Magnetic Excitations in Spin-Orbit Coupled \(d^4\) Mott Insulator on Square Lattice

Alirea Akbari and Giniyat Khaliullin
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

(Dated: July 17, 2014)

We study the magnetic order and excitations in strong spin-orbit coupled, Van Vleck-type, \(d^4\) Mott insulators on a square lattice. Extending the previous work, we include the tetragonal crystal field splitting and explore its effects on magnetic phase diagram and magnon spectra. Two different ordered phases, with in-plane and out-of-plane orientation of the staggered moments, are found for the higher and lower values of the crystal field splitting, respectively. The magnetic excitation spectra for paramagnetic and magnetically ordered phases are calculated and discussed in the context of a candidate spin-orbit \(d^4\) Mott insulator \(\text{Ca}_2\text{RuO}_4\).

I. INTRODUCTION

In a solid, five-fold orbital degeneracy of a \(d\)-electron level is lifted by crystal field potential as well as by covalency effects. In case of local cubic symmetry, two subsets of \(d\)-orbitals with two-fold \(e_g\) and three-fold \(t_{2g}\) symmetry, separated by a large energy of the order of \(10Dq \sim 2 - 3\) eV, are formed. The remaining degeneracy of orbitals – which adds up to that of spin – has to be lifted one way or another, involving dynamical Jahn-Teller effect and interionic exchange interactions. If the latter mechanism dominates, the spin and orbital degrees of freedom strongly couple to each other and are described by a family of so-called Kugel-Khomskii-type model\(^\text{1}\).

General behavior of Kugel-Khomskii Hamiltonians is very complex because of the frustrated nature of orbital interactions, in particular in the case of \(t_{2g}\) orbitals where the higher degeneracy enhances quantum effects\(^\text{12}\). In addition to that, \(t_{2g}\) triplet has an unquenched orbital angular momentum \(L\), and relativistic spin-orbit coupling (SOC) \(\lambda(S \cdot L)\) is active. When \(\lambda\) is comparable to the strength of exchange interactions, spin-orbit coupling effects become of a nonperturbative nature. In that case, it is more convenient to represent the spin-orbital exchange Hamiltonians in terms of ionic multiplets in which SOC is already included\(^\text{2}\). Often, it is sufficient to keep the lowest-lying ionic multiplet with \(2S + 1\) degeneracy: this results in effective, "pseudospin \(\tilde{S}\)" Hamiltonians describing low-energy magnetic properties of a material.

By construction, pseudospins \(\tilde{S}\) inherit the spatial shape and bond-directional nature of orbitals and their interaction\(^\text{3}\). Thus, the pseudospin Hamiltonians may strongly deviate from a conventional, spin-isotropic Heisenberg models, even in a simplest case of just twofold Kramers degeneracy with \(\tilde{S} = 1/2\). As an example, exchange interactions between \(t_{2g}\) ions with pseudospins \(\tilde{S} = 1/2\) obtain large Ising term with an unusual, bond-dependent alternation of the "Ising-axes"\(^\text{4,5}\), leading to unconventional magnetic states. The pseudospin Hamiltonians for \(\tilde{S} > 1/2\) receive in addition strong biquadratic and multipolar interactions\(^\text{6,7}\). Experimental studies of the iridium oxides hosting pseudospin physics\(^\text{8,9}\) have boosted general interest in strong spin-orbit coupled magnetism (see Ref.\(^\text{12}\) for the recent review).

