Spin-Orbit Excitons in a Correlated Metal: Raman Scattering Study of Sr₂RhO₄

Lichen Wang[®],^{1,*} Huimei Liu,^{1,2,†} Valentin Zimmermann[®],¹ Arvind Kumar Yogi[®],^{1,3} Masahiko Isobe[®],¹

Matteo Minola⁰,¹ Matthias Hepting⁰,^{1,‡} Giniyat Khaliullin⁰,¹ and Bernhard Keimer⁰,[§]

¹Max Planck Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

²Institute for Theoretical Solid State Physics and Würzburg-Dresden Cluster of Excellence ct.qmat,

IFW Dresden, Helmholtzstrasse 20, 01069 Dresden, Germany

³UGC-DAE Consortium for Scientific Research (CSR), Indore Centre, University Campus,

Khandwa Road, Indore (M.P.) 452001, India

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Using Raman spectroscopy to study the correlated 4*d*-electron metal Sr_2RhO_4 , we observe pronounced excitations at 220 meV and 240 meV with A_{1g} and B_{1g} symmetries, respectively. We identify them as transitions between the spin-orbit multiplets of the Rh ions, in close analogy to the spin-orbit excitons in the Mott insulators Sr_2IrO_4 and α -RuCl₃. This observation provides direct evidence for the unquenched spin-orbit coupling in Sr_2RhO_4 . A quantitative analysis of the data reveals that the tetragonal crystal field Δ in Sr_2RhO_4 has a sign opposite to that in insulating Sr_2IrO_4 , which enhances the planar *xy* orbital character of the effective J = 1/2 wave function. This supports a metallic ground state, and suggests that *c*-axis compression of Sr_2RhO_4 may transform it into a quasi-two-dimensional antiferromagnetic insulator.

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Ever since the seminal work of Mott [1], correlationdriven metal-insulator transitions have been a major focal theme of solid-state research. A multitude of electronic phases-including unconventional magnetism, charge order, and superconductivity-have been identified in proximity to the Mott transition of complex materials, and increasingly elaborate models have been devised for their theoretical description [2,3]. Spectroscopy provides some of the most powerful diagnostic abilities of the strength and influence of electronic correlations close to a metal-insulator transition, as epitomized by the singleorbital Hubbard model [4]. In its insulating state, all electrons are bound to atomic sites and can propagate incoherently via excited states with unoccupied and doubly occupied sites. In the metallic state, coherent quasiparticle bands appear at the Fermi level, but the atomic states remain visible as incoherent Hubbard bands [5]. The intensity ratio between coherent and incoherent features in the spectral function can be used to assess the proximity to the metal-insulator transition. Experimental realizations of the single-orbital Hubbard model are rare, however, and in materials for which the Hubbard model is believed to be relevant (such as the cuprate and nickelate superconductors with one hole in the *d*-electron shell), the Hubbard bands tend to overlap with electronic interband transitions, thus confounding spectroscopic studies.

Recent attention has turned to correlated-electron materials with multiple active d orbitals, which are more common and can spawn an even larger variety of electronic phases. The excitation spectra of Mott-insulating systems with multiple active d orbitals are characterized by intraatomic multiplets generated by the interplay of crystal field, Hund's rule, and spin-orbit interactions; prominent examples are Mott-insulating iridates and ruthenates [6–9]. In metallic systems, the coherent quasiparticles form multiple Fermi surfaces, which are subject to a complex set of instabilities as demonstrated by recent research on ironbased superconductors [10]. Owing to the complex electronic structure of correlated multiband metals, research has largely focused on the ground state and low-energy fermionic excitations near the Fermi level, whereas at least close to a metal-insulator transition, much of the spectral weight is believed to be concentrated in incoherent remnants of atomic multiplet excitations-analogs of the Hubbard bands in single-orbital compounds.

