

## Magnetic excitations in the square-lattice iridate $\text{Ba}_2\text{IrO}_4$

J. P. Clancy <sup>1,2</sup> H. Gretarsson,<sup>1</sup> A. Lupascu <sup>1</sup> J. A. Sears,<sup>1</sup> Z. Nie,<sup>1</sup> M. H. Upton,<sup>3</sup> Jungho Kim <sup>3</sup> Z. Islam,<sup>3</sup> M. Uchida <sup>4,\*</sup> D. G. Schlom,<sup>5,6</sup> K. M. Shen,<sup>4,6</sup> and Young-June Kim <sup>1</sup>

<sup>1</sup>*Department of Physics, University of Toronto, Toronto, Ontario M5S 1A7, Canada*

<sup>2</sup>*Department of Physics and Astronomy, McMaster University, Hamilton, Ontario L8S 4L8, Canada*

<sup>3</sup>*Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA*

<sup>4</sup>*Laboratory of Atomic and Solid State Physics, Department of Physics, Cornell University, Ithaca, New York 14853, USA*

<sup>5</sup>*Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA*

<sup>6</sup>*Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853, USA*

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We report a resonant inelastic x-ray scattering investigation of ultrathin epitaxial films of  $\text{Ba}_2\text{IrO}_4$ , and compare their low-energy magnetic and spin-orbit excitations to those of their sister compound  $\text{Sr}_2\text{IrO}_4$ . Due to the  $180^\circ$  Ir-O-Ir bond, the bandwidth of the magnon and spin orbiton is significantly larger in  $\text{Ba}_2\text{IrO}_4$ , making it difficult to describe these two types of excitations as separate well-defined quasiparticles. Both types of excitations are found to be quite sensitive to the effect of epitaxial strain. In addition, we find that the  $d$ -level inversion observed in  $\text{Sr}_2\text{IrO}_4$  is absent in  $\text{Ba}_2\text{IrO}_4$ , as predicted in recent theoretical studies. Our results illustrate that the magnetic properties of  $\text{Ba}_2\text{IrO}_4$  are substantially different from those of  $\text{Sr}_2\text{IrO}_4$ , suggesting that these materials need to be examined more carefully with electron itinerancy taken into account.

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### I. INTRODUCTION

Iridium-based transition metal oxides have emerged as a rich source for novel phenomena driven by strong spin-orbit coupling (SOC) effects [1–5]. In particular, the layered perovskite iridate  $\text{Sr}_2\text{IrO}_4$  is considered as the prototypical  $j_{\text{eff}} = \frac{1}{2}$  spin-orbit Mott insulator, whose ground state arises due to a complex interplay between crystal electric field, SOC, and electronic correlation [1]. In addition, the strong parallels between  $\text{Sr}_2\text{IrO}_4$  and  $\text{La}_2\text{CuO}_4$ , the parent compound of the high  $T_c$  cuprates, have led to natural associations with superconductivity [6–9] and have inspired extensive research into the properties of doped  $\text{Sr}_2\text{IrO}_4$ . However, in spite of several theoretical predictions, the experimental realization of iridate superconductivity through chemical substitution has proven elusive [6,7,9]. Physical properties and key issues of  $\text{Sr}_2\text{IrO}_4$  have been discussed in recent review articles [4,5].

Despite great interest in  $\text{Sr}_2\text{IrO}_4$ , its sister compound  $\text{Ba}_2\text{IrO}_4$  has received comparatively little experimental attention, largely due to the difficulty of sample synthesis. Since  $\text{Ba}_2\text{IrO}_4$  is metastable under ambient conditions, high-pressure ( $P > 6$  GPa) synthesis is required to obtain bulk  $\text{Ba}_2\text{IrO}_4$  samples [10]. A quick glance at the existing data seems to suggest that these two compounds are magnetically similar.  $\text{Ba}_2\text{IrO}_4$  and  $\text{Sr}_2\text{IrO}_4$  display identical magnetic transition temperatures ( $T_N = 240$  K) and very similar magnetically ordered structures [11]. Angle-resolved photoemission (ARPES) and x-ray absorption spectroscopy studies report that the electronic structures of these two

compounds are also quite similar [12–14]. This is somewhat surprising given that there exists an important structural difference between the two materials. The  $\text{IrO}_6$  octahedra are rigidly aligned in  $\text{Ba}_2\text{IrO}_4$ , just as the  $\text{CuO}_6$  octahedra in cuprates, while these octahedra are rotated by  $\sim 11^\circ$  about the  $c$  axis in  $\text{Sr}_2\text{IrO}_4$ . This gives rise to key structural differences in terms of Ir-O-Ir bond angles ( $180^\circ$  vs  $158^\circ$ ) and local distortions of the  $\text{IrO}_6$  octahedra (7% vs 4.5% axial elongation). The straight bond is expected to increase hybridization and make  $\text{Ba}_2\text{IrO}_4$  more itinerant, which puts into question the applicability of the  $j_{\text{eff}} = \frac{1}{2}$  pseudospin model for this material. Indeed, recent theoretical studies have pointed out the shortcomings of the pseudospin model [15] and significant mixing of the  $t_{2g}$ ,  $e_g$ , and oxygen  $p$  states [16]. Increased hybridization also suggests a stronger superexchange interaction between the pseudospins in  $\text{Ba}_2\text{IrO}_4$ , which seems to be supported by theoretical calculations [15,17]. A recent two-magnon Raman scattering study also seems to indicate the superexchange in  $\text{Ba}_2\text{IrO}_4$  is about 20%–30% larger than that in  $\text{Sr}_2\text{IrO}_4$  [18].

