Spin-Orbit-Induced Orbital Excitations in Sr$_2$RuO$_4$ and Ca$_2$RuO$_4$: A Resonant Inelastic X-ray Scattering Study

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High-resolution resonant inelastic X-ray scattering (RIXS) at the oxygen K-edge has been used to study the orbital excitations of Ca$_2$RuO$_4$ and Sr$_2$RuO$_4$. In combination with linear dichroism X-ray absorption spectroscopy, the ruthenium 4d-orbital occupation and excitations were probed through their hybridization with the oxygen p-orbitals. These results are described within a minimal model, taking into account crystal field splitting and a spin-orbit coupling $\lambda_{so} = 200$ meV. The effects of spin-orbit interaction on the electronic structure and implications for the Mott and superconducting ground states of (Ca,Sr)$_2$RuO$_4$ are discussed.

I. INTRODUCTION

The relativistic coupling between electronic spin and orbital momentum was long thought to have marginal influence on electrons in solids. Following the prediction and observation of topological surface states on Bi-based compounds$^1$, this paradigm has changed. Discovery of novel quantum phases realized through strong spin-orbit interaction is now a vivid field of research$^2$. The demonstration of spin-orbit coupling driving a new type of Mott insulating state in layered iridates$^3$ is a good example of this. It has been proposed that doping of this effective $J_{1/2}$-Mott insulating state could lead to an exotic type of superconductivity$^4$, where Cooper pairs are composed of strongly spin-orbit coupled electrons.

In this context, it is interesting to study other systems that display Mott physics and superconductivity in conjunction with strong spin-orbit interaction. The 4d-transition metal oxide system Ca$_{2-x}$Sr$_x$RuO$_4$ represents such a case. For $x = 0$, the system is a Mott insulator, whose exact nature is not clarified$^9$. At the opposite stoichiometric end ($x = 2$), the system has a superconducting ground state ($T_c = 1.5$ K) originating from a correlated Fermi liquid$^{12}$. Although triplet $p$-wave superconductivity was proposed early on, the mechanism and symmetry class of the superconducting order parameter is still debated$^{13-17}$.

A fundamental question is how strongly spin-orbit interaction influences the electrons in these materials and whether it has an impact on the Mott insulating and superconducting ground states? Current experimental evidence for a strong spin-orbit interaction stems from absorption spectroscopy$^{18-20}$, that has revealed a considerable admixture of the ruthenium $t_{2g}$ orbitals. More recently, spin-resolved photoemission spectroscopy has reported spin-polarized bands in Sr$_2$RuO$_4$$^{21,22}$. However, the most direct consequence of strong spin-orbit interaction – the splitting of $t_{2g}$ states – has not yet been probed directly by experiments. Orbital excitations transferred across this splitting are in fact not accessible to optical spectroscopies. Furthermore, the Ru $L$-edge ($\sim 3$ keV)$^9$ is currently inaccessible to high-resolution RIXS instrumentation (as it lies right between soft and hard X-ray optics).

To overcome these experimental challenges, we access here the Ru 4d-orbital excitations through their hybridization with oxygen $p$-orbitals. Exploiting a combination of X-ray absorption (XAS) and oxygen K-edge resonant inelastic X-ray spectroscopy (RIXS), we provide direct evidence for a splitting of the ruthenium $t_{2g}$ states. Our RIXS study of Ca$_2$RuO$_4$ and Sr$_2$RuO$_4$ reveals excitations that allow an estimation of the spin-orbit coupling, in the same fashion as for the iridates$^{23,24}$. These results suggest a spin-orbit coupling $\lambda_{so} \sim 200$ meV – only about two times weaker than in the iridates. We conclude by discussing the Mott insulating and superconducting states in Ca$_{2-x}$Sr$_x$RuO$_4$.

II. METHODS

High-quality single crystals of Sr$_2$RuO$_4$ and Ca$_2$RuO$_4$ were grown by the flux-feeding floating-zone technique$^{25,26}$. The samples were aligned $ex$-situ and cleaved
in-situ using the top-post method, to access momenta along the Ru-O bond direction. Oxygen K-edge X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) experiments were carried out at the ADvanced REsonant Spectroscopy (ADRESS) beamline at the Swiss Light Source (SLS)\textsuperscript{27,28}. Absorption spectra were measured in fluorescence-yield mode, using both horizontally and vertically polarized light. The RIXS spectrometer was set to have a fixed scattering angle of 130 degrees and an energy resolution of 29 meV (HWHM) at the oxygen K-edge. All spectra were recorded at $T = 20$ K. XAS matrix elements and RIXS momentum $Q = (h,k,l)$ were varied by changing the incident angle $\theta$ (see inset Fig. 2(a)).