Here we report the observation of such incoherent spectral features in a carefully selected multiorbital *d*-electron metal. The system we have chosen is Sr_2RhO_4 , a square-planar compound with electronically active Rh ions in the $4d^5$ configuration—i.e., one hole in the t_{2g} subshell of the *d*-electron manifold in the nearly octahedral crystal field. Prior angle-resolved photoemission (ARPES) and quantum transport experiments have reported multiple Fermi surface sheets with sharp fermionic quasiparticles, as expected for a

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stoichiometric metal free of any major sources of electronic disorder [11–18]. In contrast to the more widely studied unconventional superconductor Sr_2RuO_4 (with Ru in $4d^4$ configuration) [19-21], tilt distortions of the RhO₆ octahedra narrow the electronic bands, thus effectively enhancing the correlation strength. Conversely, the isoelectronic compound Sr_2IrO_4 (with Ir in $5d^5$ configuration) is Mott insulating because the larger spin-orbit coupling (SOC) of the 5d electrons splits the t_{2g} manifold into a pseudospin J = 1/2 ground state and J = 3/2 excited state, thus further narrowing the electronic bands [22]. Owing to the single hole in the t_{2q} manifold, the intra-atomic multiplet excitations of Sr_2IrO_4 comprise a simple set of $J = 1/2 \rightarrow 3/2$ excitations (termed "spin-orbit excitons") that are optically inactive but observable by Raman and resonant x-ray scattering spectroscopies [6,7]. We have used polarizationresolved electronic Raman scattering to detect incoherent but well-defined spin-orbit exciton features in Sr₂RhO₄, and show that quantitative analysis of the Raman spectra is a rich source of information on the electronic structure of this strongly correlated metal, complementary to prior experiments on the coherent fermionic quasiparticles.

Experiment.—The single crystals of Sr₂RhO₄ were grown with the optical floating-zone technique (see the Supplemental Material [23] for experimental details). We have collected Raman data covering the energy range up to about 500 meV with four different incident and scattered photon polarizations: xx, x'x', x'y', and xy, corresponding to the $A_{1g} + B_{1g}$, $A_{1g} + B_{2g}$, $B_{1g} + A_{2g}$, and $B_{2g} + A_{2g}$ representations of the D_{4h} point group [26], respectively. The antisymmetric A_{2a} contribution should be negligible here, as there is no clear sign of time-reversal and/or chiral symmetry breaking in Sr_2RhO_4 . We thus assume that x'y' and xyrepresent B_{1g} and B_{2g} spectra, respectively. The observed sharp phonon peaks (Fig. 1 and [23]) are consistent with a factor-group analysis and similar to phonon spectra in the isostructural Sr₂IrO₄ [27], and are indicative of the high quality of our crystals. Whereas most of the data were taken with the 632.8 nm excitation line of a He-Ne laser, similar spectra were observed with the 532 nm line [23].

Figure 1 shows that the Raman scattering intensity in Sr_2RhO_4 is dominated by excitations centered around 230 meV. The peaks are rather broad (the widths are about 150 meV at 7 K) yet well-defined even at room temperature [23]. The *xx* channel comprising both A_{1g} and B_{1g} signals exhibits the largest intensity. Since the $xy:B_{2g}$ signal is weak, the x'x' channel $A_{1g} + B_{2g}$ is dominated by the A_{1g} spectra. For the quantitative analysis of the data, we extract the pure A_{1g} spectra from the raw data in two different ways, as xx - x'y' and x'x' - xy, which yield nearly identical results [23]. Their average is presented in Fig. 2, along with the $x'y': B_{1g}$ spectra. Compared to the B_{1g} symmetry, the A_{1g} signal is stronger, and its peak position is lower by about 20 meV.



FIG. 1. Raman spectra taken with the 632.8 nm (1.96 eV) excitation line in different scattering geometries. Sharp peaks below 100 meV are phonons. The dashed lines at 220 meV and 240 meV indicate the peak positions for broad electronic scattering signals. Small peaks between 100 and 170 meV can be attributed to multiphonons, as in other transition metal oxides (see, e.g., Ref. [28]). Left inset: the light polarization directions with respect to Rh ions (black dots). Right inset: the *xx* spectra measured at 7 K and 295 K.

