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# Electronic excitations in $5d^4 J = 0 Os^{4+}$ halides studied by RIXS and optical spectroscopy

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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<sub>2</sub>OsCl<sub>6</sub>, 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  $\Delta_{CT} = 4.6$  eV. With  $J_H/\zeta = 1.3$ , K<sub>2</sub>OsCl<sub>6</sub> is in the intermediate-coupling regime. In a  $t_{2g}$ -only Kanamori picture, the above values correspond to  $\zeta^{\text{eff}} = 0.41$  eV and  $J_H^{\text{eff}} = 0.28$  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 K<sub>2</sub>OsCl<sub>6</sub>, the bromides K<sub>2</sub>OsBr<sub>6</sub> and Rb<sub>2</sub>OsBr<sub>6</sub> show about 12-14 % smaller values of 10 Dq and  $\Delta_{CT}$ , while the spin-orbit-entangled intra- $t_{2g}$  excitations below 2 eV and hence  $\zeta$  and  $J_H$  are reduced by less than 4 %. Furthermore, the Mott gap in K<sub>2</sub>OsBr<sub>6</sub> 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 [1-5]. Prominent examples are  $t_{2q}^5$  iridates with spin-orbit entangled J = 1/2 moments [6– 8]. Compounds with edge-sharing IrO<sub>6</sub> octahedra have been predicted to show bond-directional Kitaev-type exchange couplings [9]. This has raised hopes to realize the Kitaev model on tricoordinated lattices, where strong exchange frustration yields an intriguing quantum spin liquid [10–12]. Experimentally, the dominant bond-directional character of exchange interactions has been demonstrated for honeycomb Na<sub>2</sub>IrO<sub>3</sub> [13, 14]. Remarkably, Kitaev exchange has been found to have a very different effect for J = 1/2 moments on an *fcc* lattice with corner-sharing IrO<sub>6</sub> octahedra as realized in the double perovskite Ba<sub>2</sub>CeIrO<sub>6</sub>. There, antiferromagnetic Kitaev coupling counteracts the geometric frustration of isotropic Heisenberg exchange [15]. For face-sharing IrO<sub>6</sub> octahedra as in the Ir<sub>2</sub>O<sub>9</sub> dimer compounds Ba<sub>3</sub>MIr<sub>2</sub>O<sub>9</sub>, spin-orbit coupling competes with strong intra-dimer hopping that yields quasimolecular orbitals. Still, RIXS studies for  $M = Ce^{4+}$ and  $In^{3+}$  established the spin-orbit entangled  $J_{dim} = 0$  and  $J_{\rm dim} = 3/2$  character of the respective quasimolecular magnetic moments [16, 17].

For a  $t_{2g}^4$  configuration in cubic symmetry, dominant spinorbit coupling  $\zeta$  is expected to yield a non-magnetic J=0ground 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 [18–21]. In this scenario, a magnetic amplitude mode equivalent to a Higgs mode is expected, which has been proposed for antiferromagnetic Ca<sub>2</sub>RuO<sub>4</sub> [18, 22]. In this layered  $4d^4$  compound, one has to consider the tetragonal crystal-field splitting  $\Delta_{\rm CF}$  [21, 23–28] 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, 30]. 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=0state have been studied by RIXS in  $4d^4$  K<sub>2</sub>RuCl<sub>6</sub> [31] and in the  $5d^4$  Ir<sup>5+</sup> double perovskites  $A_2BIrO_6$  (A = Ba, Sr; B = Y, Gd, Lu, Sc) [32–36]. Among these,  $Sr_2YIrO_6$  and  $Ba_2YIrO_6$ were reported to host magnetic order [37, 38] which has been attributed to the presence of  $5d^5 \text{ Ir}^{4+}$  and  $5d^3 \text{ Ir}^{6+}$  defects [39]. Pyrochlore Yb<sub>2</sub>Os<sub>2</sub>O<sub>7</sub> with  $5d^4$  Os<sup>4+</sup> ions exhibits a trigonal distortion and a defect-induced magnetic response [40]. For  $K_2RuCl_6$ , the possible role of vibronic effects has been discussed [41].

