A new spin-anisotropic harmonic honeycomb iridate

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Abstract

The physics of Mott insulators underlies diverse phenomena ranging from high temperature superconductivity to exotic magnetism. Although both the electron spin and the structure of the local orbitals play a key role in this physics, in most systems these are connected only indirectly — via the Pauli exclusion principle and the Coulomb interaction. Iridium-based oxides (iridates) open a further dimension to this problem by introducing strong spin-orbit interactions, such that the Mott physics has a strong orbital character. In the layered honeycomb iridates this is thought to generate highly spin-anisotropic interactions, coupling the spin orientation to a given spatial direction of exchange and leading to strongly frustrated magnetism. The potential for new physics emerging from such interactions has driven much scientific excitement, most recently in the search for a new quantum spin liquid, first discussed by Kitaev [1]. Here we report a new iridate structure that has the same local connectivity as the layered honeycomb, but in a three-dimensional framework. The temperature dependence of the magnetic susceptibility exhibits a striking reordering of the magnetic anisotropy, giving evidence for highly spin-anisotropic exchange interactions. Furthermore, the basic structural units of this material suggest the possibility of a new family of structures, the ‘harmonic honeycomb’ iridates. This compound thus provides a unique and exciting glimpse into the physics of a new class of strongly spin-orbit coupled Mott insulators.

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Quantum spin systems are characterized by small moments where the spin orientation is decoupled from the crystal lattice, in contrast to Ising-like spin systems that often apply to higher spin states. In the Heisenberg model describing spin-isotropic exchange between neighboring spins, spatial anisotropies of the exchange suppress long-range order [2], but do not lead to anisotropy of the magnetic susceptibility. Striking examples of this are quasi-1D and -2D systems where the exchange differs by orders of magnitude for neighbors along distinct crystallographic directions [3, 4]. The spin-orbit interaction introduces magnetic anisotropy by coupling the spin to the symmetry of the local orbital environment. Although in spin-\(1/2\) systems the crystal field does not introduce single-ion anisotropy (due to Kramer’s protection of the spin-\(1/2\) doublet), it can — via spin-orbit — introduce spin-anisotropies in the \(g\)-factor and in the exchange interactions. The strength of the spin-orbit coupling varies by orders of magnitude between the 3\(d\) and 5\(d\) transition metals. In the former, quenching of the orbital moment decouples the orbital wavefunction from the spin, giving a \(g\)-factor anisotropy that is typically small and an even smaller spin-anisotropy. For example, spin-\(1/2\) copper in a tetragonal crystal field has a \(g\)-factor anisotropy of order 10\%, whereas the spin-anisotropy of exchange is of the order of 1\% [4].

The stronger spin-orbit coupling of the 5\(d\) transition metals is known to give rise to larger magnetic anisotropies. In materials with edge-shared IrO\(_6\) octahedra, spin-anisotropy of the exchange between neighboring effective spin-\(1/2\) states is enhanced by the interference of the two simplest exchange paths across the planar Ir-O\(_2\)-Ir bond. Jackeli and Khaliullin (JK) suggested that in the honeycomb iridates this mechanism may lead to extreme spin-anisotropy where, in the limiting case, the only non-vanishing exchange is for the spin component normal to the Ir-O\(_2\)-Ir plane [5–7]. In the honeycomb lattice, such an interaction couples different orthogonal spin components on the three bonds for each site; no single exchange direction can be simultaneously satisfied, leading to strong frustration. It is the possibility of engineering spin-anisotropy coupled to spatial exchange pathways that has spurred intense scientific research, particularly in connection to the search for quantum spin-liquids [1, 5–7]. However, whether the spin-anisotropic exchange interaction that is coupled to the Ir-O\(_2\)-Ir bonding plane is realized in such materials remains an intense subject of scientific debate [8–10], highlighting the need for the discovery of new materials with related structures and strongly anisotropic exchange interactions.

