Spin-Orbital Entanglement Emerging from Frustration in the Kugel-Khomskii Model

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Abstract. We investigate the zero-temperature phase diagrams of the bilayer square-lattice Kugel-Khomskii (d^9) model involving entangled and singlet phases using mean-field cluster approach. This diagram includes interlayer singlet phase observed in copper fluoride K_3Cu_2F_7 and exotic entangled spin-orbital phases. For a monolayer case, realized in K_2CuF_4, we perform similar calculations at finite temperature and show that the alternating-orbital ferromagnet decays first to an entangled uniform ferromagnet and then to a paramagnet.

It has been shown that quantum fluctuations are enhanced near the orbital degeneracy and could suppress long-range order in the Kugel-Khomskii (KK) model [1], called below the d^9 model. This model was introduced long ago for a perovskite KCuF_3 [2], a strongly correlated system with a single hole within degenerate e_g orbitals at each Cu^{2+} ion. Kugel and Khomskii showed that alternating orbital (AO) order can be stabilized by a purely electronic superexchange mechanism. This happens for strongly frustrated orbital superexchange [3], and columnar Ising-type of order is obtained [4] in the two-dimensional quantum compass model. This model exhibits nontrivial symmetry properties which may be employed to perform efficient calculations for square compass clusters [5].

Orbital order occurs in a number of compounds with active orbital degrees of freedom, where strong Coulomb interaction localizes electrons (or holes) and gives rise to spin-orbital superexchange [6]. When spin and orbital pseudospins couple to each other, their order is usually complementary — AO order accompanies ferromagnetic (FM) spin order, and ferro-orbital (FO) order coexists with antiferromagnetic (AF) spin order. However, the above Goodenough-Kanamori rules, see also [3], are not satisfied in cases when spin-orbital entanglement (SOE) dominates [7], as for instance in the spin-orbital d^1 model on a triangular lattice [8].

The spin-orbital superexchange KK model for Cu^{2+} (d^9) ions in KCuF_3 with S = 1/2 spins and e_g orbitals described by \( \tau = 1/2 \) pseudospin was derived from the degenerate Hubbard Hamiltonian with hopping \( t \), intraorbital Coulomb interaction \( U \) and Hund’s exchange \( J_H \) [9]. It describes the Heisenberg SU(2) spin interactions coupled to the orbital problem by superexchange \( J = 4t^2/U \),

\[
\mathcal{H} = -\frac{1}{2} J \sum_{(ij)\gamma} \left\{ r_1 \Pi_{(ij)}^\gamma + r_2 \Pi_{(ij)}^{\gamma*} \left( \frac{1}{4} - \tau_i^\gamma \tau_j^\gamma \right) + r_3 \Pi_{(ij)}^{\gamma*} \left( \frac{1}{2} - \tau_i^\gamma \right) \left( \frac{1}{2} - \tau_j^\gamma \right) \right\} - E_z \sum_i \tau_i^z.
\]

(1)
where \(\{r_1, r_2, r_3\}\) depend on \(\eta \equiv J_H/U\) [9], and \(\gamma = a, b, c\) is the bond direction. In a bilayer two \(ab\) planes are connected by interlayer bonds along the \(c\) axis [10] (a monolayer has only bonds within a single \(ab\) plane). Here

\[
\Pi^s_{(ij)} = \frac{1}{4} - S_i \cdot S_{i+\gamma}, \quad \Pi^t_{(ij)} = \frac{3}{4} + S_i \cdot S_{i+\gamma}, \quad (2)
\]

are projection operators on a spin triplet (singlet) configuration on a bond \(\langle ij\rangle\), and \(\tau^\gamma_i\) are the orbital operators for bond direction \(\gamma = a, b, c\). They are defined in terms of Pauli matrices \(\{\sigma_i^x, \sigma_i^z\}\) as follows:

\[
\tau^a(b)_i \equiv \frac{1}{4} (-\sigma_i^z \pm \sqrt{3}\sigma_i^x), \quad \tau^c_i \equiv \frac{1}{2} \sigma_i^z. \quad (3)
\]

Finally, \(E_z\) is the crystal-field splitting which favors either \(x \equiv x^2 - y^2\) (if \(E_z > 0\)) or \(z \equiv 3z^2 - r^2\) (if \(E_z < 0\)) orbitals occupied by holes. Thus the model Eq. (1) depends on two parameters: \(E_z/J\) and \(\eta\).

