Unquenched $e_g^1$ orbital moment in the Mott insulating antiferromagnet KOsO$_4$

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I. INTRODUCTION

In condensed matter, especially when containing heavy ions, spin-orbit coupling (SOC) often leads to phenomena that are lacking without SOC. Examples of recent interest include the original topological insulators# behavior arising from the Rashba effect, unconventional metal-insulating transitions, compensating spin and orbital moments$^{2,3}$ and the magneto crystalline anisotropy (MCA) that is so important in spintronics applications. Whereas SOC within a $t_{2g}$ manifold in a $\text{MO}_6$ octahedron ($\mathcal{M}=$transition metal) has a long history# and has been intensively discussed recently in several specific contexts$^{2-4}$, corresponding effects in an $e_g$ manifold have rarely been considered due to the conventional wisdom that the $e_g$ subshell ensures a perfectly quenched orbital moment. From this viewpoint, heavy transition metal oxides containing $\text{MO}_4$ tetrahedra are of great interest, since the crystal field splitting leads to partially filled orbitals in the $e_g$ manifold.

About a century ago, monoclinic crystals of two toxic, volatile materials OsO$_4$ and RuO$_4$ were synthesized. These are presumably textbook band insulators albeit with remarkably high (8+) formal charges. Although existing data on these crystals are limited, the effects of SOC have been investigated from the chemical viewpoint since the 1990s# and generally found to be minor. In 1985, the heptavalent $\text{MO}_4$ ($\mathcal{M}=$alkali metal) compounds were synthesized by Levason et al., who determined they formed in the tetragonal scheelite crystal structure$^{2,3}$; KOsO$_4$ has been often synthesized from the mixture of KO$_2$ and Os metal as a precursor for preparation of the superconductor KO$_2$OsO$_6$# but no further investigation of physical properties have been published.

KOsO$_4$ seems to be insulating, though detailed resistivity data are not yet available$^{17,18}$.

Recently Yamaura et al. determined the crystal structure parameters and measured the susceptibility and specific heat$^{19}$. The Curie-Weiss moment is $\mu_{\text{eff}}=1.44\ \mu_B$, 20% reduced from the spin-only moment, and the Neel temperature is $T_N=37$ K. These authors suggested that magnetic frustration in this distorted diamond lattice may be necessary to account for observations. However, the conventional ratio of Curie-Weiss to ordering temperatures $|\theta_{\text{CW}}|/T_N \approx 1.8$ is small (i.e. no frustration) so other factors must be considered.

In this paper we study the electronic structure of KOsO$_4$, with special attention to the interplay between strong correlation and SOC. The small ligand field splitting of the $e_g$ orbitals due to distortion of the OsO$_4$ tetrahedron plays an important role in determining the occupied orbital in the Mott insulating state, and may become active in effects arising from SOC as well. The modest $t_{2g}-e_g$ crystal field splitting ($\Delta_e=1.7\ eV$) and large SOC strength ($\sim 0.3\ eV$) brings in another effect of crystallinity that impacts the effects of SOC. This splitting is especially small considering that in another Os$^{7+}$ compound, the double perovskite Ba$_2$NaOsO$_6$, $\Delta_e=6\ eV$ is extremely large. Results are analyzed in terms of magnetization densities, Wannier functions, and spin-orbital occupation numbers. Symmetry reduction due to SOC when the spin lies in the [100] direction is found to have great consequence.
II. STRUCTURE AND CALCULATION METHODS

KO\textsubscript{2}O\textsubscript{4} crystallizes in the scheelite-like structure (space group: \textit{I}4\textsubscript{1}/\textit{a}, No. 88). In this tetragonal structure with two formula units (f.u.) per primitive cell, the lattice parameters are \textit{a}=5.652 Å and \textit{c}=12.664 Å\textsuperscript{10} leading to the ratio of \textit{c}/\sqrt{2}\textit{a} = 1.58. The Os sublattice forms an elongated diamond lattice; this ratio is unity for the cubic diamond lattice. The K and Os atoms sit at the \textit{4b} sites (0, \frac{1}{2}, \frac{5}{8}) and \textit{4a} sites (0, \frac{1}{2}, \frac{1}{8}), respectively. The O atoms lie on the 16\textit{f} sites (0.1320, 0.0160, 0.2028). In the OsO\textsubscript{4} tetrahedron, all Os-O bond lengths are 1.81 Å, and the O-Os-O bond angles are either 114° or 107°, compared to 109.5° for a regular tetrahedron. Similar distortion is observed in the band insulator OsO\textsubscript{4} and KRuO\textsubscript{4} where both RuO\textsubscript{4} and KRuO\textsubscript{4} have nearly ideal tetrahedra\textsuperscript{21,22}. This difference suggests that the distortion is due to chemical difference between Os and Ru ions.