We have synthesized single crystals of a polytype of Li\(_2\)IrO\(_3\) in which we reveal the effect of
FIG. 1. Single crystal of $H\langle1\rangle$-Li$_2$IrO$_3$ and the Ir lattice structure. (A) Single crystal oriented to be parallel to the crystallographic axes shown in (C), (B) 3D view and (C) projection in the $ab$ plane. In (B) gray shading emphasizes the Ir (purple balls) honeycomb rows that run parallel to the $a \pm b$ diagonals, alternating upon moving along the $c$-axis. For simplicity only Li ions (grey balls) located in the center of Ir honeycombs are shown. In (B) and (C) the rectangular box indicates the unit cell. Comparing (A) and (C) we note that the $\sim 70^\circ$ angle between honeycomb rows is evident in the crystalline morphology.

the spin-anisotropy of exchange across the Ir-O$_2$-Ir bond from the temperature dependence of the anisotropic magnetic susceptibility. The crystals are synthesized as described in Methods. As shown in Figure 1A, the crystals are clearly faceted and typically around $100 \times 100 \times 200 \mu$m$^3$ in size. In contrast to the monoclinic structure of the layered iridate, we find that these materials are orthorhombic and belong to the non-symmorphic space group $Cccm$, with lattice parameters $a = 5.9119(3)$ Å, $b = 8.4461(5)$ Å, $c = 17.8363(10)$ Å (see SI I in published version for details of the crystallography). The structure (shown in Figure 1B and C) contains two interlaced honeycomb planes, the orientation of which alternate along the $c$ axis. The angle $\phi_0$ between the honeycomb planes is fixed by the geometry of the edge shared bonding of the IrO$_6$ octahedra (see Figures 2A and 4A ). For cubic octahedra $\cos \phi_o = 1/3$, namely $\phi_o \approx 70^\circ$, as shown in Figure 2A. The x-ray refinement (see SI II in published version) indicates that the stoichiometry is Li$_2$IrO$_3$, such that the Ir oxidation state is Ir$^{4+}$, 5$d^5$ with an effective Ir local moment of $J_{\text{eff}} = 1/2$. The possibility of Li deficiency in our samples could lead to some Ir$^{5+}$ sites, however this is not expected to have a marked effect on the magnetism; in the case that spin-orbit coupling dominates over the Coulomb
interaction, Ir$^{5+}$ 5d$^4$ is non-magnetic. This is supported by studies of NaIrO$_3$ which are consistent with octahedrally coordinated Ir$^{5+}$ being close to non-magnetic [11]. We denote our crystal structure $^H\langle 1 \rangle$-Li$_2$IrO$_3$, where $^H\langle 1 \rangle$ refers to the single, complete $^H$ honeycomb row.

FIG. 2. Temperature dependence of the magnetic susceptibility and its anisotropy. (A) Each Ir is surrounded by one of two planar, triangular environments indicated by blue and red shaded triangles, located at $\sim 35^\circ$ either side of the $b$-axis. (B) The anisotropy of the magnetic susceptibility as measured by torque and the direct (SQUID) susceptibility (inset) are shown as a function of temperature for all three crystallographic directions. An anomaly indicates the onset of magnetic order at $T_N = 38$ K. (C) The ratios of the anisotropic susceptibility tend to simple fractional values dictated by the $g$-factor anisotropy of the local planar iridium environment. (D) $\sin(2\theta)$ fits to the anisotropy $\alpha_{bc}$ illustrating the change of sign at $\sim 75$K.
In the inset of Figure 2B, the raw magnetic susceptibility shows a magnetic anomaly at 38 K, suggesting an absence of strong frustration. Due to the smallness of our samples and sensitivity to sample misalignment, the anisotropy at high temperatures could not be quantitatively resolved to high accuracy using SQUID magnetometry. To do so, we utilized torque magnetometry, which exclusively probes magnetic anisotropy and is sufficiently sensitive to measure single crystals of \( \sim 10 \mu \text{m} \) dimensions. The magnetic anisotropy, \( \alpha_{ij} = \chi_i - \chi_j \) \((i, j \in a, b, c)\) is shown in Figure 2B and agrees well with the low temperature magnetization data.

