Topological states in pyrochlore iridates: Long-range anisotropy strongly competing with spin-orbit interaction

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In the search for topological phases in correlated electron systems, iridium-based pyrochlores A$_2$Ir$_2$O$_7$ – materials with 5d transition-metal ions – provide fertile grounds. Several novel topological states have been predicted but the actual realization of such states is believed to critically depend on the strength of local potentials arising from distortions of IrO$_6$-cages. We test this hypothesis by measuring with resonant x-ray scattering the electronic level splittings in the $A=\text{Y, Eu}$ systems, which we show to agree very well with ab initio electronic structure calculations. We find, however, that not distortions of IrO$_6$-octahedra are the primary source for quenching the spin-orbit interaction, but strong long-range lattice anisotropies, which inevitably break the local cubic symmetry and will thereby be decisive in determining the system’s topological ground state.

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Introduction – The discovery that in solids with weakly interacting electrons the spin-orbit interaction can induce insulating states of topological nature, prompts the intriguing question what kind of topological phases can develop in correlated electron systems, in which it is well-known that the Coulomb interactions between electrons can qualitatively change the character and properties of the electronic ground state [1–7]. Intra and inter-orbital electron-electron interactions are very substantial in 3d transition metal compounds such as copper-oxides and transition metal compounds, such as iridates, the interesting situation arises that these interactions meet on the same energy scale. The way in which this competition plays out delicately depends on the local energy, $E$, and will thereby be decisive in determining the system’s topological ground state.

In the pyrochlore iridates of the type $A_2$Ir$_2$O$_7$ that we consider here, with $A=\text{Sm, Eu, Lu and Y}$, five electrons occupy the three Ir $t_{2g}$ orbitals, which reside on Ir$^{4+}$ ions inside corner linked IrO$_6$ octahedra, see Fig. [1]. This leaves one hole in the $t_{2g}$ shell to which 6 distinct $t_{2g}$ quantum states (3 orbital and 2 spin) are available. When the local symmetry is cubic, so that it does not lift the degeneracy of the three $t_{2g}$ orbitals, the strong SOC splits the $t_{2g}$ states up into a pure $j=3/2$ quadruplet and a pure $j=1/2$ doublet. The doublet is higher in energy and therefore accommodates the hole. Any additional crystal-field splitting, for instance of tetragonal or trigonal symmetry, lifts the degeneracy of $t_{2g}$ states and competes with the SOC, thus tending to quench the orbital moment. As the SOC is driving the formation of electronic states of topological nature, the outcome of this competition is decisive for the actual realization of any type of non-trivial topological ground state in pyrochlore iridates [8–7].

