Orbital order, stacking defects and spin-fluctuations in the $p$-electron molecular solid RbO$_2$

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We examine magnon and orbiton behavior in localized O$_2$ anti-bonding molecular $\pi^*$ orbitals using an effective Kugel-Khomskii Hamiltonian derived from a two band Hubbard model with hopping parameters taken from ab initio density functional calculations. The considerable difference between intraband and interband hoppings leads to a strong coupling between the spin wave dispersion and the orbital ground state, providing a straightforward way of experimentally determining the orbital ground state from the measured magnon dispersion. The near degeneracy of different orbital ordered states leads to stacking defects which further modulate spin-fluctuation spectra. Proliferation of orbital domains disrupts long-range magnetic order, thus causing a significant reduction in the observed Néel temperature.

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Correlated systems have generated considerable interest in the literature in recent years. The discovery of high temperature superconductors and the subsequent development and application of correlated methods like LDA+U [1] and DMFT [2], has led to remarkable success in dealing with strongly correlated systems. At integer filling, strongly correlated systems are typically insulating and often show antiferromagnetic behavior arising from exchange or superexchange processes. Such systems include the undoped cuprates, where there is one hole per site that can hop in a square lattice of Cu $d_{x^2-y^2}$ orbitals, and heavy fermion materials like CeCuIn$_5$ where the Ce 4$f$ orbitals weakly couple to the valence states. Multi-band correlated systems can also show orbital ordering; the earliest successful application of LDA+U found orbital ordering in the KCuF$_3$ system [3].

Since correlated behavior is typically the domain of materials with 3$d$ and 4$f$ orbitals, comparatively little attention has been given to the study of correlated behavior in $p$ orbital systems. However, local moment magnetism in $2p$ orbitals has been implicated in several systems, such as at polar oxide vacancies [4] and substitutions [5]. The occurrence of $2p$ orbital moments at $p$-type LaAlO$_3$/SrTiO$_3$ interfaces [6] is still the only viable explanation of the insulating character that is observed in these interfaces, where the electron count would suggest metallic interface states. Alkali hyperoxides, to be discussed below, comprise another likely example. Recent calculations [7] suggest that doping of $d^0$ (no $d$ electrons) magnetic systems can stabilize or even enhance $2p$ magnetic moments in systems such as ZnO nanowires [8].

Recently, there has been significant interest in studying correlations in solid molecular systems, such as SrN [9], which consists of Sr octahedra containing either isolated N atoms or N$_2$ dimers, with calculations predicting that the magnetic moment is strongly confined to the anionic N$_2^-$ dimers. Calculations on the Rb$_4$O$_6$ system [9] and Cs$_4$O$_6$ [10] suggest that these systems would be a half-metallic ferromagnets particularly useful for spintronic applications, due to the reduced spin-orbit interaction in $p$ orbitals. However, these calculations were done within weakly correlated density functional theory; more recent calculations using LDA+U [11] suggest that the valence charge separates to give a mixture of magnetic hyperoxide O$_2^-$ anions and nonmagnetic peroxide O$_2^{2-}$ anions, and an insulating ground state. There seems to be some experimental disagreement as to whether Rb$_4$O$_6$ is conducting [12] or insulating [11]. In Rb$_4$O$_6$ the three different orientations of the O$_2$ dimers along the principle axes of the crystal give rise to frustration of the magnetic order.

Our interest here is in the alkali hyperoxides, taking RbO$_2$ as a specific example. Solovyev [13] has provided a study of the sister compound KO$_2$, considering the large spin-orbit coupling (SOC) limit. We present here an alternative viewpoint for RbO$_2$, based on the supposition that SOC is not so large an effect, so orbital moments are quenched by the crystal field, making the conventional real $p_x,p_y$ orbitals the natural basis for studying spin and orbital phenomena in RbO$_2$. Experimental measurement of the Landé $g$-factor [14] yields values close to 2, indicating a mostly spin moment, rather than the $g = 4/3$ value expected for large spin orbit coupling.