At temperatures that are high relative to the exchange interaction energy scale, we expect that only the \( g \)-factor affects the magnetic anisotropy. We find that the ratio of the anisotropic susceptibilities \( \alpha_{ij}/\alpha_{jk} \) asymptotically approach simple fractions at high temperature (above \( \sim 100 \) K, see Figure 2C). Specifically, each Ir is in a three-fold local planar environment with (almost) equidistant neighbors and thus the Ir \( g \)-factor anisotropy can be captured by ascribing each honeycomb plane susceptibility components parallel, \( \chi_{\parallel} \) and perpendicular, \( \chi_{\perp} \) to the plane (consider Figure 2A). This constrains the three components of susceptibility at high temperature to be equally spaced; \( 2\chi_b = \chi_a + \chi_c \) (see SI II) and the anisotropy ratios to be \( \alpha_{ba}/\alpha_{ac} = -1/2, \alpha_{bc}/\alpha_{ac} = 1/2, \alpha_{bc}/\alpha_{ab} = 1 \), just as we observe. This observation places constraints on the ordering of the principal components of the spin-anisotropic \( g \)-factor at all temperatures.

In \( \mathcal{H} \text{Li}_2\text{IrO}_3 \) the principal components of susceptibility tend to diverge upon lowering temperature. The inverse susceptibilities extrapolate to a negative temperature intercept, indicating predominantly antiferromagnetic exchange interactions. Above 200 K, \( 1/\chi \) (in both \( a \) and \( b \) directions) is approximately linear in temperature with a Curie-Weiss slope giving \( \mu_{eff} \approx 1.6 \mu_B \), which is consistent with a \( J_{eff} = 1/2 \) magnetism. The striking reordering of the principal components of susceptibility, leads to strong deviations from Curie-Weiss behavior as the temperature is lowered: \( \alpha_{bc} \) changes sign at \( T \approx 75 \) K (Figure 2D). This is in stark contrast to spin-isotropic Heisenberg exchange systems where the low temperature susceptibility reflects the \( g \)-factor anisotropy observed at high temperatures, even in the presence of spatially-anisotropic exchange \cite{4}. The change of sign of \( \alpha_{bc} \) arises because \( \chi_b \) softens, becoming an order of magnitude greater than \( \chi_a \) and \( \sim 5 \times \chi_c \) (Figure 2B).

The observed ten fold increase in \( \chi_b \) cannot be driven by the \( g \)-factor of the local iridium environment, whose geometric constraints are temperature independent (see SI I & II). The
temperature dependence of $\chi_b$ must therefore arise from spin-anisotropic exchange. We note that all the $c$-axis bonds have the Ir-O$_2$-Ir plane normal to the $b$-axis, whether they preserve or rotate between the two honeycomb orientations (see the full structure in SI I Fig. ??A in the published version and a schematic in Fig. 3A - green shading indicate the Ir-O$_2$-Ir planes). This is the only Ir-O$_2$-Ir plane that is normal to a crystallographic axis, providing evidence for spin-anisotropic exchange across these links. This may arise from the mechanism suggested by JK in the context of the Kitaev model (see also SI III in the published version).

The softening of $\chi_b$ is truncated at 38 K by an antiferromagnetic instability. Within the ordered state, the magnetization increases linearly with applied field (Figure 3C and $\tau/H$ in 3B). At sufficiently high magnetic fields $H^*$, the magnetization kinks abruptly. This corresponds to an induced moment of $\approx 0.1 \mu_B$. Above $H^*$, the finite torque signal reveals that the induced moment is not co-linear with the applied field, consistent with the finite slope observed at these fields in Figure 3C. This shows that in the phase above $H^*$ the induced magnetization along the field direction is not yet saturated, but keeps growing with increasing field (the value is well below the expected saturated Ir moment of $\sim 1 \mu_B$ for $J_{eff} = 1/2$). The angular dependence of both the slope of the linear regime and the kink field $H^*$, exhibit an order of magnitude anisotropy with field orientation (Figure 3D and 3E). Such strong anisotropy in a spin-$1/2$ system highlights the strong orbital character arising from the spin-orbit coupling, again in contrast to spin-$1/2$ Heisenberg anti-ferromagnetism.

