Robustness of Basal-Plane Antiferromagnetic Order and the $J_{\text{eff}} = 1/2$ State in Single-Layer Iridate Spin-Orbit Mott Insulators


1 London Centre for Nanotechnology and Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom
2 Diamond Light Source Ltd, Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, United Kingdom
3 Royal Commission for the Exhibition of 1851 Research Fellow, Interface Analysis Centre, University of Bristol, Bristol BS2 8BS, United Kingdom
4 Deutsches Elektronen-Synchrotron DESY, 22607 Hamburg, Germany
5 Laboratory for Quantum Magnetism, ICMP, Ecole Polytechnique Federale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
6 Laboratory for Neutron Scattering, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
7 DPMC-MaNEP, University of Geneva, CH-1211 Geneva, Switzerland
8 National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
9 Scottish Universities Physics Alliance, School of Physics, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, United Kingdom

The magnetic structure and electronic ground state of the layered perovskite Ba$_2$IrO$_4$ have been investigated using x-ray resonant magnetic scattering. Our results are compared with those for Sr$_2$IrO$_4$, for which we provide supplementary data on its magnetic structure. We find that the dominant, long-range antiferromagnetic order is remarkably similar in the two compounds and that the electronic ground state in Ba$_2$IrO$_4$, deduced from an investigation of the x-ray resonant magnetic scattering $L_3/L_2$ intensity ratio, is consistent with a $J_{\text{eff}} = 1/2$ description. The robustness of these two key electronic properties to the considerable structural differences between the Ba and Sr analogues is discussed in terms of the enhanced role of the spin-orbit interaction in 5d transition metal oxides.

DOI: 10.1103/PhysRevLett.110.117207 PACS numbers: 75.25.–j, 71.70.Ej, 75.40.Cx, 78.70.Ck

Transition metal oxides containing a 5d element are increasingly attracting attention as an arena in which to search for novel electronic states [1–4]. These are proposed to derive from the strong spin-orbit interaction (SOI) in the 5d $^5$ ions, from which a Mott-like insulator then emerges through the action of relatively weak electronic correlations which would otherwise lead to a metallic state. Direct evidence for the existence of a $J_{\text{eff}} = 1/2$ ground state in Sr$_2$IrO$_4$ was provided by x-ray resonant magnetic scattering (XRMS) experiments, which revealed a much stronger resonance at the $L_3$ edge than at the $L_2$ [6].

The structural similarity of the single-layer iridates to La$_2$CuO$_4$ adds further impetus to the study of these materials, opening as it does a possible route to the discovery of new families of superconductors [7]. In this context, a particularly interesting compound is Ba$_2$IrO$_4$, since structurally it is a closer 5d analogue of La$_2$CuO$_4$ than the Sr compound. Ba$_2$IrO$_4$ crystallizes in the K$_2$NiF$_4$-type structure (space group $I4/mmm$) with 180° Ir-O-Ir bonds in the basal plane (Fig. 1) and with a 7% tetragonal distortion of the IrO$_6$ octahedra along the [0 0 1] direction [8]. In contrast, in Sr$_2$IrO$_4$, there is a tetragonal distortion of 4% [9] and a staggered, correlated rotation of the IrO$_6$ octahedra by 11° about the c axis that reduces the space group symmetry to $I4_1/acd$. This generates a larger unit cell, $\sqrt{2}a \times \sqrt{2}b \times 2c$, under the rotation of the original cell by 45°.

From a theoretical point of view, both the tetragonal distortion and the presence or otherwise of octahedral rotations have significant consequences for the electronic and magnetic properties. First, it should be noted that the $J_{\text{eff}} = 1/2$ state itself is only strictly realized in a system of cubic symmetry [10]. Second, the loss of inversion symmetry in Sr$_2$IrO$_4$ gives rise to a finite Dzyaloshinskii-Moriya (DM) interaction, allowing the formation of non-collinear magnetic structures [11]. Both of these effects on the magnetism in Ba$_2$IrO$_4$ and Sr$_2$IrO$_4$ have been investigated using $ab$ initio methods [12].