III. RESULTS

In Fig. 1 and 2, X-ray absorption spectra recorded on Ca$_2$RuO$_4$ and Sr$_2$RuO$_4$ are shown for different light polarizations and incident angles $\theta$. Good agreement with previous XAS work\textsuperscript{18,19} is found whenever overlap in temperature, polarization, and incident angle is present. As generally observed on cuprates\textsuperscript{29}, iridates\textsuperscript{24} and ruthenates\textsuperscript{18,19}, the $t_{2g}$ and $e_g$ states can be probed through oxygen-hybridization on both the apical and planar oxygen sites, that have slightly different absorption resonance energies\textsuperscript{29}.

By varying light polarization and incident angle $\theta$, matrix elements favor different $p$-orbitals – see top panels of
Fig. 3. (color online) Resonant Inelastic X-ray Scattering (RIXS) spectra for different momentum transfers $Q_{1} = (h, 0)$ as indicated on Ca$_2$RuO$_4$ (left) and Sr$_2$RuO$_4$ (right), recorded using linear-horizontal light tuned to the planar oxygen K-edge. For visibility, all spectra are given an individual vertical offset. Solid lines are fits to a Gaussian (approximately resolution limited elastic line), an anti-symmetric Lorentzian (gray-shaded component) and a quadratic background.

IV. RIXS

Next, we turn to the resonant inelastic X-ray spectra recorded on Ca$_2$RuO$_4$ and Sr$_2$RuO$_4$. In Fig. 2(c), the incident-photon-energy dependence of the RIXS spectra across apical and planar oxygen K-resonances on Ca$_2$RuO$_4$ is shown for linear horizontal light polarization at incident angle $\theta = 75^\circ$. Besides elastic scattering, three pronounced excitations are resolved at the planar oxygen edge. Those at $\sim 2$ and $\sim 4$ eV, correspond approximately to the $t_{2g}$ to $d_{3z^2-r^2}$ and $d_{xy}$-$d_{yz}$ splittings and are hence assigned to be $dd$-excitations. In the following, focus is on the low-energy excitations found at $0.3 - 0.5$ eV for both Ca$_2$RuO$_4$ and Sr$_2$RuO$_4$—see Fig. 3. These excitations are non-dispersive and reside at energy scales well above optical phonon branches. Furthermore, as Ca$_2$RuO$_4$ is an insulator, a plasmon scenario is very unlikely. These are also incompatible with a simple $t_{2g}$ crystal field splitting, which is expected to be much smaller than 300 meV.
V. INTERPRETATION

To gain further insight into the nature of this excitation, we start by discussing the $t_{2g}$ states. Linear dichroism effects on X-ray absorption spectra yield information about the orbital hole occupation $n_{xy}^z$ = $n_{yz}^z$ and $n_{xz}^z$. For example, on the planar oxygen site, $p_{x/y} - d_{xy}$ and $p_{z} - d_{xz/yz}$ hybridizations are dominating, whereas $p_{x/y} - d_{xz/yz}$ is leading at the apical site. Using light polarization to emphasize the $p_x$ or $p_y$ channel, absorption is enhanced on the apical site if hole orbital occupation $n_{xy}^z$ = $n_{yz}^z$ is high. Likewise, the planar absorption resonance will be enhanced for large $d_{xy}$-occupation. As a result, apical and planar absorptions cannot both be strong at the same time.

The proportion between planar and apical XAS peak amplitudes is an experimental measure of the ratio $R_3 = [n_{xy}^z/(n_{yz}^z + n_{xz}^z)]^{18,24}$. Judging from peak amplitudes$^{18}$, $R_3 \sim 1.23(2)$ and $\sim 0.17(2)$ respectively in Sr$_2$RuO$_4$ and Ca$_2$RuO$_4$ – see Fig. 4(b). There is, however, a caveat related to the tetragonal distortion of the apical oxygen (6% and −2% in Sr$_2$RuO$_4$ and Ca$_2$RuO$_4$ respectively) leading to slightly under- and over-estimation of $n_{xy}^z$. Assuming (as done for iridates materials$^{24}$) that the hybridization strength decays as $r^{-3.5,31}$, where $r$ is the Ru-O bond length, $n_{xy}^z$ would be overestimated by $\sim 20\%$ in Sr$_2$RuO$_4$ and underestimated by 5% in Ca$_2$RuO$_4$. Therefore, $1 < R_3 < 1.25$ for Sr$_2$RuO$_4$ and $0.15 < R_3 < 0.2$ for Ca$_2$RuO$_4$ (Fig. 4) – the latter being consistent with the conclusion of early XAS work at 90 K using circular polarized light$^{18}$.