The MO$_2$ systems (M=Li,Na,Rb,Cs) exhibit complex phase diagrams and low temperature antiferromagnetism [15]. The phase diagrams at low temperature consist of several structural changes which are minor symmetry lowering distortions from the room temperature (averaged) tetragonal phase which is comparable to a distorted rock salt structure with O$_2^-$ ions playing the role of the anion, with the molecular axis pointing along the $c$ direction, shown in Fig. [16]. The Jahn-Teller effect causes the O$_2$ molecules to tilt away from the tetragonal axis, an effect which is difficult to reproduce in a non-magnetic LDA calculation. Below $194\, K$, RbO$_2$ shows incommensurate superstructure and a mixture of pseudotetragonal,
The interacting Hamiltonian is
\[ H = \sum_{\alpha, \beta} \sum_{i, j} t_{\alpha i, \beta j} c_{\alpha i}^\dagger c_{\beta j} + \frac{U}{4} \sum_{i, x, y} n_{i x} n_{i y} \]
where \( i, j \) run over sites and \( \alpha, \beta \in \{x, y\} \). We apply second-order perturbation theory to \( H \) to get an effective Kugel-Khomskii (KK) \([21]\) type Hamiltonian
\[ H_{KK} = H_{KK}^{nn} + H_{KK}^{nnn} \]
for nearest and next nearest neighbor interactions,
\[ H_{KK}^{nn} = \sum_{\langle i, j \rangle} \left\{ \frac{1}{4} (J_{xy} + J_{xx}) (S_i \cdot S_j - \frac{3}{4}) + \frac{1}{2} J_{xy} (\tau_i^x \tau_j^y + \tau_i^y \tau_j^x) + \frac{1}{2} J_{xx} (\tau_i^x \tau_j^x + \tau_i^y \tau_j^y) - \frac{1}{2} (J_{xx} - J_{xy}) \tau_i^x \tau_j^y (S_i \cdot S_j + \frac{1}{2}) \right\} \]
\[ H_{KK}^{nnn} = \sum_{\langle i, j \rangle} \left\{ \frac{1}{4} J_{xy} (S_i \cdot S_j - \frac{3}{4} + \tau_i^x \tau_j^x (S_i \cdot S_j + \frac{1}{2}) + J_1 (\tau_i^x \tau_j^y + \tau_i^y \tau_j^x) (S_i \cdot S_j + \frac{1}{2}) \right\} \]
in terms of parameters \( J_{xy} = 4t_{xy}^2/U, J_{xx} = 4t_{xx}^2/U, J_1 = 4t_{xy}^2/U, J_2 = J_0 + J_3 \) where terms with
ical results, we select Pauli matrices that operate in orbital space. For numer-
spin wave spectrum for xy ordering (blue dotted). Also, the solid, ABAB stacking and red dashed, ABCD stacking), and p-type ordering for both stackings as described in text (black dotted).

FIG. 2. (Color online) (a) Spin wave spectrum for RbO for p-type ordering for both stackings as described in text (black solid, ABAB stacking and red dashed, ABCD stacking), and spin wave spectrum for xy ordering (blue dotted). Also, the nearly dispersionless orbital spectrum is shown for p-type orderings (black dash-dot line). (b) Spin wave spectrum for ferroorbital ordering, which is orthorhombic symmetry.

A single \( \tau \pm \) operators have been neglected. The parameter \( J_0 = \pm (J_\sigma - J_\pi) \) depends on the direction of the bond between \( i \) and \( j \). The \( \tau \) operators can be represented as Pauli matrices that operate in orbital space. For numerical results, we select \( U = 3 \) eV, which is equivalent to \( U_{\text{eff}} = U - J \) for intraorbital \( U \) and Hund’s exchange \( J \) found previously [13] for the \( \pi^* \) orbitals in KO via the constrained LDA method [22]. This gives \( J_{xx} = 1.54 \) meV, \( J_{xy} = 4.8 \) meV, \( J_\sigma = 3.89 \) meV, and \( J_\pi = 0.34 \) meV.

