Dimensionality Driven Spin-Flop Transition in Layered Iridates

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Using resonant x-ray diffraction, we observe an easy c-axis collinear antiferromagnetic structure for the bilayer Sr$_2$IrO$_4$, a significant contrast to the single layer Sr$_2$IrO$_4$ with in-plane canted moments. Based on a microscopic model Hamiltonian, we show that the observed spin-flop transition as a function of number of IrO$_2$ layers is due to strong competition among intra- and inter-layer bond-directional pseudo-dipolar interactions of the spin-orbit entangled $J_{\text{eff}}=1/2$ moments. With this we unravel the origin of anisotropic exchange interactions in a Mott insulator in the strong spin-orbit coupling regime, which holds the key to the various types of unconventional magnetism proposed in 5$d$ transition metal oxides.

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Despite the long history of research on magnetism in insulating oxides, magnetism in 5$d$ transition-metal oxides (TMO) with strong spin-orbit coupling (SOC) is only now beginning to be explored. Since the recent discovery of the SOC-driven Mott insulator with $J_{\text{eff}}=1/2$ states in Sr$_2$IrO$_4$ [1, 2], a wide array of theoretical proposals have been put forward for novel types of quantum magnetism and topological phases of matter [3–9]. The magnetism in the strong SOC limit has two fundamentally novel aspects: (i) orbitals of different symmetries are admixed by SOC and thus the magnetic exchange interactions are multidirectional, which is evident in particular from the “cubic” shape of the $J_{\text{eff}}=1/2$ Kramers doublet wavefunction relevant for tetravalent iridates [1–5]; (ii) the quantum phase inherent in the $J_{\text{eff}}=1/2$ states can strongly suppress the isotropic Heisenberg coupling via a destructive interference among multiple superexchange paths, and lead to large anisotropic exchange couplings, of the form of pseudo-dipolar (PD) and Dzyaloshinsky-Moriya (DM) interactions [3]. This provides a mechanism for frustrated magnetic interactions that are predicted to lead to unconventional magnetism, such as the Kitaev model with spin liquid ground state [3, 5, 10]. By contrast, magnetic interactions in the weak SOC limit are predominantly of isotropic Heisenberg type weakly perturbed by the anisotropic couplings.

The central theoretical premise underlying various iridates is that the Kramers pair of $J_{\text{eff}}=1/2$ states is the correct starting point. Strictly speaking, however, the exact $J_{\text{eff}}=1/2$ states are realized only in cubic symmetry and in the large Coulomb correlation limit. Although it has been shown that in Sr$_2$IrO$_4$, having tetragonal symmetry at the Ir site, the ground state wave function is indeed close to the $J_{\text{eff}}=1/2$ state [2], it is not a priori obvious that this should also be the case for other iridates with symmetries lower than cubic. Further, the $J_{\text{eff}}=1/2$ states are also perturbed by the hopping term, the effect of which should be more pronounced in iridates with small charge gap such as the Sr$_3$Ir$_2$O$_7$ [11], a bilayer variant of the single layer Sr$_2$IrO$_4$. Experimentally, a clear signature of the unique features of the interactions inherent to the $J_{\text{eff}}=1/2$ moments, e.g. strong PD couplings, has yet to be seen, especially in (Na,Li)$_2$IrO$_3$ [12, 13], the candidate material for realization of the Kitaev model.

In this Letter, we report a direct manifestation of the strong PD interactions in Sr$_3$Ir$_2$O$_7$, which result from the $J_{\text{eff}}=1/2$ states that are robust despite the proximity of Sr$_3$Ir$_2$O$_7$ to the metal-insulator transition (MIT) boundary. Using resonant x-ray diffraction (RXD), we find in Sr$_3$Ir$_2$O$_7$ a G-type antiferromagnetic (AF) structure with c-axis collinear moments, in contrast to ab-plane canted AF found for Sr$_2$IrO$_4$. The observed spin-flop transition as a function of number of IrO$_2$ layers does not accompany an orbital reconstruction, which shows that the strong inter-layer PD couplings, supported by the three-dimensional (3D) shape of the $J_{\text{eff}}=1/2$ wavefunction, are indeed responsible for the spin-flop transition. Employing the microscopic model Hamiltonian of Ref. [3], we show that in wide – and realistic – parameter ranges, the same microscopic parameters describing the $J_{\text{eff}}=1/2$ electronic states lead to easy-ab-plane moments for the single layer Sr$_2$IrO$_4$ and c-axis collinear moments for Sr$_3$Ir$_2$O$_7$. This implies that the transition occurs only as a function of dimensionality, which is a consequence of the robustness of $J_{\text{eff}}=1/2$ states (albeit perturbed to some extent) against strong quasi-3D hopping amplitudes.