The spectra in Figs. 1 and 2 are highly unusual for clean metals with well-defined quasiparticles [13], which typically only exhibit a featureless electronic continuum (as exemplified by Sr_2RuO_4 [29,30].) A magnetic (e.g., two-magnon [26,31]) origin of the strong Raman scattering at



FIG. 2. Experimental spectra in A_{1g} and B_{1g} channels (gray lines) after extracting the low-energy phonon peaks. The fit curves (black) include a Lorenztian tail of the elastic line (thin gray), and the spin-orbit exciton bands *B* (blue) and *C* (red). Their peak positions and intensities are calculated theoretically (see text), while the Lorenztian linewidths are adjusted to fit the experimental data.

230 meV is unlikely, as the largest intensity is seen in the A_{1g} channel with parallel polarization. On the other hand, Raman features with closely similar line shapes were observed in the Mott insulators Sr_2IrO_4 [6] and α -RuCl₃ [32,33], and assigned to transitions between the intra-ionic J = 1/2 and J = 3/2 states [7]. These spin-orbit excitons have been found to persist also in lightly doped metallic iridates [31,34] (although in this case, doping-induced disorder complicates the interpretation of the spectra). Moreover, the energy scale of 230 meV in Sr₂RhO₄ is very similar to the spin-orbit splitting $\frac{3}{2}\lambda$ with $\lambda \sim 160$ meV (slightly reduced from a Rh⁴⁺ free-ion value of ~190 meV [35] by covalency effects). Remarkably, spin-orbit levels in the range of 200-250 meV have been predicted by quantum chemistry calculations for Sr_2RhO_4 [36]. The above considerations have led us to develop a theory for Raman scattering from spin-orbit excitons based on a localized model, which describes most aspects of our data on a quantitative level. Note that the theory does not address the width of the excitonic profiles, which is slightly larger in Sr_2RhO_4 than in Sr_2IrO_4 [6] and α -RuCl₃ [32], likely due to interaction with fermionic quasiparticles.

Theory.-In an octahedral crystal field, the Rh4+ ion contains a single hole in the t_{2g} orbital level, hosting spin s = 1/2 and effective orbital l = 1 moments. The crystal field induced by the tetragonal distortion, $\frac{1}{3}\Delta(n_{yz}+n_{zx}-2n_{xy})=\Delta(l_z^2-\frac{2}{3})$, splits this level into an xy singlet and an xz/yz doublet [Fig. 3(a)]. On the other hand, the spin-orbit coupling $\lambda(l \cdot s)$ forms multiplets with total angular momentum J = 1/2 and 3/2. The combined action of these interactions results in a level structure comprising the ground state Kramers doublet A with an effective spin 1/2, and two excited doublets B and C derived from the J = 3/2 quartet states with $J_z = \pm 3/2$ and $J_z = \pm 1/2$, respectively; see Fig. 3(b). Explicit forms of the corresponding spin-orbit entangled wave functions can be found in the Supplemental Material [23], and their spatial shapes at representative Δ/λ values are illustrated in Fig. 3(c). With respect to the ground state A level, the energies of B and C doublets read as

$$E_{\rm B} = \frac{3}{4}\lambda + \frac{1}{2}\Delta + \frac{1}{2}R, \qquad E_{\rm C} = R,$$
 (1)

where $R = \sqrt{\frac{9}{4}\lambda^2 + \Delta^2 - \lambda\Delta}$. For $\Delta > 0$ ($\Delta < 0$), the B level is higher (lower) than the C level; see Fig. 3(c).