Here, we employ RIXS at the Os  $L_3$  edge and optical spectroscopy to study stoichiometric single crystals of the  $5d^4$  halides K<sub>2</sub>OsCl<sub>6</sub> and  $A_2$ OsBr<sub>6</sub> 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], 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  $5d^4$  iridates [32–35]. 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 [43–45], and for the purpose of studying the local electronic ex-

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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  $\Gamma$ , X, K, and L. Lower right: photos of a K<sub>2</sub>OsBr<sub>6</sub> crystal and of the thin, transparent sample of K<sub>2</sub>OsCl<sub>6</sub> that has been studied in infrared transmittance. The size of the latter amounts to approx. 0.5 mm×0.3 mm×0.12 mm.

citations the compounds may be viewed as being composed of undistorted, well separated  $OsX_6$  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<sub>2</sub>OsCl<sub>6</sub>, allowing for a straightforward determination of the charge-transfer energy  $\Delta_{CT}$ .

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– 34, 40, 46]. In contrast, optical spectroscopy is most sensitive to electric-dipole-active absorption features such as intersite excitations across the Mott gap or excitons [30, 47, 48], 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 [49-52]. Interesting examples studied by both techniques are, e.g., the  $3d^2$  vanadates  $RVO_3$  [48, 52, 53] or the excitations from J = 1/2 to 3/2 in the  $4d^5$  Kitaev material  $\alpha$ -RuCl<sub>3</sub> [54–56]. 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  $E_{\rm in} = 10.870$  keV, we achieve a resolution  $\delta E = 63$  meV, i.e.,  $\delta E / E_{in} \approx 6 \times 10^{-6}$ . 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] or infrared spectroscopy on  $K_2OsCl_6$  [57]. For  $K_2OsCl_6$ , we will show below that the combination of the two techniques resolves all ambiguities.



FIG. 2. Magnetic susceptibility  $\chi$  of K<sub>2</sub>OsCl<sub>6</sub> and K<sub>2</sub>OsBr<sub>6</sub>. Both compounds show dominant temperature-independent Van-Vleck paramagnetism. For comparison, we show  $\chi$  of the J = 1/2iridium sister compounds with a sizable Curie-Weiss contribution.

# I. SINGLE-CRYSTAL GROWTH AND CRYSTAL STRUCTURE

Single crystals of K<sub>2</sub>OsCl<sub>6</sub> and of the bromides  $A_2$ OsBr<sub>6</sub> with A = K and Rb were grown starting from commercially available dihydrogen hexahalogenoosmate(IV) H<sub>2</sub>OsCl<sub>6</sub>, resp. H<sub>2</sub>OsBr<sub>6</sub> 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<sub>2</sub>OsBr<sub>6</sub> and K<sub>2</sub>OsCl<sub>6</sub> are shown in Fig. 1.

At room temperature, these K<sub>2</sub>PtCl<sub>6</sub>-type compounds show a cubic crystal structure with space group  $Fm\bar{3}m$  [43–45], see Fig. 1. The Os<sup>4+</sup> 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]. At 45 K, K<sub>2</sub>OsCl<sub>6</sub> exhibits a phase transition to a tetragonal phase [44]. For K<sub>2</sub>OsBr<sub>6</sub>, 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].

### II. MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility  $\chi$  of K<sub>2</sub>OsCl<sub>6</sub> and K<sub>2</sub>OsBr<sub>6</sub> is plotted in Fig. 2. 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<sup>+</sup>, Os<sup>4+</sup>, Cl<sup>-</sup>, and Br<sup>-</sup>,  $\chi = \chi_{VV} + \chi_{dia}$ . Via tabulated values [59], we estimate  $\chi_{dia}^{Cl} = -2.1 \cdot 10^{-4}$  emu/mol and  $\chi_{dia}^{Br} = -2.7 \cdot 10^{-4}$  emu/mol. This yields experimental values of the Van-Vleck contribution of  $\chi_{VV}^{Cl} = 9.6 \cdot 10^{-4}$  emu/mol and  $\chi_{WV}^{Br} = 10.2 \cdot 10^{-4}$  emu/mol.