VI. MODEL

This mixing of $d^\pm$, $d^\pm_x$, and $d^\pm_{x'y'}$ orbitals, where $\pm$ refers to the electronic spin, can be explained by a non-negligible spin-orbit interaction $\lambda_{so}$.$^{18,21,22,32,33}$ Calculations including crystal field effects and spin-orbit interaction but neglecting the Hund’s coupling$^{34}$ have described very successfully the band structure of Sr$_2$RuO$_4$ and Sr$_2$RhO$_4$.$^{21,22}$ Following this spirit, the simplest Hamiltonian describing the $t_{2g}$ states reads:

$$H = \lambda_{so} L \cdot S + \frac{\Delta}{3} (L_z)^2$$

where $S$ and $L$ are the spin and orbital momentum operators and $\lambda_{so}$ is the spin-orbit coupling constant.$^{23,24,35}$ The intra-$t_{2g}$ crystal field splitting $\Delta$ is defined so that $\Delta > 0$ lifts $d_{xy}$ above $d_{xz}$ and $d_{yz}$. Diagonalizing Eq. 1 in the ($d_{xy}^\pm$, $d_{xz}^\pm$, $d_{yz}^\pm$)-subspace$^{23,35}$ (neglecting $e_g$-states) yields the eigenstates $\psi_1^\pm = d_{xy}^\pm \pm i d_{yz}^\pm / \sqrt{2}$, $\psi_2^\pm = d_{xz}^\pm \pm i d_{yz}^\pm / \sqrt{2}$ and $\psi_3^\pm = d_{xz}^\pm + i d_{yz}^\pm / \sqrt{2}$ with hole/electron occupancy:

$$n_{xy}^z = \frac{(2\delta - 1 + C)^2}{4} \quad \text{and} \quad n_{yz}^z = n_{xz}^z - 2C$$

where $\delta = \Delta/\lambda_{so}$ and $C = \sqrt{9 + 40(\delta - 1)}$ – see Fig. 4. The Eigenenergies ($E_3$, $E_2$ and $E_1$) are split by:

$$E_3 - E_1 = \frac{\lambda_{so} C}{2} \quad \text{and} \quad E_3 - E_2 = \frac{\lambda_{so}}{4} (C + 3 + 2\delta).$$

Notice that in the limit $\delta = 0$ (the case of (Ba,Sr)$_2$IrO$_4$)$^{3,24,30}$, then $E_2 = E_1$ are degenerate (see Fig. 4(a)) and $E_3 - E_1 = 1.5\lambda_{so}$. In the opposite limit $\lambda_{so} \to 0$, $E_3 - E_1 = \Delta$. Within this simple model, our observations $R_3 = n_{xy}^z/(n_{yz}^z + n_{xz}^z)$ and the RIXS excitation at $\sim 350$ meV can be explained using the two adjustable parameters $\Delta$ and $\lambda_{so}$.

For example, for Sr$_2$RuO$_4$ where $R_3 \approx 1.2(2)$, we find $\Delta/\lambda_{so} \approx 0.55(5)$ (see Fig. 4). This implies that $E_2 - E_0 = 1.4\lambda_{so}$ and $E_2 - E_1 = 2.1\lambda_{so}$. Assuming that the peak feature at $\sim 350$ meV (Fig. 3(b)) results from the average of two broad excitations ($E_3 - E_2$ and $E_3 - E_1$) leads us to $\lambda_{so} \sim 200$ meV and hence $\Delta \sim 100$ meV. This value of $\lambda_{so}$ is comparable to the theoretical expectation for Ru$^{21,36}$ and what has been extracted from spin resolved ARPES$^{21}$. Notice that the $E_2 - E_1 \sim \Delta/2 \approx 50$ meV splitting – possibly accessible through indirect RIXS processes – is expected near the elastic line but not resolved in this experiment.

