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Electronic excitations in $5d^4$ $J = 0$ Os⁴⁺ halides studied by RIXS and optical spectroscopy

P. Warzanowski,¹ M. Magnaterra,¹ P. Stein,¹ G. Schlicht,¹ Q. Faure,^{2,3} Ch. J. Sahle,² T. Lorenz,¹

P. Becker,⁴ L. Bohatý,⁴ M. Moretti Sala,⁵ G. Monaco,⁶ P.H.M. van Loosdrecht,¹ and M. Grüninger¹

¹ Institute of Physics II, University of Cologne, 50937 Cologne, Germany

²*ESRF, The European Synchrotron, 71 Avenue des Martyrs, CS40220, 38043 Grenoble Cedex 9, France*

3 *Laboratoire Leon Brillouin, CEA, CNRS, Universit ´ e Paris-Saclay, CEA-Saclay, 91191 Gif-sur-Yvette, France ´*

4 *Sect. Crystallography, Institute of Geology and Mineralogy, University of Cologne, 50674 Cologne, Germany*

⁶*Dipartimento di Fisica e Astronomia "Galileo Galilei", Universita di Padova, I-35121 Padova, Italy `*

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We demonstrate that the cubic antifluorite-type halides K_2OsCl_6 , K_2OsBr_6 , and Rb_2OsBr_6 are excellent realizations of non-magnetic $J = 0$ compounds. The magnetic susceptibility shows the corresponding Van-Vleck type behavior and no sign of defects. We investigate the electronic excitations with two complementary techniques, resonant inelastic x-ray scattering (RIXS) and optical spectroscopy. This powerful combination allows us to thoroughly study, e.g., on-site intra- t_{2g} excitations and t_{2g} -to- e_g excitations as well as inter-site excitations across the Mott gap and an exciton below the gap. In this way, we determine the electronic parameters with high accuracy, altogether yielding a comprehensive picture. In K_2OsCl_6 , we find the spin-orbit coupling constant $\zeta = 0.34$ eV, Hund's coupling $J_H = 0.43$ eV, the onset of excitations across the Mott gap at $\Delta = 2.2$ eV, the cubic crystal-field splitting 10 Dq = 3.3 eV, and the charge-transfer energy Δ_{CT} = 4.6 eV. With J_H/ζ = 1.3, K_2 OsCl₆ is in the intermediate-coupling regime. In a t_{2q} -only Kanamori picture, the above values correspond to ζ^{eff} = 0.41 eV and J_H^{eff} = 0.28 eV, which is very close to results reported for related $5d^4$ iridates. In the tetragonal phase at 5 K, the non-cubic crystal field causes a peak splitting of the $J = 1$ state as small as 4 meV. Compared to K₂OsCl₆, the bromides K₂OsBr₆ and Rb₂OsBr₆ show about 12-14 % smaller values of 10 Dq and Δ_{CT} , while the spin-orbit-entangled intra- t_{2g} excitations below 2 eV and hence ζ and J_H are reduced by less than 4%. Furthermore, the Mott gap in K_2OsBr_6 is reduced to about 1.8 eV.

The family of 5d transition-metal compounds features Mott-insulating quantum materials in which strong spin-orbit coupling plays the central role [\[1–](#page-10-0)[5\]](#page-10-1). Prominent examples are t_{2g}^5 iridates with spin-orbit entangled $J = 1/2$ moments [\[6–](#page-10-2) [8\]](#page-11-0). Compounds with edge-sharing $IrO₆$ octahedra have been predicted to show bond-directional Kitaev-type exchange couplings [\[9\]](#page-11-1). This has raised hopes to realize the Kitaev model on tricoordinated lattices, where strong exchange frustration yields an intriguing quantum spin liquid [\[10](#page-11-2)[–12\]](#page-11-3). Experimentally, the dominant bond-directional character of exchange interactions has been demonstrated for honeycomb $Na₂IrO₃$ [\[13,](#page-11-4) [14\]](#page-11-5). Remarkably, Kitaev exchange has been found to have a very different effect for $J = 1/2$ moments on an *fcc* lattice with corner-sharing $IrO₆$ octahedra as realized in the double perovskite Ba_2CeIrO_6 . There, antiferromagnetic Kitaev coupling counteracts the geometric frustration of isotropic Heisenberg exchange [\[15\]](#page-11-6). For face-sharing $IrO₆$ octahedra as in the Ir₂O₉ dimer compounds $Ba₃MIr₂O₉$, spin-orbit coupling competes with strong intra-dimer hopping that yields quasimolecular orbitals. Still, RIXS studies for $M = Ce^{4+}$ and In³⁺ established the spin-orbit entangled $J_{\text{dim}} = 0$ and $J_{\text{dim}} = 3/2$ character of the respective quasimolecular magnetic moments [\[16,](#page-11-7) [17\]](#page-11-8).

For a t_{2g}^4 configuration in cubic symmetry, dominant spinorbit coupling ζ is expected to yield a non-magnetic $J=0$ ground state. However, strong exchange interactions give rise to a dispersion of magnetic excited states, and if the dispersion is large enough, these may condense and drive magnetism of excitonic Van-Vleck-type that is also called singlet magnetism [\[18](#page-11-9)[–21\]](#page-11-10). In this scenario, a magnetic amplitude mode equivalent to a Higgs mode is expected, which has been proposed for

antiferromagnetic Ca_2RuO_4 [\[18,](#page-11-9) [22\]](#page-11-11). In this layered $4d^4$ compound, one has to consider the tetragonal crystal-field splitting Δ_{CF} [\[21,](#page-11-10) [23](#page-11-12)[–28\]](#page-11-13) and that spin-orbit coupling is smaller than in 5d materials such that the physics is governed by the ratio $\Delta_{\rm CF}/\zeta > 2$ [\[29,](#page-11-14) [30\]](#page-11-15). For dominant non-cubic $\Delta_{\rm CF}$, d^4 compounds turn into spin $S = 1$ magnets. Considering (nearly) cubic symmetry, the local intra- t_{2q} excitations from the $J=0$ state have been studied by RIXS in $4d^4$ K₂RuCl₆ [\[31\]](#page-11-16) and in the $5d^4$ Ir⁵⁺ double perovskites A_2B IrO₆ (A = Ba, Sr; B = Y, Gd, Lu, Sc) [\[32–](#page-11-17)[36\]](#page-11-18). Among these, $Sr₂YIrO₆$ and $Ba₂YIrO₆$ were reported to host magnetic order [\[37,](#page-11-19) [38\]](#page-11-20) which has been attributed to the presence of $5d^5$ Ir⁴⁺ and $5d^3$ Ir⁶⁺ defects [\[39\]](#page-12-0). Pyrochlore $Yb_2Os_2O_7$ with $5d^4$ Os^{4+} ions exhibits a trigonal distortion and a defect-induced magnetic response [\[40\]](#page-12-1). For K_2RuCl_6 , the possible role of vibronic effects has been discussed [\[41\]](#page-12-2).

Here, we employ RIXS at the Os L_3 edge and optical spectroscopy to study stoichiometric single crystals of the $5d⁴$ halides K_2OsCl_6 and A_2OsBr_6 with $A = K$ and Rb. In the magnetic susceptibility, we do not find any indication of magnetic defects. Our results establish these materials as a reference for $J = 0$ systems in the intermediate regime between LS coupling for $J_H/\zeta \to \infty$ and jj coupling for $J_H/\zeta \to 0$. We show that $J_H/\zeta = 1.3$ is equivalent to $J_H^{\text{eff}}/\zeta^{\text{eff}} = 0.8$ in the Kanamori scheme [\[42\]](#page-12-3), which considers only t_{2g} orbitals. Our result for $J_H^{\text{eff}}/\zeta^{\text{eff}}$ is in excellent agreement with the values reported for $5d⁴$ iridates [\[32](#page-11-17)[–35\]](#page-11-21). The antifluorite-type Os compounds combine several properties which are advantageous for a precise determination of the electronic parameters. At room temperature, they show cubic symmetry [\[43–](#page-12-4) [45\]](#page-12-5), and for the purpose of studying the local electronic ex-

⁵*Dipartimento di Fisica, Politecnico di Milano, I-20133 Milano, Italy*

FIG. 1. Left: Face-centered cubic crystal structure of A_2 Os X_6 at 300 K. The Os X_6 octahedra (X = Cl, Br) are plotted in red and the A^+ ions ($A = K$, Rb) in gray. Top right: sketch of the first Brillouin zone of the *fcc* lattice with the high-symmetry points Γ , X, K, and L. Lower right: photos of a K_2OsBr_6 crystal and of the thin, transparent sample of K_2OsCl_6 that has been studied in infrared transmittance. The size of the latter amounts to approx. $0.5 \text{ mm} \times 0.3 \text{ mm} \times 0.12 \text{ mm}$.

citations the compounds may be viewed as being composed of undistorted, well separated $\text{Os}X_6$ octahedra with, to first approximation, negligible interactions between them. This yields well-defined, narrow RIXS peaks even at high energy such as the charge-transfer excitations at 4.6, 5.7, and 8.0 eV in K_2OsCl_6 , allowing for a straightforward determination of the charge-transfer energy $\Delta_{\textrm{CT}}$.