Our spectroscopic data establish a J=0 ground state of the  $5d^4$  configuration of Os<sup>4+</sup>, cf. Sect. IV. 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,  $\mu_B$  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, 61], 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  $\chi^{\rm Cl}_{VV,mod}$  =  $8.8\cdot10^{-4}$  emu/mol and  $\chi^{\rm Br}_{VV,mod}$  =  $8.6 \cdot 10^{-4}$  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  $8 \times 50 \,\mu\text{m}^2$  (V  $\times$  H) at the sample position. Incident  $\pi$  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 [62-64]. 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]. 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]. 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].

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 <sup>4</sup>He 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<sub>2</sub>OsCl<sub>6</sub> was lapped to a suitable thickness and polished with  $CeO_2$  in propanol, while the sample of K<sub>2</sub>OsBr<sub>6</sub> was measured as grown. The sample thickness amounts to  $d = 120(5) \ \mu m$  for K<sub>2</sub>OsCl<sub>6</sub> 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<sub>2</sub>OsCl<sub>6</sub> at 300 K in the range from 1 to 6 eV using a Woollam VASE ellipsometer.

# IV. RESULTS ON K<sub>2</sub>OsCl<sub>6</sub>

### A. Resonance behavior

To study the resonance behavior and to maximize the RIXS intensity, we collected low-resolution RIXS spectra of K<sub>2</sub>OsCl<sub>6</sub> for different incident energies at T = 20 K for a transferred momentum  $q = (7 \ 7 \ 6)$ , see Fig. 3b). With the energy loss being independent of  $E_{in}$  for all of the observed RIXS peaks, we find the two distinct resonance energies  $E_{in} = 10.870$  keV and 10.8735 keV, as shown in Fig. 3c). These can be attributed to  $t_{2g}$  resonance and  $e_g$  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  $10 Dq \approx 3.5$  eV. This agrees with the strong RIXS peak at about 3.5 eV energy loss that exhibits  $e_q$ 



FIG. 3. **Resonance behavior of K**<sub>2</sub>**OsCl**<sub>6</sub> **at** T = 20 **K.** a) Lowresolution RIXS spectra for incident energy  $E_{in} = 10.870$  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  $E_{in}$ . The integration interval is chosen to be  $\pm 0.4$  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).

### **B.** Character of RIXS features

Based on the resonance behavior, we distinguish three different kinds of excitations: intra- $t_{2g}$  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  $\zeta$ 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  $E_{\rm in} = 10.8375$  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 2.7 eV 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,  $|5d_{OS}^4 3p_{CI}^6\rangle \rightarrow |5d_{OS}^5 3p_{CI}^5\rangle$ . The peaks at 4.6 eV and 5.7 eV both show  $t_{2g}$  resonance and hence can be attributed to  $|t_{2q}^5 3p_{\rm Cl}^5\rangle$  final states. Roughly, these two excited states with  $t_{2q}^5$  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. This suggests an overlap between an on-site crystal-field excitation to  $e_q$  orbitals and the lowest charge-transfer excitation to  $t_{2q}$  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,  $\Delta_{\rm CT} = 4.6 \, {\rm eV}$ .

