Magnetically Hidden Order of Kramers Doublets in $d^1$ Systems: Sr$_2$VO$_4$

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We formulate and study an effective Hamiltonian for low-energy Kramers doublets of $d^1$-ions on a square lattice. We find that the system exhibits a magnetically hidden order in which the expectation values of the local spin and orbital moments both vanish. The order parameter responsible for a time-reversal symmetry breaking has a composite nature and is a spin-orbital analog of a magnetic octupole. We argue that such a hidden order is realized in the layered perovskite Sr$_2$VO$_4$.

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The ions with odd number of electrons have ground states which are at least doubly degenerate. The latter, known as Kramers degeneracy, is protected by time-reversal symmetry [1]. In Mott insulators the exchange interactions between Kramers doublets often induce a time-reversal symmetry breaking phase lifting the local degeneracy. As a result, a magnetic state with a well defined ordered pattern of local magnetic moments is formed at low temperatures, which, in turn, leads to the new Bragg peaks in neutron scattering experiments.

The above conventional picture may, however, fail for the insulating systems in which the local and non-local interactions between magnetically active degrees of freedom compete with each other. This competition may lead to a spontaneous time-reversal symmetry breaking through the development of a more complex order parameter, while the magnetic dipole moments of spin and orbital origin, being locally entangled, would remain disordered across the transition. The resulting order can be thus hidden to some experimental probes.

In this Letter we show that such a magnetically hidden order may be realized in transition-metal compounds. In the following we focus on a system of $d^1$ ions with partially filled $t_{2g}$ levels on a square lattice, like the layered insulating compound Sr$_2$VO$_4$ [2, 3]. Here, a square lattice of V$^{4+}$ ions is formed in the $ab$-plane by corner-shared VO$_6$ octahedra, elongated along the c-axis. Sr$_2$VO$_4$ undergoes a phase transition on cooling at around $T_c \approx 100$ K. The crystal structure remains tetragonal across the transition, the $c/a$ ratio jumps to a somewhat higher value, and the magnetic susceptibility shows a sharp drop near $T_c$ [4]. It has been suggested that a (weakly) first-order transition to an antiferromagnetic and orbitally ordered state could be responsible for the observed anomalies [4]. However, the neutron scattering experiments were not able to detect any magnetic order in the low temperature phase [2]. The nature of the ordered phase still remains experimentally unknown. Theoretically, as a possible candidate, a nontrivial orbital-stripe order coexisting with collinear antiferromagnetic spin order with large unit cell has been proposed [5].

Here, based on the microscopic theory, we propose that an unusual symmetry-breaking phase, induced by spin-orbit coupling and compatible with tetragonal crystal symmetry, is realized in Sr$_2$VO$_4$. We argue that the staggered ordering of composite spin-orbital objects, magnetic octupoles, is responsible for the phase transition. There is no static order of either spin or orbital magnetic moments in the ground state, hence the absence of magnetic Bragg peaks.

The octupolar order has thus far been discussed primarily in the context of $f$-electron systems [6, 7]. The peculiar physics of $t_{2g}$ orbitals in tetragonal compounds uncovered here shows that this unusual state is well hosted by $d$-electron systems, too.