For the study of orbital and electronic excitations in Mott insulators, RIXS and optical spectroscopy are complementary techniques. In the case of inversion symmetry, RIXS at the transition-metal L edge is in particular sensitive to local, parity-conserving excitations between d orbitals $[29, 31]$ $[29, 31]$ [34,](#page-11-22) [40,](#page-12-1) [46\]](#page-12-6). In contrast, optical spectroscopy is most sensitive to electric-dipole-active absorption features such as intersite excitations across the Mott gap or excitons [\[30,](#page-11-15) [47,](#page-12-7) [48\]](#page-12-8), while local excitations between d orbitals mainly contribute in a phonon-assisted process, i.e., they become electric-dipoleactive by the simultaneous excitation of a symmetry-breaking phonon [\[49](#page-12-9)[–52\]](#page-12-10). Interesting examples studied by both techniques are, e.g., the $3d^2$ vanadates RVO_3 [\[48,](#page-12-8) [52,](#page-12-10) [53\]](#page-12-11) or the excitations from $J = 1/2$ to 3/2 in the $4d^5$ Kitaev material α - $RuCl₃$ [\[54](#page-12-12)[–56\]](#page-12-13). In the infrared data, weak phonon-assisted absorption features can only be detected in the transparent range with excitation energies smaller than the Mott gap. In comparison, RIXS offers the possibility to observe the corresponding orbital excitations also for larger excitation energies but with limited energy resolution. At the Os L_3 edge with an incident energy $E_{\text{in}} = 10.870 \text{ keV}$, we achieve a resolution $\delta E = 63$ meV, i.e., $\delta E/E_{\text{in}} \approx 6 \times 10^{-6}$. In contrast, the Fourier spectrometer employed for infrared measurements offers a resolution better than 0.1 meV. Accordingly, it is more difficult to determine the electronic parameters by using only one of the two techniques, as discussed, e.g., for RIXS on $Yb_2Os_2O_7$ [\[40\]](#page-12-1) or infrared spectroscopy on K_2OsCl_6 [\[57\]](#page-12-14). For K_2OsCl_6 , we will show below that the combination of the two techniques resolves all ambiguities.

FIG. 2. Magnetic susceptibility χ of K_2OsCl_6 and K_2OsBr_6 . Both compounds show dominant temperature-independent Van-Vleck paramagnetism. For comparison, we show χ of the $J = 1/2$ iridium sister compounds with a sizable Curie-Weiss contribution.

I. SINGLE-CRYSTAL GROWTH AND CRYSTAL **STRUCTURE**

Single crystals of K_2OsCl_6 and of the bromides A_2OsBr_6 with $A = K$ and Rb were grown starting from commercially available dihydrogen hexahalogenoosmate (IV) H₂OsCl₆, resp. H_2OsBr_6 and the respective halide KCl or ABr. The educts were dissolved in stoichiometric ratio in diluted hydrochloric (resp. hydrobromic) acid. For the potassium compounds, single crystals of several mm size were achieved by slow, controlled evaporation of the solvent at 293 K during a typical growth period of one to two weeks. For the Rb compound, crystals were of sub-mm size due to the low solubility. Examples of K_2OsBr_6 and K_2OsCl_6 are shown in Fig. [1.](#page-1-0)

At room temperature, these K_2PtCl_6 -type compounds show a cubic crystal structure with space group $Fm\overline{3}m$ [\[43–](#page-12-4)[45\]](#page-12-5), see Fig. [1.](#page-1-0) The Os^{4+} ions are located on an *fcc* lattice. The stoichiometry of all three compounds has been verified on small crystals by x-ray diffraction in the cubic phase [\[58\]](#page-12-15). At 45 K, K_2OsCl_6 exhibits a phase transition to a tetragonal phase [\[44\]](#page-12-16). For K_2OsBr_6 , the structural transition at 220 K to a phase with tetragonal symmetry is followed by a phase transition to a monoclinic phase at 200 K [\[45\]](#page-12-5).

II. MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility χ of K₂OsCl₆ and K₂OsBr₆ is plotted in Fig. [2.](#page-1-1) We observe a temperature-independent susceptibility without any indication of a Curie-Weiss contribution of defects. The constant value $\chi = 7.5 \cdot 10^{-4}$ emu/mol can be attributed to a dominant Van-Vleck term and a small diamagnetic contribution of the closed shells of K^+ , Os^{4+} , Cl[−], and Br[−], $\chi = \chi_{VV} + \chi_{dia}$. Via tabulated values [\[59\]](#page-12-17), we estimate $\chi_{\text{dia}}^{\text{Cl}} = -2.1 \cdot 10^{-4}$ emu/mol and $\chi_{\text{dia}}^{\text{Br}} = -2.7 \cdot$ 10[−]⁴ emu/mol. This yields experimental values of the Van-Vleck contribution of $\chi_{VV}^{\text{Cl}} = 9.6 \cdot 10^{-4}$ emu/mol and $\chi_{VV}^{\text{Br}} = 10.2 \cdot 10^{-4} \text{ emu/mol}.$

Our spectroscopic data establish a $J = 0$ ground state of the $5d⁴$ configuration of Os⁴⁺, cf. Sect. [IV.](#page-2-0) The corresponding Van-Vleck susceptibility is given by

$$
\chi_{\rm VV} = \frac{N}{V} 2\mu_B^2 \sum_n \frac{|\langle n|L_z + gS_z|0\rangle|^2}{E_n - E_0},\tag{1}
$$

where $|0\rangle$ and $|n\rangle$ denote the ground state and excited states, respectively, $E_n - E_0$ is the respective energy difference, S_z and L_z refer to the z components of spin and orbital angular momentum, μ_B is the Bohr magneton, and N/V denotes the density of Os ions. In the most simple picture, one can consider only the matrix elements from the $J = 0$ ground state to the lowest excited state, the $J = 1$ triplet, assuming that all other excitation energies are infinite. The corresponding matrix element equals $|\langle 1 | L_z + gS_z | 0 \rangle|^2 = 6$. With an excitation energy of 0.35 eV (see below), this yields $\chi_{VV}^{J=1} = 11 \cdot 10^{-4}$ emu/mol. As a more sophisticated alternative, we calculate the matrix elements via *Quanty* [\[60,](#page-12-18) [61\]](#page-12-19), using the electronic parameters that result from our thorough analysis of the spectroscopic data discussed below. For the 209 possible excited states of a $5d^4$ configuration, we find that only two states contribute significantly. About 90 % arise from the $J = 1$ state at about 0.35 eV, while 10 % stem from a state with one electron in the e_a orbitals at about 3.5 eV. The two matrix elements are similar, hence the contribution of the second term is suppressed by about a factor 10 due to the higher excitation energy. We find $\chi_{VV,mod}^{\text{Cl}} = 8.8 \cdot 10^{-4}$ emu/mol and $\chi_{VV,mod}^{\text{Br}} =$ 8.6 · 10⁻⁴ emu/mol, in reasonable agreement with the experimental result.