As mentioned above, the spin-orbit excitons interact with the underlying electronic continuum, so that their spectral features are broadened. In the following, we focus on the polarization dependence of the exciton peak energies and intensities, leaving the line shape effects aside. To this end, we adopt the Fleury-Loudon theory, which describes the Raman scattering intensity in terms of spin exchange



FIG. 3. Energy levels for the t_{2g} hole in tetragonal crystal field (a) without and (b) with spin-orbit coupling. In the hole language used here, $\Delta > 0$ corresponds to the oxygen octahedra with longer $z \parallel c$ axis as in Sr₂RhO₄. (c) Excitation energies E_B and E_C as a function of Δ/λ . The vertical gray stripes at $\Delta/\lambda \sim 0.4$ and $\Delta/\lambda \sim -0.5$ correspond to Sr₂RhO₄ with $\lambda \simeq 154$ meV and $\Delta \simeq 60$ meV (this work), and Sr₂IrO₄ with $\lambda \simeq 380$ meV and $\Delta \simeq -190$ meV (Ref. [7]), respectively. The spatial shapes of the t_{2g} hole wave functions in these two compounds are displayed; note a more flat, *xy*-type shape of the ground-state wave function in Sr₂RhO₄, in contrast to more out-of-plane *xz/yz* character in Sr₂IrO₄.

operators, with proper form factors encoding the scattering geometry [26,37].

In the present context, the Raman light scattering involves two subsequent optical transitions of *d* electrons between neighboring Rh ions, and creates a spin-orbit exciton in the final state, as illustrated in Fig. 4. As exactly the same intersite hoppings via doubly occupied intermediate states also appear in the derivation of the spinorbital exchange interactions between ions, the Raman scattering operator \mathcal{R} can be expressed via the corresponding exchange Hamiltonian. Based on this observation [37], we can write down the Raman operators of A_{1g} and B_{1g} symmetries as $\mathcal{R}_{A_{1g}/B_{1g}} = (\mathcal{R}_x \pm \mathcal{R}_y)$, where \mathcal{R}_γ with $\gamma \in \{x, y\}$ is the spin-orbital exchange operator acting on nearest-neighbor $\langle ij \rangle || \gamma$ bonds. For the t_{2g} orbital systems with spin one-half, it has the following structure (neglecting Hund's coupling corrections) [23,38]:

$$\mathcal{R}_{\gamma} \propto \sum_{\langle ij \rangle_{\gamma}} \left[(4\mathbf{s}_i \cdot \mathbf{s}_j + 1) \mathcal{O}_{ij}^{(\gamma)} - l_{\gamma i}^2 - l_{\gamma j}^2 + \tau^2 (l_{zi}^2 + l_{zj}^2) \right], \quad (2)$$

where the orbital operator $\mathcal{O}_{ij}^{(x)} = [(1 - l_y^2)_i(1 - l_y^2)_j + (l_y l_z)_i(l_z l_y)_j] + [y \leftrightarrow z]$, and $\mathcal{O}_{ij}^{(y)}$ follows by symmetry (replacing $y \rightarrow x$). The orbital angular momentum operators $l_x = i(d_{xy}^{\dagger}d_{zx} - d_{zx}^{\dagger}d_{xy})$, etc.

In Eq. (2), all terms but the last originate from the t_{2g} - t_{2g} orbital hoppings [38], while the τ term stands for a contribution from nondiagonal t_{2g} - e_{g} hopping \tilde{t} . Relative



FIG. 4. Schematic of (a),(b) t_{2g} - t_{2g} and (c) t_{2g} - e_g intersite hoppings (dashed lines) in the Raman photon-in photon-out (orange zigzag arrows) scattering process, creating spin-orbit excitations $A \rightarrow B/C$ (wavy lines) on site *i*. In the intermediate virtual state, site *j* is occupied by two holes (filled and empty circles) which experience intraionic Coulomb interaction (not shown). (d) t_{2g} - e_g hopping between d_{xy} and $d_{3x^2-r^2}$ orbitals, generated by the rotations of the oxygen octahedra around z || caxis by angle α . In Sr₂RhO₄, $\alpha = 10.5^{\circ}$ [39].

to the t_{2g} - t_{2g} hopping t, it is given by $\tau \equiv \tilde{t}/t = \sin 2\alpha (t_{pd\sigma}/t_{pd\pi})$, where α quantifies the deviation of the Rh–O–Rh bond angle from the ideal 180°; see Fig. 4(d). This contribution can be sizeable even for small α , due to the stronger σ -type overlap $t_{pd\sigma}$ between O-p and Rh- e_g orbitals, as compared to the $t_{pd\pi}$ overlap for t_{2g} states.