The spin-orbital model Eq. (1) describes also CuO\(_2\) planes in La\(_2\)CuO\(_4\), where indeed \(U \gg t\) and large \(E_z/J_H \approx 0.27\) favors holes within \(x\) orbitals [9]. The superexchange between Cu\(^{2+}\) ions \(\sim 0.127\) eV reoccurs there the experimental value. In this paper we consider the model Eq. (1) for K\(_3\)CuF\(_7\) bilayer and K\(_2\)CuF\(_4\) monolayer compound where nearly degenerate \(e_g\) orbitals are expected. It has been shown that the magnetic state of K\(_3\)CuF\(_7\) is described by the interlayer valence bond (VB) phase [11] with AO configuration whereas K\(_2\)CuF\(_4\) undergoes a pressure driven phase transition (PT) from the FM phase with alternating orbitals at low pressure to the AF phase with with \(x\) orbitals uniformly occupied [12].

The simplest approach is a single-site mean field (MF) approximation applied to the model Eq. (1). It excludes any spin fluctuations so the spin projectors \(\Pi^s_{(ij)}\) \((\Pi^t_{(ij)})\) can be replaced by their mean values depending on the assumed magnetic order. In the orbital sector we apply then the MF decoupling for the products \(\{\tau_i^\gamma \tau_{i+\gamma}^\gamma\}\) along the axis \(\gamma\):

\[
\tau_i^\gamma \tau_{i+\gamma}^\gamma \simeq \langle \tau_i^\gamma \rangle \tau_{i+\gamma}^\gamma + \tau_i^\gamma \langle \tau_{i+\gamma}^\gamma \rangle - \langle \tau_i^\gamma \rangle \langle \tau_{i+\gamma}^\gamma \rangle. \quad (4)
\]

As order parameters we take \(t^a \equiv \langle \tau_i^a \rangle\) and \(t^c \equiv \langle \tau_i^c \rangle\) for a chosen site \(i = 1\) (which is sufficient in the orbital sector as \(t^b = -t^a - t^c\)) and we assume two orbital sublattices: each neighbor of the site \(i\) is rotated by \(\pi/2\) in the \(ab\) plane meaning that \(\langle \tau_{i+\gamma}^a \rangle = \rho^{(a)}\). The self-consistency equations can be solved analytically and the phase diagram can be obtained by comparing the ground state energies for different points in the \((E_z/J, \eta)\) plane (see Ref. [10]). One finds two classes of solutions: (i) uniform orbital configurations \((t^c = \pm 1/2, t^a(b) = \mp 1/4)\) for global FO order, and (ii) nontrivial AO order with orbitals staggering from site to site in \(ab\) planes.

In a better cluster MF (or Bethe-Peierls-Weiss) approach, introduced to capture the effects of quantum fluctuations, one divides the bilayer square lattice into separate cubes containing 8 sites each and treats the bonds inside a cube exactly, while the bonds connecting different cubes are included in MF. This approach has at least three advantages over the single-site MF: (i) spins can fluctuate, (ii) elementary cell can double, and (iii) ordered phases may be characterized by an independent spin-orbital order parameter. The MF leads in a cluster to five order parameters: magnetic \(s \equiv \langle S_i^z \rangle\), orbital \(t^{a(b)} \equiv \langle \tau_1^{a(b)} \rangle\), and spin-orbital \(v^{a(b)} \equiv \langle S_i^z \tau_1^{a(b)} \rangle\). The self-consistency equations can be solved only numerically by iterative Lanczos diagonalization of a cluster followed by the update of the mean fields (for details see Ref. [10]). To capture the effect of the SOE we first obtain the phase diagram assuming \(v^{a(b)} \equiv s t^{a(b)}\) (factorizable SO mean field)—see Fig. 1(a) and then performed the calculation with true \(v^{a(b)}\) to get Fig. 1(b).

