CalIrO$_3$: a Spin-Orbit Mott Insulator Beyond the $j_{\text{eff}} = 1/2$ Ground State

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In CaIrO$_3$ electronic correlation, spin-orbit coupling, and tetragonal crystal field splitting are predicted to be of comparable strength. However, the nature of its ground state is still object of debate, with contradictory experimental and theoretical results. We probe the ground state of CaIrO$_3$ and assess the effective tetragonal crystal field splitting and spin-orbit coupling at play in this system by means of resonant inelastic x-ray scattering. We conclude that insulating CaIrO$_3$ is not a $j_{\text{eff}} = 1/2$ iridate and discuss the consequences of our finding to the interpretation of previous experiments. In particular, we clarify how the Mott insulating state in iridates can be readily extended beyond the $j_{\text{eff}} = 1/2$ ground state.

Spin-orbit coupling is the main ingredient for $5d$ transition metal oxides to form novel electronic states of matter, such as the recently discovered Mott insulating state in Sr$_2$IrO$_4$. This insulating behavior is unexpected in iridates perovskites as, for a half-filled shell with spatially extended orbitals, electronic correlation was thought to be negligible. Instead, the role of electronic correlation is enhanced here by spin-orbit coupling, through the formation of the so-called $j_{\text{eff}} = 1/2$ ground state. Its realization arises from the interaction of strong spin-orbit coupling ($\zeta \sim 0.5$ eV) and cubic crystal field ($10Dq \sim 3$ eV), and is perturbed by short- and long-ranged anisotropies which could cause departures from the $j_{\text{eff}} = 1/2$ ground state. A small, but sizable tetragonal contribution $|\Delta| \sim 0.01$ eV to the cubic crystal field $10Dq$ was detected in both Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$, with opposite signs, in agreement with recent theoretical calculations. In these cases, however, $|\Delta | \ll \zeta \ll 10Dq$ and the $j_{\text{eff}} = 1/2$ ground state in Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$ is not in doubt. Structural distortions are instead more pronounced in the insulating perovskite Sr$_2$IrO$_4$; thus the cubic symmetry of the crystal field is expected to be drastically lowered and the $j_{\text{eff}} = 1/2$ ground state to be severely altered. The robustness of the $j_{\text{eff}} = 1/2$ ground state against structural distortions, in particular octahedral rotations and elongations, as well as chemical substitution has been mostly tested by means of resonant X-ray magnetic scattering (RMXS), on the basis of the nearly vanishing intensity at the L$_2$ absorption edge. Following this criterion, a number of “$j_{\text{eff}} = 1/2$ iridates” have been identified, including CaIrO$_3$. However, this interpretation has been widely controversioned. Indeed, a unified picture has not been reached yet: the interpretation of RMXS results was supported by LDA+SO+U calculations, but contradicted by ab-initio quantum chemistry calculations. The latter predict a large splitting of the $t_{2g}$ states that give rise to a strongly unbalanced occupation of the $xy$, $yz$ and $zx$ orbitals, while for the $j_{\text{eff}} = 1/2$ ground state the three orbitals contribute with an equal weight of 1/3. Remarkably, despite contradicting evidences about the details of the electronic ground state, consensus is reached on the magnetic interactions, with a strong antiferromagnetic coupling along the $c$-axis and a weak ferromagnetic one along the $a$-axis, which stabilize canted long range antiferromagnetism and characterize CaIrO$_3$ as a quasi-one-dimensional antiferromagnet.