In general, the operator \mathcal{R}_{γ} (2) creates spin, orbital, and composite spin-orbital excitations in the Raman spectra. To proceed further, we need to express this operator in terms of the A, B, and C Kramers doublet states. The mapping onto the spin-orbit basis is straightforward (the details are provided in the Supplemental Material [23]). As a result, we obtain the Raman operators of the A_{1g} and B_{1g} symmetries, and evaluate their matrix elements corresponding to the transitions from the ground state A to the excited states B and C. Neglecting nonlocal spin correlations in paramagnetic Sr₂RhO₄, we arrive at the following intensities of the B and C excitons in the A_{1g} scattering channel:

$$A_{1g} \begin{cases} I_{\rm B} = \frac{1}{4} c_{\theta}^{6} + \frac{1}{2} c_{\theta}^{2} (1 + s_{\theta}^{2})^{2}, \\ I_{\rm C} = \frac{3}{4} s_{\theta}^{2} c_{\theta}^{2} (1 + s_{\theta}^{2})^{2} + s_{\theta}^{2} c_{\theta}^{2} (c_{\theta}^{2} + 4\tau^{2})^{2}. \end{cases}$$
(3)

In the B_{1g} channel, we obtain

$$B_{1g} \begin{cases} I_{\rm B} = \frac{5}{4} c_{\theta}^{6} + \frac{1}{2} c_{\theta}^{2} (1 + s_{\theta}^{2})^{2}, \\ I_{\rm C} = \frac{3}{4} s_{\theta}^{2} c_{\theta}^{2} (1 + s_{\theta}^{2})^{2}. \end{cases}$$
(4)

Here, $c_{\theta} \equiv \cos \theta$, $s_{\theta} \equiv \sin \theta$, and the angle $0 < \theta < (\pi/2)$ given by $\tan 2\theta = 2\sqrt{2\lambda}/(\lambda - 2\Delta)$ depends on the relative

strength of the tetragonal field Δ/λ . It decides the spatial shapes of the spin-orbit wave functions shown in Fig. 3(c), and thus determines the intersite hopping amplitudes and Raman matrix elements. The τ term contributes only to the A_{1g} intensity.

We note that within the present nearest-neighbor hopping model, the spin-orbit excitons do not contribute to the B_{2g} scattering. In reality, however, a small contribution $\propto (t'/t)^4$ to the B_{2g} signal is expected (and possibly present in Fig. 1) due to longer-range hoppings t'.

Equations (1), (3), and (4) fully determine the spin-orbit exciton peak positions and intensities in the Raman spectra, as a function of three parameters: λ , Δ , and τ . We recall that τ accounts for the t_{2g} - e_g hopping, and its value is determined by the $t_{pd\sigma}/t_{pd\pi}$ ratio (for a given angle α).

Discussion.—The above theory with $\lambda = 154 \text{ meV}$, $\Delta = 60 \text{ meV}$, and $t_{pd\sigma}/t_{pd\pi} = 1.2$ reproduces the experimental spectra (Fig. 2) very well. The deviations can be attributed to the particle-hole continuum, possible excitonphonon sidebands, and multiple excitons. Regarding the latter, we note that multiple exciton creation requires at least two subsequent intersite hoppings between the J = 1/2 and J = 3/2 levels, which are small in compounds with 180° exchange bonding. Therefore, the double-exciton peaks are not clearly visible in the perovskites Sr₂RhO₄ and Sr₂IrO₄. In contrast, such intersite hoppings are strong in Kitaev materials with 90° bonding, and pronounced double-exciton peaks have indeed been observed in α -RuCl₃ [32,33].

