Novel magnetic state in $d^4$ Mott insulators

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We show that the interplay of strong Hubbard interaction $U$ and spin-orbit coupling $\lambda$ in systems with the $d^4$ electronic configuration leads to several unusual magnetic phases. While in the atomic limit the system is in a non-magnetic $J = 0$ singlet state, we find that the competition between superexchange and atomic spin-orbit coupling dramatically changes the local moment, which challenges the conventional wisdom that local moments are well-defined in a Mott insulator. Most notably, we find that in the Mott limit at strong $U$ there is a phase transition from a non-magnetic insulator of uncoupled $J = 0$ singlets to an orbitally entangled ferromagnetic insulator. We identify candidate materials and present predictions for Resonant X-ray Scattering (RXS) signatures for the unusual magnetism in $d^4$ Mott insulators and contrast them with the well-studied $d^5$ case.

Introduction: The interplay of strong interactions and spin-orbit coupling (SOC) has recently taken center stage in condensed matter research. The discovery of topological band insulators [1] has fueled tremendous interest in materials with strong spin-orbit coupling, while strong correlations have produced exciting phenomena, ranging from high $T_c$ superconductivity [2] to colossal magnetoresistance [3]. These two features naturally combine in the $5d$ transition metal materials, which hold the potential of hosting new phases of matter with entangled spin, orbital and charge degrees of freedom. Already there are many predictions for exotic topological matter, for example the topological Mott insulators [4] and Weyl semi-metals [5]. Recent experiments demonstrating that Sr$_2$IrO$_4$ is an unusual Mott insulator with a half filled $J = 1/2$ band resulting from strong SOC [6] have prompted the search for Weyl semi-metals in iridium pyrochlores [7].

We emphasize that most of the focus in this field to date has been on iridium based materials with a $d^5$ electronic configuration. In the limit of strong spin orbit coupling the $t_{2g}$ orbitals are split into $J = 1/2$ and $J = 3/2$ multiplets. For the $d^5$ configuration, all of the $J = 3/2$ states are filled and the only low-energy degree of freedom is a single hole in the $J = 1/2$ manifold which is sufficient to understand most phenomena. This picture is often given in terms of non-interacting atomic levels, but it also holds in the strongly interacting limit for the $d^5$ configuration.

The physics is dramatically different for other fillings. Mott insulators with $d^1$ and $d^2$ configuration have been shown to exhibit exotic magnetic phases [8, 9] in the presence of large SOC. In the $d^1$ case, SOC is quenched in a cubic environment [10] and the problem reduces to a conventional spin-only model. This leaves only the $d^4$ case, which has been largely ignored because it is expected that large SOC and strong interactions give rise to a non-magnetic state in the atomic limit [9], though see [11].

We show that contrary to the above expectation, the $d^1$ configuration has a rich magnetic phase diagram as a function of SOC and Hubbard $U$. In particular, at large $U$ there is a quantum phase transition from the expected non-magnetic insulator of local $J = 0$ singlets to a ferromagnetic insulator with a nonzero local moment as SOC is reduced. This moment arises from superexchange-induced mixing, at a single site, of magnetic states largely from the higher energy triplet with the singlet. Our result provides an interesting counterexample to the commonly held notion that Mott insulators have well defined local moments that cannot be affected by small perturbations (compared to the interaction scale $U$). We then present predictions for Resonant X-ray Scattering (RXS), which has proven to be an indispensable tool for studying local magnetic states. Considering resonant enhancement coming from virtual excitations to the $J = 1/2$ intermediate states in the $d$- orbitals, we find that the scattering cross-section at the $L_2$ edge is about an order of magnitude larger than at the $L_3$ edge. This is an indication of weight in the local state coming from the $J = 1$ triplet. In contrast, experiments on the $d^5$ Sr$_2$IrO$_4$ find suppressed signal at the $L_2$ edge.