In this Letter, we use resonant inelastic X-ray scattering (RIXS) at the Ir L$_3$ edge to solve the puzzle of the ground state in CaIrO$_3$. RIXS is a powerful technique for the study of correlated electron systems mostly devoted to the study of high-$T_c$ superconducting and insulating cuprates in the past years. Recently, RIXS was applied to the investigation of magnetic excitations in correlated iridium oxides. Following the initial theoretical suggestion of Ament et al., it was demonstrated that magnon dispersion could be studied in Sr$_2$IrO$_4$ and Sr$_3$Ir$_2$O$_7$. In the present work, we focus on the inelastic response of CaIrO$_3$ in the energy range relevant to spin-orbital excitations, and we determine the effective tetragonal crystal field and spin-orbit coupling acting on $t_{2g}$ levels by comparing the results to a single-ion model. We obtain $\zeta = 0.52$ and $\Delta = -0.71$ eV and therefore conclude that the departure of CaIrO$_3$ from the $j_{\text{eff}} = 1/2$ state is unambiguous, in agreement with ab-initio calculations.

RIXS measurements were performed at the new inelastic X-ray scattering beamline of ESRF (ID20-UPBL06). Two different set-ups were used in order to optimize the flux and energy-resolution of the beamline. The incident radiation was monochromatized by a high heat-load double crystal Si(111) monochromator and a post-monochromator for further bandwidth reduction. In the high energy-resolution mode, a Si(844) back-scattering channel-cut reduced the incident photon bandwidth down to 15 meV at 11.215 keV; in the low energy-resolution set-up, a Si(311) channel-cut monochromator provided a bandwidth of about 350 meV. A Kirkpatrick-Baez mirror system focused the X-rays to a spot size of $10 \times 20$ (V\times H) $\mu$m$^2$ at the sample position. The scattered X-rays were energy-analyzed by a Rowland-type...
Fig. 1 shows a low energy-resolution RIXS map of CaIrO$_3$. In RIXS, the incident photon energy is tuned to an absorption edge, the $L_3$ in our case, corresponding to the transition of an electron from the $2p_{3/2}$ to the 5d states, thus creating a deep core hole. The system then relaxes to a less excited final state by filling the core hole with the same or another electron, possibly creating a low energy excitation. The incident energy is scanned across the $L_3$ absorption line and spectra are recorded up to 12 eV energy loss. An elastic line and magnetic excitations are found close to the zero energy loss line. At increasing energy losses, we assign features to intra-$t_{2g}$ ($t_{2g}^e \rightarrow t_{2g}^o$, $t_{2g}$-to-$e_g$ ($t_{2g}^o \rightarrow t_{2g}^e e_g^o$) and charge-transfer (CT) excitations (as indicated in the figure), following previous RIXS studies \[28, 33\]. In this work, we concentrate on intra-$t_{2g}$ excitations only. Their intensity (including that of the elastic line and magnetic excitations) is enhanced for incident photon energies about 3 eV below the main absorption peak. This is a common feature of several iridium oxides, which was observed in both RMXS and RIXS experiments \[4, 26\]. It can be understood by considering the electronic structure of an Ir$^{4+}$ ion in a large cubic crystal field: with 5 electrons filling the 5d states, $e_g$ states are empty and one hole is left in the $t_{2g}$ states. The maximum of the absorption line (11.219 keV) corresponds to the transition of an electron into the 5d $e_g$ state, while the contribution of the $t_{2g}$ states is minor, as it scales with the number of unoccupied final states. On the other hand, it is reasonable to assume that intra-$t_{2g}$ excitations are more effectively probed when a $2p_{3/2}$ electron is directly promoted in the 5d $t_{2g}$ state, i.e. for incident photon energies tuned at $\sim 10Dq$ below the main absorption line (11.216 keV).

For the high resolution measurements, we fixed the incident photon energy at 11.216 keV to enhance $t_{2g}$ excitations. A representative spectrum is shown in Fig. 2. The low energy range comprises the elastic line and a broad structure of magnetic origin, not discussed here. The 0.3-1.6 eV energy range is dominated by two intense broad features (B and C) and a weak, energy-resolution limited peak (A), similar to the excitation spectrum of Na$_2$IrO$_3$ and Li$_2$IrO$_3$ \[28, 29\]. The assignment of features B and C to local excitations across crystal field split states \[28\] was initially debated \[34\], but then supported by recent calculations \[35\]. We therefore assign features B and C of Fig. 2 in analogy to the case of Na$_2$IrO$_3$ and Li$_2$IrO$_3$. The assignment of features B and C is further strengthened by \textit{ab-initio} calculations for CaIrO$_3$ predicting a splitting of the $j_{\text{eff}} = 3/2$ states by 0.6-0.7 eV \[10\], in agreement with the energy difference of about 0.6 eV for features B and C found in our experiment.