The subtlety of the magnetic anisotropy due to the local distortion was discussed in the theoretical study by Bogdanov and co-workers [19]. On a local level, competition between octahedral distortions and longer-range ligand-field effects from the highly charged  $\text{Ir}^{4+}$  ions is believed to reverse the order of the low-lying  $d$  levels in  $\text{Sr}_2\text{IrO}_4$ , but not in  $\text{Ba}_2\text{IrO}_4$ . The net result is to suppress the effect of the tetragonal distortion in  $\text{Ba}_2\text{IrO}_4$  [19]. However, the weak Ising exchange anisotropy could not explain the basal plane ordering direction observed experimentally [11], and various additional interactions such as the interlayer exchange interaction [20], single-ion anisotropy, and pseudoquadrupolar interaction [21] have been suggested to explain the magnetic structure. In addition, Solovyev *et al.* suggested that the pseudospin model

\*Present address: Department of Physics, Tokyo Institute of Technology, Tokyo 152-8551, Japan.

is inadequate for  $\text{Ba}_2\text{IrO}_4$  due to the increased hybridization, and higher-order terms arising from itinerancy of the system should be considered [15]. Unfortunately, there have been only limited experimental studies on  $\text{Ba}_2\text{IrO}_4$  to test these theories, mainly due to the difficulty with growing single crystal samples.

In this paper, we examine the magnetic Hamiltonian of  $\text{Ba}_2\text{IrO}_4$  by studying thin film samples. In the absence of high-quality single crystal samples, thin films provide an important avenue for studying the underlying physics of this material. Epitaxial film growth [14,22,23] offers an elegant alternative to the high-pressure synthesis techniques required for  $\text{Ba}_2\text{IrO}_4$  [10], providing a method for both stabilizing the crystal structure and exerting a high level of control over key structural parameters. To probe characteristic excitations of such thin film samples, we use resonant inelastic x-ray scattering (RIXS) to map out the dispersion of magnetic and orbital excitations. RIXS is a momentum-resolved and element-specific probe of elementary excitations such as magnons or orbitons [8,24,25]. We compare the RIXS spectra of  $\text{Ba}_2\text{IrO}_4$  thin film samples with those obtained for  $\text{Sr}_2\text{IrO}_4$ , and found that despite the overall similarity of the magnetic excitation spectra, the magnetic energy scales in  $\text{Ba}_2\text{IrO}_4$  differ significantly from those in  $\text{Sr}_2\text{IrO}_4$ . The magnon and spin-orbital excitations are no longer well separated in  $\text{Ba}_2\text{IrO}_4$ , making it difficult to justify the use of the pseudospin model to describe magnetic properties. In addition, we confirm that the magnetic anisotropy is reversed in  $\text{Ba}_2\text{IrO}_4$  as predicted in Ref. [19]. Our results show that the structural differences between square-lattice iridates make the magnetic properties of  $\text{Ba}_2\text{IrO}_4$  distinct from those of  $\text{Sr}_2\text{IrO}_4$ .

## II. EXPERIMENTAL DETAILS

Measurements were performed on two ultrathin  $\text{Ba}_2\text{IrO}_4$  samples prepared by molecular beam epitaxy: one 20-nm ( $\sim 15$  unit cells) film grown on a  $\text{PrScO}_3$  (PSO) substrate, and one 13-nm ( $\sim 10$  unit cells) film grown on  $\text{GdScO}_3$  (GSO). A more detailed description of the synthesis procedure can be found in Ref. [14]. Reflection high-energy electron diffraction (RHEED) was used to monitor the films throughout the growth process, and to verify that there was no evidence of lattice relaxation. After synthesis, a combination of low-energy electron diffraction (LEED) and x-ray diffraction was used to confirm the phase purity, crystallinity, and lattice constants of the films. In addition, the ARPES data [14] provide confirmation that the electronic structures of thin film samples are comparable to bulk crystals. The degree of lattice mismatch in these two samples is somewhat different, with the PSO sample approaching unstrained bulk material ( $\Delta a/a = -0.2\%$ ) and the GSO sample exhibiting a sizable compressive strain ( $\Delta a/a = -1.4\%$ ). The effect of epitaxial strain on the crystal structure of  $\text{Ba}_2\text{IrO}_4$  is illustrated in Fig. 1(a). Bulk single crystals of  $\text{Sr}_2\text{IrO}_4$  were synthesized using the self-flux technique, as described in Ref. [26]. Throughout this paper, we will compare the RIXS spectra for  $\text{Ba}_2\text{IrO}_4$  thin film samples with those for  $\text{Sr}_2\text{IrO}_4$  single crystals. This is justified for the following two reasons. First, the magnetic structure of the thin film samples remains unchanged from that of single crystal samples [27]. Second, we note that Lupascu *et al.* reported that