The paper is organized as follows: we start by describing the multi-orbital Hubbard model relevant for oxides with $d^4$ configuration. We then diagonalize it exactly for a two-site system with strong SOC and large $U$, which helps us to build intuition about the problem. In the Mott limit, the two-site calculation is expected to provide a reliable description of local properties and the nature of the magnetic interactions between neighboring sites. It also provides the basis for calculating RXS cross-sections which can be used to verify the unusual ferromagnetic Mott insulator. Following the exploration of the local physics, we propose an effective magnetic model on a lattice that leads to a Ginzburg-Landau description of the magnetic phase transition. We conclude by identifying some specific materials among the ruthenates and osmates with a $d^4$ electron count where this phase transition could be observed by using strain to modify the effective interaction strength and SOC.

Hamiltonian: We consider a three-orbital Hubbard model with SOC that captures the essence of $4d^4$ or $5d^4$ materials with an octahedral cage of oxygen surround-
ing each transition metal ion (as occurs in, e.g., the perovskites, double perovskites and pyrochlores). The crystal field splitting between the $t_{2g}$ orbitals and the $e_g$ orbitals is the largest energy scale and for $d^4$ filling, only the $t_{2g}$ levels are relevant. The Hamiltonian has the following form:

$$H = H_{hop} + \sum_i (H_{i,U} + H_{i,SOC})$$

where

$$H_{hop} = \sum_{ij} \sum_{\alpha\beta} \sum_{\sigma\sigma'} \left( t_{ij}^{\alpha\sigma,\beta\sigma'} c_{i\alpha\sigma}^\dagger c_{j\beta\sigma'} + \text{h.c.} \right)$$

$$H_{i,U} = \lambda \sum_{\alpha\beta} \sum_{\sigma\sigma'} \langle \sigma \cdot 1 \rangle_{\alpha\beta,\sigma} c_{i\alpha\sigma}^\dagger c_{i\beta\sigma'}$$

$$H_{i,U} = U \sum_{\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} + (U - 3J_H) \sum_{\alpha>\beta,\sigma} n_{i\alpha\sigma} n_{i\beta\sigma} + (U - 2J_H) \sum_{\alpha>\beta,\sigma} n_{i\alpha\sigma} n_{i\beta\sigma} - J_H \sum_{\alpha>\beta} \left( c_{i\alpha\uparrow}^\dagger c_{i\beta\downarrow} c_{i\beta\uparrow} c_{i\alpha\downarrow} + \text{h.c.} \right)$$

Here $c_{i\alpha\sigma}^\dagger$ ($c_{i\alpha\sigma}$) creates (annihilates) an electron at site $i$ in orbital $\alpha$ with spin $\sigma$. $t_{ij}^{\alpha\sigma,\beta\sigma'}$ is the hopping matrix element from the state $\beta\sigma'$ at site $j$ to $\alpha\sigma$ at site $j$. For simplicity we will consider only nearest neighbor hopping, and take it to be diagonal in both spin and orbital space ($t_{ij}^{\alpha\sigma,\beta\sigma'} \rightarrow t_{ij}^{\alpha\sigma,\beta\sigma}$). $U$, $J_H$ and $\lambda$ are intra-orbital interaction strength, Hund’s coupling and SOC strength respectively. $\langle \sigma \cdot 1 \rangle_{\alpha\beta,\sigma}$ are the matrix elements of atomic SOC in the $t_{2g}$ basis. Note that the $t_{2g}$ orbitals have an effective orbital momentum $L = -1$. Unless mentioned otherwise, all energy scales are measured in units of $t$.

**Two-site results:** We solve the multi-orbital Hubbard model described in Eq. 1 for a two-site system using exact diagonalization. As a function of $\lambda$ and $U$ the two-site system shows three different magnetic states as shown in Fig. 1(a): (i) a non-magnetic state ($J = 0$) in the large $\lambda$ limit, (ii) a ferromagnet with $J = 2$ for small $\lambda$ and moderate $U$ and (iii) a different ferromagnet with $J = 1$ at large values of $U$ and small $\lambda$. The magnetic phases can be understood easily in some limiting cases. The $J = 0$ state at large $\lambda$ and small $U$ corresponds to a band insulator with a completely filled $J = 3/2$ manifold. The post-perovskite material NaIrO$_3$ and perovskites BaOsO$_3$ and CaOsO$_3$ are believed to be in such a state [12, 13]. With increasing $U$, this band insulator smoothly crosses over into a $J = 0$ Mott insulator, consistent with recent Gutzwiller and Dynamical Mean-Field Theory calculations [13]. We will discuss the non-magnetic Mott insulator in greater detail below. In the limit of small $\lambda$ and moderate $U$, the $J = 2$ ferromagnet is essentially the Stoner ferromagnet seen in SrRuO$_3$ [14].