In the following we discuss the spin-orbit excitations (features B and C in Fig. 2) in more detail. Although of mostly local origin, it should be mentioned that they show a weak, but non negligible dispersion versus momentum transfer, in the order of 0.05 eV, indicating that they retain some non-local character. In the present work, however, we aim at determining the size of the effective tetragonal crystal field splitting and spin-orbit coupling in CaIrO$_3$ and the fine details of the band struc-
corresponding eigenvalues, the eigenstates of $H$ will be neglected. In fact, their bandwidth is one order of magnitude smaller than the energy at which these excitations occur, and therefore inter-site interactions can be considered as small perturbations to the local crystal field. The effective parameters $\Delta$ and $\zeta$ then include any kind of renormalization due to non-local effects. A dedicated study of the transferred momentum dependence of such excitations is, however, desirable.

The spectra were fitted to three Pearson functions: feature A turns out to be energy-resolution limited, at an energy of about 0.42 eV, very similar to the value reported for $\text{Na}_2\text{IrO}_3$ and $\text{Li}_2\text{IrO}_3$ [28]. Features B and C are centered at 0.66 and 1.22 eV, respectively, which correspond to the largest intra-$t_{2g}$ splitting ever reported in iridium oxides. In order to better understand the nature of these excitations, and to assess the effective tetragonal crystal field. The weak momentum transfer dependence of these excitations suggests a dominant intra-site character, for which a local model is justified. Since $10Dq$ is sufficiently large ($10Dq \sim 3$ eV), $5d$ $e_g$ states are neglected and the interacting Hamiltonian for one hole in the $5d$ $t_{2g}$ states is then written as

$$H = \zeta \mathbf{L} \cdot \mathbf{S} - \Delta L_z^2, \tag{1}$$

in which tetragonal crystal field splitting ($\Delta < 0$ for compressed octahedra) and spin-orbit coupling are treated on equal footing. For $\Delta = 0$, the ground state is represented by the $|\jmath_{\text{eff}} = 1/2\rangle$ doublet and the excited states by the $|\jmath_{\text{eff}} = 3/2\rangle$ quadruplet. For arbitrary values of $\zeta$ and $\Delta$, the eigenstates of $H$ are three non-degenerate Kramers doublets, which we generically label $|0, \pm\rangle$, $|1, \pm\rangle$ and $|2, \pm\rangle$ ($|0, \pm\rangle$ being the ground state wave function). The corresponding eigenvalues, $E_0$, $E_1$ and $E_2$, are reported, for example, in Ref. [17]. Here we are interested in transitions from the $|0, \pm\rangle$ ground state to the $|1, \pm\rangle$ and $|2, \pm\rangle$ excited states. The corresponding energies, relative to the ground state, at which the RIXS transitions occur, are given by

$$\varepsilon_1 = E_1 - E_0 = \frac{\zeta}{4} \left[ 3 + \delta + \sqrt{9 + \delta(\delta - 2)} \right], \tag{2}$$

$$\varepsilon_2 = E_2 - E_0 = \frac{\zeta}{2} \sqrt{9 + \delta(\delta - 2)}, \tag{3}$$

where $\delta = 2\Delta/\zeta$. These are reported in Fig. 3 as a function of $\Delta$ for $0.45 < \zeta < 0.55$ eV. For $\Delta = 0$, $\varepsilon_1 = \varepsilon_2 = 3\zeta/2$ as the $|1, \pm\rangle$ and $|2, \pm\rangle$ states merge into the $|\jmath_{\text{eff}} = 3/2\rangle$ quadruplet when the $\jmath_{\text{eff}} = 1/2$ ground state is realized. In general, however, the energy of the two RIXS excitations is a function of both $\Delta$ and $\zeta$.