Experiments were carried out at the 4-IDD and 6-ID beamlines at the Advanced Photon Source, with incident photon energy tuned to Ir L$_{2,3}$ edges. A horizontal scattering geometry was used with $\pi$-polarized incident beam. The polarization of the scattered x-rays was ana-
FIG. 1. (a) Crystal structure of Sr$_3$Ir$_2$O$_7$ as reported in Ref. 10. Every neighboring IrO$_6$ octahedra are rotated in opposite sense about the c-axis by $\approx 12^\circ$. (b) Magnetic order has a c-axis collinear G-type antiferromagnetic structure. The up and down magnetic moments correlate with counterclockwise and clockwise rotations of the IrO$_6$ octahedra, respectively.

FIG. 2. (a) l scan measured in $\pi - \sigma$ polarization channel showing magnetic Bragg peaks. (b) Integrated intensities at each peak obtained from rocking curves (red dots). Red solid (green dashed) line is bilayer structural factor expected for antiferromagnetic (ferromagnetic) alignment of two adjacent IrO$_2$ planes in a bilayer expressed by $\cos^2 \frac{2\pi d}{c} \sin^2 \frac{2\pi f}{c}$. (c) Temperature dependence of (0 1 19) peak.
the easy axis also lies in the $bc$ plane. Taking these two data together, it is unambiguously determined that the magnetic Bragg peaks of $(1 0 l)$ and $(0 1 l)$ are associated with the $c$-axis component of the magnetic moment. With the provision of $k=0$ ordering, the magnetic structure is uniquely solved as shown in Fig. 1(b) [19].

Having determined the magnetic structure, we now analyze the origin of distinct magnetic orderings in layered iridates. In the case of single layer $\text{Sr}_2\text{IrO}_4$, it has been shown [3] that DM couplings can be gauged away by a proper rotation of quantization axes, and the magnetic anisotropy is solely decided by the bond-directional PD interactions whose sign and hence the moment direction is controlled by the tetragonal distortion parameter $\theta$ alone (while $\eta = J_H/U$, the ratio of Hund’s exchange and the local Coulomb repulsion, scales the magnitude of the PD terms and magnon gaps). In the bilayer $\text{Sr}_3\text{Ir}_2\text{O}_7$ case, however, one may expect strong inter-layer couplings since the spin-orbit entangled wavefunction in iridates is spatially of 3D shape [1–3]. This suggests that magnetic states in iridates may strongly vary with dimensionality as number of planes are increased, unlike the case of cuprates with spin-only moments that reside on planar orbitals.

The magnetic interactions for intra- and inter-layer bonds of neighboring iridium ions can be expressed in the following common form (with differing coupling constants for inter- and intra-layer bonds):

$$\mathcal{H}_{ij} = J_{ij} \vec{S}_i \cdot \vec{S}_j + \Gamma_{ij} S_i^z S_j^z + \vec{D}_{ij} \cdot [\vec{S}_i \times \vec{S}_j],$$  \hspace{1cm} (1)

where the first term stands for isotropic AF exchange $J_{ij}$, the second term describes symmetric anisotropy $\Gamma_{ij}$ that includes PD terms driven by Hund’s exchange and those due to staggered rotations of octahedra [3]. The latter also induce DM interaction, with DM vector $\vec{D}_{ij}$ parallel to $c$-axis on all bonds, while its direction is staggered. For intra-layer bonds, the coupling constants are identical to those for the single layer case, derived in Ref. [3] in terms of $\eta$, $\theta$, and the octahedra rotation angle $\alpha$. We
have extended the same derivation to inter-layer bonds (the expressions are somewhat lengthy and are given in the Supplementary Material). The Hamiltonian supports two types of ordered states: a canted AF structure with moments in ab-plane and a collinear AF order with moments along c-axis, with AF inter-layer stacking in both cases. We obtained a classical phase boundary between these phases marking a spin-flop transition as a function of $\eta$ and $\theta$. The result is shown as a solid line in Fig. 4(a). The dashed line in the same figure shows the spin-flop transition for the single-layer compound. It is evident that the AF order with $c$-axis moments has a wider stability window in the bilayer compound than in the single-layer one, which is primarily due to the PD interaction acting on the $c$-axis bond. One may note that the same set of parameters in the wide parameter space, bounded by the solid and dashed lines in Fig. 4(a), leads to in-plane moments for single layer Sr$_2$IrO$_4$ and c-axis moments for bilayer Sr$_3$Ir$_2$O$_7$; i.e., the spin-flop transition occurs without an accompanying “orbital” reconstruction.