![FIG. 1: (a) Magnetic phase diagram of the two-site $d^4$ system in the $U-\lambda$ plane. It consists of three phases: a non-magnetic ($J = 0$) phase and two different ferromagnetic phases ($J = 2$ and $J = 1$). (b) A magnetic phase transition occurs as a function of $\lambda$ in the Mott limit ($U/t = 40$ and $J_H = 0.2U$). The total $J$-moment changes from $J = 1$ to $J = 0$ at $\lambda_c/t \approx 0.185$. The local $J$-moment also changes from $J_s \approx 1$ to $J_t \approx 0$ at the phase transition. The local $S_i$ and $L_i$ moments, on the other hand, do not change across this phase transition.

![FIG. 2: Schematic rationalization for ferromagnetic superexchange. For the antiferromagnetic configuration (a), the intermediate state has a higher energy, due to Hund’s coupling on the $d^3$ site, than the corresponding state in the ferromagnetic case (b). To make use of these virtual processes, the “down” electrons in (b) must also occupy different orbitals.

ferromagnetic state must exist for small $\lambda$, we next turn to an analysis of the competition between the ferromagnetic superexchange interaction and SOC and show that it leads to a phase transition from an unusual ferromag-
Magnetic Mott insulator to a non-magnetic insulator with increasing $\lambda$ as shown in Fig. 1(b). More importantly, the local $J$ moment changes from $J_1 \approx 1$ to $J_1 \approx 0$. This challenges the generally accepted notion that the local moment is a robust quantity in Mott insulators. A generalization of the two-site result to the thermodynamic limit will be discussed below.

**RXS scattering cross-section:** We now make predictions for RXS cross-sections, which can be used to identify the ferromagnetic insulator. For Mott insulators, RXS matrix elements are usually calculated in the free ion approximation\cite{6, 16}. However, to include non-local effects, which we will show is crucial for understanding the $d^4$ ferromagnetic Mott insulator, we need to generalize the expression for RXS amplitude as follows \cite{15}

$$\Delta f(\omega) \propto \text{Tr} \left[ \rho \sum_n \frac{(\mathbf{e} \cdot \mathbf{D})^\dagger |\psi_n\rangle \langle \psi_n| \mathbf{e} \mathbf{D}}{E_n - E_G - \hbar \omega - i\Gamma_n} \right]$$

(5)

where $\rho$ is the reduced density matrix at the scattering site, and the trace is over atomic states in the $d^4$ configuration. $\mathbf{e} (\mathbf{e}')$ is the incoming (outgoing) polarization, $\mathbf{D}$ is the dipole operator, $|\psi_n\rangle$ is an excited state (in the $d^5$ configuration) with energy $E_n$, and $E_G$ is the ground state energy. $\Gamma_n$ is the inverse life time of the excited state $|\psi_n\rangle$.

The $L_2$ and $L_3$ edges correspond to excitations from $2p_{1/2}$ and $2p_{3/2}$ levels to the intermediate $d^5$ states respectively. The $d^5$ states are also split by SOC into $J = 1/2$ and $J = 3/2$ multiplets, with a single hole occupying the $J = 1/2$ levels being lower in energy. Because of this we consider only the resonant enhancement from these $J = 1/2$ states.