Including spin fluctuations in this approach stabilizes three VB phases absent in the single-site approach. These are VB\(_z\), VB\(_m\) and PVB phases, see Fig. 1(a). The VB\(_z\) replaces
ordinary antiferromagnet in the negative $E_z$ region of the phase diagram and involve interlayer singlets accompanied by FO$_z$ configuration which can smoothly evolve for growing $\eta$ towards AO configuration in the VB$m$ being the phase observed in K$_3$Cu$_2$F$_7$ by Manaka et al. [11]. Here we explain it for realistic $\eta \simeq 0.14$. In the PVB (plaquette VB) phase spin singlets are pointing uniformly in $a$ or $b$ direction within the cluster and the clusters form a checkerboard pattern so the unit cell is doubled. Other phases, i.e., FM, G-AF$_x$ and A-AF, exhibit long range magnetic order and can be obtained in ordinary MF approach (see Ref. [10]).

A different class of phases stems from the non-factorizable SO mean field and involves SOE — these are the ESO, EPVB and PVB-AF phases shown in Fig. 1(b). The PVB-AF phase connects PVB and G-AF$_x$ phases by second order PTs and is characterized by fast changes in orbital order and appearance of global magnetization. The ESO phase has no magnetization and weak FO order. When $E_z$ grows, the ESO phase does change continuously into the EPVB configuration, being an entangled precursor of the PVB phase with highly non-uniform AF magnetization. As shown in Ref. [10], both ESO and EPVB are characterized by strong on-site SOE defined as $r^{a,b} \equiv v^{a,b} - s^{a,b}$.

Using the same cluster MF approach as above one can easily study the properties of the KK model for a single layer at zero and finite temperature $T$. At $T = 0$ one finds the phase diagram of the form shown in the Fig. 2(a). In the low-$\eta$ region it involves only AF and PVB phases and the VB$z$ is replaced by AF$_z$ one in the absence of the second layer. The PVB area is strongly elongated in the horizontal directions and caps AF$_z$ down to $E_z < -2J$ where one finds a narrow stripe of a paramagnetic (PM) phase separating PVB from FM$_z$ phase (FM phase with FO$_z$ order). The presence of paramagnetizm at $T = 0$ shows that a monolayer system is even more frustrated than a bilayer. The $E_z$-induced FM-AF$_x$ PT above $\eta \simeq 0.225$ agrees with the one observed in K$_3$CuF$_4$ (see Ref. [12]) with $E_z$ acting as uniaxial pressure.

In the Fig. 2(b) we show the thermal evolution of spin and orbital order parameters and SOE for a point ($E_z = -2.1J, \eta = 0.19$) lying in the FM area of the monolayer phase diagram. This evolution involves passage through the FM$_z$ phase and ends in the PM phase. The FM magnetization $s$ exhibits critical behaviour staying close to 1/2 in the FM phase and dropping quickly to zero at the FM$_z$-PM PT. The orbital parameters $\{t^a, t^b\}$ show inverse bifurcation at
Figure 2. Panel (a)— phase diagram of the $d^9$ monolayer model at $T = 0$. Shaded (yellow) area marks singlet phase with spin disorder. Panel (b)— spin $s$ and orbital $t_{a,b}$ order parameters, on-site $r_{a,b}^a$ and bond $R_{a,b}^a$ SOE parameters (multiplied by 100) for point $(E_z = -2.1 J, \eta = 0.19)$, marked with thick (red) arrow in (a), as functions of temperature. Thermal evolution of the system involves intermediate FMz phase before reaching PM phase.

the FM-FMz PT being the end of the AO order but remain finite in the paramagnet which is induced by finite $E_z$. The on-site SOE represented by $r_{a,b}^a$ are small everywhere but in FMz phase they become relatively large which suggests that the FMz is an entangled phase. The bond SOE defined by $R_{a,b}^a = \langle S_1^a S_{i}^a r_{i}^a r_{a,b}^a \rangle - \langle S_1^a S_{i}^a \rangle \langle r_{i}^a r_{a,b}^a \rangle$ take considerable values only in the PM phase and shows rather purely statistical covariance than a true quantum effect.

Summarizing, we have shown exotic types of order with spin-orbital entanglement in a bilayer system at $T = 0$ and entangled intermediate phase between ferromagnet and paramagnet for a monolayer at finite temperature. Within the same cluster MF approach we were able to capture the most important experimental features of both types of the Kugel-Khomskii systems.

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