It may happen that the lowest spin-orbit ionic state has no degeneracy, \(\tilde{S} = 0\), and hence it is nonmagnetic. Such is the case of transition metal ions with \(t_{2g}\) configuration, where the spin \(S = 1\) and orbital \(L = 1\) moments form a singlet ground state\(^\text{10}\). Compounds with such nominally nonmagnetic ("Van Vleck-type") ions may still undergo magnetic transitions, due to mixing of the ground state \(\tilde{S} = 0\) level with higher-lying \(\tilde{S} = 1, 2\) multiplets by virtue of intersite exchange interaction\(^\text{11}\). Because of SOC, the transitions between multiplets with different \(\tilde{S}\) are magnetically active. In a solid, they become dispersive bands and have been observed in cobalt\(^\text{13,14}\) and iridium\(^\text{15}\) oxides. Magnetic order in systems with \(\tilde{S} = 0\) can be thus viewed as a Bose condensation of excitonic \(\tilde{S} = 1\) band. A hallmark of such magnetism is the presence of soft amplitude mode\(^\text{17}\) corresponding here to the length fluctuations of the total angular momentum \(\tilde{S} = S + L\), in addition to conventional spin waves.

Theory of the exchange interactions and exciton magnetism in Van Vleck-type \(t_{2g}\) systems has been developed recently in Ref.\(^\text{14}\) and ruthenium oxide \(\text{Ca}_2\text{RuO}_4\) was suggested as a possible candidate material, based on the experimental observation\(^\text{18}\) of an unquenched SOC in this compound. In this paper, we consider magnetic order and excitations in more detail, with a particular focus on the effects of tetragonal distortion generally present in most perovskites.

II. MODEL HAMILTONIAN

Having in mind a layered perovskite structure of \(\text{Ca}_2\text{RuO}_4\), we consider square lattice of \(t_{2g}\) ions which are assumed to have a low-spin configuration with spin \(S = 1\) and orbital \(L = 1\) moments. Intraionic SOC generates three levels at energies 0, \(\lambda\), and \(3\lambda\), corresponding to the spin-orbit multiplets with total angular momentum \(\tilde{S} = 0, 1, 2\). We neglect the highest, \(\tilde{S} = 2\) multiplet at energy \(3\lambda\); this is justified if the exchange interactions are not too strong as compared to SOC parameter \(\lambda\). The remaining ionic degrees of freedom include ground state singlet \(|s\rangle\) and \(\tilde{S} = 1\) triplet \(|T_{0,\pm 1}\rangle\) states. In a \(|M_S, M_L\rangle\) basis, the wave-functions read as
The Hamiltonian Eq. (1) can be either paramagnetic or antiferromagnetic. There are two different magnetic phases, namely ferromagnetic and easy-plane (M∥ab) orderings. For the fixed crystal-field splitting δ, for the fixed crystal-field splitting δ = 0.2λ, the condensate density ρ and the staggered moment M values versus δ, for the fixed J = 0.2λ.

III. GROUND STATE PROPERTIES

Depending on the relative strength of the exchange J and SOC λ parameters, the ground state of effective Hamiltonian Eq. (1) can be either paramagnetic or antiferromagnetic. There are two different magnetic phases, with out-of-plane M∥c and in-plane M∥ab orientations of the staggered moments. The M-orientation is decided by the competition between the exchange J and the crystal-field δ couplings. We calculate below classical energies of magnetically ordered states, and obtain from them a phase diagram and ordered moment values.
A. Phase diagram

Magnetic phase I (M || c): This state is obtained by a condensation of the $T_z$-component of $\vec{S} = 1$ triplet: $T_z \rightarrow \sqrt{\rho_1}$. The corresponding classical energy gain is:

$$E_{g1} = -\rho_1 \mu_1 = -\frac{1}{4\kappa_1} (\kappa_1 - \beta_1)^2,$$

where $\rho_1 = \frac{1}{2} (1 - \frac{3}{2} \frac{\beta_1}{\kappa_1})$ is the condensate density, and $\mu_1 = \frac{1}{2} (\kappa_1 - \beta_1)$. We note that the constant $-\mu$ has a physical meaning of chemical potential. The condensate density and hence the magnetic moments are determined by the interaction parameters $\kappa_1 = \frac{2\beta}{J}$ and $\beta_1 = \lambda + \frac{2}{3} \delta$. The magnetic phase transition sets in at $\kappa_1 = \beta_1$ (i.e., when $\mu_1$ becomes zero); this gives the critical value of the exchange constant $J$ as $J^* = (3\lambda + 2\delta)/22$.