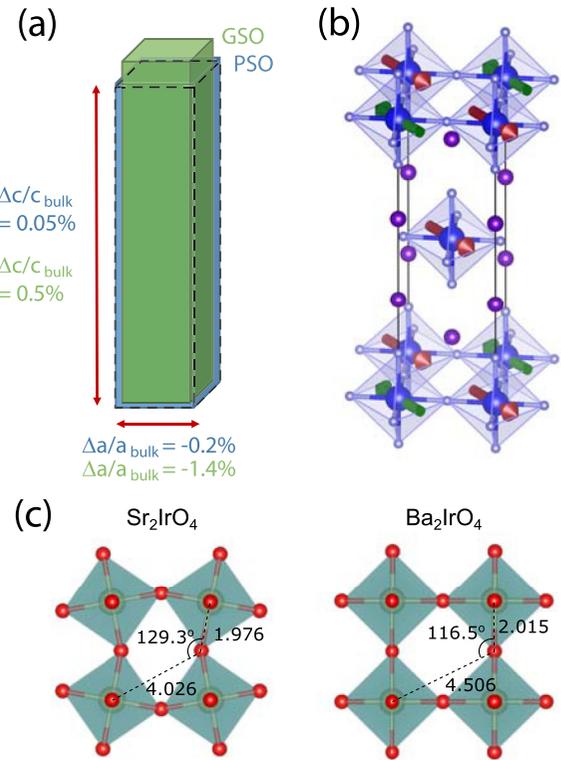


FIG. 1. (a) Effect of epitaxial strain on the crystal structure of  $\text{Ba}_2\text{IrO}_4$ . The unit cell of bulk  $\text{Ba}_2\text{IrO}_4$  is illustrated by the dashed black lines. Epitaxial strains generated by  $\text{PrScO}_3$  (PSO, blue) and  $\text{GdScO}_3$  (GSO, green) substrates have been magnified by a factor of 10. (b) The collinear antiferromagnetic ground state of  $\text{Ba}_2\text{IrO}_4$ . (c) A comparison of Ir-O-Ir bond geometry in  $\text{Sr}_2\text{IrO}_4$  and  $\text{Ba}_2\text{IrO}_4$ .

RIXS data for thin film  $\text{Sr}_2\text{IrO}_4$  are quite similar to those for bulk single crystal  $\text{Sr}_2\text{IrO}_4$  [28]. The zone-boundary magnon energy shifts slightly due to epitaxial strain, but the spin-orbit exciton energy is the same in both thin film and single crystal samples.

Ir  $L_3$ -edge RIXS measurements were performed using the MERIX spectrometer on Beamline 30-ID-B at the Advanced Photon Source. A channel-cut Si-(8,4,4) secondary monochromator, and a spherical (2 m radius) diced Si-(8,4,4) analyzer crystal were used to obtain an overall energy resolution of 45 meV [full width at half maximum (FWHM)]. To reduce the strong elastic scattering contribution from the sample and substrate, measurements were carried out in horizontal scattering geometry, with a scattering angle close to  $2\theta = 90^\circ$  and at  $T = 10$  K. To maximize the inelastic scattering from the films, measurements were performed near grazing incidence, with an angle of incidence  $\alpha < 1^\circ$ . In this grazing-incidence geometry, the photon polarization is roughly along the crystallographic  $c$  direction.

## III. EXPERIMENTAL RESULTS

Results from the RIXS measurements on the essentially unstrained film,  $\text{Ba}_2\text{IrO}_4$  on PSO, are presented in Fig. 2. Figure 2(a) shows representative energy scans collected at

