis and AF order within (a, b) planes], (*ii*) G-AF phase (staggered in all three directions), and (*iii*) orbital valence bond (OVB) phase described below. Consider first a single bond along c axis in the $J_{\rm H} \to 0$ limit. The lowest energy of $-J/2$ is obtained when the spins are FM, and the orbitals a and b form a singlet. Then both the retraceable [Fig. 1(a)] and fluctuating [Fig. 1(b)] terms contribute equally to the FM superexchange [4]. As pointed out by Shen, Xie, and Zhang [8], the best energy is obtained when the singlets occur at every second bond. The system self-organizes into an OVB state, with FM singlet bonds separated by AF bonds with disordered $\{a, b\}$ orbitals. This dimerized state survives when the quantum corrections due to the coupling between spin and orbital variables are included [9].

In contrast, in C-AF phase the orbital correlations follow from the one-dimensional AF Heisenberg chain, weakly coupled to the neighboring chains at finite η [4]. This resonating OVB state is favored only at large Hund's exchange $\eta > \eta_c$, where $\eta_c \simeq 0.095$ [see Fig. 2(a)]. Indeed, at realistic $\eta = 0.116$ the C-AF order occurs in LaVO$_3$ [6], but G-AF phase is observed instead in YVO$_3$ at low temperature $T < T_{N1}$ ($T_{N1} = 77$ K) [7]. It can be explained by including the JT effect which favors a distorted structure with orbital ordering [7, 10]. Such ordering is promoted by the JT term [4],

$$H_{\rm JT} = -2V \sum_{\langle ij\rangle \| c} \tau_i^z \tau_j^z + V \sum_{\langle ij\rangle \| (a,b)} \tau_i^z \tau_j^z , \qquad (4)$$

and competes with the orbital disorder, either in the OVB or in C-AF phase. When η increases, the orbital fluctuations along the c axis are enhanced, and a larger value of V/J is needed to stabilize the G-AF phase [Fig. 2(a)].

Finally, we evaluated the exchange constants within (a,b) planes (J_{ab}) and along c axis (J_c) in various phases, given by the orbital correlations [4]:

$$J_{ab} = \frac{1}{4}\left[1-\eta(R+r)+(1+2\eta R-\eta r)\langle n_{ia}n_{ja}\rangle^{(b)}\right], \tag{5}$$

$$J_c = \frac{1}{2}\left[(1+2\eta R)\left\langle\vec{\tau}_i\cdot\vec{\tau}_j+\frac{1}{4}\right\rangle^{(c)}-\eta r\left\langle\tau_i^z\tau_j^z+\frac{1}{4}\right\rangle^{(c)}-\eta R\right]. \tag{6}$$

In the OVB phase the orbitals are disordered, $\langle n_{ia}n_{ja}\rangle^{(b)}=\frac{1}{4}$, and one finds,

$$J_{c1}=-\frac{1}{4}(1+\eta)R, \qquad J_{c2}=\frac{1}{8}(1-2\eta R-\eta r), \tag{7}$$

alternating along c axis [Fig. 2(b)]. With increasing η, the FM (AF) interactions J_{c1} (J_{c2}) on singlet (intersinglet) bonds are enhanced (reduced) in the OVB phase [Fig. 2(b)]. The in-plane AF interactions J_{ab} are stronger (here c orbitals contribute) than J_{c2}, but they are further reduced when the orbital ordering (with $\langle\tau_i^z\rangle\neq 0$ and $\langle n_{ia}n_{ja}\rangle^{(b)}<\frac{1}{4}$) occurs in the C-AF phase. Taking realistic values $t\simeq 0.2$ eV and $\eta=0.116$ one finds similar FM and AF exchange constants: $J_c\simeq -6.4$ and $J_{ab}\simeq 7.1$ meV, the values expected for LaVO$_3$ [6]. The magnetic properties of YVO$_3$ are more puzzling [7] — they are dominated by the competition between the orbital ordering and orbital fluctuations at finite T, as we will discuss elsewhere [9].

Summarizing, we presented a competition between the OVB phase and two AF phases: C-AF phase stabilized by increasing Hund's interaction $\propto J_{\rm H}$, and G-AF phase stabilized by the JT term $\propto V$. Although the OVB phase is not observed in cubic vanadates, it suggests that the tendency towards dimerization in the orbital sector is generic and might be expected to play an important role also in the C-AF phase of YVO$_3$ at $T>T_{N1}$.

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