For Sr$_2$IrO$_4$, the consequences of these structural features for the electronic and magnetic properties have been comprehensively explored in a number of experimental and theoretical studies [5,6,11,13]. By contrast, for Ba$_2$IrO$_4$ there are a number of important open questions, including whether or not its ground state can reasonably be assigned as $J_{\text{eff}} = 1/2$ and the exact nature of its magnetic
structure. The latter question is of particular relevance to the prospect of Ba₂IrO₄ becoming the parent compound of a new family of unconventional, magnetically mediated superconductors. Both cuprate and pnictide superconductors, for example, emerge when doping destabilizes long-range antiferromagnetic order, and in each case obtaining a microscopic understanding of the magnetic groundstate of the parent compound has played a pivotal role in our knowledge [14,15]. From a range of bulk probes and muon spin rotation (μSR) it is known that Ba₂IrO₄ exhibits a magnetic transition below ~240 K [8], close to the magnetic transition in Sr₂IrO₄ of T_N ~ 230 K, below which the magnetic moments in Sr₂IrO₄ form a canted antiferromagnetic structure [6]. Whether or not the ferromagnetic moment resulting from the canting is inimical for superconductivity when Sr₂IrO₄ is doped to form a metal is another important open question.

In this Letter we report the results of our XRMS investigation of Ba₂IrO₄, which addresses both the question of the magnetic structure in Ba₂IrO₄ and the relevance of the J_eff = 1/2 description to its electronic groundstate. Our results are compared with corresponding measurements on Sr₂IrO₄, for which we also supply supplementary data, and discussed in terms of current theoretical models. The major achievement of our study is to establish that both antiferromagnetic order and the J_eff = 1/2 state are, to a remarkable degree, robust to structural distortions in the single layered iridate perovskites.

The XRMS measurements were performed at the Ir L₂ (12.831 keV) and L₃ (11.217 keV) edges, probing dipolar transitions from 2p₁/₂ to 5d and from 2p₃/₂ to 5d, respectively. The experiment on the Ba₂IrO₄ crystal was conducted at the I16 beam line of the Diamond Light Source, Didcot, UK. The XRMS study on Sr₂IrO₄ was performed at the P09 beam line [16] of Petra III, at DESY, Germany. An Au (3 3 3) crystal and a pyrolytic graphite (0 0 8) crystal were exploited to analyze the polarization of the scattered beam on I16 and on P09, respectively.

In Ba₂IrO₄, with the photon energy tuned to be close to the L₃ edge (11.222 keV) and the sample cooled to 50 K, sharp peaks were found at the reciprocal lattice points (1 1 1/2) with L even. These peaks existed in the rotated photon polarization channel σ − π only (see Fig. 2(a)) as expected from the selection rules for XRMS arising from dipolar transitions [17]. We thus deduce that the Ir⁴⁺ magnetic moments order in an antiferromagnetic structure, with a doubling of the unit cell along the in-plane directions (√2a × √2b), described by a magnetic propagation vector of k = [1 1/2 0].

In Fig. 2(c) we present the energy dependence of the magnetic scattering at (1 1 1/2) together with x-ray absorption near edge structure (XANES) measurements for energies in the vicinity of the L₃ and L₂ edges. The most

![FIG. 1 (color online). The left-hand panel shows the crystal structure of Ba₂IrO₄. Perovskite IrO₆ layers, where the Ir atoms (grey) lie at the center of corner sharing oxygen (red) octahedra, are separated by Ba atoms (light green). The right-hand panel shows the basal-plane antiferromagnetic structure of the Ba₂IrO₄, where the magnetic moments are pointing along the [1 1 0] direction.](image)

![FIG. 2 (color online). (a) L scans across the (1 1 1/2) magnetic reflection, T = 50 K in Ba₂IrO₄. (b) The temperature dependence of the (1 1 1/2) magnetic reflection in Ba₂IrO₄. The solid blue line is a fit to a power law. (c) Resonant enhancement of the (1 1 1/2) magnetic reflection across the L₂,₃ edges at T = 50 K in Ba₂IrO₄. The solid black line shows the XANES spectra normalized to the number of initial states. The blue spheres and red triangles show the intensity of the (1 1 1/2) reflection. The black dashed line demarcates the integrated white line used to calculate the branching ratio.](image)
notable features of this data are the existence of a well-defined resonance at the $L_3$ edge, and the complete absence of a response at the $L_2$ edge within experimental uncertainty. Concerted attempts to find a magnetic response at the $L_2$ edge by investigating various magnetic reflections all ended in failure. In their study of Sr$_3$IrO$_4$, Kim et al. [6] argued that the observed large XRMS intensity ratio, $I_{L_1}/I_{L_2}$, served as a unique fingerprint of the $J_{\text{eff}} = 1/2$ state, since for the pure $J_{\text{eff}} = 1/2$ state $I_{L_3}$ is identically zero. Our results, interpreted in this spirit, establish that even in the presence of a large tetragonal distortion, Ba$_2$IrO$_4$ belongs to the same class of $J_{\text{eff}} = 1/2$ spin-orbit Mott insulators as Sr$_3$IrO$_4$.