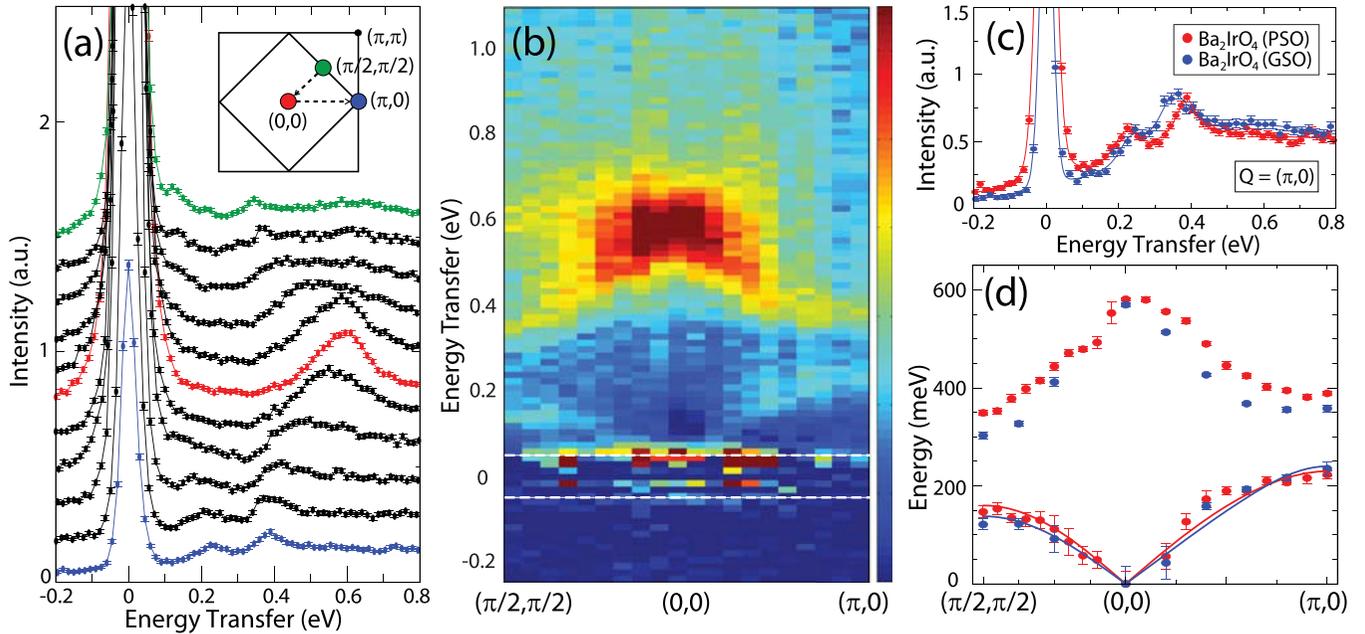


FIG. 2. (a) Representative energy scans performed on 20-nm thin film  $\text{Ba}_2\text{IrO}_4$  grown on a PSO substrate. Colored spectra were obtained at the high-symmetry points of the magnetic Brillouin zone shown in the inset. The top 5 spectra correspond to the scans obtained along the  $(0, 0)$ - $(\pi/2, \pi/2)$  momentum transfer direction, while the bottom 5 were obtained for  $(0, 0)$ - $(\pi, 0)$ . Spectra have been offset vertically for illustrative purposes. Inset: The magnetic Brillouin zone for  $\text{Ba}_2\text{IrO}_4$ . (b) Color contour map showing the dispersion of the low-energy magnon ( $\sim 0$ –250 meV) and spin-orbit exciton ( $\sim 350$ –650 meV) modes in  $\text{Ba}_2\text{IrO}_4$ . The elastic scattering contribution has been subtracted from this panel in order to highlight the inelastic features. The position of the elastic line is denoted by dashed white lines. (c) Strain dependence of magnetic and orbital excitations in  $\text{Ba}_2\text{IrO}_4$  grown on PSO ( $-0.2\%$  strain, red) and GSO ( $-1.4\%$  strain, blue) substrates. (d) Dispersion of magnon and spin-orbit exciton modes in thin film  $\text{Ba}_2\text{IrO}_4$ . The magnetic dispersion can be fit to a Heisenberg  $J$ - $J'$ - $J''$  model (solid red and blue lines).

high-symmetry points throughout the magnetic Brillouin zone. Here, the scattering intensity is plotted as a function of energy transfer  $\Delta E$ . The distinguishing features of these spectra are (1) a strong, resolution-limited elastic line ( $\Delta E = 0$ ), (2) a dispersive magnetic excitation, or magnon, at low energy ( $\Delta E < 250$  meV), and (3) a dispersive orbital excitation, or spin-orbit exciton, at higher energy ( $350 < \Delta E < 650$  meV). Figure 2(b) shows a color intensity map constructed out of energy scans similar to those of Fig. 2(a). In order to emphasize the inelastic features, the elastic scattering contribution has been subtracted from the data sets.

A direct comparison of  $\text{Ba}_2\text{IrO}_4$  and  $\text{Sr}_2\text{IrO}_4$  spectra, obtained under equivalent experimental conditions, is provided in Fig. 3(a). The energy of the magnon mode at  $\mathbf{Q} = (\pi, 0)$ , which provides a measure of the full magnetic bandwidth, is significantly larger in  $\text{Ba}_2\text{IrO}_4$  ( $223 \pm 4$  meV) than  $\text{Sr}_2\text{IrO}_4$  ( $178 \pm 4$  meV). This difference in bandwidth ( $\sim 25\%$ ) is qualitatively consistent with predictions based on quantum chemistry calculations by Katukuri *et al.* [17]. One important consequence of the larger bandwidth in  $\text{Ba}_2\text{IrO}_4$  is the proximity of the magnon mode and the spin-orbiton mode. These two modes are well separated in  $\text{Sr}_2\text{IrO}_4$ , but the larger bandwidth in  $\text{Ba}_2\text{IrO}_4$  pushes the magnon mode up and the spin-orbiton mode down as shown in Fig. 3(a). This is also clearly shown in the dispersion plot of Fig. 2(d), in which these two modes seem to come close to each other in energy as they approach the  $(\pi, 0)$  point. In many other iridates described by the  $j_{\text{eff}} = \frac{1}{2}$  picture, the  $j_{\text{eff}} = \frac{1}{2}$  and  $j_{\text{eff}} = \frac{3}{2}$

states are well separated, meaning that the magnon and spin orbiton can be treated as separate quasiparticles. In  $\text{Ba}_2\text{IrO}_4$ , however, the lack of such a clear separation between the  $j_{\text{eff}} = \frac{1}{2}$  and  $j_{\text{eff}} = \frac{3}{2}$  states indicates that a full understanding of these collective excitations will require consideration of all six bands in  $t_{2g}$  manifolds.