III. SPECTROSCOPIC MEASUREMENTS

All RIXS experiments were performed at beamline ID20 of the European Synchrotron Radiation Facility. Incident photons from three consecutive U26 undulators were monochromatized by a Si(111) high-heat-load monochromator and either a successive Si(664) backscattering-channel-cut or a Si(311) channel-cut post-monochromator at 10.870 keV with a final bandwidth of 18 meV or 0.29 eV, respectively. The monochromatic X-ray beam was focused by a mirror system in Kirkpatrick-Baez geometry to $8 \times 50 \,\mu m^2$ (V \times H) at the sample position. Incident π polarization in the horizontal scattering plane was used. We specify the transferred momentum q in reciprocal lattice units. First, we studied the resonance behavior of K_2OsCl_6 at the Os L_3 edge by measuring lowenergy-resolution RIXS spectra with the incident energy in the range from 10.866 to 10.880 keV. Then, the incident energy was tuned to 10.870 keV to maximize the intra- t_{2q} excitations. RIXS spectra were measured using the 2 m analyzer/detector arm of the spectrometer. The $Si(6,6,4)$ reflection of a diced Si(5,5,3) analyzer crystal was utilized in conjunction with a pixelated area detector [\[62](#page-12-20)[–64\]](#page-12-21). The overall energy resolution of the setup was 63 meV for the high-energy-resolution spectra and 0.29 eV for the low-energy-resolution spectra, respectively, as estimated by the full width at half maximum of quasielastic scattering from a piece of adhesive tape. To determine the energy-loss scale of the spectrometer, we first define its origin at the center of mass of the rocking curve of a diced Si(664) analyzer crystal using quasielastic scattering from a piece of adhesive tape. Then, the increment of the scale is determined mainly by the analyzer Bragg angle and detector position. The combination of RIXS and optics allows us to examine the accuracy of this approach up to high energies. Comparing the excitation energy of a RIXS peak with the corresponding feature in the optical data at 2117 meV (see below), we find that the two values agree within about 1 %. This excellent result is in line with a previous study of the precision of the RIXS energy scale for energies up to 150 meV [\[65\]](#page-12-22). For a consistent analysis, we have anchored the RIXS energy loss scale using the optical value of 2117 meV. The RIXS measurements were performed using a dynamic helium gas flow cryostat as described elsewhere [\[66\]](#page-12-23). RIXS data were collected at 20 K and 300 K on a (111) surface, with (001) and (110) lying in the horizontal scattering plane. All RIXS spectra are corrected for energy-dependent self absorption [\[67\]](#page-12-24).

Infrared transmittance measurements in the energy range from 0.1 to 2.5 eV were performed using a Bruker IFS 66/v Fourier-transform spectrometer equipped with a continuousflow ⁴He cryostat. The transmittance $T(\omega)$ was measured at several temperatures in the range from 5 to 300 K. We employed thin plane-parallel samples with a cubic (111) surface. The sample of K_2OsCl_6 was lapped to a suitable thickness and polished with $CeO₂$ in propanol, while the sample of K_2OsBr_6 was measured as grown. The sample thickness amounts to $d = 120(5) \mu m$ for K₂OsCl₆ and $d = 170(7) \mu m$ for K_2OsBr_6 . We determined the complex optical conductivity $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ from the complex index of refraction $n(\omega) + i\kappa(\omega)$, which, in turn, can be derived from $T(\omega)$. The imaginary part $\kappa(\omega)$ depends sensitively on the absolute value of $T(\omega)$. In the transparent range with $\kappa \ll n$, the real part $n(\omega)$ is nearly constant and can be obtained from the period of the Fabry-Pérot interference fringes which arise from multiple reflections within the sample. To study the optical response in the non-transparent range above the Mott gap, we performed ellipsometry measurements on K_2OsCl_6 at 300 K in the range from 1 to 6 eV using a Woollam VASE ellipsometer.

IV. RESULTS ON K_2 OsCl₆

A. Resonance behavior

To study the resonance behavior and to maximize the RIXS intensity, we collected low-resolution RIXS spectra of K_2OsCl_6 for different incident energies at $T = 20 K$ for a transferred momentum $q = (7 7 6)$, see Fig. [3b](#page-3-0)). With the energy loss being independent of E_{in} for all of the observed RIXS peaks, we find the two distinct resonance energies $E_{\text{in}} = 10.870 \,\text{keV}$ and 10.8735 keV, as shown in Fig. [3c](#page-3-0)). These can be attributed to t_{2q} resonance and e_q resonance, i.e., resonance enhancement of the initial x-ray absorption part of the RIXS process in which a $2p$ core electron is promoted to either a t_{2g} or an e_g orbital, respectively. The difference of the two resonance energies gives a first estimate of the cubic crystal-field splitting $10 Dq \approx 3.5 \text{ eV}$. This agrees with the strong RIXS peak at about 3.5 eV energy loss that exhibits e_g

FIG. 3. Resonance behavior of K_2OsCl_6 at $T = 20 K$. a) Lowresolution RIXS spectra for incident energy $E_{\text{in}} = 10.870 \text{ keV}$ and 10.8735 keV, i.e., at t_{2g} and e_g resonance, respectively. Arrows indicate peak energies and their color the resonance behavior. b) Lowresolution resonance map of the RIXS intensity based on RIXS spectra measured with different E_{in} for $q = (7 7 6)$. c) Normalized integrated intensity of the RIXS peaks as a function of $E_{\rm in}$. The integration interval is chosen to be ± 0.4 eV around the peak energy. With the exception of the 4.6 eV peak, all peaks show either t_{2g} or e_g resonance.

resonance behavior and corresponds to an excitation from a t_{2g} orbital to an e_g orbital. Cuts of the resonance map at the two resonance energies are shown in Fig. [3a](#page-3-0)).

B. Character of RIXS features

Based on the resonance behavior, we distinguish three different kinds of excitations: intra- t_{2q} excitations, crystal-field excitations to e_g orbitals, and charge-transfer excitations. At low energy loss, up to about 2 eV, all RIXS features exhibit

 t_{2g} resonance and can be attributed to intra- t_{2g} excitations. Their excitation energies mainly reflect spin-orbit coupling ζ and Hund's coupling J_H . These intra- t_{2g} excitations will be addressed below by high-resolution RIXS measurements and optical transmission measurements. At higher energy loss, the RIXS peaks in the range from 2.7 to 4.6 eV are resonantly enhanced for $E_{\text{in}} = 10.8375 \text{ keV}$ and correspond to crystal-field excitations to e_g orbitals, $|t_{2g}^4\rangle \rightarrow |t_{2g}^3 e_g^1\rangle$. We will show below that the lowest e_g excitation at $2.7eV$ can be identified with the high-spin $S = 2$ multiplet with ⁵E symmetry. The energy of this high-spin state is reduced by Hund's coupling J_H , and the ⁵E multiplet becomes the d^4 ground state if J_H dominates over the cubic crystal-field splitting 10 Dq.

At still higher energy loss, we observe charge-transfer excitations, $|5d_{\rm Os}^4 3p_{\rm Cl}^6\rangle \rightarrow |5d_{\rm Os}^5 3p_{\rm Cl}^5\rangle$. The peaks at 4.6 eV and 5.7 eV both show t_{2q} resonance and hence can be attributed to $|t_{2g}^5 3p_{\text{Cl}}^5\rangle$ final states. Roughly, these two excited states with t_{2g}^5 configuration can be identified with $J = 1/2$ and 3/2 on the Os site. The peak at 8.0 eV energy loss shows e_q resonance and corresponds to excitations from Cl 3p to Os $5d e_q$ orbitals. The RIXS peak at 4.6 eV is the only one that resonates both at 10.870 keV and at 10.8735 keV, see lower panel of Fig. [3.](#page-3-0) This suggests an overlap between an on-site crystal-field excitation to e_g orbitals and the lowest charge-transfer excitation to t_{2g} orbitals. Note that the energy difference of about 3.4 eV between the peaks at 8.0 eV and 4.6 eV confirms our first rough estimate of $10 Dq \approx 3.5$ eV. Accordingly, we identify the peak energy of the lowest charge-transfer excitation with the charge-transfer energy, $\Delta_{CT} = 4.6 \text{ eV}$.