In our case, the only solution with physical meaning is found by imposing $\varepsilon_1 = 0.66$ and $\varepsilon_2 = 1.22$ eV (white dots in the diagram of Fig. 3), from which one obtains $\zeta = 0.52$ and $\Delta = -0.71$ eV. The value of $\zeta$ compares favourably with previous estimates in other iridium oxides [8, 12, 26, 28], and in particular to the recently calculated value of 0.47 eV by Bogdanov et al. [19] for the specific case of $\text{CaIrO}_3$. The sign of $\Delta$ is consistent with structural studies reporting a compression of the $\text{IrO}_6$ octahedra [8], while its magnitude implies a minor contribution of the $xy$ orbital to the ground state wave function (only 10%), in agreement with ab-initio quantum chemistry calculations which predict a splitting of $t_{2g}$ states in the absence of spin-orbit coupling in the order of 0.63-0.76 eV [19]. Noteworthy, $|\Delta|$ is more than one order of magnitude larger than that of the prototypical $\jmath_{\text{eff}} = 1/2$ compounds, $\text{Sr}_2\text{IrO}_4 (\Delta = -0.01$ eV) [8] and $\text{Ba}_2\text{IrO}_4 (\Delta = 0.05$ eV) [17]. Therefore, $|\Delta| > \zeta$ and we
can safely state that CaIrO3 is not a $j_{\text{eff}} = 1/2$ iridate, with a dominant $(|yz, \mp\rangle \pm |zx, \mp\rangle)/\sqrt{2}$ character of the ground state wave-function.

We now discuss the size and direction of the magnetic moments in comparison to existing experimental results and the sign of magnetic interactions. The size of the magnetic moments is a function of both $\zeta$ and $\Delta$ [17]: with the above determined values, the expectation value for the $z$ component of the magnetic moment turns out to be 1.7 $\mu_B$ in CaIrO3, i.e. larger than the magnetic moment of 1 $\mu_B$ expected for a perfectly localized $j_{\text{eff}} = 1/2$ state. Following the interpretation of magnetization data of Ref. [14] we conclude that the magnetic moments in CaIrO3 are canted along the $b$‐axis, with a canting angle of $\sim 2^\circ$, i.e. about $21^\circ$ away from the local $z$-axis of the IrO6 octahedra. It should be noted here that the discrepancy between RMXS and RIXS results is reconciled in view of their non-trivial dependence on magnetic moment direction [17]. Indeed, considering the actual value of $\Delta$ and $\zeta$, and the direction of the magnetic moments, one obtains a Ir $L_2/L_3$ RMXS intensity ratio of 0.1%, which is below the detectability limit of 0.3% reported in the experiment [14] (the calculated Ir $L_2/L_3$ RMXS intensity ratio would be 24% in the case of magnetic moments aligned along the local $z$-axis). Magnetic interactions giving rise to the stripe-type canted antiferromagnetism of CaIrO3 discussed above were explained in the framework of an ideal $j_{\text{eff}} = 1/2$ state [14], for which theoretical arguments [30] predict antiferromagnetic (ferromagnetic) coupling along the corner-sharing (edge-shared) bonds. CaIrO3 seems to obey these rules. However, as long as the occupancy of the $yz$ and $zx$ orbitals is identical and their phase relation preserved, the same theoretical arguments apply and the sign of the magnetic interactions remains unchanged. Indeed, the fact that the coupling is ferromagnetic along $a$ and antiferromagnetic along $b$, despite the severe departure of CaIrO3 from the $j_{\text{eff}} = 1/2$ ground state, is also supported by quantum chemistry calculations [14].