Both B and C excitations feed into the A_{1g} and B_{1g} channels, but with unequal spectral weights (Fig. 2). The overall peak position thus depends on the scattering geometry. The A_{1g} peak is more intense than B_{1g} due to t_{2g} - e_g hopping; the opposite is expected in Ba₂IrO₄ with no octahedral rotations.

The relative order of the A_{1g} and B_{1g} peak positions uniquely determines the sign of the tetragonal field Δ , and our data firmly exclude $\Delta < 0$ values (Supplemental Material [23]). The obtained $\Delta/\lambda \simeq 0.4$ ratio is rather small, implying that all components of the orbital moment remain unquenched. While the relative strength of Δ and λ is comparable to that in Sr₂IrO₄ with $\Delta/\lambda \simeq -0.5$ [7], the signs of Δ in these compounds are opposite, despite similar lattice structures. The difference likely originates from screening of the lattice Madelung potential (which gives a large negative Δ in Sr₂IrO₄ [36]) in metallic Sr₂RhO₄, so that the ligand field $\Delta > 0$ of the apically elongated (by 5% [40]) octahedra dominates. It should be interesting to include such screening effects in quantum chemistry calculations [36].

The positive (negative) Δ values increase (reduce) the planar *xy* orbital character of the effective J = 1/2 wave function (Fig. 3). Consequently, the in-plane effective hopping amplitude in Sr₂RhO₄ (Sr₂IrO₄) is enhanced (suppressed) from its $\Delta = 0$ value of $t_{\text{eff}} = \frac{2}{3}t$. This effect

cooperates with the reduced spin-orbit coupling to support a metallic ground state in Sr_2RhO_4 , and suggests that *c*-axis compression (changing the sign of Δ) may trigger a metalto-insulator transition.

Our results on the spin-orbit excitons with energy \sim 230 meV are complementary to ARPES data, which mostly probe coherent fermionic quasiparticles at and near the Fermi level [11,12,41,42]. Results from both probes indicate a major influence of the spin-orbit coupling on the electronic structure and dynamics. Remarkably, however, the ARPES data suggest strong orbital polarization in favor of out-of-plane xz/yz hole states, whereas the Raman data are more isotropic with preferential xy character. The coexistence of spin-orbit excitons and fermionic quasiparticles with different orbital admixtures calls for a more elaborate description of our data, for instance via a dynamical mean-field theory approach to Raman scattering [43].

In summary, using Raman spectroscopy we have observed spin-orbit excitons in Sr₂RhO₄, as a direct signature of the spin-orbit entangled nature of correlated electrons in this Fermi-liquid metal. From the polarization dependence of the exciton peaks, we have quantified the spin-orbit and tetragonal crystal field parameters, which determine the orbital shapes of the corresponding wave functions. We found that the tetragonal field in Sr₂RhO₄ increases the planar xy orbital character of the effective J = 1/2 wave function, thereby supporting the metallic ground state. This finding calls for x-ray absorption and light-polarized ARPES studies of the orbital character of the electronic bands in Sr₂RhO₄. Our results also suggest that flattening of the RhO₆ octahedra may drive Sr₂RhO₄ into a Mott-insulating state, similar to the metal-insulator transition in Ca2RuO4 [44]. More generally, our results demonstrate that coherent fermionic quasiparticles and incoherent, atomiclike excitations can coexist in multiorbital metals, and that detailed analysis of the latter features can yield interesting insights into the microscopic interactions underlying the electronic structure. The experiments we have presented on a disorder-free system with a relatively simple electronic structure thus open up a potentially rich source of information on electronic correlations in other multiband metals.

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L. W. and H. L. contributed equally to this letter.

*lichen.wang@fkf.mpg.de †huimei.liu@ifw-dresden.de †hepting@fkf.mpg.de \$b.keimer@fkf.mpg.de

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