The width of the $L_3$ resonance is FWHM $L_3 = 7.6(1)$ eV, comparable to the values found in Sr$_2$IrO$_4$ and in Sr$_3$Ir$_2$O$_7$ [6,18]. The position of the resonance, similarly to those of Sr$_2$IrO$_4$ and Sr$_3$Ir$_2$O$_7$, is 3 eV below the $L_3$ white line. From the analysis of the XANES spectra, we find a very large branching ratio $\text{BR} = 5.45$ [19]. This is a further confirmation of the strong SOI regime in Ba$_2$IrO$_4$.

The thermal evolution of the antiferromagnetic order was determined by performing $\theta - 2\theta$ scans of the $(\frac{1}{2} \frac{1}{2} 10)$ reflection in the $\sigma - \pi$ channel at the energy (11.219 keV) that maximizes the XRMS response. Figure 2(b) shows the integrated intensity obtained by fitting a Lorentzian shape to the individual scans as a function of temperature. The transition appears to be second order, and from the fit to a $A(1-\frac{\Delta}{T_N})^2\beta$ function we obtain the Neel temperature $T_N = 241(2)$ K and $\beta = 0.25(4)$, in good agreement with the values found by $\mu$SR measurements [8].

In order to determine the magnetic structure of Ba$_2$IrO$_4$, we performed azimuthal scans of the $(\frac{1}{2} \frac{1}{2} 10)$ magnetic reflection. This method consists in measuring $\theta - 2\theta$ scans for different $\Psi$ angles, rotating the sample around the scattering vector. From the azimuthal modulation of the intensity of the XRMS signal it is possible to determine the orientation of the magnetic moments in an antiferromagnetic material [20]. Figure 3 shows the azimuthal dependence of the $(\frac{1}{2} \frac{1}{2} 10)$ reflection (blue solid points). The dashed black line, solid blue line and dotted red line are the azimuthal dependencies calculated by means of the FDMNES package [21] for three different orientations of the moments, $m \parallel [001]$ ($\Gamma_2$), $m \parallel [110]$ ($\Gamma_3$), and $m \parallel [1-10]$ ($\Gamma_1$), that are the allowed magnetic structures and irreducible representations ($\Gamma_i$) according to group theory calculations [22]. The experimental curve most closely resembles the calculation for the $\Gamma_3$ representation. We therefore conclude unambiguously that Ba$_2$IrO$_4$ exhibits a basal-plane antiferromagnetic order with the magnetic moments pointing along the [1 1 0] direction. The magnetic structure of Ba$_2$IrO$_4$ is shown in Fig. 1.

To understand the dependence of the $J_{\text{eff}} = 1/2$ state and the associated Hamiltonian on symmetry and lattice distortions, we have investigated the magnetic structure of Sr$_2$IrO$_4$. In particular we focus on the polarization and azimuthal dependencies of the XRMS, neither of which have been reported [6]. With the photon energy tuned to the Ir $L_3$ edge, well defined magnetic peaks were found at the $(1 0 4n)$ and $(0 1 4n + 2)$ Bragg positions, which are forbidden within the $I4_1/acd$ space group and correspond to the $(\frac{1}{2} \frac{1}{2} 2L)$ peaks observed in the Ba$_2$IrO$_4$ [as illustrated in the inset of Fig. 4(c)]. Figures 4(a) and 4(b) shows the $L$ scan and the energy scan of the $(1 0 24)$ magnetic reflection at the Ir $L_3$ edge at $T = 90$ K. The well-defined $L$ scan supports the existence of a long-range antiferromagnetic order. The Lorentzian shape of the energy scan (FWHM$_{L_3} = 6.26(9)$ eV) and the absence of any $\sigma - \sigma$ scattering mechanism confirms the magnetic nature of the peaks, similarly to Ba$_2$IrO$_4$. These results are in agreement with the first XRMS study of Sr$_3$IrO$_4$ [6].