Magnetic phase II (M || ab): The magnetic moment is in the ab-plane corresponding to the condensation of $T_x \rightarrow \sqrt{\rho_2}$. The ground state energy can be represented in the form as above,

$$E_{g2} = -\rho_2 \mu_2 = -\frac{1}{4\kappa_2} (\kappa_2 - \beta_2)^2,$$

but with different parameters: $\rho_2 = \frac{1}{2} (1 - \frac{3}{2} \frac{\beta_2}{\kappa_2})$ and $\mu_2 = \frac{1}{2} (\kappa_2 - \beta_2)$, where $\kappa_2 = \frac{2}{3} \delta + \frac{2}{3} J$ and $\beta_2 = \lambda - \frac{2}{3} \delta$. The magnetic phase transition line is given by $\kappa_2 = \beta_2$, and the critical value $J^2 = (3\lambda - \delta)/19$.

Using the above results, we find a phase diagram as shown in Fig. (1b). At small crystal fields $\delta$, the exchange anisotropy terms in Eq. (4) select out-of-plane $M$-direction. However, already quite small tetragonal splitting $\delta$ stabilizes the in-plane magnetic order, which corresponds to the case of Ca$_2$RuO$_4$.

B. Staggered Magnetisation

The magnetic moment of present singlet-triplet system is represented by the following operator:

$$M = -i\sqrt{6} (T - T^\dagger) - ig_J (T^\dagger \times T),$$

with $g_J = 1/2$. In magnetic phases with condensed bosons, the first term of this operator obtains finite expectation value [at the ordering wave-vector $(\pi, \pi)$]. Using the above results for condensate amplitudes, we find that the staggered magnetic moment in phase I is:

$$M_1 = \sqrt{6} (1 - \eta_1) ; \quad J > J^*_1,$$

where $\eta_1 = \frac{3}{2} \frac{\beta_1}{\kappa_1}$. The same equation holds for the magnetic moment in phase II, but with $\eta_2 = \frac{3}{2} \frac{\beta_2}{\kappa_2}$ and $J > J^*_2$. Parameters $\beta_{1,2}$ and $\kappa_{1,2}$ have been given above.

The numerical results for the staggered moment as a function of parameters $\delta$ and $J$ are shown in Fig. [2] A clear trace of the phase transition from PM to magnetic phases, and a discontinuous spin-reorientation transition between phases I and II are observed.

Condensate densities [Fig. [2]b] and staggered moments [Fig. [2]c] critically depend on $J/\lambda$ ratio. However, they are not sensitive to the value of anisotropy parameter $\delta$ [Fig. [2]d,e] whose major effect is the stabilization of phase II with in-plane magnetic moments.

IV. EXCITATION SPECTRA

A. Magnon dispersions

We consider now spin excitations above the ground state. Technically, we follow early works [21,22] which extended a linear spin-wave theory to singlet-triplet models. We handle the particle-number constraint on average only, neglecting magnon interaction effects.

Within this approximation, spin excitations in the paramagnetic phase follow directly from Eqs. (1-3), after the Bogoliubov transformation of the $T$ operators (in momentum space). For $T_z$ component, this gives

$$\omega_z(k) = (\lambda - \frac{1}{3} \delta) \sqrt{1 + a_z \phi_k} , \quad a_z = \frac{3\lambda + 2\delta}{3\lambda - \delta} ,$$

where $\phi_k = \frac{1}{2} (\cos k_x + \cos k_y)$ is a square lattice form-factor. Because of tetragonal symmetry, the $T_z$ and $T_y$ modes are degenerate:

$$\omega_{z/y}(k) = (\lambda - \frac{1}{3} \delta) \sqrt{1 + a_{z/y} \phi_k} , \quad a_{z/y} = \frac{3\lambda - \delta}{\lambda - \delta} .$$