Unlike previous studies [23,26] on the KK Hamiltonian, which contained only a single parameter \( t \) for both intraorbital and interorbital hopping, we consider here a KK-type Hamiltonian where the hoppings between orbitals channels are significantly different than hoppings within an channel, as shown in Fig. 2a. One previous study [26] concluded that due to unusual symmetries present, the KK Hamiltonian could not describe the observed order and gapped excitations. In the present work, the broken symmetry of the hoppings in this model should avoid these difficulties. These hoppings will lead to the orbital ground state having a significant impact on the spin wave dispersion, which should be measurable in experiment.

To proceed with spin/orbital wave theory a reference ground state for both the spin and orbital systems must be chosen. From here on, we will consider the electronic structure from the hole perspective, so that there is a single hole per site. We restrict our magnetic order to be antiferromagnetic between with nearest neighbors.

The ground state orbital ordering for this model is where antiferroorbital (AFO) ordering occurs in planes so that a given site with, say, \( |x\) occupied would have second neighbors (first neighbors in the plane) with \( |y\) occupied. We refer to this ordering as p-type. This ordering frustrates the first neighbor orbitals, so alternate stackings of the planes will be very close in energy and may be degenerate. For these orderings, the spin wave dispersion \( \omega_k^p \) and orbital wave dispersion \( \nu_k^p \) are given by

\[
\omega_k^p = \sqrt{(8J)^2 - [4J_{xy}\gamma_m(k) + 4J_{xx}\gamma_n(k)]^2}
\]

\[
\nu_k^p = \sqrt{(\frac{1}{2}J_1\gamma_2(k))^2}
\]

where \( J_1 = \sqrt{J_\pi J_\sigma} \) and \( \gamma_2(k) = \frac{1}{2}(\cos k_x + \cos k_y) \). Here, the effect of different stackings is contained in the structure factors \( \gamma_m(k) \) and \( \gamma_n(k) \). First we consider the case of ABAB stacking, where any given site has the same orbital occupation as the sites at displacements \((0,0,c)\) and \((0,0,-c)\) from it. This results in structure factors given by

\[
\gamma_m(k)^{\text{ABAB}} = \cos \left( \frac{1}{2} (k_x + k_y) \right) \cos \left( \frac{1}{2} k_z \right)
\]

\[
\gamma_n(k)^{\text{ABAB}} = \cos \left( \frac{1}{2} (k_x - k_y) \right) \cos \left( \frac{1}{2} k_z \right).
\]

An alternate stacking, ABCD, where each site has the opposite orbital occupation as the sites above and below in the \( \hat{z} \) direction, has structure factors of

\[
\gamma_m(k)^{\text{ABCD}} = \cos \frac{k_x}{2} \cos \frac{k_y}{2} \cos \frac{k_z}{2} + i \sin \frac{k_x}{2} \sin \frac{k_y}{2} \sin \frac{k_z}{2}
\]

\[
\gamma_n(k)^{\text{ABCD}} = \cos \frac{k_x}{2} \cos \frac{k_y}{2} \cos \frac{k_z}{2} - i \sin \frac{k_x}{2} \sin \frac{k_y}{2} \sin \frac{k_z}{2}.
\]

The dispersions are depicted in Fig. 2a.

An alternate orbital ordering we consider is where the ordering within planes are ferroorbital (FO) ordering. This ordering is not stable to orbital fluctuations within our KK model, however it may be stabilized in RbO by effects not considered here, such as the Jahn-Teller distortion that causes the cattling of the O₂ molecules. This ordering is of particular interest because if the stacking of planes is AFO, then the nearest neighbor spin exchange is maximized. With this orbital ordering (hereafter referred to as xy ordering), the spin sublattices have different dispersions due to the swapping of \( J_\pi \) and \( J_\sigma \) in each plane. The Kugel-Khomskii Hamiltonian yields a spin wave dispersion of

\[
\omega_k^{\tau \pi} = \sqrt{A_m^2 - (8J_{xy}\gamma(k))^2} \pm A_d
\]