Experimental RIXS results – We use Resonant Inelastic X-ray Scattering (RIXS) [8] to measure directly the energy of the different configurations of a hole in the Ir $t_{2g}$ shell of Y$_2$Ir$_2$O$_7$ and Eu$_2$Ir$_2$O$_7$ and to determine in that way the crystal-field energy splittings of these states. The single crystals of Eu$_2$Ir$_2$O$_7$ and powder samples of Y$_2$Ir$_2$O$_7$ were grown by solid-state synthesis (see Supplementary Material). RIXS is a second-order scattering technique and can directly probe the electronic transitions within the Ir 5d manifold due to two subsequent electric dipole transitions ($2p \rightarrow 5d$ followed by $5d \rightarrow 2p$) [8,9]. It is therefore a valuable technique for detecting transitions between crystal-field split Ir 5d levels and has been utilized for a variety of iridates [10–12]. We determine the splittings by measuring the $d$-$d$ transition energies at the iridium $L_3$ edge, with an incident energy, $E_i = 11.217$ keV, chosen to maximize the res-
The RIXS spectra of both Y$_2$Ir$_2$O$_7$ and Eu$_2$Ir$_2$O$_7$ (Fig. 2) show sharp features below 1.5 eV, corresponding to transitions within the Ir $t_{2g}$ levels, and a strong intense peak stretching from 2 to 5 eV that according to the calculations, see below, corresponds to d-d transitions between the Ir $t_{2g}$ and $e_g$ levels. The position refinement for the three main peaks apart from the zero-loss peak results in $E_1 = 0.53 \pm 0.05$ (0.54 $\pm$ 0.03), $E_2 = 0.98 \pm 0.05$ (1.00 $\pm$ 0.03) and $E_3 = 3.90 \pm 0.05$ eV (3.70 $\pm$ 0.05 eV) for Y$_2$Ir$_2$O$_7$ (Eu$_2$Ir$_2$O$_7$). Using a first, empirical ansatz we fit the energies of the three peaks to the eigenvalues of an effective single-ion Hamiltonian for the $t_{2g}$ orbitals of the form $H_0 = \lambda \cdot s + \Delta t_{z}^2$, where $\lambda$ is the SOC strength and $\Delta$ the $t_{2g}$ crystal-field splitting (see Supplementary Material). The latter tends to quench the Ir orbital moment and is usually identified with distortions of the IrO$_6$ octahedra [6–13]. The fit of the RIXS data to the effective $\lambda$-$\Delta$ model results in parameters $\lambda = 0.41$ and $\Delta = 0.59$ eV for Y-227 and $\lambda = 0.43$ and $\Delta = 0.54$ eV for Eu-227. The value for $\lambda$ for both these materials agrees very well to values of 0.39–0.49 eV that can be extracted from electron spin resonance measurements on Ir$^{4+}$ impurities [15]. The magnitudes of $\Delta$, 0.54–0.59 eV, however, are surprisingly large. To understand the size and elucidate the microscopic origin of this large crystal-field splitting – a crucial energy scale in determining the topological ground state of the electronic system – we have carried out a set of detailed ab initio calculations of the Ir d-level electronic structure on a series 5d$^5$ pyrochlore iridates: Sm-, Eu-, Lu- and Y-227.

Ab initio calculation of d-d excitations – To investigate in detail the electronic structure and the essential interactions in the A$_2$Ir$_2$O$_7$ iridates, we rely on ab initio many-body techniques from wave-function-based quantum chemistry [10]. To calculate the local electronic multiplet structure with this wave-function-based methodology we use embedded clusters of IrO$_6$ octahedra and a farther-out solid-state environment that reproduces the Madelung field in the cluster region, see Refs. [17, 18].

Multiconfiguration self-consistent-field (MCSCF) and
TABLE I: Relative energies of the split $j = 3/2$ states $E_1$ and $E_2$ as well as $t_{2g}^4 e_g^1$ excitation energies in 227 iridates. The energies are the result of ab initio spin-orbit multireference configuration-interaction calculations, see text. The experimental values for EuIr$_2$O$_7$ and Y$_2$Ir$_2$O$_7$ determined from their RIXS spectra in Fig. 2 are shown in bold, within brackets.

|        | $E_1$  | $E_2$  | $t_{2g}^4 e_g^1$  |
|--------|--------|--------|-------------------|
| Sm$_2$Ir$_2$O$_7$ | 0.61   | 0.91   | 3.41–4.75         |
| Eu$_2$Ir$_2$O$_7$ | 0.60 (0.54) | 0.91 (1.00) | 3.39–4.72 (3.70) |
| Lu$_2$Ir$_2$O$_7$ | 0.57   | 0.92   | 3.49–4.88         |
| Y$_2$Ir$_2$O$_7$  | 0.58 (0.53) | 0.94 (0.98) | 3.48–4.84 (3.90) |

The d-d level splittings calculated for cuprates, such as La$_2$CuO$_4$ and Sr$_2$CuO$_3$, and iridates, such as Sr$_2$IrO$_4$, by similar quantum-chemical techniques are in close agreement to the experimental values of these excitation energies. Also for the 227 iridium pyrochlores that we consider here, we observe that the calculated excitation energies of the 5$d$ multiplets (the values of $E_1$, $E_2$ and $E_3$), see Table I, are in close agreement with the ones obtained from our RIXS experiments.