**Low-energy effective Hamiltonian.** We first introduce the local degrees of freedom and then discuss the exchange interactions between them. The V$^{4+}$ ion has a single unpaired electron residing in the $t_{2g}$ manifold of $xy$, $xz$, and $yz$ orbitals. The tetragonal elongation of the oxygen octahedra along the $z \parallel c$-axis only partly lifts the threefold orbital degeneracy: The $xy$ orbital is pushed to a higher energy, while $xz$ and $yz$ orbitals remain degenerate. The orbital angular momentum is unquenched and the spin-orbit coupling is active. We thus start with a local Hamiltonian $H_0 = \Delta_{cf}(\frac{3}{2}I_z^2 - I_z^4) - \lambda \vec{S} \cdot \vec{S}$ consisting of a tetragonal crystal field $\Delta_{cf}$ and a spin-orbit coupling $\lambda$. Here $\vec{S}$ is an electron spin, and $I_z$ is an effective angular momentum with $|\langle I_z = 0 \rangle| = |\langle xy \rangle|$, $|\langle I_z = \pm 1 \rangle| = \frac{1}{\sqrt{2}}(|\langle xz \rangle| \pm |\langle yz \rangle|)$. The total magnetic moment $\vec{M} = 2\vec{S} + \vec{L}$, where $\vec{L} = -\kappa \vec{I}$ is a true angular momentum and $\kappa$ is a so-called covacency factor of order one [1]. The eigenstates of $H_0$ are spanned by three sets of Kramers doublets. The corresponding local level structure is schematically shown in Fig. 1(a). Concerning the energy scales involved, the *ab initio* study of Sr$_2$VO$_4$ electronic structure suggests $\Delta_{cf} \approx 80$ meV [2], and $\lambda \approx 30$ meV for free V$^{4+}$ ion is known experimentally [1]. In what follows, we retain only the two low-energy levels and neglect the one located at high energy $\sim \Delta_{cf}$. We label Kramers partners within a doublet by isospin index $\uparrow$ and $\downarrow$ ($s^z = \pm \frac{1}{2}$), while the two doublets are denoted by pseudoorbital index $\pm$ ($s^z = \pm 1$). The wave functions of the ground state doublet, $\sigma^z = +1$, are

$$|\uparrow\rangle_+ = |+1, \uparrow\rangle, \quad |\downarrow\rangle_+ = |-1, \downarrow\rangle.$$  

(1)
We find the dominant part of the Hamiltonian and discuss later energy Kramers doublets \((1)\) and \((2)\). We first consider ions. The effective Hamiltonian is obtained by projecting of interest here, \(\theta\) reality associated with the gradient of their phases determined by orbital angular momentum [see Fig. 1(b)].

The first excited level, located at an energy \(\delta = \lambda + \frac{1}{4}(2\Delta_{cf} - \lambda)(1/\cos 2\theta + 1)\), has the following eigenstates:

\[
\begin{align*}
\lvert \uparrow \rangle &= \sin \theta \lvert -1, \uparrow \rangle + \cos \theta \lvert 0, \downarrow \rangle, \\
\lvert \downarrow \rangle &= \sin \theta \lvert 1, \downarrow \rangle + \cos \theta \lvert 0, \uparrow \rangle,
\end{align*}
\]

where \(\tan 2\theta = 2\sqrt{2}\lambda/(\lambda - 2\Delta_{cf})\). In the limit \(\Delta_{cf} \gg \lambda\) of interest here, \(2\theta \sim \pi\) and \(\delta \sim \lambda\).

We now discuss the interactions between neighboring ions. The effective Hamiltonian is obtained by projecting the corresponding \(t_{2g}\) superexchange model of Ref. \([8]\) onto the reduced Hilbert space spanned by the two low energy Kramers doublets \((1)\) and \((2)\). We first consider the dominant part of the Hamiltonian and discuss later the effects of a finite Hund’s coupling. We find

\[
\mathcal{H} = J \sum_{\langle ij \rangle} (\sigma_i \cdot \sigma_j + \frac{1}{4})(1 \pm \sigma_i^z)(1 \pm \sigma_j^z) - \frac{\delta}{2} \sum_i \sigma_i^z, \tag{3}
\]

where the first term describes the exchange coupling between the neighboring states, the \(SU(2)\) isospin degrees of freedom are represented by \(\sigma_i\), and Pauli matrices \(\sigma_i\) denote pseudo-orbitals, referred to as simply orbitals from now on (not to be confused with original \(t_{2g}\) orbitals). The upper (lower) sign is taken for a bond along \(a(b)\) direction, \(J = t^2/U\), where \(t\) is a transfer integral and \(U\) stands for the Coulomb repulsion. The local level splitting \(\delta\) between two Kramers doublets is given by the second term.

