Testing the Validity of the Strong Spin-Orbit-Coupling Limit for Octahedrally Coordinated Iridate Compounds in a Model System Sr$_3$CuIrO$_6$

X. Liu,$^{1,*}$ Vamshi M. Katukuri,$^2$ L. Hozoi,$^2$ Wei-Guo Yin,$^1$ M. P. M. Dean,$^1$ M. H. Upton,$^3$ Jungho Kim,$^3$ D. Casa,$^3$ A. Said,$^3$ T. Gog,$^3$ T. F. Qi,$^{4,5}$ G. Cao,$^{4,5}$ A. M. Tsvelik,$^1$ Jeroen van den Brink,$^2$ and J. P. Hill$^1$

$^1$Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA
$^2$Institute for Theoretical Solid State Physics, IFW Dresden, Helmholtzstrasse 20, 01069 Dresden, Germany
$^3$Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA
$^4$Center for Advanced Materials, University of Kentucky, Lexington, Kentucky 40506, USA
$^5$Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506, USA

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The electronic structure of Sr$_3$CuIrO$_6$, a model system for the 5$d$ Ir ion in an octahedral environment, is studied through a combination of resonant inelastic x-ray scattering and theoretical calculations. Resonant inelastic x-ray scattering spectra at the Ir $L_3$ edge reveal an Ir $t_{2g}$ manifold that is split into three levels, in contrast to the expectations of the strong spin-orbit-coupling limit. Effective Hamiltonian and $ab$ initio quantum chemistry calculations find a strikingly large noncubic crystal field splitting comparable to the spin-orbit coupling, which results in a strong mixing of the $j_{\text{eff}} = \frac{1}{2}$ and $j_{\text{eff}} = \frac{3}{2}$ states and modifies the isotropic wave functions on which many theoretical models are based.

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A new type of Mott physics has recently been discussed in the 5$d$ transition metal oxides [1–3]. In contrast with the more familiar 3$d$ Mott insulators, for which new physical phenomena originate from the large on-site Coulomb interaction, $U$, in 5$d$ transition metal oxides the strong electron correlation has been argued to be driven by a large spin-orbit coupling (SOC). Iridates are an important example in this category and have attracted much attention recently [1–19]. In particular, iridates in which the iridium atom sits in an octahedral oxygen cage have been classified as narrow-band Mott insulators. It is argued that a strong SOC splits the occupied $t_{2g}$ orbitals into two sets of narrow bands corresponding to $j_{\text{eff}} = \frac{1}{2}$ and $j_{\text{eff}} = \frac{3}{2}$ states. For the important case of the Ir$^{4+}$, 5$d^5$ ion, this puts one electron in the $j_{\text{eff}} = \frac{1}{2}$ state and even a small $U$, then gives rise to Mott insulating behavior. Further, because of the isotropic nature of the resulting wave functions [3], this has important consequences for the magnetic superexchange interactions and has led to predictions of an array of interesting physics, including quantum spin liquids [5,7,9–12], topological insulators [2,4], and superconductivity [14].

The strong SOC limit assumes local cubic symmetry with perfect IrO$_6$ octahedra. In reality, all of the proposed physical realizations of these models have nonideal octahedra. Examples include the pyrochlores $R_2$Ir$_2$O$_7$ ($R =$ Y, Sm, Eu, and Lu), the hexagonal lattice systems $A_2$IrO$_4$ ($A =$ Li, Na), the hyperkagome lattice compound Na$_2$IrO$_4$ and the square lattice compounds (Ba, Sr)$_2$IrO$_4$. To date these have mostly been treated in the strong SOC limit. There are signs though, that this may not always be appropriate. For example Na$_2$IrO$_3$ has been thought to be a realization of the Kitaev model on a honeycomb lattice [5]. However, it was found recently to be antiferromagnetically ordered in a zigzag pattern [20,21], contradicting theoretical predictions based on the strong SOC limit. This is suggestive of significant noncubic crystal fields and indeed very recently theorists have begun to consider this question [22,23]. Thus, understanding the interplay of SOC and noncubic crystal fields and experimentally determining their size are crucial requirements for any realistic model for the iridates.