To examine the effect of epitaxial strain on the RIXS spectra, representative energy scans performed on two  $\text{Ba}_2\text{IrO}_4$  films are plotted in Fig. 2(c). These scans have been collected at the  $(\pi, 0)$  zone-boundary position, where the energy of the magnon mode is at its maximum. Note that epitaxial strain does shift the peak positions but the difference is much smaller than that between  $\text{Ba}_2\text{IrO}_4$  and  $\text{Sr}_2\text{IrO}_4$  shown in Fig. 3(a). As the magnitude of the compressive strain grows larger, the energy of the magnon mode is enhanced, while that of the spin-orbiton mode is reduced. Similar strain-induced tuning of the zone-boundary magnon energy has also been observed in thin film  $\text{Sr}_2\text{IrO}_4$  [28], where the magnetic bandwidth can be lowered (raised) by the application of a moderate tensile (compressive) strain. However, by measuring the full dispersion of the magnetic excitations, as shown in Fig. 2(d), a more detailed picture of the strain dependence emerges. Each scan at a given momentum was fit using a fit function consisting of elastic-line (resolution-limited pseudo-Voigt), magnon (Gaussian), spin-orbiton (Lorentzian, Gaussian), and electron-hole continuum/background (broad Gaussian). Only magnon and spin-orbiton positions are plotted in Fig. 2(d).

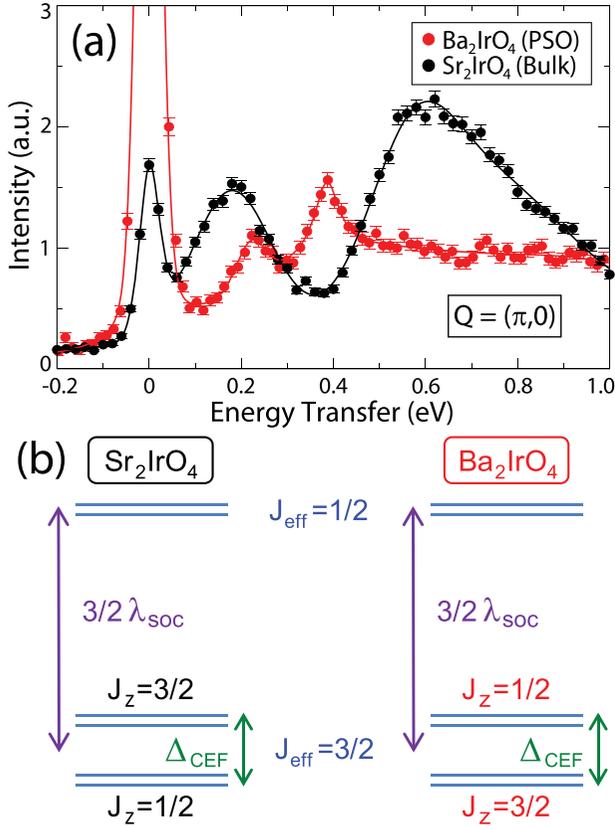


FIG. 3. (a) Representative excitation spectra measured at the  $(\pi, 0)$  zone-boundary position for thin film  $\text{Ba}_2\text{IrO}_4$  (20 nm, PSO substrate) and bulk single crystal  $\text{Sr}_2\text{IrO}_4$ . Both spectra were obtained using grazing incidence geometry. (b) The orbital energy level schemes implied by the spectra in (a). Note that the sign of the non-cubic crystal field splitting must be opposite in  $\text{Ba}_2\text{IrO}_4$  ( $\Delta_{\text{CEF}} > 0$ ) and  $\text{Sr}_2\text{IrO}_4$  ( $\Delta_{\text{CEF}} < 0$ ).

## IV. DISCUSSION

### A. Magnon dispersion relation

To analyze the magnetic dispersion relation, we employ a  $J$ - $J'$ - $J''$  pseudospin model. This is the same phenomenological model which has previously been used to describe magnon dispersion in  $\text{Sr}_2\text{IrO}_4$  [8] ( $J = 60$ ,  $J' = -20$ ,  $J'' = 15$  meV). Substantial ferromagnetic next-nearest coupling was introduced to account for the observed large zone-boundary dispersion. Similarly sizable zone-boundary dispersion is also observed for  $\text{Ba}_2\text{IrO}_4$ , and the dispersion relation is reasonably well described with  $J \approx 85$ ,  $J' \approx -15$ ,  $J'' \approx 10$  meV for the PSO film. Similar parameters are also obtained from fitting the GSO film data ( $J \approx 82$ ,  $J' \approx -19$ ,  $J'' \approx 16$  meV). The much larger value of  $J$  in  $\text{Ba}_2\text{IrO}_4$  can be understood from the  $180^\circ$  Ir-O-Ir bond angle according to the Goodenough-Kanamori rule. However, the further neighbor interactions in  $\text{Ba}_2\text{IrO}_4$  are almost as large as the values in  $\text{Sr}_2\text{IrO}_4$ . This is difficult to understand in the superexchange picture, since the next-nearest-neighbor hopping paths in  $\text{Ba}_2\text{IrO}_4$  are very different from those in  $\text{Sr}_2\text{IrO}_4$  due to the absence of  $\text{IrO}_6$  octahedral rotations [see Fig. 1(c)]. It is possible that superexchange involving  $j_{\text{eff}} = \frac{3}{2}$  might account for this,

although no such calculation has been reported. However, we would like to point out that the large zone-boundary dispersion could be explained using the so-called ring exchange as discussed in the context of  $\text{La}_2\text{CuO}_4$  [29], which could indicate considerable electron itinerancy (breakdown of the assumption of large Hubbard  $U$ ). It should be noted that recent *ab initio* calculations have demonstrated that interplane and symmetric anisotropic interactions are required in order to reproduce the observed magnetic structure of  $\text{Ba}_2\text{IrO}_4$  [20]. However, the small size of these terms (estimated to be  $\sim 0.5$ – $3.5$  meV) means that their contribution to the dispersion is overshadowed by the much stronger in-plane isotropic exchange interactions.