The ground state properties.— The interaction between the isospins \(\sigma_i\) in Eq. \((3)\) depends on the orbital occupations through the operator \((1 \pm \sigma_i^z)(1 \pm \sigma_i^z)\). Since this operator is non-negative, the isospin exchange is purely antiferromagnetic (or equal to zero). This suggests that in the classical limit, \(\langle \sigma_i \sigma_j \rangle = -\frac{1}{4}\), the expectation value of the first term in the Hamiltonian vanishes and all orbital configurations are degenerate. This extensive classical degeneracy, inherent to the coupled spin-orbital systems \([8]\), is lifted here by the second term of the Hamiltonian \(\mathcal{H}\), selecting uniform orbital order with \(\sigma^z = \pm 1\). The antiferromagnetic ordering of isospins \(\sigma_i\) is then stabilized.

While the ground state in terms of staggered order of isospins may, at a first glance, look conventional, its physical properties are in fact very unusual and depend on the spatial orientation of the order parameter \(\bar{m} \equiv \langle \bar{S}_Q \rangle\) \(Q = (\pi, \pi)\) is the ordering wave vector. To illustrate this, we express the isospin \(\sigma\) in terms of the original, physical spin \(\vec{S}\) and angular momentum \(\vec{L}\), operators:

\[
s^x(y) = S^x(y)(\langle l_x \rangle^2 - \langle l_y \rangle^2), \quad s^z = S^z. \tag{4}
\]

The in-plane components of isospins are represented by a composite object, which is, remarkably enough, a spin-orbital analog of a magnetic octupole. On the other hand, the axial component is equivalent to the physical spin. Thus, in-plane ordering of isospins \(\langle \bar{m} \parallel z \rangle\) corresponds to a staggered order of magnetic octupoles, while the axial one \(\langle \bar{m} \parallel z \rangle\) corresponds to a magnetic dipolar order. In the former case, the local expectation values of both spin and angular moments are exactly zero: \(\langle \bar{S}_i \rangle = \langle \bar{l}_i \rangle = 0\). This can be explicitly verified using the wave functions \((1)\) of the ground state doublet: the in-plane \(g\)-factor of this doublet \(g_{ab} \equiv 0\). In the case of a dipolar order, \(\bar{m} \parallel z\), we find again a somewhat unusual picture: the value of ordered magnetic moments is strongly suppressed, \(\langle M^z \rangle = 1 - \kappa \ll 1\), because of compensation between spin and orbital magnetic moments. In the absence of covalency, i.e. \(\kappa = 1\), both \(\langle M \rangle\) and \(g_e = 2(1 - \kappa)\) vanish.

The effective Hamiltonian \((3)\), with isospin rotational symmetry, cannot select a direction of the order parameter \(\bar{m}\): The latter can be rotated from a purely dipolar character to a purely octupolar one at no energy cost. In other words, a Goldstone mode describing the out-of-plane rotation of isospins corresponds physically to fluctuations between dipolar and octupolar orderings. However, the \(SU(2)\) isospin symmetry is only approximate and is broken by Hund’s coupling \(J_H\), neglected so far. Finite \(J_H\) induces the anisotropy term, which in the present case is of easy-plane form \(\mathcal{H}_{\alpha}(i,j) = -\alpha J_s \sigma_i^z \sigma_j^z\), with \(\alpha = 2J_H/U \ll 1\). It confines the isospins in the plane and selects the staggered octupolar order, with vanishing dipolar moments \(\langle \tilde{S}_i \rangle\) and \(\langle \tilde{l}_i \rangle\) on every site. The emergence of this highly unusual state in an apparently simple \(d^1\) Mott insulator like \(Sr_2\)VO\(_4\) is surprising, given that its single-hole counterpart, \(d^0\) perovskite \(La_2CuO_4\), is a conventional antiferromagnet. The origin of new physics here is due to an unquenched spin-orbit coupling, the significance of which is being recognized in the context of various phenomena \([10, 11, 12, 13, 14]\).
Excitation spectra.— We now turn to the excitation spectrum above the octupolar ordered state. We first study the Hamiltonian \( \mathcal{H} \) at a mean-field level, decouple it into isospin and orbital sectors, and discuss later the interactions between them. We employ isospin (orbital) wave representation for \( \hat{s}_i \) (\( \hat{a}_i \)) operators in terms of Holstein-Primakoff bosons \( b_i \) (\( a_i \)) and diagonalize the harmonic part of the mean-field Hamiltonian.