The occurrence of both  $t_{2g}$  resonance and  $e_g$  resonance behavior of charge-transfer excitations has previously been observed in, e.g.,  $5d^5$  K<sub>2</sub>IrBr<sub>6</sub> [68],  $5d^4$  Yb<sub>2</sub>Os<sub>2</sub>O<sub>7</sub> [40], and  $5d^2$  Ba<sub>2</sub>YReO<sub>6</sub> [32]. In the present case of K<sub>2</sub>OsCl<sub>6</sub>, 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<sub>2</sub>OsCl<sub>6</sub>, in agreement with the notion that interactions between the well separated OsCl<sub>6</sub> octahedra are very small, at least for  $t_{2g}$  orbitals.

### C. Intra- $t_{2g}$ excitations of $K_2OsCl_6$ in RIXS

High-resolution RIXS spectra of the intra- $t_{2g}$  excitations reveal four peaks at about 0.3, 0.6, 1.3, and 2.1 eV, see Fig. 4. 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. 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  $e_g$  orbitals on the intra- $t_{2g}$ 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, 42]. Note, however, that these values correspond to a  $t_{2g}$ -only scenario, i.e.



FIG. 4. Intra- $t_{2g}$  excitations of  $K_2OsCl_6$  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  $K_2OsCl_6$  at 20 K at L, X, and close to  $\Gamma$ . The latter data were measured in the vicinity of  $\Gamma$  to avoid the strong contribution of Bragg scattering right at  $\Gamma$ . 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  $\zeta$ , as discussed below. The low-energy RIXS peaks at 0.3 eV and 0.6 eV reflect strong spin-orbit coupling, which splits the  ${}^3T_1$  multiplet into the J = 0 ground state with  $\Gamma_1$  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, 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**<sub>2</sub>**OsCl**<sub>6</sub>. 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- $t_{2g}$  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 [69–74]. For both  $5d^4$  and  $5d^2$ , also the degeneracy of the  ${}^{1}T_2$  and  ${}^{1}E$  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, indeed indicates a finite splitting between the cubic multiplets with a weaker feature on the high-energy side, as discussed in K<sub>2</sub>RuCl<sub>6</sub> and Ba<sub>2</sub>YIrO<sub>6</sub> [31, 33].

Overall, the excitation spectrum agrees with previous RIXS results on  $5d^4$  iridates [32–35]. RIXS data of Yb<sub>2</sub>Os<sub>2</sub>O<sub>7</sub> [40] also show the two low-energy modes below 1 eV but the intra $t_{2a}$  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<sub>2</sub>Os<sub>2</sub>O<sub>7</sub> due to a trigonal distortion [40]. In  $4d^4$  K<sub>2</sub>RuCl<sub>6</sub>, the equivalent of the lower three features have been observed [31]. The  ${}^{1}A_{1}$  peak at 2.1 eV thus far was only observed as a very weak feature in Sr<sub>2</sub>YIrO<sub>6</sub> [32]. Comparing two data sets measured at the equivalent X points (5 5 6) and (7 7 6), see Fig. 4, we find that the  ${}^{1}A_{1}$  peak is suppressed in the latter, which has been recorded with a scattering angle  $2\theta$  close to 90°. This geometry typically is chosen to suppress elastic Thomson scattering, explaining the absence of this peak in previous measurements on  $5d^4$  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. 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<sub>2</sub>OsCl<sub>6</sub> and b) K<sub>2</sub>OsBr<sub>6</sub>. In K<sub>2</sub>OsCl<sub>6</sub>, 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 <sup>1</sup>A<sub>1</sub> intra- $t_{2g}$  excitation is observed at 2.117 eV, and the many narrow lines around it correspond to phonon sidebands. In contrast to the <sup>1</sup>A<sub>1</sub> 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<sub>2</sub>OsBr<sub>6</sub> show the Mott gap at 1.8 eV at 5 K and a very similar temperature dependence. In K<sub>2</sub>OsBr<sub>6</sub>, the exciton is observed around 1.6-1.7 eV.

the scattered light is perpendicular to the incident  $\pi$  polarization. This suggests that the  ${}^{1}A_{1}$  feature is observable only for parallel polarization, which is supported by simulations using *Quanty* [60, 61].