Our calculations were carried out with the local (spin) density approximation [L(S)DA] and its extensions, as implemented in the accurate all-electron full-potential code \textit{wien2k}\textsuperscript{24}. Since we are interested in possible competition between large SOC and strong correlation effects in magnetic systems, we compare all of the LDA, LSDA, LSDA+SOC, LSDA+U, and LSDA+U+SOC approaches. An effective on-site Coulomb repulsion \textit{U} was used for LDA+U calculations; since Os\textsuperscript{7+} is a \textit{d}\textsuperscript{1} ion which is not occupied by more than one electron, the Hund’s rule coupling \textit{J} between two electrons of the same spin was set to zero. To analyze the partially filled Os complex, the Wannier function approach implemented in \textit{fplo} and \textit{wien2k} has been used\textsuperscript{24,25}. Calculations of the Wannier function including SOC are available only in the latter. In \textit{wien2k}, the following muffin-tin radii are adopted: 2.02 for Os, 1.4 for O, 2.2 for K (in units of a.u.). The extent of the basis was determined by \textit{R_{MT}K_{MAX}}=7. The Brillouin zone was sampled with a sufficiently dense \textit{k}-mesh of 13×13×6.

III. THE UNDERLYING ELECTRONIC STRUCTURE

Figure\textsuperscript{2} displays the LDA total and atom-projected densities of states (DOSs), which demonstrates the strong \textit{p}−\textit{d} hybridization not only in the most relevant Os \textit{e}\textsubscript{g} bands (denoted as the molecular \textit{e}\textsuperscript{*} orbitals) but also in more tightly bound oxygen orbitals around -7 eV. This hybridization of transition metal \textit{d} character into O 2\textit{p} bands is common but is not particularly relevant and is little discussed. The narrow bands reflect moderately binding molecular orbitals. Some nearly pure oxygen bands lie in the -6 to -3 eV range. The \textit{t}\textsubscript{2} bands centered around 2 eV are a mixture of Os \textit{t}\textsubscript{2g}, and all O 2\textit{p} orbitals, while the \textit{e}\textsuperscript{*} set is a mixture of \textit{e}\textsubscript{g} and mostly \textit{p}\textsuperscript{π}.

Before considering the complications of spin polarization, correlation effects, and SOC, we consider the basic underlying features of the electronic structure. Supposing formal charges of K\textsuperscript{1+}, Os\textsuperscript{7+}, and O\textsuperscript{2−} ions, the crystal field \textit{e}\textsubscript{g}−\textit{t}\textsubscript{2g} splitting is expected to be 0.8 eV, about half of the calculated splitting \textit{\Delta_{eg}} = 1.7 eV which is the full ligand field splitting.

The LDA nonmagnetic band structure in the Os 5\textit{d}}
FIG. 3: (Color online) LDA Os 5$d$ band structure of non-magnetic KOsO$_4$, showing the $e_g$-$t_{2g}$ crystal field splitting of ~1.8 eV. The partially filled $e_g$ bands, which are colored with the corresponding Wannier orbitals, lie on the range of -0.3 to 0.3 eV. In units of $(\pi/a, \pi/a, \pi/c)$, the symmetry points shown are $H = (100)$, $N = (\frac{1}{2}\frac{1}{2}0)$, and $P = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$.