The occurrence of both t_{2g} resonance and e_g resonance behavior of charge-transfer excitations has previously been observed in, e.g., $5d^5$ K₂IrBr₆ [\[68\]](#page-12-25), $5d^4$ Yb₂Os₂O₇ [\[40\]](#page-12-1), and $5d^2$ Ba₂YReO₆ [\[32\]](#page-11-17). In the present case of K₂OsCl₆, the charge-transfer excitations are particularly well-defined and yield comparably narrow RIXS peaks. For instance the 5.7 eV peak shows a full width at half maximum of 0.6 eV. This suggests that the charge-transfer excitations to t_{2g} orbitals are well localized in non-magnetic K_2OsCl_6 , in agreement with the notion that interactions between the well separated $OsCl₆$ octahedra are very small, at least for t_{2g} orbitals.

C. Intra- t_{2g} excitations of K_2 OsCl₆ in RIXS

High-resolution RIXS spectra of the intra- t_{2q} excitations reveal four peaks at about 0.3, 0.6, 1.3, and 2.1 eV, see Fig. [4.](#page-4-0) The local, on-site character of these excitations is highlighted by the insensitivity of the peak energies to the transferred momentum q, i.e., the absence of a measurable dispersion, see Fig. [5.](#page-4-1) For a first assignment, we neglect spin-orbit coupling, $\zeta = 0$, and assume 10 $Dq = \infty$ for the cubic crystal-field splitting. In this case, the effect of the e_q orbitals on the intra- t_{2q} excitations vanishes. In a d^4 configuration there are 15 t_{2g}^4 states. Inter-orbital Coulomb interactions lift their degeneracy and yield a nine-fold degenerate ${}^{3}T_{1}$ ground state and the ${}^{1}T_{2}$, ${}^{1}E$, and ${}^{1}A_{1}$ excited states. The latter is expected at $5J_{H}$, while ${}^{1}T_{2}$ and ${}^{1}E$ show an energy of $2J_{H}$ [\[25,](#page-11-23) [42\]](#page-12-3). Note, however, that these values correspond to a t_{2g} -only scenario, i.e.

FIG. 4. Intra- t_{2g} excitations of K_2 OsCl₆ at the X point. RIXS spectra at $q = (5 5 6)$ and $(7 7 6)$ reveal four peaks at 0.3, 0.6, 1.3, and 2.1 eV with little temperature dependence. For clarity, the data are plotted with an offset. The inset highlights the ${}^{1}A_1$ peak at 2.1 eV which is suppressed for a scattering angle $2\theta = 90^\circ$, see main text.

FIG. 5. Low-energy RIXS features in K_2 OsCl₆ at 20 K at L, X , and close to Γ. The latter data were measured in the vicinity of Γ to avoid the strong contribution of Bragg scattering right at Γ. Dashed lines indicate peak positions at X . The dispersion is negligible, highlighting the local character of the intra- t_{2g} excitations. Additionally, data at (7.72 7.72 5.01) demonstrate the suppression of elastic Thomson scattering for $2\theta = 90^\circ$.

 $10 Dq = \infty$, they are not suitable to estimate J_H for realistic values of 10 Dq and ζ , as discussed below. The low-energy RIXS peaks at 0.3 eV and 0.6 eV reflect strong spin-orbit coupling, which splits the ${}^{3}T_1$ multiplet into the $J = 0$ ground state with Γ_1 symmetry and two excited states of $J = 1 \; (\Gamma_4)$ and $J = 2(\Gamma_3 + \Gamma_5)$ character, respectively. The two contributions to the $J = 2$ peak at about 0.6 eV are expected to split in energy for finite values of the cubic crystal-field splitting $10 Dq$. The fact that our RIXS data still show a single peak, cf. Fig. [5,](#page-4-1) indicates that the splitting is much smaller than the energy resolution $\delta E = 63$ meV. A finite Coulomb-induced splitting of the $J=2$ states is most relevant in cubic $5d^2$ compounds.

FIG. 6. Optical conductivity $\sigma_1(\omega)$ of K_2OsCl_6 . Note the logarithmic scales. The strong absorption features above the Mott gap at 2.2 eV have been measured by ellipsometry, while the data in the transparent range below the gap with much smaller values of $\sigma_1(\omega)$ are based on the transmittance $T(\omega)$. The latter is suppressed below the noise level above 2.2 eV and around 0.6 eV, limiting the maximum value of $\sigma_1(\omega)$ that can be determined via $T(\omega)$ for the given sample thickness. Below the Mott gap, $\sigma_1(\omega)$ shows (phononassisted) intra- t_{2g} excitations in agreement with RIXS (arrows depict the RIXS intra- t_{2g} peak energies). Additionally, $\sigma_1(\omega)$ reveals an exciton around 2.0 eV and two tiny features at about 0.95 and 1.25 eV that can be assigned to inter-site overtones of the low-energy intra t_{2g} excitations.

In these electron analogs of the two- t_{2g} -hole $5d^4$ configuration, the $J = 2$ multiplet has the lowest energy and its splitting for finite $10 Dq$ determines the local ground state, which may lead to exotic multipolar phases [\[69](#page-12-26)[–74\]](#page-13-0). For both $5d⁴$ and $5d^2$, also the degeneracy of the 1T_2 and 1E multiplets is lifted for finite 10 Dq . The asymmetric line shape of the RIXS peak around 1.3 eV at 20 K and 300 K, cf. Fig. [4,](#page-4-0) indeed indicates a finite splitting between the cubic multiplets with a weaker feature on the high-energy side, as discussed in K_2RuCl_6 and $Ba₂YIrO₆$ [\[31,](#page-11-16) [33\]](#page-11-24).

Overall, the excitation spectrum agrees with previous RIXS results on $5d^4$ iridates [\[32](#page-11-17)[–35\]](#page-11-21). RIXS data of $Yb_2Os_2O_7$ [\[40\]](#page-12-1) also show the two low-energy modes below 1 eV but the intra t_{2q} features at higher energies are hidden by a broad band that has been attributed to defects. Furthermore, the energy of the lowest excitation is much smaller in $Yb_2Os_2O_7$ due to a trig-onal distortion [\[40\]](#page-12-1). In $4d^4$ K₂RuCl₆, the equivalent of the lower three features have been observed [\[31\]](#page-11-16). The ${}^{1}A_1$ peak at 2.1 eV thus far was only observed as a very weak feature in $Sr₂YIrO₆$ [\[32\]](#page-11-17). Comparing two data sets measured at the equivalent X points (5 5 6) and (7 7 6), see Fig. [4,](#page-4-0) we find that the ${}^{1}A_1$ peak is suppressed in the latter, which has been recorded with a scattering angle 2θ close to 90° . This geometry typically is chosen to suppress elastic Thomson scattering, explaining the absence of this peak in previous measurements on $5d⁴$ compounds. An example for the successful suppression of the elastic line for $2\theta = 90^\circ$ is given by the data for (7.72 7.72 5.01) in Fig. [5.](#page-4-1) In contrast, the data for (5 5 6) were measured with $2\theta = 66^\circ$ and accordingly show a more pronounced elastic line. For $2\theta = 90^\circ$, the polarization of

FIG. 7. Temperature dependence of $\sigma_1(\omega)$ close to the Mott gap in a) K_2 OsCl₆ and b) K_2 OsBr₆. In K_2 OsCl₆, the onset of excitations across the Mott gap is observed at 2.2 eV at 5 K. This onset is washed out with increasing temperature since additional processes with simultaneous annihilation of thermally excited phonons reduce the total excitation energy in the Urbach tail. The ${}^{1}A_1$ intra- t_{2q} excitation is observed at 2.117 eV, and the many narrow lines around it correspond to phonon sidebands. In contrast to the ${}^{1}A_1$ peak, the absorption band between 1.9 and 2.1 eV has no counterpart in RIXS and can be assigned to an exciton. For comparison, the data of K_2OsBr_6 show the Mott gap at 1.8 eV at 5 K and a very similar temperature dependence. In K_2OsBr_6 , the exciton is observed around 1.6-1.7 eV.

the scattered light is perpendicular to the incident π polarization. This suggests that the ${}^{1}A_1$ feature is observable only for parallel polarization, which is supported by simulations using *Quanty* [\[60,](#page-12-18) [61\]](#page-12-19).