For the antiferromagnetically ordered phases, we introduce two sublattices labeled by A and B. It is convenient also to introduce the sublattice dependent phase shifts $T_A \rightarrow iT$, $T_B \rightarrow -iT$, and work within the extended Brillouin zone (BZ). Then, after the Fourier transformation $T_k = \sum_i e^{ik \cdot r_i} T_i$ in Eqs. (1-3), we arrive at the following momentum-space Hamiltonian:

$$H = \sum_k (H^x_k + H^y_k + H^z_k)$$

$$= \sum_k (\lambda - \frac{3}{2} \delta - 4 J \phi_k) T^\dagger_{k,z} T_{k,z} - \frac{5}{3} J \phi_k (T_{k,z} T_{k,z} + h.c.)$$

$$+ \left[ (\lambda - \frac{1}{3} \delta + \frac{10}{3} J \phi_k) T^\dagger_{k,x} T_{k,x} - \frac{3}{2} J \phi_k (T_{k,x} T_{k,x} + h.c.) \right] + \left[ x \rightarrow y \right],$$

Magnetic order in singlet-triplet models implies condensation of a particular component of the triplet state, i.e., it mixes-up coherently with the ground state singlet. In order to describe this process, we introduce $T \rightarrow s^\dagger t$ with $n_s + n_t = 1$, and transform the basis as follows:

$$t_x = \tilde{s} \sin \theta + \tilde{t}_x \cos \theta,$$

$$s = \tilde{s} \cos \theta - \tilde{t}_x \sin \theta ,$$

with

$$\tilde{s} = s \sin \theta + \tilde{t}_x \cos \theta.$$
where \( \alpha = z(x) \) for phase I (II). A new \( \tilde{s} \) boson is then condensed. Fluctuations of \( t_a \) represent amplitude fluctuations, while remaining two (uncondensed) components of the triplet become transverse magnons. The basis-rotation angle \( \theta \) is determined by minimization of the classical energy \( E_C \) of Hamiltonian Eq. (10), which results in \( \sin \theta = \sqrt{\rho} \) and \( E_g = -\rho \mu \), with condensate densities \( \rho_{1,2} \) and potentials \( -\mu_{1,2} \) for phases I and II, correspondingly, as given in a previous section.

We consider first the magnetic phase I. After the above transformations, quadratic part of the Hamiltonian Eq. (10) takes the following form:

\[
H^i_k = A^i_k \tilde{t}^i_{k,z} \tilde{t}^i_{k,z} + \frac{1}{2} B^i_k \left( \tilde{t}^i_{k,z} \tilde{t}^i_{-k,z} + h.c. \right), \tag{12}
\]

where

\[
A^i_k = \kappa_1 \left[ 1 + \frac{\phi_k}{2} (1 + 11 \eta_1) \right],
\]

\[
B^i_k = \kappa_1 \left[ \frac{\phi_k}{22} (1 - 11 \eta_1) \right]. \tag{13}
\]

Diagonalization of Eq. (12) gives the amplitude mode dispersion:

\[
\omega_z (k) = \sqrt{ (A^i_k - B^i_k) (A^i_k + B^i_k) } = \sqrt{ \kappa_1^2 + \beta_2^2 \phi_k } \tag{14}
\]

The transverse components \( t_{x/y} \) are degenerate in phase I. Accounting for the chemical energy shift \( -\mu (n_x + n_y) \), we find the corresponding quadratic Hamiltonian for \( x/y \) modes in a form of Eq. (12) again, with the following constants

\[
A^x_k = A^y_k = \kappa_1 - \delta + \frac{5}{11} \kappa_1 \phi_k,
\]

\[
B^x_k = B^y_k = \frac{9}{22} \kappa_1 \phi_k, \tag{15}
\]

where \( \kappa_1 = (\kappa_1 + \beta_1)/2 \). This gives spin-wave dispersions

\[
\omega_{x/y} (k) = (\kappa_1 - \delta) \sqrt{1 + \frac{19}{22} \frac{\kappa_1 \phi_k}{\kappa_1 - \delta}} \tag{16}
\]

for the magnetic phase I with \( M \parallel c \).