IV. EFFECTS OF CORRELATION AND SOC

A primary emphasis in our study of this system is to assess the interplay in an $e_g$ system between strong correlations, which prefer full occupation of certain orbitals and usually increase spin polarization, and SOC which mixes spin-orbitals and complicates all aspects of the electronic structure while inducing the orbital moment and magnetocrystalline anisotropy (MCA). It was mentioned above that including correlation effects in the LSDA+U method leads to preferred occupation of the $d_{z^2}$ orbital, which has 84 meV lower on-site (crystal field) energy than $d_{x^2-y^2}$ due to the distortion of the OsO$_4$ tetrahedron. The band structures including the lower part of the $t_{2g}$ complex, and the DOS of the $e_g$ bands alone for the energetically preferred AFM state are displayed in Figs. 4 and 5, respectively. These figures have been constructed to allow identification of individual effects of $U$ and SOC.

Before proceeding with a description of the full electronic structure and then the spin density itself, we review the energy differences arising from the various interactions.
TABLE I: Effect of correlation $U$ on the relative energies $\Delta E$ (in units of meV/f.u.) and Os orbital moments $M_L$ (in units of $\mu_B$) for each of four spin quantization directions and for FM and AFM alignments. $M_L$ of Os is antialigned to the spin moment of Os, which is $\sim 0.4 \mu_B$ for the insulating states. The spin moments contributed by O ions are $0.24 - 0.32 \mu_B$/O in LSDA+SOC, increasing to $\sim 0.4 \mu_B$/O for LSDA+SOC+U. $U = 2$ eV was used for LSDA+SOC+U calculations.

|            | [100] | [001] | [110] | [111] |
|------------|-------|-------|-------|-------|
| LSDA+SOC  | $\Delta E$ | 0     | 4.6   | 2.3   | 3.7   |
| LSDA+U+SOC| $\Delta E$ | 0     | 14.4  | 3.0   | 10.6  |
| LSDA+SOC  | $M_L$  | -0.134| -0.014| -0.136| -0.052|
| LSDA+U+SOC| $M_L$  | -0.184| 0.007 | -0.183| -0.053|

A. Magnetic Energy Differences

As expected from the peak at $E_F$ in the DOS (see Fig. 2) and Stoner instability, FM is energetically favored over the nonmagnetic state, by 26 meV/f.u. Our fixed spin moment calculations of the interacting susceptibility lead to $N(E_F)=1.58$, above the Stoner instability criterion of unity, and $N(E_F)=4.09$ states/eV-f.u.-spin gives the Stoner parameter $I=0.39$ eV, similar to the value observed in Ba$_2$NaOsO$_6$. Within metallic LSDA where exchange coupling might be considered some mixture of double exchange, RKKY, and superexchange, the FM ground state lies 5.5 meV/f.u. below the observed AFM state.

To assess the effects of SOC before including correlation corrections, we display MCA energies with LSDA+SOC+U leads to a Mott insulating state.

B. LSDA+SOC+U leads to a Mott insulating state

The lowest and highest bands (Fig. 4) in the $e_g$ manifold extending over the regime of $-0.25$ to $+ 0.5$ eV are the Os spin up and down $d_{z^2}$ bands, respectively. In the quarter filled $e_g$ manifold, the $d_{z^2}$-$d_{x^2-y^2}$ degeneracy lifting is 0.2 eV, i.e. the $e_g$ degeneracy is already split (presumably, self-consistently by occupation of the $d_{z^2}$ orbital and resulting Jahn-Teller distortion). Applying the on-site Coulomb repulsion $U$ starting from small values leads to an MIT (gap opening) at the critical value $U_c \approx 1.2$ eV, which is near the bottom of the range of expected values for Os. As shown in the bottom panel of Fig. 4 for $U=2$ eV and spin along the [100] direction, the top of the occupied band has a flat region around the N point, giving rise to a one-dimension-like peak and sharp discontinuity in the DOS at the top of the band, evident in Fig. 5. Other band maxima at $\Gamma$ and midway between $\Gamma$ and N are (somewhat accidentally) degenerate with the flat band at N. The occupied bandwidth is 0.2 eV. As shown by red dashed lines in the band structure of Fig. 4 inclusion of SOC has negligible effect on the occupied state (position and dispersion) but lowers the uppermost $e_g$ band (primarily minority spin) by 0.15 eV. This shift corresponds to a small decrease in the exchange splitting of the unoccupied $e_g$ orbital.