with \( A_m = 8J_{xy} - J_\pi [2 - \cos(k_x) - \cos(k_y)] \) and \( A_d = (J_\sigma - J_x) [\cos(k_x) - \cos(k_y)] \), and is shown in Fig. 2a.
Thus far, the orderings considered all preserve tetragonal symmetry, but orthorhombic and monoclinic low temperature phases of RbO$_2$ exist. The final orbital ordering we consider is FO ordering for every site in the crystal, hereafter called xx ordering, which is orthorhombic symmetry. This has spin-wave dispersion $\omega_{k}^{xx} = \sqrt{A_{k} - B_{k}^2}$ where $A_{k} = 8J_{xx} + \frac{1}{4}(J_{x} - J_{x} \cos k_{x} - J_{y} \cos k_{y})$ and $B_{k} = 8J_{xx}\gamma(k)$. Again, this configuration is not stable with respect to orbital fluctuations, but it may be stabilized by effects not considered here, which a study of KO$_2$ indicates is the case 27. The magnon dispersions is shown in Fig. 2b.

| Orbital Order |
|---------------|
| xx | xy | p-ABAB | p-ABCD |
| $E_o$ | -12.680 | -12.680 | -14.795 | -14.795 |
| $E_S$ | -0.411 | -3.266 | -2.333 | -2.288 |
| $E_D$ | 0 | 0 | -0.010 | -0.010 |
| $E_{tot}$ | -13.091 | -15.946 | -17.138 | -17.093 |

TABLE I. Energies contributing to the ground state energy in meV. $E_o$ is the classical ground state energy, $E_S(E_D)$ is the quantum correction from spin/orbital-wave theory.

The ground state energies for these four orbital orderings are listed in Table I where we find that the ABAB stacking of planar orbital ordering is the lowest energy. For an average nearest neighbor spin exchange of $\tilde{J} = 3.17$ meV (in p-type orderings), high temperature series expansion 28 would predict $T_N \approx 1.4 J = 51 K$, much higher than the observed $T_N = 15 K$. The frustrated exchanges within planes would reduce this value somewhat, but not enough to give a prediction reasonably close to the experimental transition.

As expected, the two stackings examined for the planar orbital ordering are very nearly degenerate, with only quantum fluctuations in the spin waves breaking the degeneracy at this level of approximation. It is rather clear that due to the strong asymmetry between hopping within an orbital channel and hopping between orbital channels, the orbital ground state significantly impacts the spin wave spectrum and could be inferred from a measurement of the low temperature magnons. The planar orbital orderings don’t significantly impact the spin wave dispersion, so even if the stacking is disordered magnon excitations should be coherent. Energetically the next state above p-type ordering is the xy ordering, which is $\sim 1.2$ meV $\approx 14 K$ higher in energy than p-type ordering. Above this temperature orbital domains should proliferate. The strong modulation of exchange constants at the domain boundaries should nucleate magnetic domains 29, leading to the low observed Néel temperature of RbO$_2$ of 15 K.

Orbitons are quite difficult to measure experimentally. They do not couple directly to neutrons, the standard measurement technique for magnons. Recently orbitons have been measured in titanates via X-rays 30, but the inference of the orbital dispersion is very indirect. The measured dispersion is negligible, suggesting 30 that X-rays modulate bonds resulting in a much bigger scattering from two-orbitons than from single orbitons. It may be that in narrow band molecular oxide systems the X-rays will create single orbiton excitations with all bond modulation inside a unit cell. If that is the case, the X-ray measured dispersion in RbO$_2$ should be clearly observable, if a similar experiment can be done. Neglected here is the Jahn-Teller effect which rotates the O$_2$ molecules and breaks the orbital degeneracy, which will select a particular ground state orbital ordering.

We have examined independent magnon and orbiton excitations in RbO$_2$ within spin/orbital wave theory, finding considerable coupling between the easily measured magnon excitations and the difficult to measure orbital ground state. This strong coupling arises from the large anisotropy in the hopping parameters in the O$_2$ $\pi^*$ bands. This indicates that MO$_2$ materials are attractive for studying the interplay between orbital ordering and p-electron magnetism. E. R. Y. and W. E. P were supported by DOE SciDAC Grant No. DE-FC02-06ER25794. The authors would like to thank J. Kuneš, R. T. Scalettar, and C. Felser for stimulating conversation.

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