The magnetic scattering cross-section, as a function of scattering angle, is calculated from the two-site model in the ferromagnetic state. The results are shown in Fig. 3(a). If $\rho$ had contributions only from the $J = 0$ state, which would be the case in the atomic limit, there could not be any magnetic scattering. The non-zero signal results from significant contribution to $\rho$ from the higher energy local $J = 1$ states. This has significant consequences for the RXS cross-section: the $L_2$ edge is enhanced by about an order of magnitude more than the $L_3$ edge. This is in sharp contrast from the $d^5$ case, relevant for iridates, also shown in Fig. 3(b). The $L_2$ edge is suppressed in iridates.

In Fig. 4(a) and (b) we show a comparison between two-site and atomic $\sigma - \sigma$ scattering cross-sections for the $L_2$ and $L_3$ edges respectively. In the $d^4$ configuration, the two-site result deviates significantly from the atomic result for the ferromagnetic phase. For the non-magnetic phase, the atomic and two-site results agree. For comparison, we have also shown the atomic and two-site calculations for the $d^5$ configuration in Fig. 4, where the atomic limit calculation is adequate. The picture that emerges from our analysis is that the non-magnetic phase is well described by the atomic picture with $J = 0$ singlets at each site while the ferromagnetic phase implies significant occupation of the local $J = 1$ states. In the next section, we use this insight to construct an effective spin-orbital model and produce a Ginzburg-Landau theory for the phase transition.

**Magnetic Hamiltonian and Ginzburg-Landau theory:**

The simplest spin-orbital Hamiltonian that we can write
down which includes SOC and superexchange mediated by only the lowest-lying virtual state is (see Supplementary material for details [15])

\[
\hat{H} = -\frac{J_{FM}}{2} \sum_{(ij)} \mathbf{S}_i \cdot \mathbf{S}_j \mathcal{P}(\mathbf{L}_i + \mathbf{L}_j = 1) + \frac{\lambda}{2} \sum_i L_i \cdot \mathbf{S}_i \tag{6}
\]

where \(S_i = 1\) and \(L_i = 1\) are local \(S\) and \(L\) moments at site \(i\). From the Goodenough-Kanamori analysis shown in Fig. 2, it is easy to see that the superexchange scale \(J_{FM} \sim \mathcal{O}(t^2/U)\). Each bond is projected by \(\mathcal{P}(\mathbf{L}_i + \mathbf{L}_j = 1)\) on to the total \(L = 1\) space, while the factor of \(1/2\) in the SOC term comes from rewriting the SOC Hamiltonian in the \(L - S\) coupling scheme relevant for the \(d^4\) configuration. While the combination of spin-orbit interaction and ferromagnetic exchange are sufficient to produce a phase transition, the projection operator is necessary to capture the orbital entanglement in the ferromagnet. We have checked explicitly against the exact diagonalization results that this model accurately describes the magnetic phase transition at the two-site level shown in Fig. 1(a) [15].

As described earlier, the non-magnetic phase can be understood quite simply as a local singlet at each site. The ferromagnetic phase, on the other hand, can be described as a Bose-Einstein condensation (BEC) of magnetic excitations to the \(J = 1\) state, induced by the ferromagnetic superexchange interaction. To this end we define the operators \(s_i^\dagger\) which creates a singlet at site \(i\) while \(T_{i,(0,\pm)}\) creates a triplet carrying \(J_z = 0, \pm 1\) at site \(i\) [17, 18]. By calculating the matrix elements of \(S\) and \(L\) operators in the singlet-triplet space, we get

\[
S_i^\alpha = -\sqrt{\frac{2}{3}} \left(T_{i,s}^\dagger s_i^\dagger T_{i\alpha} - \frac{1}{2} \epsilon_{\alpha \beta \gamma} T_{i\beta}^\dagger T_{i\gamma}\right)
\]

\[
L_i^\alpha = \sqrt{\frac{2}{3}} \left(T_{i,s}^\dagger s_i^\dagger T_{i\alpha} - \frac{1}{2} \epsilon_{\alpha \beta \gamma} T_{i\beta}^\dagger T_{i\gamma}\right) \tag{7}
\]