C. Effects of SOC on spin and orbital moments

In the following text and in Table 1 we quote atomic moments from contributions within the inscribed spheres, which are somewhat smaller than the full value. We remind that the occupied “$d_{z^2}$” orbital that is occupied before including SOC is rather strongly hybridized with 2p orbitals of the surrounding O ions, so the spin magnetization of $1 \mu_B$ is distributed over oxygen as well as Os. The moment values should be considered in conjunction with the spin density isocontours pictured in Fig. 4.

For all spin orientations we have considered the Os spin moment is $M_S \approx 0.4 \mu_B$. This value is almost independent of $U$ in the range $0-5$ eV that we have studied. The O net spin $M_S=0.07 \mu_B$/O aligns parallel to that of the nearest neighbor Os. The sum of the full atom moments
must be unity, so atomic values are around 0.5 and 0.12 $\mu_B$ for Os and O, respectively, versus the atomic sphere values just quoted. Including SOC reduces the Os spin moment by 10%, transferring some of it to neighboring O $M_S$ due to rehybridization. For [100] and [110] spin directions, increasing $U$ increases $|M_L|$ from $\sim 1/3$ $M_S$ at $U = 0$ to $1/2$ $M_S$ at $U = 2$ eV. For [001] spin orientation $M_L$ is essentially vanishing for any value of $U$ (Table I).

D. Behavior of the spin density

The spin density isocontour plots displayed in Fig. 6 for metallic ($U=0$) and AFM insulating ($U = 2$ eV) phases are instructive. Even in the metallic, uncorrelated case both positive and negative lobes of spin density appear on both Os and O ions, indicating more complexity than strong (but typically simple) $p - d$ hybridization. Since in this limit the lower Hubbard band is fully polarized (only spin-up states), the negative polarization arises from polarization within the filled nominally O 2p
bands at lower energy. The net spin of O lies in 2p orbital whose orientation reflects $\pi$ antibonding character with Os $d_{xz}$, $d_{yz}$ orbitals. A small negative spin density is induced in a linear combination of the $p_x$, $p_y$ orbitals, in the local coordinate system. The Os spin lies as expected mainly the $d_{zx}$ orbital, with some admixture of $d_{x^2-y^2}$ accounting for the square versus circular symmetry of the spin density in the equatorial plane of Os. A small but clear admixture of $d_{xy}$ and $d_{xz}$ character appears as a negative spin density (blue), and is necessary to provide the Os orbital moment.

In the correlated ($U=2$ eV) insulating state, Os stills has mainly the $d_{zx}$ character for spin up. However, the circular symmetry indicating $d_{yz} - id_{xz}$ character for spin down shows up much more clearly. Unexpectedly, this same development of $p_x - ip_y$ shows up on the O ions in the down spin region, while the up spin $p_x$ character is nearly undisturbed.

To generate the complex-valued, mixed-spin Wannier function $W(r)$ of the occupied band, we projected from $(\frac{3}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{3}{2})$ as a trial function in the Wien2Wannier package. Figure 7 presents isocontour plots of $|W(r)|^2$ for two directions of the spin. Consistent with Eqs. 2 and 3 below, the spin-down parts are $d_{xz}$-like in the [100] direction and $d_{xz} + id_{yz}$-like in the [001] direction. The spin-up parts are $d_{xz}$-like in the both directions, but have the negative lobe of square shape, instead of spherical one.

V. ANALYSIS OF SPIN-ORBIT COUPLING IN THE $e_g$ CASE

Now we address the effects of SOC, especially the appearance of a surprisingly large orbital moment in an $e_g$ subshell which should not produce an orbital moment, through analysis of occupation matrices and the associated Wannier function. SOC effects in the $e_g$ channel tend to be relegated to the background because $e_g$ contains only orbital $m = 0$ and $m = \pm 2$ $d$ orbitals, which are not coupled by the electron spin $s = \frac{1}{2}$. Note however that this is strictly true only in the spherical (isolated ion) limit and for orbital moments along the axis of quantization i.e. the direction of the spin. Indeed we find negligible orbital moments for spin along [001]. Crystalline effects break this orbital-moment killing symmetry.

