Orbital occupancies and the putative $j_{\text{eff}} = 1/2$ groundstate in Ba$_2$IrO$_4$: a combined oxygen K edge XAS and RIXS study

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The nature of the electronic groundstate of Ba$_2$IrO$_4$ has been addressed using soft X-ray absorption and inelastic scattering techniques in the vicinity of the oxygen K edge. From the polarization and angular dependence of XAS we deduce an approximately equal superposition of $xy$, $yz$ and $zx$ Ir$^{4+}$ 5d orbitals. By combining the measured orbital occupancies, with the value of the spin-orbit coupling provided by RIXS, we estimate the crystal field splitting associated with the tetragonal distortion of the IrO$_6$ octahedra to be small, $\Delta \approx 50(50)$ meV. We thus conclude definitively that Ba$_2$IrO$_4$ is a close realization of a spin-orbit Mott insulator with a $j_{\text{eff}} = 1/2$ groundstate, thereby overcoming ambiguities in this assignment associated with the interpretation of X-ray resonant scattering experiments.

The comprehensive characterisation of the groundstate of a system forms the basis for understanding its physical properties. In the case of the new class of spin-orbit induced Mott insulating iridium oxides, the so-called $j_{\text{eff}} = 1/2$ groundstate has been proposed to explain the unexpected transport properties of Sr$_2$IrO$_4$ (and related compounds)$^{1,2}$ and is more generally central to the prediction of the novel electronic phases in iridates. Naively one might predict that a 5d transition-metal oxide (TMO) would be metallic because of the large extension of its orbitals and reduced electronic correlations. However, the large spin-orbit coupling present in the 5d transition-metal leads to the lifting of degeneracies in the groundstate manifold, allowing diminished electronic correlations to play an enhanced role. Accordingly, Sr$_2$IrO$_4$ turns out in fact to be an antiferromagnetic insulator with properties reminiscent of 3d TMO Mott insulators$^3$.

Valuable insight into the physics of Sr$_2$IrO$_4$ and related materials can be obtained within the frame of a single-ion model, in which 5d $e_g$ states are neglected and one hole fills the $t_{2g}$ states, which are subject to tetragonal crystal field splitting ($\Delta$) and spin-orbit coupling ($\zeta$)$^4$$^5$. For magnetic moments oriented along the (110) direction, the ground state wave function is written as$^8$

$$|0, -\rangle = \frac{C_0 (|xy, -\rangle - i |xy, +\rangle) / \sqrt{2} + |yz, +\rangle + i |zx, -\rangle}{\sqrt{2} + C_0^2},$$

with $2C_0 = 1 - \delta - \sqrt{9 + \delta (\delta - 2)}$ ($C_0 \leq 0$), where $\delta = 2\Delta/\zeta$. Theoretically, a pure $j_{\text{eff}} = 1/2$ ground state is realized for $\Delta = 0$ only, with an equal occupation of the $xy$, $yz$ and $zx$ orbitals. Instead, for $\Delta \gg \zeta$ the $(|xy, -\rangle - i |xy, +\rangle) / \sqrt{2}$ state is stabilized, while for $\Delta \ll -\zeta$ the ground state reduces to $(|yz, +\rangle + i |zx, -\rangle) / \sqrt{2}$.

Compelling, microscopic evidence for the existence of a $j_{\text{eff}} = 1/2$ ground state in iridium oxides was first provided by X-ray resonant magnetic scattering (XRMS) experiments. It was argued that the near vanishing of the L$_2$/L$_3$ magnetic Bragg peak intensity ratio provides a unique signature of the $j_{\text{eff}} = 1/2$ groundstate$^{8,10}$. The subsequent application of XRMS to several compounds led to the identification of a number of other “$j_{\text{eff}} = 1/2$ iridates”, such as Sr$_3$Ir$_2$O$_7$$^{10}$$^{12}$, Ba$_2$IrO$_4$$^{13}$, CaIrO$_3$$^6$ and Ca$_4$IrO$_7$$^{14}$. However, early on Chapon and Lovesey$^{15}$ raised doubts on this interpretation. More recently, some of the present authors further clarified the situation by showing that the Ir L$_2$ edge XRMS cross-section is identically zero irrespective of the tetragonal crystal field splitting of $t_{2g}$ states when the magnetic moments lie in the $ab$-plane$^8$. Therefore, a zero L$_2$/L$_3$ XRMS intensity ratio is a necessary, but not sufficient condition for the $j_{\text{eff}} = 1/2$ groundstate to be realized in iridate perovskites with in-plane easy magnetic axis. Sr$_2$IrO$_4$$^9$ and Ba$_2$IrO$_4$$^{13}$ fall exactly in this category.