where \(\alpha, \beta, \gamma = x, y\) or \(z\), \(T_{i,z}^\dagger = T_{i,0}^\dagger\), \(T_{i,x}^\dagger = (T_{i,1}^\dagger - T_{i,-1}^\dagger)/\sqrt{2}\) and \(T_{i,y}^\dagger = i(T_{i,1}^\dagger + T_{i,-1}^\dagger)/\sqrt{2}\). Upon substituting these operators in the Hamiltonian, we obtain an effective action from the saddle point approximation[19]. Close to the magnetic phase transition, we assume \(\langle s_i \rangle \approx 1\) and \(\langle T_{i\alpha} \rangle = \phi_{i\alpha} \ll 1\), and thereby obtain the Ginzburg-Landau functional, up to second order in \(\phi_{i\alpha}\), as

\[
\mathcal{L} = \frac{\lambda}{2} \sum_{i\alpha} \left[ \phi_{i\alpha} \phi_{i\alpha}^\dagger \right] \left[ \begin{array}{c} 1 \\ 0 \\ 0 \end{array} \right] \left[ \begin{array}{c} \phi_{i\alpha} \\ \phi_{i\alpha} \end{array} \right] - \eta J_{FM} \sum_{(ij),\alpha} \left[ \phi_{i\alpha} \phi_{j\alpha} \right] \left[ \begin{array}{c} 1 \\ a \\ a \end{array} \right] \left[ \begin{array}{c} \phi_{j\alpha} \\ \phi_{j\alpha} \end{array} \right] \tag{8}
\]

where \(\eta\) and \(a\) are parameters of \(\mathcal{O}(1)\) which depend on details of the model. This can be solved easily by a Bogoliubov transformation which gives a gap function \(\Delta_k = \sqrt{(\lambda/2 - \eta J_{FM} f(k))^2 - (a \eta J_{FM} f(k))^2} \) where \(f(k) = \sum_\delta \cos(k,\delta)\) and \(\delta\) is nearest-neighbor position. For ferromagnetic superexchange, it closes at \(k = 0\) when \(\lambda_{c}/J_{FM} = 2\eta(1 + |a|)\) or \(\lambda_{c} \sim \mathcal{O}(t^2/U)\) where \(z\) is the coordination number, thereby generating a condensate of triplets in the ground state and consequently a phase transition into a ferromagnet.

**Materials:** We propose candidate materials from the double perovskite family which can be tuned across the magnetic transition by chemical substitution and/or pressure. They have the general formula \(A_2BB'O_6\) where \(A\) is an alkaline earth element while \(B\) and \(B'\) are two different transition metal ions, ordered in a 3D checkerboard pattern. If we choose the \(B\) sites to have completely filled shells, the bandwidth is suppressed, giving rise to a Mott insulator. When combined with a 4d or 5d element on the \(B'\) site, we have the ideal model system where large SOC competes with \(J_{FM}\). Of particular interest to us is \(La_2ZnRuO_6\) which is an insulator with Ru in \(d^4\) configuration. Two different samples grown by two different groups have shown very different magnetic states. One group has found a ferromagnetic state with \(T_C \approx 165K\) [21], while the other found a non-magnetic state [22]. We believe \(La_2ZnRuO_6\) is very close to the phase boundary and small differences in the lattice parameter may be the origin of this discrepancy. An RXS study under pressure will be an ideal experiment to observe the phase transition. Another closely related material is \(La_2MgRuO_6\) [21], which is also a promising candidate.

**Comments:** During the final stages of our work we came across Ref.[11] which also identifies a superexchange-driven magnetic phase transition in a \(d^4\) Mott insulator. However, there are significant differences in our results. We obtain a phase transition from a non-magnetic insulator to an entangled ferromagnetic insulator, consistent with the Goodenough-Kanamori analysis, whereas Ref.[11] predicts an anti-ferromagnetic phase and further identifies \(Ca_2RuO_4\) as a candidate material. Experimentally \(Ca_2RuO_4\) is known to show weak ferromagnetism [20] whose explanation would require additional Dzyaloshinskii-Moriya type interactions. Our proposal, on the other hand, naturally explains the weak ferromagnetism as arising from superexchange that is itself ferromagnetic.