Our peak assignment assumes cubic symmetry and neglects the phase transition from cubic to tetragonal symmetry at 45 K. However, the RIXS data measured at 20 K and 300 K fully agree with each other, see Fig. [4,](#page-4-0) suggesting that the non-cubic splitting is much smaller than the energy resolution $\delta E = 63$ meV. This is supported by the infrared data, which were measured with $\delta E = 0.25$ meV. A thorough analysis of the temperature dependence of the infrared data reveals a noncubic splitting of about 4 meV, as discussed below.

D. Optical conductivity of K_2OsCl_6

Based on the different selection rules, optical spectroscopy and RIXS are complementary techniques. The optical conductivity $\sigma_1(\omega)$ is dominated by electric-dipole-active transitions. Considering the orbital and electronic excitations in a Mott insulator, the dominant absorption features arise from *inter-site* processes such as excitations across the Mott gap,

in our case $|d_i^4 d_j^4\rangle \rightarrow |d_i^3 d_j^5\rangle$, or charge-transfer excitations $|5d_{\text{Os}}^4 3p_{\text{Cl}}^6 \rangle \rightarrow |5d_{\text{Os}}^5 3p_{\text{Cl}}^5 \rangle$. In Fig. [6,](#page-4-2) the Mott gap corresponds to the steep rise of $\sigma_1(\omega)$ above 2.2 eV. In contrast, RIXS at the Os L edge is dominated by on-site excitations [\[32](#page-11-17)[–34,](#page-11-22) [40,](#page-12-1) [46\]](#page-12-6), as discussed above, in particular for incident energies tuned to t_{2g} resonance. In the presence of inversion symmetry, on-site crystal-field excitations such as the intra t_{2q} excitations are parity forbidden in $\sigma_1(\omega)$ but can become weakly allowed for instance in a phonon-assisted process. The corresponding spectral weight is several orders of magnitude smaller. Such weak features can only be studied for energies below the Mott gap where they are not hidden by stronger absorption processes, see Fig. [6.](#page-4-2)

1. Intersite excitations in $\sigma_1(\omega)$

Concerning the strong absorption features in $\sigma_1(\omega)$ above the Mott gap, we have to distinguish charge-transfer excitations between Cl and Os states from Mott-Hubbard excitations between Os states on different sites. One expects a larger spectral weight for the charge-transfer excitations due to the larger hopping matrix elements between Cl $3p$ and Os 5d states compared to Os inter-site hopping. Accordingly, the strongest peak at about 6 eV can be assigned to a charge-transfer excitation, in agreement with the RIXS feature at 5.7 eV. The three peaks in $\sigma_1(\omega)$ between 2 and 4 eV correspond to Mott-Hubbard excitations involving t_{2q} states, $|t_{2g_i}^4 t_{2g_j}^4\rangle \rightarrow |t_{2g_i}^3 t_{2g_j}^5\rangle$. Their energy mainly reflects the onsite Coulomb repulsion U , while the splitting is caused by J_H and ζ . In $4d^4$ Ca₂RuO₄, the relative spectral weight of these bands has been employed to estimate ζ [\[30\]](#page-11-15). Comparing $\sigma_1(\omega)$ with the RIXS data, we emphasize that the origin of the RIXS features between 2 and 4 eV is very different. RIXS shows on-site excitations to e_q states, as demonstrated by the resonance behavior. The pronounced difference between the two techniques is based on the on-site energy U that has to be paid in the optical Mott-Hubbard excitations. In $\sigma_1(\omega)$, Mott-Hubbard excitations to e_g states $|t_{2g_i}^4 t_{2g_j}^4\rangle \rightarrow |t_{2g_i}^3 (t_{2g}^4 e_g^1)_{j}\rangle$ are expected to occur roughly $10 Dq$ higher in energy than the corresponding t_{2q} bands, i.e., above about 6 eV. In K₂OsCl₆, these processes hence overlap with the charge-transfer excitations discussed above.

The onset of excitations across the Mott gap can be determined very well from the transmittance $T(\omega)$ which is strongly suppressed by the steep increase of absorption. This limits the accessible frequency window in our measurement on a single crystal with thickness $d = 120 \,\mu \text{m}$, see Fig. [6.](#page-4-2) At 5 K, the onset is at Δ = 2.2 eV. With increasing temperature, the onset shifts to lower energy, roughly to 1.9 eV at 300 K, while the slope of the steep increase in $\sigma_1(\omega)$ is reduced, see Fig. [7a](#page-5-0)). The change of slope shows that the main origin of this shift is not a possible small temperature dependence of the gap itself. The enhanced absorption below 2.2 eV predominantly can be attributed to thermally activated phononassisted excitations across the gap, i.e., the Urbach tail.

Below the Mott gap, the optical data show three additional absorption bands that are absent in the RIXS data. The

FIG. 8. Intra- t_{2g} excitations of \mathbf{K}_2 OsCl₆ in $\sigma_1(\omega)$. The panels depict excitations from $J = 0$ to a) $J = 1$, i.e, Γ_1 to Γ_4 ; b) the split $J = 2$ states, i.e., Γ_1 to Γ_5 and Γ_3 ; c) the split 1T_2 and 1E states; and d) ${}^{1}A_1$. Each panel covers a window of the same width, 120 meV. In each panel, the vertical black line denotes the bare electronic (zerophonon) energy, while the red line shows the fit result of the RIXS data. In $\sigma_1(\omega)$, the spectral weight is dominated by phonon sidebands. In b), the transmittance around the peak maximum is suppressed below the noise level, which limits the measurable range of $\sigma_1(\omega)$. In d), the horizontal black lines denote phonon sidebands at $E_{1_{A_1}} \pm E_{\text{ph}}$ with $E_{ph} = 7$, 13, and 21 meV.

strongest one is observed between 1.9 and 2.1 eV, which is very close to the Mott gap, see Fig. [7a](#page-5-0)). This feature is well separated from the 1A_1 intra- t_{2q} excitation at 2.117 eV. Its spectral weight is comparable to the weak intra- t_{2g} excitations but the absence of a corresponding RIXS feature strongly points to a different origin. We therefore assign it to an exciton with $5d^3$ and $5d^5$ configurations on neighboring Os sites. This exciton is stabilized by nearest-neighbor Coulomb attraction and may induce a local relaxation of the Cl_6 octahedra. In this case, the substructure of this absorption feature tentatively can be attributed to phonon sidebands. The exciton scenario is strongly supported by the data of K_2OsBr_6 , in which both the Mott gap and the excitonic absorption feature are shifted to lower energy by about 0.3-0.4 eV, see Fig. [7b](#page-5-0)). In contrast, the intra- t_{2g} excitation energies are very similar in K_2OsBr_6 and K_2OsCl_6 , as discussed in Sect. [V.](#page-9-0)

FIG. 9. Temperature dependence of $\sigma_1(\omega)$ across the structural **phase transition at 45 K.** a) Excitations to $J = 1$, cf. Fig. [8a](#page-6-0)). Data have been offset for clarity. b) Corresponding peak energies as a function of temperature. The peak splitting below 45 K reflects the non-cubic crystal field.

The two other below-gap absorption bands without a counterpart in RIXS are the two tiny features in $\sigma_1(\omega)$ at about 0.95 and 1.25 eV, see Fig. [6.](#page-4-2) We attribute also these bands to inter-site excitations. They can be explained as a combination and overtone of the intra- t_{2q} excitations at about 0.35 eV and 0.65 eV, i.e., the simultaneous excitation of intra- t_{2a} excitations on two neighboring Os sites. In the honeycomb compound α -RuCl₃ it has been shown that such double or even triple excitations may carry sizable spectral weight [\[55\]](#page-12-27). Due to interaction effects, the peak energies do not have to perfectly match the simple sum of the individual excitation energies.