By now, the $j_{\text{eff}} = 1/2$ groundstate of Sr$_2$IrO$_4$ has been verified by a number of experimental techniques, including optical conductivity, O K edge XAS, ARPES$^2$, XRMS$^8$ and RIXS$^{10,17}$, and the tetragonal crystal
field has been shown to be small \[18\]. Like the benchmark compound, it was suggested that $\text{Ba}_2\text{IrO}_4$ is a spin-orbit Mott insulator \[19\], and indeed recent ARPES measurements suggest that $\text{Sr}_2\text{IrO}_4$ and $\text{Ba}_2\text{IrO}_4$ have qualitatively similar band structures \[20\]. The crystal structure and the magnetic properties of the two compounds, however, are significantly different. In both $\text{Sr}_2\text{IrO}_4$ and $\text{Ba}_2\text{IrO}_4$ the apical Ir-O bonds are longer than the in-plane bonds, but with differences of 4% and 7%, respectively \[3 \[14\], implying a larger tetragonal distortion in the latter compound. Additionally, in $\text{Sr}_2\text{IrO}_4$ the IrO$_6$ octahedra have a staggered rotation about the c axis by $\sim 12^\circ \[3\]$, such that the in-plane Ir-O-Ir angles are not 180°, while in $\text{Ba}_2\text{IrO}_4$ the Ir-O-Ir bonds are straight \[19\]. The combination of a larger tetragonal distortion and the absence of octahedra rotation has mainly two effects: i) the crystal field potential acting on the central Ir ion is different in the two compounds. \textit{Ab initio} quantum chemistry calculations by L. Hozoi \textit{et al.}\[21\] show that the local Ir-O bonding sets a different energy order of the Ir t$_{2g}$ levels for the two compounds in the absence of spin-orbit coupling; in the \textit{electron} representation, the lowest, doubly occupied t$_{2g}$ level is xy in $\text{Ba}_2\text{IrO}_4$, and yz/zx in $\text{Sr}_2\text{IrO}_4$. ii) the inversion symmetry at the O site between adjacent Ir ions is preserved and Dzyaloshinsky-Moriya-type (DM) interaction is suppressed. DM interaction in $\text{Sr}_2\text{IrO}_4$ is responsible for the canting of the magnetic moments, which in turn produces a finite ferromagnetic component below 240 K \[3\]; $\text{Ba}_2\text{IrO}_4$, instead, does not exhibit a net magnetic moment at any temperature \[19\].

Thus taking into account all of the above facts, the question of whether or not the $j_{\text{eff}} = 1/2$ groundstate is realised in $\text{Ba}_2\text{IrO}_4$ is an interesting but open one. Here we address this question by presenting the results of oxygen K edge XAS and RIXS which allow us to directly determine the occupancy of the xy, yz and zx orbitals in the groundstate of Eq. 1., and to estimate the tetragonal crystal field.

O K edge x-ray absorption spectroscopy (XAS) and resonant inelastic x-ray scattering (RIXS) data were taken at the ID08 soft x-ray beam line of the European Synchrotron Radiation Facility, Grenoble. XAS spectra were collected in total-fluorescence-yield mode to ensure the highest bulk sensitivity. RIXS spectra were measured with the AXES spectrometer working at a fixed scattering angle of 130°. The energy-resolution of the incident photons was better than 100 meV, while the overall energy-resolution of the RIXS spectra was 180 meV, as determined by measuring the off-resonant elastic scattering of amorphous graphite. The photon polarization was determined by measuring the off-resonant elastic scattering, and was set to be either horizontal (H) or perpendicular (V) to the scattering plane. The photons impinge onto the sample at an angle $\theta$ with respect to the normal of the sample surface. RIXS measurements were performed at $\theta = 25^\circ$ (specular geometry); in this geometry, spectra taken with horizontal and vertical polarization (4 hours each) were found to be similar, and therefore were summed up to reduce the error bars. The temperature of the sample was kept below 50 K during the whole experiment. The sample, a single crystal of $\text{Ba}_2\text{IrO}_4$ (of $\sim 0.5 \times 0.5 \times 0.2$ mm$^3$ size), synthesized at the National Institute for Materials Science (NIMS) by the slow cooling technique under pressure \[19\], was oriented having the (010) and (001) crystallographic direction in the horizontal plane. Note that in this geometry the vertical polarization is always parallel to the (100) axis, while the direction of the horizontal polarization relative to the sample changes with $\theta$ according to $\mathbf{e}_H = (0, \cos \theta, \sin \theta)$.