**Conclusion:** We have provided evidence for a \(d^4\) ferromagnetic Mott insulator, despite the fact that each site in the atomic limit has no moment. RXS scattering cross sections are a direct probe of this unusual entangled magnetic state and we predict, in sharp contrast to the \(d^3\) iridates, that the \(L_3\) edge magnetic scattering is suppressed by an order of magnitude compared to the \(L_2\) edge.

While we have focussed on the unusual ferromagnetic state at large \(U\) and \(\lambda\), the phase diagram in Fig. 1(a) is considerably richer, allowing for a broader exploration of magnetic and metal-insulator phase transitions.

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Novel magnetic state in \(d^4\) Mott insulators

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In this supplement we provide details on the following:

1. Derivation and validation of the minimal spin-orbital Hamiltonian used to describe the magnetic phase transition from a non-magnetic phase with local \(J = 0\) singlets to a novel ferromagnetic phase in \(d^4\) Mott insulators.
2. A general theory for calculating Resonant X-ray Scattering amplitude including non-local effects.

MAGNETIC HAMILTONIAN

As discussed in the main text, the sign of the super-exchange is ferromagnetic and it can be easily understood from a Goodenough-Kanamori analysis in the \(\lambda = 0\) limit. Here, we present a detailed derivation and validation of the spin-orbital Hamiltonian in Eq. 6 of the main text.

In the atomic limit with no SOC, the \(d^4\) Mott insulator has \(L_i = 1\) and \(S_i = 1\) at each site. For two sites, the ground state with \(d^4 - d^4\) configuration is a direct product state

\[
|\Psi_{GS}\rangle = |S_1 = 1\rangle \otimes |L_1 = 1\rangle \otimes |S_2 = 1\rangle \otimes |L_2 = 1\rangle \tag{1}
\]

which can give rise to total \(L = 2, 1\) or 0 and total \(S = 2, 1\) or 0, all of which are degenerate with energy \(E_G\). From second order perturbation theory, the magnetic exchange term that captures the correction to the atomic ground state energy has the form of the atomic state with \(d^4\) configuration and energy \(E_n\).

\[
\tilde{H}' = H_{\text{hop}} \left[ \sum_n \frac{|\psi_n\rangle\langle\psi_n|}{E_G - E_n} \right] H_{\text{hop}} \tag{2}
\]

where

\[
H_{\text{hop}} = -t \sum_{\alpha, \sigma} \left( c_{\alpha \sigma}^\dagger c_{2\alpha \sigma} + h.c. \right) \tag{3}
\]

is the kinetic energy and \(|\psi_n\rangle\) is the intermediate exited atomic state with \(d^3 - d^3\) configuration and energy \(E_n\). Let us now examine the excited states. The ground state for \(d^3\) has \(L_i = 0\) and \(S_i = 3/2\) while \(d^5\) has \(L_i = 1\) and \(S_i = 1/2\) in its ground state. So, the lowest lying excited state, which we will call \(|\psi_1\rangle\), can have total \(L = 1\) and total \(S = 2\) or 1. If \(|\psi_1\rangle\) contributes to the exchange interaction in Eq. 2, it will be the dominant term.

To see if \(|\psi_1\rangle\) contributes to the magnetic exchange energy, we need to examine how \(H_{\text{hop}}\) connects \(|\Psi_{GS}\rangle\) to the excited state. The form of \(H_{\text{hop}}\) in Eq. 3 is invariant under rotations in both spin and orbital space. It, therefore, commutes with total \(L^2\) and total \(S^2\) operators and only connects states with the same total \(L\) and total \(S\). \(|\psi_1\rangle\) has \(L = 1\), and consequently the energy gain from the exchange term is maximized if \(|\Psi_{GS}\rangle\) is in the \(L = 1\) state. Similarly, only the \(S = 2\) and \(S = 1\) components of \(|\Psi_{GS}\rangle\) gains energy via virtual excitations to \(|\psi_1\rangle\). If we consider only the dominant contribution from \(|\psi_1\rangle\) to the magnetic exchange energy, the magnetic Hamiltonian in Eq. 2 can be written in terms of spin and orbital projection operators as

\[
\tilde{H}' \approx -J_d |S = 2\rangle \langle L = 1| L = 1 \langle S = 2| - J_1 |S = 1\rangle \langle L = 1| L = 1 \langle S = 1| \tag{4}
\]

where

\[
J_i = \frac{|\langle \psi_1 | H_{\text{hop}} | \Psi_{GS} (L = 1, S = i) \rangle|^2}{|E_G - E_1|} \tag{5}
\]