To gain insights into the competing magnetic interactions, consider first the case in which there is no octahedral rotation ($\alpha=0$). Whereas the intra-layer anisotropic coupling $\Gamma$ can change sign as a function of $\theta$, favoring $c$-axis collinear (in-plane canting) structure when $\theta$ is larger (smaller) than $\theta_c \approx \pi/4$, the inter-layer PD term $\Gamma_c$ always favors $c$-axis collinear structure irrespective of the value of $\theta$, so that there is a competition between intra- and inter-layer PD terms when $\theta<\theta_c$, which is resolved in Sr$_3$Ir$_2$O$_7$ in favor of the $c$-axis collinear AF order. We find that these PD terms can be considerably large compared to the case of 3d TMOs, e.g., cuprates [20]: for realistic values of $\eta$ and $\theta$, the PD couplings can be as large as 0.1~0.3 $J$. Now, restoring finite $\alpha$ we find that emerging DM interactions further stabilize this structure. Indeed, as seen in the phase diagram [Fig. 4(a)], even at $\eta=0$ (in which case there would be no magnetic anisotropy in the single-layer case [3]) the AF order with $c$-axis moments is favored due to DM terms. The reason is that (in contrast to the case of Sr$_2$IrO$_4$) the DM interactions in bilayer Sr$_3$Ir$_2$O$_7$ cannot be simultaneously gauged away, because the intra- and inter-layer bonds prefer different canting angles.

The observed dimensionality driven spin-flop transition, which is rare in TMOs, is a natural consequence of the electronic ground state close to $J_{\text{eff}}=1/2$ states with multidirectional [see Fig. 4(b)] and strong anisotropic couplings. Indeed, it is seen that Sr$_3$Ir$_2$O$_7$ has a similar degree of deviation from the exact $J_{\text{eff}}=1/2$ states (for which $L_2$ RXD intensity is zero) as in the single layer Sr$_2$IrO$_4$ [2], as evidenced by the smallness of $L_2$ intensity ($I_{L_2}/I_{L_3} < 1\%$) as shown in Fig. 4(c). By contrast, in TMOs with polarized orbitals, adding another layer would generally not affect the magnetic structure unless accompanied by an orbital transition; for example in cuprates, the planar $x^2-y^2$ orbitals cannot mediate strong anisotropic inter-layer couplings. We find robust $J_{\text{eff}}=1/2$ states in Sr$_3$Ir$_2$O$_7$, a system lying close to the borderline of MIT with strong hopping amplitudes and a dimensionality greater than two. The validity of $J_{\text{eff}}=1/2$ picture has also been confirmed recently [21] in CaIrO$_3$, a post-perovskite material with edge-sharing geometry relevant to the Kitaev model, pointing out that the $J_{\text{eff}}=1/2$ states may be more generally applicable beyond the Ruddelsden-Popper series.

It remains to be clarified how the observed $c$-axis collinear structure can be reconciled with the reported unusual magnetic effects, such as weak ferromagnetism, diamagnetism, and magnetoresistivity observed at rather low magnetic fields below 1 T applied in the in-plane direction [15]. A possible scenario is that the moment may be canted off from the $c$-axis with the in-plane component appearing at different propagation vector $q$’s. An alternative possibility is that an additional order parameter is present and is responsible for the above magnetic effects. More investigations are needed to resolve these issues.

In summary, we have revealed – through the observation of spin-flop transition in layered iridates – a direct manifestation of the PD interactions that are expected for $J_{\text{eff}}=1/2$ states and are the essential component of the unique magnetism proposed in 5$d$ TMOs with strong SOC. For bilayer iridate Sr$_3$Ir$_2$O$_7$, these interactions lead to the collinear AF ground state with moments directed along the $c$-axis, in contrast to easy-plane canting AF structure of Sr$_2$IrO$_4$. The strong dependence of magnetic structure on the number of IrO$_2$ planes reflects the spin-orbit entangled nature of wavefunctions, which are spatially of 3D shape and support strong inter-layer couplings, unlike the case of, e.g., cuprates with planar orbitals. The resulting competition between intra- and inter-layer PD (and also DM) interactions is tuned by the octahedral rotation and tetragonal distortion, giving rise to the moment reorientation. Our experimental confirmation of robust $J_{\text{eff}}=1/2$ states in a system close to a MIT and their strongly non-Heisenberg interactions strengthens the expectation for novel magnetism in correlated oxides with strong SOC.

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