In this Letter, we experimentally determine the SOC and crystal field splitting in a model iridate, Sr$_3$CuIrO$_6$ [24], which has only small distortions of the IrO$_6$ octahedra. We find that there is strong mixing of the $j_{\text{eff}} = \frac{1}{2}$ and $j_{\text{eff}} = \frac{3}{2}$ states and that, even in this case, it is not appropriate to work in the strong SOC limit. An important consequence of this mixing is that the wave functions are no longer isotropic and the magnetic superexchange interactions are modified away from the conventional picture. These results suggest that the conventional $j_{\text{eff}} = \frac{1}{2}$ Mott insulator picture of many of the currently interesting octahedrally coordinated iridates needs to be revisited in light of these effects.

Before presenting the results in detail, we first note that there are several unique features of this study of Sr$_3$CuIrO$_6$ that make it ideal for probing these effects. First, the oxygen octahedra are very well separated from each other and therefore one does not need to consider hybridization effects between them [25]. Second, the octahedra themselves only have relatively small distortions—the Ir-O bond lengths vary by less than 2% (full details of the structure are provided below), so that noncubic crystal fields are expected to be small. Third, we use the technique of resonant inelastic x-ray scattering (RIXS) to probe the energy and momentum dependence of the excitation...
spectrum. This technique has the advantage of probing only the orbital and magnetic excitations associated with the Ir sites, making interpretation of the spectra straightforward. This, combined with the fact that the iridium-derived electronic states are well localized, allows us to compare to the theoretical models with substantial precision. We observe six well-defined electronic transitions. By comparing with an effective model Hamiltonian and with ab initio theoretical calculations, we are able to derive a complete description of the electronic degrees of freedom.

Sr$_3$CuIrO$_6$ is a quasi-one-dimensional material with a monoclinic structure [24,26]. Individual IrO$_6$ octahedra are linked by spin-1/2 Cu$^{2+}$ ions along one direction, forming a chain structure (Fig. 1). Intersite hopping is largely suppressed due to this special structure: the $d_{x^2-y^2}$ orbital at the Cu site is essentially orthogonal to the $t_{2g}$ orbitals on the Ir site, resulting in a negligible intersite hopping integral. Even though the extended nature of the 5$d$ orbitals tends to reduce correlation effects, this special arrangement puts Sr$_3$CuIrO$_6$ in the strongly localized regime.

Single crystal Sr$_3$CuIrO$_6$ was grown with self-flux techniques. In reciprocal space, the chain direction is parallel to $Q = (1.98 \ 0 \ 1)$. In our measurements, $Q$ points at $(1.98 \ 0 \ 1) + (0 \ 13 \ 0)$ were selected along the chain direction. A single chain is shown in Fig. 1 with the local coordinates for a single IrO$_6$ octahedra marked. The O-Ir-O bonds are straight and of similar length with an effective model Hamiltonian and with ab initio theoretical calculations, we are able to derive a complete description of the electronic degrees of freedom.

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The energy and momentum dependence of the excitation spectrum was studied using RIXS [27]. The experiments were carried out at the Ir $L_3$ edge for which dipole transitions excite and deexcite a $2p_{3/2}$ core-electron to the 5$d$ orbitals. Due to the strong core-hole potential and localized nature of the Ir 5$d$ electrons in Sr$_3$CuIrO$_6$, the RIXS process is dominated by local dipole transitions which lead to intrasite $d$-$d$ excitations, an important consideration for this work. The measurements were carried out at beam line 9-1D, Advanced Photon Source, in a horizontal scattering geometry. A Si(844) secondary monochromator and a $R = 2$ m Si(844) diced analyzer were utilized. The overall energy resolution of this setup was $\sim 45$ meV (FWHM). All data were collected at 7 K.

The incident x-ray energy dependence of the RIXS spectra near the Ir $L_3$ edge is shown in Fig. 2. Three features are observed at 0.28, 0.58, and 0.81 eV in the low energy region. Importantly, these three features show the same resonant behavior as a function of incident x-ray energy, all resonating around 11.216 keV. This indicates that they all originate from initial $2p \rightarrow 5d$ transitions into the same unoccupied states within the Ir $t_{2g}$ manifold. The different energies arise from the fact that the $5d \rightarrow 2p$ deexcitation transitions create holes in different orbitals, leaving the system in different excited states at the end of the respective RIXS processes.