There is a very interesting connection between the layered honeycomb Li$_2$IrO$_3$ and the polytype studied here. The $^H(1)$-Li$_2$IrO$_3$ is distinguished by its $c$-axis bond, which either preserves or rotates away from a given honeycomb plane (see Figure 4A); in the case that all the bonds preserve the same plane, the resulting structure is the layered honeycomb system. Further polytypes can be envisioned by tuning the $c$-axis extent of the honeycomb plane before switching to the other orientation (see Figure 4B). We denote each polytype $^H(N)$-Li$_2$IrO$_3$, where $^H(N)$ refers to the number of complete honeycomb rows (see Figure 4B), and the family as the “harmonic”-honeycombs, so named to invoke the periodic connection between members. The layered compound, $^H(\infty)$-Li$_2$IrO$_3$ and the hypothetical hyper-honeycomb structure, $^H(0)$-Li$_2$IrO$_3$ are the end members of this family (see also SI IV in the published version). The edge-sharing geometry of the octahedra preserves the essential
FIG. 3. Low temperature magnetic properties of the $^H\langle 1\rangle$-Li$_2$IrO$_3$. (A) The Ir-O$_2$-Ir planes defining three orthogonal directions of the spin-exchange, one parallel to $\hat{b}$ and the other two parallel to $\hat{a} \pm \hat{c}$, labelled $+$ and $-$ ($\hat{a}$ is the unit vector along $a$). This connects to the notation used to describe the Kitaev Hamiltonian in SI III in the published version. (B) Torque signal $\tau$ divided by the applied magnetic field $H$ illustrating a linear low-field dependence and a kink at $H^*$, which is strongly angle dependent (colors correspond to angles shown in (D)). (C) Magnetization vs magnetic field applied along the $b$-axis at a temperature of 15 K. (D) & (E) The angle dependence $\theta_{ab/ac}$ of the kink field $H^*$ of the ordered state (full circles, left axes) with respect to the crystallographic axes $a, b$ and $c$. $H^*$ is correlated to the magnetization anisotropy $\alpha_{ij}$ (open circles, right axes) indicating a common moment at $H^*$ in all field orientations.

ingredients of the Kitaev model and this is universal for this family of polytypes. Each structure is a material candidate for the realization of a 3D spin liquid in the pure Kitaev limit (see SI III in the published version and for $^H\langle 0\rangle$-Li$_2$IrO$_3$ see Refs. [13–15]).

Finally, we speculate on the consequences and feasibility of making other members of the $^H\langle N\rangle$-Li$_2$IrO$_3$ family. Both the layered $^H\langle \infty\rangle$-Li$_2$IrO$_3$ and the $^H\langle 1\rangle$-Li$_2$IrO$_3$ are stable structures, implying that intermediate members may be possible under appropriate synthesis.
FIG. 4. Introducing the harmonic honeycomb series. (A) Two kinds of c-axis bonds (black links) in the harmonic honeycomb family $\mathcal{H}\langle N \rangle$-Li$_2$IrO$_3$ are shown, one linking within a honeycomb plane (for example blue to blue, top) and one that rotates between honeycomb planes (for example red to blue, bottom). For undistorted octahedra, these links are locally indistinguishable, as can be observed by the local coordination of any Ir atom (also see Figure 2A). (B) These building blocks can be used to construct a series of structures. The end members include the theoretical $N = 0$ ‘hyper-honeycomb’ [13–15] and the $N = \infty$ layered honeycomb [12]. Here $N$ counts the number of complete honeycomb rows in a section along the c-axis before the orientation of the honeycomb plane switches.

conditions. The building blocks shown in Figure 4A connect each member of the harmonic honeycomb series in a manner that is analogous to how corner sharing octahedra connect the Ruddlesden-Popper (RP) series. Indeed, despite the fact that members of the RP family are locally identical in structure, they exhibit a rich variety of exotic electronic states; including superconductivity and ferromagnetism in the ruthenates [16, 17], multiferroic behavior in the titanates [18], collosal magnetoresistance in the manganites [19] and high temperature superconductivity in the cuprates [20]. The harmonic honeycomb family is a honeycomb analogue of the RP series, and its successful synthesis could similarly create a new frontier in the exploration of strongly spin-orbit coupled Mott insulators.
A. Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, under Contract No. DE-AC02-05CH11231. TES acknowledges support National Science Foundation Graduate Research Fellowship under Grant No. DGE 1106400. JYC acknowledges n*sf-dmr 1063735 for support. RMcD acknowledges support from BES-‘Science of 100 tesla’. Work at Oxford was supported by the EPSRC (UK) grant EP/H014934/1. The work at the National High Magnetic Field Laboratory is supported via NSF/DMR 1157490.
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