For the magnetic phase II, similar calculations give the following results for the energy-momentum dispersions of the amplitude (\( x \)) and transverse (\( y, z \)) modes:

\[
\omega_x (k) = \sqrt{ \kappa_2^2 + \beta_2^2 \phi_k },
\]

\[
\omega_y (k) = \kappa_2 \sqrt{1 + \phi_k }, \tag{17}
\]

\[
\omega_z (k) = (\kappa_2 + \delta) \sqrt{1 + \frac{22}{19} \frac{\kappa_2 \phi_k}{\kappa_2 + \delta}} .
\]

It is noticed that in phase II with \( M \parallel ab \), there is no degeneracy of magnon branches, i.e., in-plane (\( y \)) and out-of-plane (\( z \)) magnons are split.

Some examples of magnon dispersion curves, representing different magnetic phases, are plotted in Figs. [3] and [4]. Fig. [3] shows the evolution of excitation spectra as a function of the crystal-field parameter \( \delta \), and their dependence on the exchange parameter \( J \) is illustrated in Fig. [4]. The features mentioned above such as a separation of the amplitude mode from the low-energy magnon modes, and splitting of the latter into two distinct branches in phase II can be noticed.

In order to see the evolution of the magnon gaps in more detail, we plot in Fig. [5] the magnetic excitation energies at the Bragg point \( Q = (\pi, \pi) \), as a function of the exchange constant \( J \) at different \( \delta \) values. In the PM phase (small \( J \)), all the branches have a finite gap. At the critical value of \( J \), gap for the amplitude mode closes. Further increase of \( J \) enhances the excitation gaps for all the branches in phase I [see panel (a)]. In phase II, there remains gapless Goldstone mode [see panels (b-d)], corresponding to a free rotation of the staggered moment within \( ab \) plane. Figs. [3][a] and (d) illustrate a transformation of spin-wave dispersions at the first order phase transitions between phases I and II.

B. Magnon Intensities

The intensity of spin excitations is given by the imaginary part the dynamic spin susceptibility which, within the present linear spin-wave approximation, takes the fol-
In the paramagnetic phase, the factors \( F_x(q) \) representing the spectral weights of \( \gamma = x, y, z \) magnon modes are given by

\[
F_x(q) = F_y(q) = \frac{54\kappa_2}{19}\phi_q; \quad F_z(q) = \frac{30\kappa_1}{11}\phi_q. \tag{19}
\]

In the magnetic phase I, we have

\[
F_x(q) = F_y(q) = \frac{27\kappa_1}{11}\phi_q; \tag{20}
\]

\[
F_z(q) = \frac{3\kappa_1}{11}(-1 + 11\eta_1)\phi_q.
\]

and, finally, for the magnetic phase II, we obtain

\[
F_x(q) = \frac{3\kappa_2}{19}(-1 + 19\eta_2)\phi_q; \tag{21}
\]

\[
F_y(q) = \frac{54\kappa_2}{19}\phi_q; \quad F_z(q) = \frac{60\kappa_2}{19}\phi_q.
\]

Magnon intensities are given by \( I(q, \omega) = \sum_\gamma \text{Im} \chi^2_q(\omega) \).

The contour plots of this quantity, multiplied by \( \sqrt{\omega} \) for clarity, are shown in Fig. 5. In the \((J - \delta)\) parameter space, five different panels in this figure correspond to the following form:

\[
\text{Im} \chi^2_q(\omega) = \left| \frac{F_y(q)}{\omega_y(q)} \right|^2 \delta(\omega - \omega_y(q)). \tag{18}
\]

In the paramagnetic phase, the factors \( F_y(q) \) representing the spectral weights of \( \gamma = x, y, z \) magnon modes are nearly equal. In phase II [panels (b-d)], which is of particular interest in the context of \( \text{Ca}_2\text{RuO}_4 \), the intensity of the highest energy (amplitude) mode is large near the critical point [see inset in panel (b)], but it fades away rather quickly at larger \( J / \lambda \) values.