We are now in the position to discuss the transport properties of iridates and their connection to the $j_{\text{eff}} = 1/2$ ground state. The latter was originally invoked to explain the insulating behaviour of Sr2IrO4 and readily extended to other “$j_{\text{eff}} = 1/2$” compounds. In Fig. [1] we explain and extend the concept of a spin-orbit Mott insulator beyond the specific case of “$j_{\text{eff}} = 1/2$” iridates. One has to consider the 5$d$ $t_{2g}$ states, whose bandwidth in the absence of perturbations would be too large for a reasonable Hubbard energy $U$ to open a gap; rather, the density of states at the Fermi energy would be only slightly reduced, as in Fig. [1] (b). Crucially, spin-orbit coupling in the absence of a tetragonal crystal field splits the otherwise degenerate $t_{2g}$ states and a half filled $j_{\text{eff}} = 1/2$ bands is isolated, with a much reduced bandwidth ($w$) compared to the original one. As $U > w$, lower (LHB) and upper (UHB) Hubbard bands are created, thus turning the system into an insulator (Fig. [1]d)) [1]. In the case of CaIrO3, however, the large tetragonal crystal field degrades the $|j_{\text{eff}} = 1/2$ ground state into the generic $|0\rangle$. Nevertheless, the smallest splitting between the $j_{\text{eff}} = 1/2$- and $j_{\text{eff}} = 3/2$-derived bands is $\zeta (\varepsilon_1$ in the limit $\Delta \rightarrow -\infty$), i.e. only a factor 3/2 smaller than that in the pure $j_{\text{eff}} = 1/2$ ground state. Therefore, for $U > w$ LHB and UHB bands are formed and the system retains its insulating character, although the ground state wave function differs significantly from $|j_{\text{eff}} = 1/2\rangle$ (indeed, $|0, \pm\rangle = \pm |xy, z\rangle$ for $\Delta \rightarrow +\infty$ and $|0, \pm\rangle = (|yz, \mp\rangle \pm |zx, \mp\rangle)/\sqrt{2}$ for $\Delta \rightarrow -\infty$). A rough estimate of $U$ in CaIrO3 can be naively extracted by adopting the interpretation, though debated [34, 35], of feature A in Fig. [2] as the excitation across the Mott gap [28]: we obtain $U \simeq 0.4$ eV which is consistent with the band gap of 0.34 eV deduced from resistivity measurements [18, 20] and places CaIrO3 in the scenario of Fig. [1] (f).

In conclusion, i) we solve the controversy concerning the ground state of CaIrO3 [14] [19]. CaIrO3 is not a $j_{\text{eff}} = 1/2$ iridate, due to the large tetragonal crystal field. Indeed, we estimate the effective tetragonal crystal field splitting and spin-orbit coupling to be $\Delta = -0.71$ and $\zeta = 0.52$ eV, respectively, by inspecting the Ir $L_3$ edge RIXS response in the energy range relevant to spin-orbital excitations. ii) We show that experimental [14] and theoretical [19] results can be reconciled in view of the nontrivial dependence of the Ir $L_2/L_3$ RMXS intensity ratio on the magnetic moment direction [17]. Furthermore, iii) we understand that the sign of magnetic interactions is unchanged with respect to the ideal

![FIG. 4. Schematic representations of the band structure in iridates with 5$d^9$ configurations in the absence of perturbations (a), with spin-orbit coupling (c) and spin-orbit coupling plus tetragonal crystal field splitting (e). Panels (b), (d) and (f) correspond to panels (a), (c) and (e), respectively, when the Hubbard term $U$ is taken into account.](image-url)
$j_{\text{eff}} = 1/2$ case because the even occupancy and the phase relation of the $yz$ and $zx$ orbitals is preserved. Finally, iv) we clarified how the Mott insulating state survives in CaIrO$_3$ despite the severe departure from the $j_{\text{eff}} = 1/2$ ground state.

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