Next, we turn to the effect of epitaxial strain. Although the  $J$ - $J'$ - $J''$  model may not be applicable for  $\text{Ba}_2\text{IrO}_4$ , it is still interesting to compare the obtained exchange interaction parameters. Although compressive strain does serve to increase the overall bandwidth, it actually does so by reducing the nearest-neighbor exchange interaction, while enhancing the second and third neighbor interactions. It is important to remember the structural difference between  $\text{Ba}_2\text{IrO}_4$  and  $\text{Sr}_2\text{IrO}_4$  and its effect on the magnetic exchange interactions. This was illustrated in the two-magnon Raman scattering studies of  $\text{Sr}_2\text{IrO}_4$  thin films by Seo and co-workers [30]. They have reported that the enhanced magnon energy with compressive strain is the result of increased hopping amplitude due to the complexity of the multiorbital nature of the pseudospin. It is interesting to note that a similar suppression of the bandwidth is not observed in the case of  $\text{Ba}_2\text{IrO}_4$  reported here. A direct comparison of the zone-boundary energy also does not show a difference [Fig. 3(d)]. Perhaps this observation points to the important role of the octahedral rotation in  $\text{Sr}_2\text{IrO}_4$ . However, future two-magnon Raman measurements on  $\text{Ba}_2\text{IrO}_4$  films could be useful in making a quantitative comparison.

### B. Spin-orbital excitations

There are also notable differences in the orbital excitations of these two materials. The spin-orbit exciton mode, originally observed by Kim *et al.* [8], corresponds to excitations between the  $j_{\text{eff}} = \frac{3}{2}$  and  $j_{\text{eff}} = \frac{1}{2}$  states, which acquire dispersion as they propagate against an antiferromagnetically ordered background. Recent RIXS measurements on  $\text{Sr}_2\text{IrO}_4$  have demonstrated that this mode exhibits a strong dependence on the photon polarization [31]. When the sample is rotated with respect to the incoming photon polarization, the RIXS matrix elements will change as follows: Scattering from wave functions with a larger in-plane orbital component is enhanced (suppressed) in grazing (normal) incidence, while scattering from wave functions with a larger out-of-plane orbital component is suppressed (enhanced). Applying this to the ideal  $j_{\text{eff}} = \frac{3}{2}$  wave functions, which can be expressed as  $|\frac{3}{2}, \pm\frac{3}{2}\rangle = (\mp|d_{yz}, \pm\sigma\rangle + i|d_{xz}, \pm\sigma\rangle)/\sqrt{2}$  and  $|\frac{3}{2}, \pm\frac{1}{2}\rangle = (\mp|d_{yz}, \mp\sigma\rangle + i|d_{xz}, \mp\sigma\rangle + 2|d_{xy}, \pm\sigma\rangle)/\sqrt{6}$ , we expect grazing incidence to result in a preferential enhancement of excitations associated with the  $j_z = \pm\frac{1}{2}$  states.

As illustrated in Fig. 3(a), the orbital excitations of  $\text{Ba}_2\text{IrO}_4$  in grazing incidence are markedly different from those of  $\text{Sr}_2\text{IrO}_4$  measured in the same geometry, but bear a striking

resemblance to those of  $\text{Sr}_2\text{IrO}_4$  measured in normal incidence [see Fig. 2(b) in Ref. [31]]. The grazing incidence data in Fig. 3(a) imply that the  $j_z = \pm \frac{1}{2}$  levels form the lower-energy  $j_{\text{eff}} = \frac{3}{2}$  states in  $\text{Ba}_2\text{IrO}_4$ , but the higher-energy states in  $\text{Sr}_2\text{IrO}_4$ . This energy level scheme is illustrated in Fig. 3(b). Note that this scheme implies that the sign of the effective noncubic crystal field splitting ( $\Delta_{\text{CEF}}$ ) must be opposite in  $\text{Ba}_2\text{IrO}_4$  and  $\text{Sr}_2\text{IrO}_4$ , despite the fact that both materials display a similar elongation of  $\text{IrO}_6$  octahedra. Since this octahedral distortion is expected to generate a positive tetragonal crystal field splitting in both systems, the apparent reversal of  $j_{\text{eff}} = \frac{3}{2}$  levels demonstrates that longer-range crystal field effects must play a significant role in these materials as pointed out in Ref. [19]. This reversal of energy levels is consistent with recent x-ray absorption measurements on  $\text{Ba}_2\text{IrO}_4$  [32] and  $\text{Sr}_2\text{IrO}_4$  [33].

A comparison of excitation spectra for  $\text{Ba}_2\text{IrO}_4$  (glancing geometry) and  $\text{Sr}_2\text{IrO}_4$  (normal geometry, as in Ref. [31]) also reveals a clear suppression of the spin-orbit exciton energy scale. The sharp exciton feature at  $\mathbf{Q} = (\pi/2, \pi/2)$  shifts from  $\sim 470$  meV in  $\text{Sr}_2\text{IrO}_4$  to  $\sim 350$  meV in  $\text{Ba}_2\text{IrO}_4$ . This trend is opposite to predictions from quantum chemistry calculations [17], and approximately four times larger than predicted by theory. This peak shift seems to be due to the larger bandwidth of the spin-orbit exciton in  $\text{Ba}_2\text{IrO}_4$ , as the zone center energy of  $\sim 600$  meV is similar to that in  $\text{Sr}_2\text{IrO}_4$  [see Fig. 3(d)]. We note that the observed bandwidth of  $\sim 250$  meV in  $\text{Ba}_2\text{IrO}_4$  is almost a factor of two larger than that of  $\text{Sr}_2\text{IrO}_4$ . However, the apparent larger bandwidth could be due to the presence of two spin-orbit exciton modes and a further investigation of the incident angle dependence is necessary to disentangle these two modes, as was done for  $\text{Sr}_2\text{IrO}_4$  [31].