V. APPLICATION TO \( \text{Ca}_2\text{RuO}_4 \)

The calcium ruthenate, \( \text{Ca}_2\text{RuO}_4 \), has a layered perovskite structure similar to that of \( \text{La}_2\text{CuO}_4 \) cuprate, and shows a Mott-insulating behavior below room temperature.\(^{22-23}\) It undergoes a magnetic phase transition at \( \sim 110 \) K, below which an antiferromagnetic order with a staggered moment \( M \simeq 1.3 \mu_B \) is observed.\(^{23}\) A sizeable value of \( LS \)-product indicates that SOC is not quenched,\(^{23}\) and hence this material may exhibit some features of the "excitonic" magnetism considered above. To our knowledge, no dynamical spin susceptibility measurements for \( \text{Ca}_2\text{RuO}_4 \) have been reported to date; some theoretical expectations are given below.

Observed \( ab \)-plane orientation of the momentum is consistent with the phase II in Fig. 2(b), which is stabilized by a compressive tetragonal distortion present in \( \text{Ca}_2\text{RuO}_4 \).

One can roughly estimate the parameters \( J / \lambda \) and blue points in Fig. 2(c), and thus represent (a) the paramagnetic phase, (b-d) the magnetic phase II (\( M \parallel ab \)), and, finally, (e) the magnetic phase I (\( M \parallel c \)).
\[ \frac{\delta}{\lambda} \] from the observed staggered moment \( M \simeq 1.3 \mu_B \) \cite{11} and the static magnetic susceptibility \( \chi \simeq 2.6 \times 10^{-3} \text{emu/m}\) \cite{12}. The moment \( M \) is determined by \( \eta_2 \) [see Eq. (7)] defining the distance to the critical point, while the susceptibility is given by

\[ \chi_{ab} = \frac{12 \mu_B^2 N_A}{\kappa_2 (1 + \eta_2)} \]

where \( N_A \) is Avogadro number. From the \( M \) and \( \chi \) equations, we find \( \eta_2 \simeq 0.85 \), and estimate the parameters \( J/\lambda \sim 0.17 \), and \( \delta/\lambda \sim 0.2 \). Magnon dispersions in \( \text{Ca}_2\text{RuO}_4 \) are then expected to resemble the plots shown in Fig. 6(b,c). These plots suggest a full magnon bandwidth of the order of \( 1.5 \lambda \sim 100 \text{ meV} \), given a spin-orbit coupling constant \( \lambda (= \xi/2) \simeq 75 \text{ meV} \) \cite{9}. The parameter \( J = \frac{\xi^2}{\eta} \simeq 13 \text{ meV} \) which follows from these estimates seems reasonable for \( t_{2g} \) systems with \( t_0 \sim 0.2 \text{ eV} \) and \( U \sim 3 \text{ eV} \). As far as the amplitude mode is concerned, the insets in Fig. 6 suggest a sizeable intensities; however, it might be difficult to identify this mode because it falls in the phonon-energy window (\( \sim 40 \text{ meV} \)).

VI. SUMMARY

We have studied here the phase diagram and magnetic excitations in Van Vleck-type \( d^4 \) Mott insulators with spin-orbit singlet ground state. As the intersite exchange interactions increase, the system makes a transition into an antiferromagnetically ordered state. For a square lattice geometry considered here, the exchange anisotropy supports a uniaxial-type magnetic order. Under a compressive strain, this order changes to the easy-plane one via a first order phase transition. We have calculated magnetic excitations over an entire phase diagram, quantifying the magnon dispersions and their intensities. We hope that the results presented here will motivate experimental studies of \( \text{Ca}_2\text{RuO}_4 \) and other potential candidate materials for excitonic-type magnetism \cite{10} by means of inelastic neutron and/or resonant x-ray scattering techniques.

We would like to thank B.J. Kim for useful discussions.

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