Next, we are interested in describing correctly only the ground state and the first excited state. We will show later higher energy states are not important for understanding the magnetic phase transition shown in Fig. 1(b) of the main text. We can, then, replace the spin projection operators in Eq. 4 by the Heisenberg form as follows

\[
\tilde{H} \approx -J_{FM} S_1 \cdot S_2 P (L_1 + L_2 = 1) \tag{6}
\]

where \(J_{FM} = (J_2 - J_1)/2\). From the Goodenough-Kanamori analysis and also from exact diagonalization, we know that \(J_2 > J_1\) and, therefore, \(J_{FM} > 0\). \(P\) is the same as \(|L = 1\rangle \langle L = 1|\) which projects the total \(L\) of the
two sites to $L = 1$, and it has the form
\[ P(L_1 + L_2 = 1) = \frac{(1 - L_1L_2)(2 + L_1L_2)}{2} \quad (7) \]

We can add to Eq. 6 the spin-orbit coupling term and generalize to a lattice in order to obtain the desired spin-orbital Hamiltonian
\[ \hat{H} = -J_{FM} \sum_{(ij)} \mathbf{S}_i \cdot \mathbf{S}_j P(L_i + L_j = 1) + \frac{\lambda}{2} \sum_i L_i \cdot S_i \quad (8) \]

We note that in our analysis, the intermediate oxygen orbitals are not taken into account explicitly. Including them, however, does not change the ferromagnetic nature of superexchange.

We now present numerical results to show that the minimal spin-orbital Hamiltonian in Eq. 8 describes the magnetic phase transition as shown in Fig. 1(b) of the main text. In Fig. 1(a) we have reproduced the exact diagonalization results for two site Hubbard model (See Eq. 1 of main text) and in Fig. 1(b) we present exact diagonalization results for two sites of the magnetic Hamiltonian in Eq. 8. By comparing the two plots, it is clear that our minimal spin-orbital Hamiltonian captures the competition between superexchange and SOC. Not only does it accurately describe the phase transition from a non-magnetic ($J = 0$) state insulator to a ferromagnetic ($J = 1$) state, it also captures the non-trivial changes in the local moment ($J_i \approx 0$ in the non-magnetic state and $J_i \approx 1$ in the ferromagnet).

**RESONANT X-RAY SCATTERING**

In this section, we describe the general theory of resonant x-ray scattering (RXS) that we have used to calculate the results shown in Figs. 3 and 4 of the main text. The starting point is the scattering amplitude. Within second order perturbation theory and the dipole approximation, the resonant scattering amplitude has the following form [1]
\[ \Delta f(\omega) \propto \sum_n \frac{\langle \Psi_{GS}|(e'\mathbf{D})^\dagger|\psi_n\rangle \langle \psi_n|\mathbf{e}\cdot\mathbf{D}|\Psi_{GS}\rangle}{E_n - E_G - \hbar\omega - i\Gamma_n} \quad (9) \]

where $|\Psi_{GS}\rangle$ is the ground state with energy $E_G$ and $|\psi_n\rangle$ is an excited state with energy $E_n$. $\Gamma_n$ corresponds to the inverse lifetime of the particular excited state $|\psi_n\rangle$ and $e(e')$ is the polarization of the incoming(outgoing) X-ray photon.