Fig. 1 shows two representative XAS spectra of $\text{Ba}_2\text{IrO}_4$ for both horizontal (black continuous) and vertical (red dashed line) polarization of the photons at $\theta = 80^\circ$.

![Fig. 1. XAS spectra of $\text{Ba}_2\text{IrO}_4$ for both horizontal (black continuous) and vertical (red dashed line) polarization of the photons at $\theta = 80^\circ$.](image1)

![Fig. 2. XAS spectra of $\text{Ba}_2\text{IrO}_4$ for both horizontal (black continuous) and vertical (red circles) polarization of the photons at (left) $\theta = 0^\circ$ and (right panel) $\theta = 80^\circ$. The corresponding experimental geometries are shown in the inset.](image2)
extended energy range from 525 to 560 eV. A linear background was subtracted by fitting the flat region at energies lower than 528 eV; the spectra were then normalized to unity on the high energy side of the edge jump. We clearly observe a pronounced polarization dependence, most notably in the pre-peak region, at energies lower than 535 eV. Typically, this region is associated with transitions of the O 1s core electrons to the 2p states hybridized with the transition metal ion unoccupied valence states; in our case, these can be mainly associated with the Ir 5d \( t_{2g} \) and e\(_g\) states. Structures at higher energies are assigned to Ba 5d and Ir 6s and 6p empty states. In Fig. 2 we highlight the polarization and angular dependence of the pre-peak region (528 to 533 eV) by focussing on the two peaks at 529.1 and 530.1 eV which arise from O 2p-Ir 5d \( t_{2g} \) hybridization. At \( \theta = 0 \) (left panel) the spectra taken with the two photon polarizations are essential identical, while for \( \theta = 80^\circ \) (right panel) the spectra are strongly affected by polarization: specifically, the low-energy peak (529.1 eV) is strongly suppressed, while the peak at higher energy (530.1 eV) is strongly enhanced when switching from H to V polarization. This behaviour reflects the anisotropy of the orbitals: at \( \theta = 0 \), \( \epsilon_V = (100) \) and \( \epsilon_H = (010) \), and the spectra are identical owing to the equivalence of the (100) and (010) directions in Ba\(_2\)IrO\(_4\); on the other hand, \( \epsilon_V = (100) \), while \( \epsilon_H \approx (001) \) at \( \theta = 80^\circ \), and the spectra look different as Ba\(_2\)IrO\(_4\) has tetragonal symmetry.

Following the work of Moon et al.\(^{22}\) on Sr\(_2\)IrO\(_4\), and in agreement with the peak assignments in La\(_2\)-Sr\(_x\)Cu\(_4\)\(_{2−x}\)\(^{23}\), Sr\(_2\)RuO\(_4\)\(^{24}\), and Ca\(_2\)RuO\(_4\)\(^{25}\), the two peaks at 529.1 and 530.1 eV of Fig. 2 arise from transitions to the 5d \( t_{2g} \) states at the apical and in-plane oxygen, respectively. Also, the broad peaks at 532 and 534 eV (indicated by triangles in Fig. 1) correspond to transitions to the to the 5d \( 3z^2−r^2 \) and \( x^2−y^2 \) states, respectively.\(^{22}\) With this assignments, 10\( Dq \) can be estimated to be about 3 eV in Ba\(_2\)IrO\(_4\).