More details of these three excitations can be seen in Fig. 3. The peak at 0.28 eV, though sharing the same resonant behavior, has much less spectral weight. This excitation is most likely from impurity states associated with defects. At higher energy loss above 2 eV, $d$-$d$ excitations into Ir $e_g$ orbitals and charge transfer excitations from oxygen 2$p$ orbitals are also observed. Here we focus on the 0.58 and 0.81 eV excitations, which are $d$-$d$ excitation within the iridium $t_{2g}$ manifold. These two peaks, especially the lower energy one, are fairly sharp. Importantly, they show no significant dispersion with momentum transfer (Fig. 3). These observations are consistent with the narrow band picture and the very localized nature of the 5$d$ electrons in Sr$_3$CuIrO$_6$.

In the ideal case for which the Ir atom sits within a regular oxygen octahedral cage, the $t_{2g}$ manifold is split into $j_{\text{eff}} = \frac{1}{2}$ and $j_{\text{eff}} = \frac{3}{2}$ states by the SOC [28]. In this effective 2 level system, only one $d$-$d$ transition is expected. Our observations clearly deviate from this ideal picture, and even without any modeling, already point to the importance of noncubic crystal fields.

**FIG. 1** (color online). The Cu-IrO$_6$-Cu-IrO$_6$ chain of Sr$_3$CuIrO$_6$. The local coordinates for the IrO$_6$ octahedra and the CuO$_6$ prism are labeled with $(x, y, z)$ and $(x', y')$, respectively.

**FIG. 2** (color online). Incident x-ray energy dependence of the RIXS spectra from Sr$_3$CuIrO$_6$ at the Ir $L_3$ edge. Three low energy features at 0.28, 0.58, and 0.81 eV are observed. These show similar resonant behavior, each peaking at 11.216 keV.
The splitting of the $d_{xy}$ field is of a similar magnitude to SOC. With the parameters crystal field.

The data at $\zeta = -0.3$ are fit with multiple Gaussian peaks. The black solid line shows the total fitting result. Individual Gaussian peaks are shown with red dashed lines, which are centered at 0.28, 0.58, 0.81, 3.14, 3.90, 4.72, and 6.20 eV, respectively. The vertical and horizontal bars indicate the excitations listed in Table I from the MRCI + SOC calculations.

In order to understand these results, we first turn to an effective Hamiltonian to describe the local Ir 5$d$ electrons. This will provide us with an intuitive description of the electronic structure. We will later see that this is consistent with a more sophisticated $ab$ initio quantum chemistry calculation for this structure. We start with a local atomic multiplet Hamiltonian in hole representation,

$$H_{\text{local}} = \lambda \sum_n \vec{L}_n \cdot \vec{S}_n + \Delta \sum_{n, \sigma} d_{n, \sigma}^* d_{n, \sigma},$$

where $\lambda$ is the strength of the SOC and $\Delta$ describes the splitting of the $d_{xy}$ from $d_{yz, zx}$ due to a nonoctahedral crystal field. $n$ is the index of the Ir sites. This Hamiltonian splits the energy levels within the $t_{2g}$ manifold into three doublets,

$$E_{0.2} = \frac{\lambda}{4} (-1 + \delta + \sqrt{9 + 2\delta + \delta^2}), \quad E_{1} = \frac{\lambda}{2},$$

where $\delta = \frac{\Delta}{\lambda}$ and $E_0$ is the ground state energy. Our RIXS spectra determine the energy differences to be $E_1 - E_0 = 0.58$ eV and $E_2 - E_0 = 0.81$ eV, which leads to $\lambda = 0.44$ eV and $\Delta = 0.31$ eV. That is, the noncubic crystal field is of a similar magnitude to SOC. With the parameters for $H_{\text{local}}$ in hand, the wave functions of the three doublets can now be determined. We find,