It is convenient to write the dipole operator $\mathbf{D}$ in second quantized form to facilitate calculation of the matrix elements in the numerator of Eq. (9). For the $L_{2(3)}$ edge, absorbing a photon promotes a core $2p$ electron to the valence $d$ shell
\[ e\cdot\mathbf{D} \approx e\cdot \hat{r} = \sum_{\alpha\sigma} e\cdot \langle d\alpha | \hat{r} | p\beta \rangle d\dagger_{\alpha\sigma}p_{\beta\sigma} + \text{h.c.} \quad (10) \]

where $\langle d\alpha | \hat{r} | p\beta \rangle \equiv R_{\alpha\beta}$ are easily determined by symmetry and tabulated

\[ R \propto \begin{pmatrix} |p_x\rangle & |p_y\rangle & |p_z\rangle \\ \langle d_{yz}\rangle & 0 & \hat{z} & \hat{y} \\ \langle d_{zx}\rangle & \hat{z} & 0 & \hat{x} \\ \langle d_{xy}\rangle & \hat{y} & \hat{x} & 0 \end{pmatrix} \quad (11) \]

The proportionality constant depends on fine details of the atomic states, but symmetry dictates that it should be the same for all combinations of $p$ and $d$ orbitals. Hence it is an overall constant which we hereafter ignore.

**Free ion approximation**: A common practice in calculating RXS matrix elements is to approximate the scattering site as a free ion [1, 2]. This usually gives a good description for Mott insulators where the scattering amplitude is primarily determined by local properties. The effect of the lattice comes only through the geometrical structure factor. Within the free ion approximation, the ground state in Eq. 9 is replaced by the atomic ground state and the excited states are replaced by atomic excited states.

**Non-local effects**: When interaction between different sites have significant effect on local properties, as in the case of the $d^4$ ferromagnetic Mott insulator, the free ion approximation breaks down. Substituting the ground state in Eq. 9 by the atomic ground state is no longer a good approximation. However, it turns out the excited states can still be substituted by the atomic exited states because the core hole generates an additional binding energy for the excited electron [1, 3].

To include the non-local effects correctly, we need to write the ground state as a direct product of states defined only on the scattering site $|\psi_n\rangle$ and states defined on the rest of the lattice $|\phi_q\rangle$
\[ |\Psi_{GS}\rangle = \sum_{pq} a_{pq}|\psi_p\rangle|\phi_q\rangle \quad (12) \]

Substituting this into Eq. 9, the matrix element in the numerator becomes
\[ \langle \Psi_{GS}|(e'\mathbf{D})^\dagger|\psi_n\rangle \langle \psi_n|\mathbf{e}\cdot\mathbf{D}|\Psi_{GS}\rangle = \sum_{pqrs} a_{pq}^* a_{pq}\langle \psi_r|\mathbf{e'}\cdot\mathbf{D}\rangle^\dagger|\psi_n\rangle \langle \psi_n|\mathbf{e}\cdot\mathbf{D}|\mathbf{\phi_s}\rangle \langle \phi_s|\phi_q\rangle \]
\[ = \sum_{pr} \rho_{pr} \langle \psi_r|\mathbf{e'}\cdot\mathbf{D}\rangle^\dagger|\psi_n\rangle \langle \psi_n|\mathbf{e}\cdot\mathbf{D}|\psi_p\rangle = \text{Tr} \left[ \rho(e'\cdot\mathbf{D})^\dagger|\psi_n\rangle\langle \psi_n|\mathbf{e}\cdot\mathbf{D} \right] \quad (13) \]

where $\rho_{pr} = \sum_q a_{rq}^* a_{pq}$ is the reduced density matrix at the scattering site. Finally, we get the desired expression for the resonant scattering amplitude with non-local effects included correctly
\[ \Delta f(\omega) \propto \text{Tr} \left[ \rho \sum_n \frac{(e'\cdot\mathbf{D})^\dagger|\psi_n\rangle \langle \psi_n|\mathbf{e}\cdot\mathbf{D}}{E_n - E_G - \hbar\omega - i\Gamma_n} \right] \quad (14) \]
As shown in Fig. 4 of the main text, the influence of the lattice on the scattering site through the super-exchange interaction is crucial in understanding the ferromagnetic $d^4$ Mott insulator.

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