First, in KOsO$_4$ the crystal field splitting $\Delta_{cf} = 1.7$ eV is not so much larger than the SOC strength, so virtual inclusion of $\gamma_2$ orbitals may be involved. Second, the OsO$_4$ tetrahedron is distorted, breaking the 2-fold $e_g$ symmetry, which is related to the Mott insulating behavior: occupation of a single $e_g$ orbital and the accompanying Jahn-Teller distortion. Finally, the higher symmetry crystalline $\hat{z}$ axis is not the easy axis, so additional complexities arise. The focus begins with the $d_{xz}$ orbital that is occupied before SOC is included, with slight admixture of other 5$d$ orbitals due to the structural symmetry breaking and the hopping.

Spin along [001]. Applying $\vec{L} \cdot \vec{S}$ to the spin-up $d_{xz}$ orbital leads to

$$\vec{L} \cdot \vec{S}(d_{xz})|\uparrow\rangle_z \propto -(|d_{xz}| + id_{yz})|\downarrow\rangle_z.$$ (2)

which are nominally unoccupied orbitals. Indeed we calculate negligible $M_L$ for this orientation, reflecting negligible intermixing of $d_{xz} \pm id_{yz}$ orbitals across the crystal field gap $\Delta_{cf}$. The main occupation amplitudes (eigenvectors of the occupation matrix) are (in $|m_L, m_J >$ notation), 0.96 for $|0, \uparrow\rangle$ and a down-spin amplitude of -0.21 for $|+1, \downarrow\rangle$ (thus decreasing the spin moment by 4%).

Spin along [100]. For in-plane [100] spin orientation SOC leads to the common picture

$$\vec{L} \cdot \vec{S}(d_{xz})|\uparrow\rangle_x \propto -i(d_{yz})|\uparrow\rangle_x - |d_{xz}||\downarrow\rangle_x.$$ (3)

Another way to approach the emergence of an orbital moment is to note that when the $d_{xz}$ orbital is expressed in the local coordinate system $X, Y, Z$ with $Z$ directed along [100], it is a linear combination of $d_{xz}$ and $d_{x^2-y^2}$ orbitals (i.e. the $e_g$ orbitals). Breaking of symmetries may induce an asymmetry in the $m_l = \pm 2$ orbitals making up $d_{x^2-y^2}$. Indeed this happens. In the local coordinate system with complex orbitals, the amplitudes of the occupation matrix eigenstate are, for $m = 0, -1, +1, -2, +2,$ respectively,

$$|\uparrow\rangle : -0.47, -0.09i, 0.11i, 0.50, 0.70, \text{ (4)}$$

$$|\downarrow\rangle : 0.01i, -0.08, 0.07, -0.07i, 0.08i.$$

The imbalance in the $m = \pm 2$ and $m = \pm 2$ occupations in the spin-up channel results in the surprisingly large (for an $e_g$ shell) orbital moment.

VI. SUMMARY

Materials such as KOsO$_4$ with $e_g$ configuration are expected to have a negligible orbital moment. We have studied the interplay of strong correlation effects and large spin-orbit coupling strength, and have found that an additional characteristic is very important: the additional symmetry breaking (after the $e_g$ symmetry breaking by the Mott insulating character) by spin-orbit coupling. The spin-direction dependent orbital moment in this Os$^{5+} e_g$ system has been analyzed and understood. The occupied orbital without spin-orbit coupling is $d_{xz}$ $\uparrow\rangle$. For spin along the [001] axis, indeed there is negligible mixing with $m \neq 0$ orbitals and the only change due to SOC is a few percent reduction in the spin moment.

For the spin along the in-plane [100] axis, however, SOC further breaks $x \leftrightarrow y$ symmetry, inducing a population imbalance in the $m = -2$ and $m = +2$ orbitals (in the local system) that drives the unexpectedly large orbital moment $M_L = -0.2\mu_B$. This moment cancels half of the Os spin moment, and the accompanying magnetocrystalline anisotropy favors [100] this spin orientation.
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