2. *Intra-t_{2g} excitations in* $\sigma_1(\omega)$

Considering the intra- t_{2g} excitations, see Figs. [4](#page-4-0) and [8,](#page-6-0) the optical data show a rich structure where RIXS finds a single peak. Apart from the very different energy resolution, the selection rules and hence the excitation mechanisms are different. K_2OsCl_6 shows inversion symmetry, therefore the electric-dipole matrix element for a local, even-parity $d-d$ excitation vanishes. Finite spectral weight appears in $\sigma_1(\omega)$ based on either a phonon-assisted process, or in the magnetic dipole channel, or due to electric quadrupolar or higher-order moments. We exemplify this by the data on the ${}^{1}A_1$ multiplet, see Fig. [8d](#page-6-0)).

At 5 K, we find a tiny zero-phonon magnetic-dipole mode at E_{1A_1} = 2117 meV. This assignment is based on the temperature dependence of the phonon-assisted electric-dipole features observed at $E_{1A_1} \pm E_{\text{ph}}$. At 5 K, we only find modes at $E_{1A_1} + E_{\text{ph}}$ for different symmetry-breaking phonons with, e.g., $E_{\text{ph}} = 7 \text{ meV}$, 13 meV, or 21 meV, as indicated in Fig. [8d](#page-6-0)) by the right ends of the horizontal black lines. With increasing temperature, these phonon modes become thermally populated and the corresponding phonon-annihilation features

FIG. 10. Energies of on-site $d-d$ excitations for a $5d^4$ configuration in a cubic crystal field. Left: First switching on $10 Dq$ separates the t_{2g}^4 states at zero energy from $t_{2g}^3 e_g^1$ states and states with more than one electron in the e_g orbitals. Middle left: Effect of J_H for 10 $Dq = 3.3$ eV and $\zeta = 0$. Here, the ${}^{3}T_1$ multiplet forms the ground state. Middle right: Spin-orbit coupling ζ yields a $J=0$ ground state and four groups of intra- t_{2g} excitations. Red circles denote the experimental energies of K_2OsCl_6 used to determine the electronic parameters. Right: Effect of a reduction of $10 Dq$ for finite J_H and ζ , mimicking the trend from K₂OsCl₆ to K₂OsBr₆.

appear at $E_{1A_1} - E_{ph}$, strongly supporting our assignment. The spectral weight of the phonon-annihilation peaks is governed by the Boltzmann factor. Hence peaks at lower energy $E_{1A_1} - E_{ph}$ with larger E_{ph} become noticeable at higher temperature. Further features above 2150 meV correspond to a progression of phonon sidebands in a vibronic Franck-Condon picture [\[49,](#page-12-9) [51\]](#page-12-28). Typically, this rich phonon-related pattern of crystal-field excitations can be resolved in measurements of transition-metal ions substituted into a host crystal [\[57\]](#page-12-14). In single crystals, this pattern usually is washed out. Exceptions have been observed in quasimolecular crystals such as K_3NiO_2 with isolated NiO₂ units [\[50\]](#page-12-29), and the rich optical spectra of K_2OsCl_6 most probably reflect the weak interactions between well separated $OsCl₆$ octahedra. A detailed assignment of the sidebands in K_2OsCl_6 has been discussed previously [\[57\]](#page-12-14).

Similar to the analysis of the ${}^{1}A_1$ peak, we use the optical data to find the bare electronic excitation energies of the intra t_{2q} excitations at 350, 609, and 1311 meV. The value 350 meV corresponds to the energy of a feature that can be assigned to a magnetic-dipole transition from $J=0$ to 1, i.e., Γ_1 to Γ_4 [\[75\]](#page-13-1). This peak splits below 45 K, see Fig. [9](#page-6-1) and discussion below, but for comparison with theory, we employ the value at 50 K in the cubic phase. The two further energies 609 and 1311 meV are deduced from the temperature dependence of those absorption bands in $\sigma_1(\omega)$, in agreement with Ref. [\[57\]](#page-12-14).

To compare the excitation energies found in RIXS and optics, we extract the RIXS peak energies for the intra- t_{2g} excitations from a fit that uses a series of Voigt profiles. We anchor the RIXS energy scale via the optical result of 2117 meV for the highest intra- t_{2g} excitation energy, as mentioned in Sec. [III.](#page-2-1) For the other low-energy RIXS peaks, this yields

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$\Gamma_4(^3T_1)$	350	383	349	388
$\Gamma_5(^3T_1)$	609	608	604	604
$\Gamma_3(^3T_1)$		631		632
1T_2	1311	1289	1285	1267
1E		1323		1312
$^{1}A_{1}$	2117	2123		2050
5E	2721	2716	2391	2381
3E	3428	3432	3033	3042

TABLE I. Experimental and calculated excitation energies. The four intra- t_{2a} energies are taken from the optical data, the two e_a levels above 2.7 eV from RIXS. Dashes denote peaks that are not resolved in the experiment. For K_2OsCl_6 (K_2OsBr_6), the parameters of the d-shell model are $10Dq = 3.27$ eV (2.85 eV), $\zeta = 0.336$ eV (0.325 eV) , $F^2 = 3.73 \text{ eV}$ (3.90 eV) , and $F^4 = 2.22 \text{ eV}$ (2.01 eV) , which corresponds to $J_H = 0.425$ eV (0.422 eV).

341(1), 607(1), 1311(9), and 1373(140) meV, where the values in parentheses state the error bar of the fit. Remarkably, the first three values agree with the optical data within less than 10 meV, see Fig. [8.](#page-6-0) This excellent result once more corroborates the local character of these excitations. For the small shoulder around 1.37 eV, the uncertainty of the peak energy is much larger. We hence neglect this value for the further analysis.

The effect of the structural phase transition at 45 K is addressed in Fig. [9.](#page-6-1) In the antifluorite halides, a non-cubic crystal field splitting Δ_{CF} is driven by tilts and rotary or libra-tional modes of the metal-ligand octahedra [\[76](#page-13-2)[–79\]](#page-13-3). In $\sigma_1(\omega)$, the absorption band at about 0.35 eV exhibits a peak splitting below 45 K. At 5 K, we observe peaks at 347 and 351 meV, i.e., $\Delta_{\exp} \approx 4$ meV. Upon increasing temperature, the splitting gradually decreases and the two peaks merge at 45 K, see Fig. [9.](#page-6-1) A similar behavior is observed for the ${}^{1}T_{2}$ excitation at 1.3 eV (not shown). This peak splitting $\Delta_{\exp} \approx 4 \text{ meV}$ of the $J = 1$ band sets the energy scale of Δ_{CF} of K₂OsCl₆. For instance for a small tetragonal field $|\Delta_{CF}| \ll \zeta$, one finds $|\Delta_{\text{CF}}| \approx 2\Delta_{\text{exp}}$ [\[30\]](#page-11-15).

E. Calculation of energy levels of K_2OsCl_6

For the analysis of the electronic parameters, we stick to cubic symmetry. In a single-site model, the relevant parameters for the energy levels are the cubic crystal-field splitting 10 Dq between t_{2g} and e_g levels, spin-orbit coupling ζ , and the Coulomb interaction within the $5d$ shell. In spherical approximation, the latter can be described by the Slater integrals F^2 and F^4 , which are used to calculate Hund's coupling $J_H = 1/14 (F^2 + F^4)$ within the entire 5d shell [\[42\]](#page-12-3). Note that $F⁰$, equivalent to Hubbard U, does not contribute to the energy splitting for a single site with a fixed number of electrons. We calculate the multiplet energies using *Quanty* [\[60,](#page-12-18) [61\]](#page-12-19). Figure [10](#page-7-0) displays the behavior as a function of $10 Dq$, J_H , and ζ . Starting with $J_H = \zeta = 0$, the cubic crystal field yields a t_{2g}^4 ground state and raises the excitation energies of the

FIG. 11. Measured and calculated RIXS spectra of K_2OsCl_6 . Solid orange lines: Simulation based on the fit result for the full d-shell model, cf. Tab. [I.](#page-7-1) To account for the polarization dependence of the $^{1}A_{1}$ transition at 2.1 eV, we consider two different values of q. Dashed: Corresponding result of the Kanamori model for $J_H^{\text{eff}} = 0.28 \text{ eV}$ and $\zeta^{\text{eff}} = 0.41 \text{ eV}$. Peak widths are adapted to the data. Offsets have been used for clarity.