In order to determine the direction of the magnetic moments in Sr$_2$IrO$_4$ we performed azimuthal scans at the Ir $L_1$ edge, $T = 90$ K. The results, together with the FDMNES calculation using the same moment direction as in the irreducible representation $\Gamma_3$ of Ba$_2$IrO$_4$, are presented in Fig. 4(c). Note the equivalence of the $\Psi$ angles in Fig. 4 with those in Fig. 3, for the correspondence of the [1 1 0] direction in $I4/mmm$ to the [1 0 0] direction in the $I4_1/acd$. By comparing the azimuthal dependence of the $(1 0 24)$ reflection in Sr$_2$IrO$_4$ with the azimuthal dependence of $(\frac{1}{2} \frac{1}{2} 10)$ reflection in Ba$_2$IrO$_4$, we deduce that in Sr$_2$IrO$_4$ the antiferromagnetic component is oriented along the [1 1 0] direction of the $I4/mmm$ reference system. We therefore conclude that the two compounds have essentially the same basal-plane antiferromagnetic structure [23].

We now turn to the discussion of our results. An effective, low-energy Hamiltonian for the layered iridates, valid in the strong SOI limit, incorporating both the effects of a tetragonal crystal field and rotation of the IrO$_6$ octahedra
One important proviso, however, is that the magnetic antiferromagnetic order observed in our experiments. Their calculations show that when the SOI is switched off, the ground state and the magnetic interactions are extremely sensitive to the local symmetry and so very different in the two systems: \( \text{Ba}_2\text{IrO}_4 \) has a hole in the \( d_{xy}/d_{yz} \) states and a strong antiferromagnetic \( J \) interaction (\(~15.4\) meV), \( \text{Sr}_2\text{IrO}_4 \) has a hole in the \( d_{xy} \) state and a ferromagnetic \( J \) interaction (\(~19.2\) meV). However, upon including the SOI, the hole acquires an equal \( d_{xy}, d_{xz}, \) and \( d_{yz} \) character in both compounds, and \( J \) in \( \text{Sr}_2\text{IrO}_4 \) becomes antiferromagnetic (\(~51.3\) meV) and almost identical to that in \( \text{Ba}_2\text{IrO}_4 \) (\(~58\) meV). Therefore, the robustness of antiferromagnetic order in the layered perovskites to structural distortions is ultimately linked to the strong SOI, which produces a ground state wave function that is three dimensional and inherently less perturbed by structural distortions.

In this Letter we have presented a detailed XRMS study of the magnetic and electronic structures of the single layered iridates \( \text{Ba}_2\text{IrO}_4 \) and \( \text{Sr}_2\text{IrO}_4 \). \( \text{Ba}_2\text{IrO}_4 \) is found to be a basal-plane commensurate antiferromagnet below \( T_N = 241 \) K. Azimuthal scans combined with group theory calculations have been employed to prove that the moments order along the \( [110] \) direction. From a comparison with XRMS data on the related compound \( \text{Sr}_2\text{IrO}_4 \), we establish that both compounds have essentially the same basal-plane antiferromagnetic structure, in spite of their structural differences. We also conclude from our results for the intensity ratio \( I_L/I_2 \) of the XRMS signal that \( \text{Ba}_2\text{IrO}_4 \) is also in the same class of \( J_{\text{eff}} = 1/2 \) spin-orbit Mott insulators as \( \text{Sr}_2\text{IrO}_4 \). Thus both the magnetic and electronic structures in the layered perovskites are remarkably robust to structural distortions, a fact that can be linked directly to the unique three-dimensional character of the \( J_{\text{eff}} = 1/2 \) state produced by the strong SOI, which renders it insensitive to the perturbations in local symmetry.

We would like to thank the Impact studentship programme, awarded jointly by UCL and the Diamond Light Source for funding the thesis work of S. Boseggia. G. Nisbet provided excellent instrument support and advice on multiple scattering at the I16 beam line. We also thank J. Strempfer and D.K. Shukla for technical support at P09. The research was supported by the EPSRC, and part of the research leading to these results has received funding from the European Community’s Seventh Framework Programme (FP7/2007–2013) under Grant No. 312284, and the Swiss NSF through Sinergia network MPBH.
*stefano.boseggia@diamond.ac.uk

[16] J. Strempfer et al. (to be published).
[23] We note that XRMS does not couple to the canting of the moments since the latter can be seen as a ferromagnetic component of the magnetic structure. As a consequence, this scattering mechanism occurs in the same position in the reciprocal lattice as the charge scattering.