The strain dependence of the spin-orbit exciton mode [Figs. 2(c) and 2(d)] suggests that epitaxial strain can also be used to tune the orbital properties of  $\text{Ba}_2\text{IrO}_4$ . As the compressive strain increases, we expect the  $c/a$  ratio to grow larger and the elongation of the  $\text{IrO}_6$  octahedra to become more pronounced. This octahedral distortion should make the noncubic crystal field splitting  $\Delta_{\text{CEF}}$  larger in  $\text{Ba}_2\text{IrO}_4$  [see Fig. 3(b)]. In principle, this suggests that it should be possible to tune  $\text{Ba}_2\text{IrO}_4$  (or  $\text{Sr}_2\text{IrO}_4$ ) to the  $\Delta_{\text{CEF}} = 0$  limit where the magnetic anisotropy vanishes, by applying an appropriate epitaxial strain. In the case of  $\text{Ba}_2\text{IrO}_4$  the required strain should be tensile (to decrease  $\Delta_{\text{CEF}}$ ), while for  $\text{Sr}_2\text{IrO}_4$  it should be compressive (to increase  $\Delta_{\text{CEF}}$ ). This conclusion is supported by recent local density approximation plus dynamical mean-field theory (LDA+DMFT) calculations on  $\text{Sr}_2\text{IrO}_4$  [34], which predict that a compressive strain of  $\sim 1\%$  would be required

to tune the local structure to the  $\Delta_{\text{CEF}} = 0$  point. It is interesting to note that the  $\Delta_{\text{CEF}} = 0$  limit in  $\text{Ba}_2\text{IrO}_4$  and  $\text{Sr}_2\text{IrO}_4$ , which restores full rotational symmetry, does not correspond to perfectly undistorted  $\text{IrO}_6$  octahedra, but rather to the point where short-range and long-range crystal field effects cancel out.

## V. SUMMARY AND CONCLUSIONS

In summary, our RIXS studies of ultrathin epitaxial films of  $\text{Ba}_2\text{IrO}_4$  reveal that the bandwidths of the low-energy magnetic and spin-orbit excitations in this material are significantly larger than those found in  $\text{Sr}_2\text{IrO}_4$ . This observation can be understood from the increased hopping due to the  $180^\circ$  Ir-O-Ir bond in  $\text{Ba}_2\text{IrO}_4$ , which suggests that itinerancy may be important for understanding the electronic structure of  $\text{Ba}_2\text{IrO}_4$ . The results of this study demonstrate that hard x-ray RIXS can provide a detailed probe of spin and orbital excitations in ultrathin film samples. This technique offers unique opportunities for the study of samples which are difficult, or impossible, to synthesize in bulk single crystal form, allowing novel materials to be investigated under a variety of highly tunable strain conditions (tensile or compressive, uniform or anisotropic). In closing, we note that the relatively high inelastic count rates in this study ( $\sim 5$  counts/s) resulted in very reasonable measurement times ( $\sim 1$ – $2$  minutes per point for the data in Figs. 2 and 3). This suggests that measurements on monolayer and bilayer thin films are entirely feasible even with hard x rays, opening up exciting possibilities for the study of multilayers, buried interfaces, and complex heterostructures.

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# Supplemental Material - Magnetic Excitations in the Square Lattice Iridate $\text{Ba}_2\text{IrO}_4$

J. P. Clancy,<sup>1,\*</sup> H. Gretarsson,<sup>1</sup> A. Lupascu,<sup>1</sup> J. A. Sears,<sup>1</sup> Z. Nie,<sup>1</sup> M. H. Upton,<sup>2</sup> Jungho Kim,<sup>2</sup> Z. Islam,<sup>2</sup> M. Uchida,<sup>3</sup> D. G. Schlom,<sup>4,5</sup> K. M. Shen,<sup>3,5</sup> and Young-June Kim<sup>1</sup>

<sup>1</sup>Department of Physics, University of Toronto, Toronto, Ontario, M5S 1A7, Canada

<sup>2</sup>Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA

<sup>3</sup>Laboratory of Atomic and Solid State Physics, Department of Physics, Cornell University, Ithaca, New York 14853, USA

<sup>4</sup>Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA

<sup>5</sup>Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853, USA

## MAGNETIC STRUCTURE

The magnetic structure of both samples was examined using REXS. Figure S1 shows Ir  $L_3$ -edge REXS data on our most highly strained film,  $\text{Ba}_2\text{IrO}_4$  on GSO. As shown in Fig. S1(a), magnetic Bragg peaks were observed at  $[1/2, 1/2, L]$  wave vectors for all integer values of  $L$ . These measurements were collected well within the mag-