Origin of d-d splittings – The very good agreement between calculated and measured d-d level splittings forms the basis for a subsequent detailed analysis of the microscopic origin of the crystal-field splitting of the 5$d$ levels. To this end, we first test the hypothesis that the splitting $\Delta$ in the effective single ion $\lambda - \Delta$ model is due to a distortion of the IrO$_6$ octahedra which lowers the local cubic symmetry to a trigonal (or even lower) symmetry. It turns out that the crystal structure of the 227’s under consideration is fully defined by just three parameters: the space group number, the cubic lattice constant $a$, and the fractional coordinate $x$ of the O at the 48f site. For $x = x_c = 5/16$, the oxygen cage around each Ir site forms an undistorted, regular octahedron.

In our 227 Ir pyrochlores, however, $x$ is always larger than $x_c$, which translates into a compressive trigonal distortion of the IrO$_6$ octahedra and hence a splitting of the 5$d$ electronic levels. To estimate how large the resulting trigonal crystal-field splitting is, we have performed a set of further ab initio calculations, but now for an idealized crystal structure with $x = x_c$ and thus undistorted octahedra. The resulting energies $E_{1g}^f$, $E_{2g}^f$ in crystals with perfect octahedra, presented in Table II, are seen to be just slightly different from the excitation energies of trigonally distorted systems. Thus local trigonal distortions of the IrO$_6$ octahedra are not the cause of the energy splitting $\Delta$ of the $t_{2g}$ orbitals.

To understand the physical origin of the large splitting $\Delta$ one needs to consider the crystal structure of the $A$-227’s in more detail. As shown in Fig. 1b, the A ions closest to a given iridium ion form a hexagonal structure in a plane parallel to two of the faces of the IrO$_6$ octahedron. It is clear that the potential generated by these six $A^3+$ ions breaks cubic symmetry even in the absence of trigonal distortions. The numerical results we obtain show that due to the large ionic charge at the A sites and the large spatial extent of the iridium 5$d$ orbitals the anisotropic, planar $A_6$ coordination actually has by far a cause for seven 5$d^5$ sites (and nondegenerate orbitals), a given electron configuration implies 1 octet, 6 sextet, 14 quartet, and 14 doublet spin states which further interact via spin-orbit coupling (SOC). To simplify the problem and reduce the computational effort, we therefore further replaced the six Ir$^{4+}$ $d^9$ NN’s by closed-shell Pt$^{4+}$ $d^9$ ions and in this manner obtain the relative MRCI energies for the spin-orbit states presented in Tables I and II (labelled MRCI+SOC).
stronger effect on the $t_{2g}$ level splitting than the trigonal distortion of the IrO$_6$ cages.

To bolster this conclusion, an underlying assumption – the interpretation of the excitation energies $E_{1,2}$ in terms of an effective $\lambda - \Delta$ model – requires crosschecking. We can do so by calculating the $t_{2g}$ crystal-field splittings directly by switching off the SOC in the quantum-chemical calculations. These calculations show that the ground-state wave function has $a_{1g}$ symmetry. The 5$d$-level splittings without SOC’s (see Table II) are only marginally different between the distorted, experimental crystal structure ($\Delta$) and the idealized, undistorted one ($\Delta^0$). Besides thus confirming that the 5$d$ splittings are due to anisotropy potentials beyond the nearest-neighbor ligand coordination shell, the values computed without SOC’s also bring additional insight into the magnitude of these splittings. Whereas the effective values for $\Delta$ in the $\lambda - \Delta$ model and RIXS data are 0.54–0.59 eV, the $ab\text{ initio}$ calculations without SOC yield $\Delta = 0.27 - 0.30$ eV, i.e., values about a factor two lower. This implies that in the pyrochlore iridates the effect of the relativistic spin-orbit coupling cannot be captured by oversimplified single-ion models like the $\lambda - \Delta$ model. Additional degrees of freedom, in particular the $t_{2g} - e_g$ couplings, the presence of anisotropic spin-orbit interactions [31] and the hybridization of the Ir $t_{2g}$ states with other orbitals in the system must be considered.