 $t_{2g}^{4-n} e_g^n$ states with $n=1$ to 4 electrons in the e_g subshell. Switching on J_H splits each of these five branches. We focus on the 15 t_{2g}^4 states. These are split into the 3T_1 ground state and the ${}^{1}T_{2}$, ${}^{1}E$, and ${}^{1}A_{1}$ excited states. The excitation energies of roughly 3/2 J_H and 4 J_H are approximately 20-25 % lower than for 10 $Dq = \infty$, reflecting a small but finite admixture of e_q character. Finally, spin-orbit coupling ζ causes a further fanning out of the energies and splits the ${}^{3}T_{1}$ ground state into three branches. In the limit of 10 $Dq = J_H = \infty$ these correspond to the eigenstates $J = 0, 1$, and 2. The intra- t_{2q} excitations within the t_{2g}^4 states form four groups of excitations that cover the range up to about 2 eV. The lowest $t_{2g}^3 e_g^1$ level corresponds to the high-spin ${}^{5}E$ state with $S = 2$. With all four spins being parallel, it is strongly favored by J_H . Even though the ${}^{5}E$ state is well separated from other levels, cf. Fig. [10,](#page-7-0) the width of this t_{2g} -to- e_g excitation is much larger than observed for the intra- t_{2g} peaks, see Fig. [11.](#page-8-0) This suggests a finite mixing with excitations across the Mott gap at 2.2 eV.

Optical studies of Os^{4+} impurities in different host crystals have reported different sets of electronic parameters [\[80–](#page-13-4) [83\]](#page-13-5). Also for optical data on single crystals of K_2OsCl_6 , it has been found that the determination of the electronic parameters is difficult [\[57\]](#page-12-14), foremost because the crystal-field splitting $10 Dq$ is hard to obtain from the optical data. The combined approach of RIXS and optics is pivotal here to resolve these ambiguities.

To determine the parameters of the d -shell model for K_2 OsCl₆, we consider the four energies of the intra- t_{2g} excitations from the optical data and the $t_{2g}^3 e_g^1$ excitations observed at 2.72 and 3.43 eV in RIXS, see red circles in Fig. [10.](#page-7-0) We neglect peaks at higher energies where an unambiguous assignment is hindered by the large number of similar excitation energies. In the fit, we minimize the absolute difference between experimental peak energies and calculated ones. This yields the parameters $10 Dq = 3.3 \text{ eV}$, $\zeta = 0.34 \text{ eV}$, $F^2 = 3.7 \text{ eV}$,

FIG. 12. Analysis based on the t_{2g} -only Kanamori model. a) The ratio $E(2)/E(1)$ varies between 1 for $J_H^{\text{eff}}/\zeta^{\text{eff}} \to 0$ and 3 for $J_H^{\text{eff}}/\zeta^{\text{eff}} \to \infty$. For K₂OsCl₆, it yields $J_H^{\text{eff}}/\zeta^{\text{eff}} \approx 3/4$. b) Comparison of the two lowest excitation energies in K_2OsCl_6 and related $5d^4$ iridates [\[32–](#page-11-17)[35\]](#page-11-21). For all of them, $J_H^{\text{eff}}/\zeta^{\text{eff}}$ is very similar.

and $F^4 = 2.2$ eV, resulting in $J_H = 0.43$ eV. Note that the value of $10 Dq$ agrees very well with our simple estimate discussed above. Figure [11](#page-8-0) compares the calculated result for direct L_3 edge RIXS [\[46\]](#page-12-6) for this parameter set with the experimental data. Overall, the peak energies as well as the relative peak intensities are well described.

The calculated excitation energies are given in Tab. [I.](#page-7-1) For the splittings of the excitations at about 0.6 and 1.3 eV, the model predicts values of 20-35 meV in cubic symmetry, which is well below the RIXS resolution limit and agrees with the energy scale observed in the optical data. Concerning the fitted energies, the deviations are less than 7 meV for four of the six energies, an excellent result. Upon a closer look, the largest deviation of 33 meV is found for the peak lowest in energy, and the intensity of this feature is underestimated. A similar observation has been reported for $4d^4$ K₂RuCl₆, where it has been discussed in terms of a possible role of vibronic coupling, i.e., a dynamic Jahn-Teller splitting of the excited $J = 1$ triplet state [\[31,](#page-11-16) [41\]](#page-12-2). For K_2OsCl_6 , our optical data resolve the vibronic sidebands in the excited states, cf. Fig. [8,](#page-6-0) but do not hint at a particular importance of vibronic effects for the feature around 0.35 eV. We find, however, that a small change in the parameters can eliminate this apparent shortcoming of the model. In a second fit, we minimize the *relative* energy difference between experiment and model. This results in the very similar parameter set $10 Dq = 3.4 \text{ eV}, \zeta = 0.34 \text{ eV},$ and $J_H = 0.42$ eV and yields the energies 358, 600, 1278, and 2139 meV for the four lowest excitations. For all four, the relative difference is less than 2.6 %, a very reasonable result. In terms of absolute energy differences, the deviation between fit and experiment is reduced to 8 meV for the peak at 350 meV while the description of the other peaks is slightly worse compared to the first fit. Finally, we have checked that inclusion of the Cl 3p orbitals and ligand-to-metal charge-transfer processes [\[60\]](#page-12-18) yields very similar results. Overall, we find $J_H/\zeta \approx 1.3$ which puts K₂OsCl₆ in the intermediate regime between LS coupling with $J_H/\zeta \to \infty$ and jj coupling for $J_H/\zeta \rightarrow 0$.

FIG. 13. Comparison of RIXS spectra of K_2OsCl_6 , K_2OsBr_6 , and $Rb₂OsBr₆$. The difference in size and electronegativity between Br and Cl ions alters the crystal-field and charge-transfer excitations. In comparison, the intra- t_{2q} peaks are less affected by the change of the ligand, as highlighted in the inset.

F. Parameters in the Kanamori model

Thus far we discussed a model that takes the entire d shell into account. In contrast, the related $5d⁴$ iridate data in Refs. [\[32](#page-11-17)[–35\]](#page-11-21) were analyzed using the Kanamori model that assumes 10 $Dq = \infty$, i.e., it considers only t_{2g} orbitals. For a comparison, it is important to quantify how the parameter values depend on the chosen model. In the Kanamori model, the only parameters are ζ^{eff} and $J_H^{\text{eff}} = 3/49 F^2 + 20/441 F^4$ [\[42\]](#page-12-3). With 10 $Dq = \infty$, the Kanamori model restores the degeneracy of ${}^{1}T_{2}$ and ${}^{1}E$ around 1.3 eV and of the Γ_{3} and Γ_{5} states of $J = 2$ around 0.6 eV, as mentioned in Sec. [IV C.](#page-3-1) Hence the model has only four intra- t_{2g} excitation energies. For simplicity, we call these energies $E(1)$ to $E(4)$, in ascending order. Simple expressions for $E(1)$ to $E(4)$ are given in Ref. [\[41\]](#page-12-2).

A fit of the four intra- t_{2q} excitation energies with the t_{2q} only Kanamori model yields $J_H^{\text{eff}} = 0.28 \text{ eV}$ and $\zeta^{\text{eff}} = 0.41 \text{ eV}$ and the energies 371, 616, 1288, and 2125 meV. A corresponding simulated RIXS spectrum is shown in Fig. [11.](#page-8-0) Similar to the result obtained for the full d shell, the relative deviation between fit and data is largest for the lowest mode. Again, a slightly different set of parameters yields excellent agreement for the lowest excitation energies. Choosing J_H^{eff} = 310 meV and ζ^{eff} = 399 meV describes the lowest three peaks of K_2OsCl_6 within 1 meV and $E(4)$ within 6%. Overall, this suggests $J_H^{\text{eff}}/\zeta^{\text{eff}} \approx 3/4$.