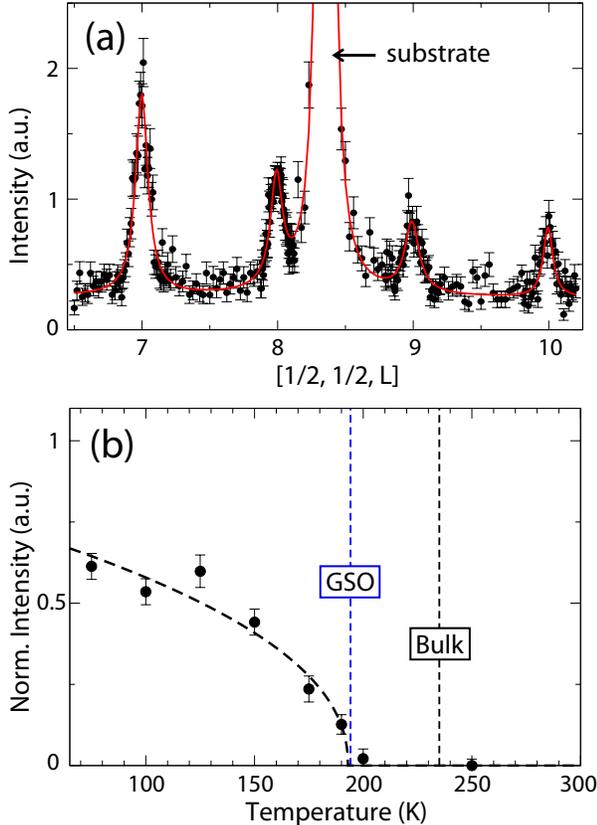


FIG. S1: (Color online) Resonant elastic x-ray scattering from 13 nm thin film  $\text{Ba}_2\text{IrO}_4$  grown on a GSO substrate. (a) A scan showing magnetic Bragg peaks along the  $[1/2, 1/2, L]$  direction. These measurements were collected in the  $\sigma\text{-}\pi'$  polarization channel at  $T = 7$  K. (b) Temperature dependence of the integrated intensity of the  $(1/2, 1/2, 7)$  magnetic Bragg peak.

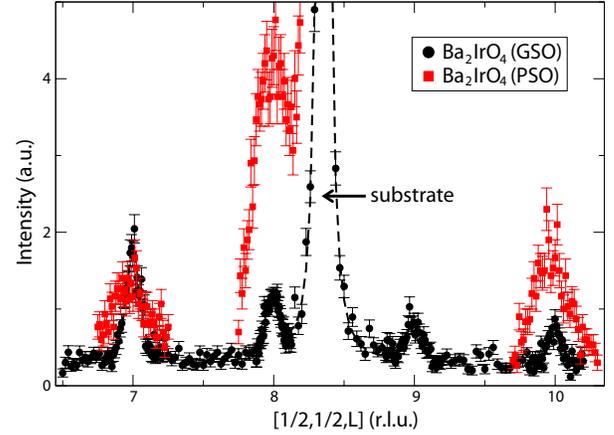


FIG. S2: (Color online) Resonant elastic x-ray scattering from  $\text{Ba}_2\text{IrO}_4$  grown on PSO and GSO substrates. A scan showing magnetic Bragg peaks along the  $[1/2, 1/2, L]$  direction for the PSO sample is plotted in red and compared with the GSO data (same data from Fig. S1). These measurements were collected in the  $\sigma\text{-}\pi'$  polarization channel at  $T = 7$  K.

netically ordered phase ( $T = 7$  K), using polarization analysis to distinguish magnetic scattering ( $\sigma\text{-}\pi'$ ) from charge scattering ( $\sigma\text{-}\sigma'$ ). This magnetic selection rule is consistent with the magnetic structure of bulk  $\text{Ba}_2\text{IrO}_4$  as reported by Boseggia *et al.*[1]: a collinear  $ab$ -plane antiferromagnet.

The observation of magnetic peaks at both  $L = \text{odd}$  and  $L = \text{even}$  implies the presence of multiple magnetic domains, with ordered moments aligning along either of the crystallographically equivalent  $[110]$  or  $[\bar{1}10]$  directions. The  $L$ -dependence of magnetic Bragg peaks for  $\text{Ba}_2\text{IrO}_4$  on PSO is compared to that of the GSO sample in Fig. S2, which illustrates that the same magnetic selection rule is followed. These results suggests that, as in the case of thin film  $\text{Sr}_2\text{IrO}_4$ [2], the modest epitaxial strain in our  $\text{Ba}_2\text{IrO}_4$  samples does not change the magnetic structure. As in previous measurements on thin film  $\text{Sr}_2\text{IrO}_4$ [2], we note that the magnetic correlations in thin film  $\text{Ba}_2\text{IrO}_4$  are highly anisotropic. Observed magnetic correlation lengths are 100 times longer within the  $ab$ -plane than along the  $c$ -axis stacking direction.

In Fig. S1(b), the temperature dependence of the  $(1/2,$

$1/2, 7)$  magnetic Bragg peak is shown. A limited number of temperature points were obtained, which prevented us from detailed analysis of the phase transition. However, it is clear that the magnetic transition temperature in this compressively strained is somewhat suppressed compared to that in a bulk sample. This observation is consistent with the behavior observed for  $\text{Sr}_2\text{IrO}_4$ [2], in which suppression of  $T_N$  was observed for the films prepared with compressive epitaxial strain.

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\* Present address: Department of Physics and Astronomy, McMaster University, Hamilton, Ontario, L8S 4L8,