To quantitatively estimate their polarization and angular dependence, the XAS spectra are fitted in Fig. 2 to two gaussian functions plus a third curve (dashed lines) to account for higher-energy features. While the position and full-width-half-maximum (\( \approx 0.55 \) eV) of the peaks are insensitive to the different geometries, it is interesting to look at the angular and polarization dependence of the corresponding spectral weights: the integrated intensity ratio of the apical and in-plane oxygen contributions is 0.71 (0.69) for vertical (horizontal) polarization at \( \theta = 0 \), and 0.64 (0.11) at \( \theta = 80^\circ \), i.e. the apical oxygen contribution is strongly suppressed, although not zeroed, in grazing incidence geometry and horizontal polarization.

The polarization and angular dependence of O K edge XAS is determined by the O 2p-Ir 5d \( t_{2g} \) hybridization strength, and the dipole matrix element governing the O 1s-2p\(_i\) transitions \( (i = x, y \text{ and } z) \). Fig. 3(a) shows the O 2p\(_i\)-Ir 5d \( t_{2g} \) orbital dependent hybridizations; the \( xy \) orbital has a finite overlap with 4 in-plane O 2p\(_x\) and 2p\(_y\) orbitals, while the \( yz \) (zx) orbital hybridizes with 2 apical O 2p\(_x\) (2p\(_y\)) and 2 in-plane O 2p\(_x\) (2p\(_z\)) orbitals. The strength of the hybridization, however, depends on the Ir-O bond length \( r \), which is different for the in-plane and apical oxygens: here we assume a power-law dependence of the hybridization strength on \( r \), i.e. \( r^{−\alpha} \), where \( \alpha = 3.5 \)\(^{26}\). From Fig. 3(b), one can understand the angular and polarization dependence of the O 1s-2p\(_i\) matrix elements, which, because of the isotropy of the O 1s orbital, is fully determined by the relative orientation of the polarization vector and the O 2p\(_i\) orbitals. It follows that the transitions to the O 2p\(_x\), 2p\(_y\), and 2p\(_z\) orbitals have \( \theta \) dependences of 0, \( \cos^2 \theta \), and \( \sin^2 \theta \) for horizontal polarization, and 1, 0 and 0 for vertical polarization, respectively. Therefore, the intensity of the feature associated with the in-plane oxygens has a \( \theta \) dependence of \( n_{xy} \cos^2 \theta + 2n_{yz} \sin^2 \theta \) for horizontal polarization, and \( n_{xy} \) for vertical polarization. Here, \( n_{xy} \) and \( n_{yz} = n_{xz} \) are the orbital occupancies of the \( xy \) and \( yz \) or \( xz \) states, respectively (\( n_{xy} + n_{yz} + n_{xz} = 1 \) in the case of Ir\(^{4+}\)). On the other hand, the intensity of the feature associated with the apical component is given by \( 1.07^{−\alpha} n_{yz} \cos^2 \theta \) for horizontal polarization, and \( 1.07^{−\alpha} n_{yz} \) for vertical polarization, where the factor \( 1.07^{−\alpha} \approx 80\% \) comes from the 7\% elongation of the IrO\(_6\) octahedra. To summarize these arguments, no angular dependence is expected in the case of vertical polarization, in agreement with the experimental findings, while the intensity of the in-plane and apical oxygens contributions are proportional to \( n_{xy} \) and \( n_{yz} \), respectively. In the case of horizontal polarization, instead, an angular dependence is expected: specifically, at normal incidence (\( \theta = 0 \)) the intensity is identical to the vertical polarization case, while at \( \theta = 80^\circ \) the int-
These considerations allow us to extract the occupancies of the $\Delta$ edge XAS (Fig. 2). We obtain $n_{xy} = 0.37 \pm 0.04$ and $n_{yz} = 0.31 \pm 0.02$. Although there appears to be a slightly higher occupancy of the $xy$ orbital ($\Delta \geq 0$), this result is also consistent with an almost even occupation of the $xy$, $yz$, and $zx$ orbitals ($n_{xy} = n_{yz} = n_{zx} = 1/3$), suggesting that Ba$_2$IrO$_4$ belongs to the class of $j_{\text{eff}} = 1/2$ iridates.