The isospin (intradoublet) and orbital (inter-doublet) excitation energies are given by \( \omega_{\mathbf{k}} = 2J_\mathbf{k}(1 - \gamma_k + \alpha \gamma_k)(1 + \gamma_k) \) and \( \Omega_{\mathbf{k}} = \sqrt{\delta(\delta + 8J_\mathbf{k} \gamma_k)} \), respectively. Here \( \gamma_k = \frac{J}{2}(\cos k_x + \cos k_y) \), \( J_s = J(1 + \sigma_i^x \sigma_j^x) \), and \( J_o = J(\sigma_i^x \sigma_j^x + \frac{1}{3}) \). At \( T = 0 \), we estimate \( J_s \simeq J \) and \( J_o \simeq -0.08J \). The dispersion relations are plotted in Fig. 2 (left) for the realistic values of the parameters (\( \delta = 2.2 \) and \( \alpha = 0.2 \) in units of \( J \)).

The in-plane isospin excitations are gapless, while the out-of-plane gap (\( \sim \sqrt{\alpha} \)) at \( \Gamma \) point is induced by easy-plane anisotropy protecting octupolar order. The weakly dispersive interdoublet excitations are centered around \( \delta \).

The above elementary excitations correspond, in fact, to the fluctuations of rather unconventional degrees of freedom. The in-plane isospin waves represent octupolar excitations, not directly coupled to the conventional spectroscopic probes such as neutrons. To make some predictions for inelastic neutron scattering experiments, we now discuss the magnetic excitations. To this end, we express the local magnetic moment \( \mathbf{M} \) in terms of isospin and orbital wave operators \( b_i \) and \( a_i \), respectively:

\[
\begin{align*}
M^x_i & \simeq (b_i + b_i^\dagger)(a_i + a_i^\dagger), \\
M^y_i & \simeq e^{i\mathbf{Q}\mathbf{r}}(a_i + a_i^\dagger), \\
M^z_i & \simeq i(1 - \kappa)e^{i\mathbf{Q}\mathbf{r}}(b_i - b_i^\dagger).
\end{align*}
\]

(5)

Here, only the leading order terms in boson operators are kept, and the isospin order parameter along \( y \)-axis is assumed. All three components of \( \mathbf{M} \) consist of fluctuating parts only. Hence, no magnetic Bragg peaks will be seen in elastic scattering. The inelastic response of the ordered state is rather nontrivial. The fluctuations of \( M^y \) component, which have the largest spectral weight of order one, are given by orbital excitations only. We thus predict well-defined interdoublet excitations at energies \( \sim \delta \) [upper curve in Fig. 2 (left)] to be observed by polarized neutrons. The out-of-plane magnetic response, \( M^z \) component in Eq. (5), corresponds to gapped out-of-plane isospin excitations. However, the small spectral weight \( \sim (1 - \kappa)^2 \) would probably make it hard to detect them. The in-plane \( M^x \) response is given by the composite isospin-orbital excitations [see Eq. (3)].