As $R_3 \sim 1/6$ for Ca$_2$RuO$_4$, it implies that $\delta \sim -1$ and hence $E_2 - E_0 = 2.1\lambda_{so}$ and $E_2 - E_1 = 1.3\lambda_{so}$. The RIXS spectra, shown in Fig. 3(a), exhibit a pronounced excitation at $\sim 340$ meV. If this is a result of an average of two excitations, once again $\lambda_{so} \sim 200$ meV is found. Thus, by including a spin-orbit coupling of 200 meV, a consistent description of the orbital hole occupation extracted from XAS and the excitations of the RIXS spectra on both Sr$_2$RuO$_4$ and Ca$_2$RuO$_4$ is obtained.

VII. DISCUSSION

Implications of spin-orbit coupling $\lambda$ in 4d-transition oxide materials have already been evaluated in a number of papers$^{10,11,15,22,32,33,36,37}$ The magnon bandwidth in Ca$_2$RuO$_4$ is, for example, predicted$^{10,11}$ to be controlled by $\sim 3\lambda/4$. Neutron experiments should be performed to test this prediction. Magnetic moments are also influenced but not uniquely defined by $\Delta/\lambda^{11}$. As the experiments on Ca$_2$RuO$_4$ suggest that $\psi_3^\pm$ is dominated by $d_{xz}/d_{yz}$ orbitals, it is possible to approximate $\psi_3^\pm = d_{xz}^\pm + i d_{yz}^\pm$. Then, both $\psi_2^+$ and $\psi_3^+$ are more elegantly expressed in spherical harmonic notation: $\psi_2^+ = [\ell_z = +\pm, s_z = \mp 1/2] = \chi^{\mp 1/2}$ and $\psi_3^+ = [\ell_z = +1, s_z = \pm 1/2] = \chi^{\mp 1/2}$. In this simplistic limit, the role of spin-orbit interaction is to split the four-fold degeneracy of $d_{xy}^\pm$ and $d_{yz}^\pm$ into two-fold degenerated $\chi^{\pm 3/2}$ and $\chi^{\pm 1/2}$ states – see Fig. 4. It has been argued that even modest Coulomb interaction $U$ is sufficient to split these $\chi^{\mp 3/2}$ and $\chi^{\pm 1/2}$ states and hence drive the Mott insulating transition$^{32,33}$. Therefore, as in layered iridates, a combination of spin-orbit interaction and electron cor-
relations may be sufficient to drive the Mott insulating ground state.

Another interesting question is how spin-orbit interaction impacts the superconducting ground state in Sr$_2$RuO$_4$. It has been suggested theoretically that ferromagnetic interactions would result in a chiral p-wave superconducting state driven by the d$_{xy}$-dominated γ-band. By contrast, if superconductivity is driven by the d$_{xz}$/d$_{yz}$-dominated α- and β-bands, then spin-orbit coupling lifts the ground state degeneracy in favor of a helical p-wave symmetry. These considerations were, however, based on the assumption that spin-orbit interaction is weak compared to the Fermi energy $E_F$. It is hence useful to compare the energy scales of superconductivity, spin-orbit coupling and the Fermi energy $E_F$. As $T_c = 1.5$ K, the superconducting gap amplitude is expected in the ~1 meV range. The Fermi energy $E_F = [h/(4\pi k_B)](A_k/m^*)^{39}$ can be estimated from the Fermi surface area $A_k$ and the quasiparticle mass $m^*$. For the γ-band, quantum oscillation experiments yield oscillation frequency $hA_k/2e\pi = 18$ kT and $m^* = 16m_e$, where $m_e$ is the free electron mass. These values imply that $E_F \sim 150$ meV, and as expected $k_BT_c/E_F \ll 1$. Similar values of $E_F$ are found for the α- and β-bands. Strong electron correlations therefore drive even the γ-electrons into the regime $\lambda_{so} \sim E_F$, where spin $S_z$ and orbital $L_z$ are no longer good quantum numbers. Cooper pairs in Sr$_2$RuO$_4$ therefore have to be composed of electronic pseudo-spins. If realized, the same would likely be true for superconductivity in layered iridates.

VIII. CONCLUSIONS AND OUTLOOK

In summary, we have performed a combined light absorption and oxygen K-edge resonant inelastic X-ray spectroscopy study of the ruthenates (Ca,Sr)$_2$RuO$_4$. Special attention was given to the Ru t$_2g$ states, probed through their hybridization with oxygen p-orbitals. Both the oxygen K-edge RIXS and absorption spectra find a consistent description within a simple model that includes crystal field splitting and spin-orbit coupling $\lambda_{so} \approx 200$ meV. In this picture, the main new observation – RIXS excitations at $\sim 350$ meV – is interpreted as holes moving across spin-orbit split t$_2g$ states.

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