Knowledge of the orbital occupancies allow us in turn to estimate the effective tetragonal crystal field splitting $\Delta$ (see Eq. 1 and related text). However, for this we first require a precise determination of the spin-orbit coupling, $\zeta$. We can then use the fact the occupancies of the $xy$, $yz$, and $zx$ orbitals are given by $n_{xy} = C_0^2/(C_0 + 2)$, $n_{yz} = n_{zx} = 1/(C_0 + 2)$, respectively, where the dependence on $\Delta$ and $\zeta$ is parametrized in $C_0$. An estimate of the spin-orbit coupling constant can then be extracted from the O K edge RIXS data. Fig. 4 shows a representative O K edge RIXS spectrum of Ba$_2$IrO$_4$ for photons impinging on the sample with an angle $\theta = 25^\circ$ (specular geometry). The spectrum shows a clear elastic line at zero energy loss and the first distinct feature is found at 0.64 eV. Higher energy features have the characteristics of resonant fluorescence emission, as verified by inspecting their incident photon energy dependence. The incident photon energy was fixed at 530.1 eV, i.e. the energy corresponding to the in-plane oxygen contribution in the O K edge XAS spectra; doing so, we expected to maximize the intensity of RIXS transitions involving orbitals hybridized with the $Ir 5d t_{2g}$ states. Therefore, in analogy to Ir L$_3$ edge RIXS, we assign this transition to the excitation of the hole from the $j_{\text{eff}} = 1/2$ ground state to the $j_{\text{eff}} = 3/2$ band. In a single ion picture, the energy cost for this transition is $3\zeta/2$, from which the value of the spin-orbit coupling constant $\zeta$ is estimated to be 0.43 eV. This value remarkably agrees with the estimate of the spin-orbit coupling in Ba$_2$IrO$_4$ ($\zeta = 0.42$ eV) given in Ref. [13] based on the Ir L$_2$ and L$_3$ XAS branching ratio.

Fig. 5 shows the calculated dependence of the orbital occupancies on the tetragonal crystal field for $\zeta = 0.43$ eV. For the derived values of the orbital occupancies given above, we calculate an effective tetragonal crystal field of 50 meV, with relatively tight constraints related to the error bars in the estimate of the XAS peak intensities, i.e. $0 \leq \Delta \leq 100$ meV. This result may be compared with the recent work of Boseggia et al. [18] on Sr$_2$IrO$_4$ who found that $-60 \leq \Delta \leq 35$ meV based on the accurate determination of the magnetic moment direction relative to the octahedra rotation by XRMS. Fig. 5 compares the calculated and observed splitting in Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$. One can speculate that $\Delta \geq 0$ in Ba$_2$IrO$_4$, while $\Delta \leq 0$ in Sr$_2$IrO$_4$, i.e. the effective tetragonal crystal field has opposite sign in the two compounds. Although one can intuitively explain this difference by invoking the elongation of the IrO$_6$ octahedra, which is more pronounced in Ba$_2$IrO$_4$ than in Sr$_2$IrO$_4$, and thus favours the occupancy of the $xy$ orbital, it should be noted that this result contradicts recent theoretical calculations by Katukuri et al. [21].

In summary, we demonstrate how the combination of soft X-ray techniques yields more information than any
one technique used in isolation, allowing us in this case to understand the link between structural distortions (octahedral rotation and elongation) and the $j_{\text{eff}} = 1/2$ groundstate in iridates. By exploiting x-ray linear dichroism at the O K absorption edge of the prototypical perovskite iridate Ba$_2$IrO$_4$, we have determined the orbital occupancies of Ir$^{4+}$ 5d groundstate to be $n_{xy} = 0.37 \pm 0.04$ and $n_{yz} = n_{zx} = 0.31 \pm 0.02$. An estimate of the effective tetragonal distortion to the cubic crystal field splitting is given by extracting the spin-orbit coupling constant ($\zeta = 0.43$ eV) from O K edge RIXS measurements. The result is that $\Delta = 50(50)$ meV i.e. very small compared with the cubic crystal field in Ba$_2$IrO$_4$ of about 3 eV. We conclude that Ba$_2$IrO$_4$ may be classified as a spin-orbit Mott insulator, with a groundstate close to the ideal $j_{\text{eff}} = 1/2$ state proposed to give rise to the novel properties of iridates. We hope that the quantitative information provided by our analysis will help refine future theoretical approaches and act as a guide to the large community of “material engineers” which exploits structural distortions to tune material properties.

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