Finite temperature transition.— We now turn to finite temperatures and show that interplay between interdoublet and intradoublet excitations leads to a first order phase transition. The in-plane ordering of isospins breaks their rotational symmetry around \( z \)-axis. Note that the uniform order of low-energy doublets, \( \sigma \equiv \langle \sigma_i^z \rangle = +1 \), conserves the tetragonal crystal symmetry, as \( xx \) and \( yz \) orbitals are equally occupied on every site. The scale of

FIG. 2: (Color online) Left: The dispersions of elementary excitations along the direction \( X(\pi, 0) \rightarrow M(\pi, \pi) \rightarrow \Gamma \) in the Brillouin zone. The lower (upper) curve corresponds to the isospin (orbital) waves. Right: The spectrum of in-plane, \( M^x \) component, magnetic excitations. It consists of a continuum of composite, isospin-orbital excitations (shaded area), and a quasiparticle part (lower curve, the width scales with intensity). The corresponding diagrams are also shown: The solid (wavy) lines denote the isospin (orbital) excitations and the open dots stand for the three-particle vertex in Eq. (6). Energies are given in units of \( J \).
Mott insulator. The present theory suggests a nontrivial magnetic excitation spectrum in the ordered state, that can be verified by neutron scattering experiments. The spin-resolved circularly polarized photoemission experiment would be another test of the present scenario. This technique measures the \( \vec{I} \cdot \vec{S} \) scalar product \( [17] \), which we predict to be \( \sim 0.5 \) in the ground state. Finally, we suggest that another candidate to exhibit octupolar order is \( \text{Sr}_2\text{NbO}_4 \), in which a more pronounced spin-orbit coupling is expected. \( \text{Sr}_2\text{NbO}_4 \) is known to be a Mott insulator \( [18] \), however, its low temperature magnetic properties have not yet been reported.

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[1] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, Oxford, 1970).

[2] M. Cyrot et al., J. Solid State Chem. 85, 321 (1990).

[3] J. Matsumo et al., Phys. Rev. Lett. 95, 176404 (2005).

[4] H.D. Zhou et al., Phys. Rev. Lett. 99, 136403 (2007).

[5] Y. Imai, I. Solovyev, and M. Imada, Phys. Rev. Lett. 95, 176405 (2005).

[6] See, e.g., Y. Kuramoto, Prog. Theor. Phys. Suppl. 176, 77 (2008), and references therein.

[7] A few exceptions include the case of frustrated magnets [T. Momoi, P. Sindzingre, and N. Shannon, Phys. Rev. Lett. 97, 257204 (2006); M.E. Zhitomirsky, Phys. Rev. B 78, 094423 (2008)], and possible order of complex e_g orbitals in ferromagnetic manganites [J. van den Brink and D. Khomskii, Phys. Rev. B 63, 140416(R) (2001)].

[8] G. Khalullin, Prog. Theor. Phys. Suppl. 160, 155 (2005).

[9] At vanishing spin-orbit coupling, \( \delta = 0 \) and the quantum effects select the spin-singlet dimer states, see G. Jackeli and D.A. Ivanov, Phys. Rev. B 76, 132407 (2007).

[10] O. Tchernyshyov, Phys. Rev. Lett. 93, 157206 (2004).

[11] S. Gangadharaiah, J. Sun, and O.A. Starykh, Phys. Rev. Lett. 100, 156402 (2008).

[12] G. Jackeli and G. Khalullin, Phys. Rev. Lett. 102, 017205 (2009).

[13] G. Chen, L. Balents, and A.P. Schnyder, Phys. Rev. Lett. 102, 096406 (2009).

[14] A. Shitade et al., Phys. Rev. Lett. 102, 256403 (2009).

[15] Our mean-field study gives a transition temperature \( T_{MF} \sim 0.74J \). Using \( t = 0.19 \) eV and \( U = 2.58 \) eV, suggested by \( ab \text{ initio} \) calculations \( [8] \), we estimate \( J \approx 14 \) meV, and find a reasonable value \( T_{MF} \sim 120 \) K.

[16] The susceptibility upturn seen at low temperatures is possibly due to spin-one \( V^{3+} \) impurities induced by the oxygen deficiency, see N. Suzuki, T. Noritake, and T. Ihoiki, Mater. Res. Bull. 27, 1171 (1992).

[17] T. Mizokawa et al., Phys. Rev. Lett. 87, 077202 (2001); G. Ghiringhelli et al., Phys. Rev. B 66, 075101 (2002).

[18] K. Isawa and M. Nagano, Physica C 357-360, 359 (2001).