$$|\phi_0\rangle = \frac{1}{1.56} (0.65 d_{x^2-y^2} + id_{xy} \pm d_{z^2}),$$

$$|\phi_1\rangle = \frac{1}{\sqrt{2}} (id_{xy} \pm d_{z^2}),$$

$$|\phi_2\rangle = \frac{1}{2.20} [2 d_{x^2-y^2} - 0.65(id_{xy} \pm d_{z^2})].$$

The above effective Hamiltonian description is simple but informative. The three doublet picture naturally explains the data with a SOC strength $\lambda$ that is consistent with earlier calculations [1]. Importantly, however, it suggests a significant noncubic crystal field, one that is comparable with the SOC—despite the small distortions of the octahedra in this material. This noncubic crystal field strongly modifies the relevant wave functions. For example, $|\phi_0\rangle$ shows significant deviation from the ideal case: instead of the expected equal admixture of the three $t_{2g}$ orbitals in the ground state, the contribution from the $d_{xy}$ orbitals is reduced by more than 30% in Sr$_3$CuIrO$_6$. This significant modification is illustrated in Fig. 4. Given that anisotropic magnetic interactions lie at the heart of much of the proposed novel phenomena for the iridates, such a modification of the wave functions would be crucial and warrants further study.

To do so, we performed $ab$ initio many-body calculations based on wave function electronic-structure theory. Complete-active-space self-consistent-field and multireference configuration-interaction (MRCI) techniques from modern quantum chemistry [29, 30] were employed, as implemented in the MOLPRO package [31]. Multiorbital and multiplet physics, SOC’s, and O 2$p$ to Ir 5$d$ charge transfer effects are all treated on an equal footing, fully $ab$ initio. The calculations were carried out on a cluster which contains a central IrO$_6$ octahedron, two nearest-neighbor CuO$_4$ plaquettes, and the adjacent Sr atoms, properly embedded in a large array of point charges that reproduces the crystal Madelung field in the cluster region.

The effect of noncubic crystal fields is studied by first turning off the SOC. Without SOC, the embedded-cluster MRCI calculations give a splitting of 0.45 eV between the $d_{x^2-y^2}$ and $d_{xy}$ levels. This value is consistent with the $\Delta$ parameter derived in the model-Hamiltonian analysis carried out above.

With spin-orbit interactions switched on [32], the MRCI calculations predict excitations within the $t_{2g}$ manifold at 0.59 and 0.91 eV. At higher energies, we find Ir $t_{2g}^1$ to $t_{2g}^0 e_g^1$ excitations between 3.2 and 4.9 eV and O 2$p$ to Ir 5$d$ charge transfer transitions between 3.5 and 5.4 eV. Further, excitation energies of $\sim$5.9 eV are predicted for the Ir $t_{2g}^1 e_g^2$ states, see Table I.
the system away from the strong SOC limit (field has a similar strength to the SOC. This drives from ideal cubic symmetry, the induced noncubic crystal distortion was reported earlier [6], recent results suggest it is smaller with the O-Ir-O bonds bending away from straight by ~7° and the O-Ir and Ir-O bonds deviating from 90° by up to 10° [21]. In all cases, the distortions are similar in magnitude or larger than the distortions present in Sr$_3$CuIrO$_6$. Thus, treating these systems as being in the strong SOC limit is likely to be incorrect. With the electronic structure and magnetic interactions highly dependant on the relative contribution from the different orbitals, the nonoctahedral crystal fields must be explicitly considered in any realistic models. Finally, we look at Sr$_2$IrO$_4$. In this system, the octahedral bond angles are 90°, and the bond lengths differ by only 4% [34]. Thus, this system may be the closest to the strong SOC limit, consistent with experimental observations [28]. However, the present study suggests that this may be the exception rather than the rule.

In summary, we have used RIXS, a microscopic model Hamiltonian, and ab initio quantum chemistry calculations to study the electronic excitations in Sr$_3$CuIrO$_6$, where Cu and IrO$_6$ octahedra form a 1-D spin chain. A three-level structure of the Ir $t_{2g}$ manifold is observed and ascribed to the lowering of the local octahedral symmetry. We show that this lowering of symmetry leads to a strong nonoctahedral crystal field, which is comparable to the spin-orbit-coupling and modifies the electronic structure, the ground state wave functions and the magnetic exchange interactions significantly. It should therefore be taken into account when modeling the magnetic behavior of all nonideal iridates. Important examples in the current literature include the pyrochlores R$_2$Ir$_2$O$_7$, the honeycomb lattice A$_2$IrO$_3$ and the hyperkagome A$_4$Ir$_3$O$_8$.

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*xl@bn.gov
xl@iphy.ac.cn

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