Conclusions – Our experimental and theoretical demonstration of the presence of large Ir $t_{2g}$ splittings in pyrochlore iridates which arise from longer-range crystal anisotropy [32, 33] and that directly compete with spin-orbit interactions, does not only change the canonical view that only, potentially weak, local distortions of IrO$_6$ octahedra tend to quench the spin-orbit coupling in these iridium pyrochlores. The broader ramification is that the rather extended nature of the 5$d$ wave functions renders the longer-range anisotropy fields to be of fundamental importance throughout the 5$d$ transition metal series. Their physical effect is particularly striking when the local ligand field symmetry is high, e.g. cubic or close-to-cubic, but the point group symmetry in the crystal is lower. This includes, for example, osmium-based pyrochlore materials [34]. Yet it is pertinent for many more crystal structures, in particular for layered quasi-2D perovskites or chain-like quasi-1D 5$d$ transition metal systems [12, 15].

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SUPPLEMENTARY MATERIAL

Crystal growth

Mixtures of Y$_2$O$_3$ and IrO$_2$ with purities of 99.99% were ground in stoichiometric molar ratios, pelletized, and then heated in air at 1000°C for 100 hours. The resulting material was reground, pressed into pellets, and resintered at the same temperature for an additional 150 hours, with two intermediate regrindings. Powder X-ray diffraction measurements confirmed the phase purity of the resulting Y$_2$Ir$_2$O$_7$ sample to within the resolution of the measurement. A single crystal of Eu$_2$Ir$_2$O$_7$ was grown by the solid state synthesis method, as previously described in detail in Ref. [35]. A mixture of polycrystalline Eu$_2$Ir$_2$O$_7$ and KF (2N) were heated up to 1100°C and next cooled down to 850°C at a rate of 2.5°C/h. Resistivity data on the resulting Eu$_2$Ir$_2$O$_7$ single-crystal shows almost metallic behavior, indicating that the sample displays slight excess of Ir, see the discussion in Ref. [34].

Single-ion $\lambda$–$\Delta$ model

In the simplest approximation, the energies of the three main peaks in the RIXS spectra can be mapped onto the eigenvalues of a single ion Hamiltonian of the form $H_0 = \mathbf{\lambda} \cdot \mathbf{s} + \Delta \mathbf{l}^2$. In the basis of $t_{2g}$ orbitals, $\lambda$ is the SOC and $\Delta$ is a tetragonal or trigonal $t_{2g}$ splitting [6, 14]. The eigenvalues of $H_0$ and the splittings among the spin-orbit $t_{2g}$ states are given by the following expressions:

$$E_0 = \lambda(-1 + \delta - \sqrt{9 + 2\delta + \delta^2})/4,$$

$$E_1 = \lambda/2,$$

$$E_2 = \lambda(-1+\delta+\sqrt{9 + 2\delta + \delta^2})/4,$$

where $E_0$ is the energy of the ground-state $j = 1/2$ doublet and $\delta = 2\Delta/\lambda$. If $E_1 - E_0$ and $E_2 - E_0$ are known from experiment, i.e., RIXS, simple estimates for $\lambda$ and $\Delta$ can be in principle derived from the relations above. In particular, $\lambda = 2(2E_{10} - E_{20})/(3-\delta)$ and $\Delta = \lambda\delta/2$, where $\delta = -\sqrt{b^2-9}$, $b = (1+3\alpha^2)/(1-\alpha^2)$, $a = E_{20}/(E_{20} - 2E_{10})$, $E_{20} = E_2 - E_0$, and $E_{10} = E_1 - E_0$. 

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