Another possibility to determine this quantity is given by the ratio $E(2)/E(1)$, which varies from 3 for LS coupling to 1 for jj coupling, see Fig. [12a](#page-8-1)). For K_2OsCl_6 with 609 meV/350 meV ≈ 1.7 , this corroborates $J_H^{\text{eff}}/\zeta^{\text{eff}} \approx 3/4$. Remarkably, very similar values of the ratio $E(2)/E(1)$ have been reported for several $5d^4$ iridates, see Fig. [12b](#page-8-1)), highlighting the close relationship of the properties of this series of $5d⁴$ compounds.

As long as the corresponding model is specified, both $J_H/\zeta \approx 1.3$ for the entire 5d shell and $J_H^{\text{eff}}/\zeta^{\text{eff}} \approx 3/4$ in the

FIG. 14. Optical conductivity of K_2OsCl_6 and K_2OsBr_6 . The main change is the shift of the Mott gap from 2.2 eV to 1.8 eV. The small offset in the K_2OsCl_6 data indicates a possible surface issue. Note that we polished this sample with $CeO₂$ in propanol, while the K_2OsBr_6 crystal was measured as grown.

 t_{2g} -only model are valid. For $J_H \approx \zeta$, the two models predict

$$
E(J=2) \approx \frac{3}{2}\zeta \left(1 + \frac{2\zeta}{10 Dq}\right) \tag{2}
$$

$$
E(2) \approx \frac{3}{2} \zeta^{\text{eff}} \tag{3}
$$

for the second excitation energy and hence $\zeta^{\text{eff}}/\zeta \approx 1.2$ in the $5d⁴$ compounds. Additionally, the different definitions of Hund's coupling yield $J_H^{\text{eff}}/J_H \approx 0.77$. Concerning the energies of the intra- t_g excitations, the t_{2g} -only Kanamori model and the model for the full d shell work equally well. The main shortcoming of both models is the intensity of the lowest excitation, which is too small in the d -shell model but too large in the Kanamori model, see Fig. [11.](#page-8-0) This suggests that the intensity of the lowest RIXS peak depends sensitively on $10 Dq$ and on the admixture of e_q character.

V. RESULTS ON THE BROMIDES

RIXS spectra of K_2OsCl_6 , K_2OsBr_6 , and Rb_2OsBr_6 are compared in Fig. [13.](#page-9-1) We find a close resemblance of the RIXS data of K_2OsBr_6 and Rb_2OsBr_6 , i.e., a very small effect of the A ion. Hence we focus on the comparison of K_2OsBr_6 and K_2OsCl_6 . The behavior is different above and below 2 eV. In RIXS we find the intra- t_{2g} excitation energies of K₂OsBr₆ at 0.34, 0.60, and 1.27 eV. Compared to K_2OsCl_6 , these are reduced by about 1% , 2% , and 3% , respectively, i.e., they are almost unaffected by the choice of the halide. In contrast, the peak energies associated to the e_q and charge-transfer excitations are reduced by about 12-14 % in K_2OsBr_6 with respect to the chloride. More precisely, the peak energies are 2.4 and 3.0 eV for the strongest $t_{2g}^3 e_g^1$ transitions and 4.0 and 4.9 eV for the charge-transfer excitations $|5d_{\text{Os}}^4 4p_{\text{Br}}^6 \rangle \rightarrow |5d_{\text{Os}}^5 4p_{\text{Br}}^5 \rangle$. The very similar intensity profile of the two compounds indicates that the main effect at high energy is captured by a renormalization of the energy scale, i.e., of 10 Dq and Δ_{CT} .

Both parameters are affected by the difference in ionic size and electronegativity.

In analogy to the discussion of K_2OsCl_6 above, we identify $\Delta_{\text{CT}}^{\text{Br}} = 4.0 \text{ eV}$ via the lowest charge-transfer excitation. Furthermore, a fit of the excitation energies using multiplet calculations yield the parameters $10Dq^{\text{Br}} = 2.9 \text{ eV}, \zeta^{\text{Br}} = 0.33 \text{ eV},$ and $J_H^{\text{Br}} = 0.42 \text{ eV}$. Compared to K_2 OsCl₆, the spin-orbit coupling constant is reduced by about 4 %, while the change of J_H is negligible, see Tab. [I.](#page-7-1) The effect of a reduction of 10 Dq on the energy levels of the multiplet model is shown in the right panel of Fig. [10.](#page-7-0) While the $t_{2g}^{3}e_{g}^{1}$ levels decrease linearly in energy, the t_{2g}^4 states hardly change. In general, lower values of 10 Dq and Δ_{CT} indicate a stronger admixture of e_q and 4p ligand character into the t_{2q} states. This, in turn, reduces the effective value of ζ . However, the large ratio of $10 Dq/\zeta \approx 10$ explains why the sizable reduction of $10 Dq$ has only a small effect on ζ .

The optical conductivity $\sigma_1(\omega)$ of K₂OsBr₆ is depicted in Fig. [14](#page-9-2) and in Fig. [7b](#page-5-0)). Note that the larger thickness $d^{\text{Br}} = 170 \,\mu\text{m}$ of the bromide sample limits the accessible values of $\sigma_1(\omega)$ to below $2(\Omega \text{cm})^{-1}$, somewhat lower than in the thinner chloride sample. The most pronounced difference to the data of K_2OsCl_6 is the value of the Mott gap, which is shifted down by about 0.4 eV to 1.8 eV at 5 K . This shift masks the 1A_1 excitation which occurs at 2.1 eV in K₂OsCl₆. Along with the Mott gap, also the excitation energy of the exciton is reduced, as already discussed in connection with Fig. [7.](#page-5-0) At lower energy, the small shifts of the intra- t_{2g} excitations of less than 1 % for the lowest excitation and about 1-2 % for the bands at 0.6 and 1.3 eV agree with the RIXS results.

VI. CONCLUSION

In conclusion, we have probed the local electronic structure of the $5d^4$ hexahalogenoosmates K_2OsCl_6 , K_2OsBr_6 , and Rb_2OsBr_6 with magnetic and spectroscopic methods. These measurements reveal non-magnetic $J = 0$ behavior, as expected for a clean $5d⁴$ system in which both defects and exchange interactions are negligible. Combining RIXS and optical spectroscopy, we can assign the multiplet excitation energies with high accuracy and extract the electronic parameters by comparison with local multiplet calculations. RIXS at the transition-metal L edge is most sensitive to on-site $d-d$ excitations, which in the optical data give rise to weak, typically phonon-assisted features. For the antifluorite-type Os halides, a central advantage of RIXS is the ability to determine 10 Dq via the observation of local excitations into the e_q subshell also above the Mott gap. Due to the weak interactions between Os X_6 (X = Cl, Br) octahedra, both the e_q excitations and the charge-transfer excitations are narrow and very well defined in RIXS. As a complementary technique, optical spectroscopy allows us to determine the small non-cubic crystalfield splitting of 4 meV below 45 K in K_2OsCl_6 . Furthermore, it is sensitive to intersite processes such as excitations across the Mott gap at 2.2 eV and reveals an exciton around 1.9- 2.1 eV. These results establish the presented compounds as realizations of clean cubic $J = 0$ systems in the intermediate coupling regime with $J_H/\zeta \approx 1.3$ or $J_H^{\text{eff}}/\zeta^{\text{eff}} \approx 3/4$. Accordingly, Coulomb interaction and spin-orbit coupling have to be taken on equal footing. This value of $J_H^{\text{eff}}/\zeta^{\text{eff}}$ is very similar to results reported for $5d^4$ iridates [\[32](#page-11-17)[–35\]](#page-11-21), highlighting the close relationship between these compounds. The comparison of the data from chloride and bromide samples shows a 20 % decrease of the Mott gap as well as a reduction of about 12- 14 % of 10 Dq and of the charge-transfer energy Δ_{CT} . Due to the large size of 10 Dq and Δ_{CT} with respect to J_H and ζ , this sizable change has only a marginal effect on intra- t_{2g} energies, which are reduced by 1-3 %. In contrast to previous studies on $5d^4$ J = 0 compounds, where the determination of ζ and J_H has turned out to be difficult, we find that both chloride and bromide samples are well described by $\zeta = 0.33$ -0.34 eV and $J_H = 0.42$ -0.43 eV. These values may serve as a solid reference for future studies on Os compounds.

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