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, 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<sub>2</sub>OsCl<sub>6</sub>

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  $|5d_{Os}^4 3p_{Cl}^6 \rangle \rightarrow |5d_{Os}^5 3p_{Cl}^5 \rangle$ . In Fig. 6, 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 [32–34, 40, 46], 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- $t_{2g}$  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.

## *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  $\zeta$ . In  $4d^4$  Ca<sub>2</sub>RuO<sub>4</sub>, the relative spectral weight of these bands has been employed to estimate  $\zeta$  [30]. 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  $|t_{2g_i}^4, t_{2g_j}^4\rangle \rightarrow |t_{2g_i}^3, (t_{2g}^4, e_g^1)_i\rangle$ are expected to occur roughly 10 Dq higher in energy than the corresponding  $t_{2q}$  bands, i.e., above about 6 eV. In K<sub>2</sub>OsCl<sub>6</sub>, 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. At 5 K, the onset is at  $\Delta = 2.2 \,\text{eV}$ . With increasing temperature, the onset shifts to lower energy, roughly to  $1.9 \,\text{eV}$  at 300 K, while the slope of the steep increase in  $\sigma_1(\omega)$  is reduced, see Fig. 7a). 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  $K_2$ OsCl<sub>6</sub> in  $\sigma_1(\omega)$ . The panels depict excitations from J = 0 to a) J = 1, i.e,  $\Gamma_1$  to  $\Gamma_4$ ; b) the split J = 2 states, i.e.,  $\Gamma_1$  to  $\Gamma_5$  and  $\Gamma_3$ ; c) the split  ${}^1T_2$  and  ${}^1E$  states; and d)  ${}^1A_1$ . 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  $E_{1A_1} \pm E_{ph}$  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). This feature is well separated from the  ${}^{1}A_{1}$  intra- $t_{2g}$  excitation at 2.117 eV. Its spectral weight is comparable to the weak intra- $t_{2q}$  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<sub>6</sub> 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). In contrast, the intra- $t_{2q}$  excitation energies are very similar in K<sub>2</sub>OsBr<sub>6</sub> and K<sub>2</sub>OsCl<sub>6</sub>, as discussed in Sect. V.



FIG. 9. Temperature dependence of  $\sigma_1(\omega)$  across the structural phase transition at 45 K. a) Excitations to J = 1, cf. Fig. 8a). 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. We attribute also these bands to inter-site excitations. They can be explained as a combination and overtone of the intra- $t_{2g}$  excitations at about 0.35 eV and 0.65 eV, i.e., the simultaneous excitation of intra- $t_{2g}$  excitations on two neighboring Os sites. In the honeycomb compound  $\alpha$ -RuCl<sub>3</sub> it has been shown that such double or even triple excitations may carry sizable spectral weight [55]. 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 and 8, 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<sub>2</sub>OsCl<sub>6</sub> 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  ${}^1A_1$  multiplet, see Fig. 8d).

At 5 K, we find a tiny zero-phonon magnetic-dipole mode at  $E_{{}^{1}A_{1}} = 2117 \text{ meV}$ . This assignment is based on the temperature dependence of the phonon-assisted electric-dipole features observed at  $E_{{}^{1}A_{1}} \pm E_{\text{ph}}$ . At 5 K, we only find modes at  $E_{{}^{1}A_{1}} + E_{\text{ph}}$  for different symmetry-breaking phonons with, e.g.,  $E_{\text{ph}} = 7 \text{ meV}$ , 13 meV, or 21 meV, as indicated in Fig. 8d) 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 Dqseparates 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  ${}^3T_1$  multiplet forms the ground state. Middle right: Spin-orbit coupling  $\zeta$  yields a J = 0ground state and four groups of intra- $t_{2g}$  excitations. Red circles denote the experimental energies of K2OsCl6 used to determine the electronic parameters. Right: Effect of a reduction of 10 Dq for finite  $J_H$  and  $\zeta$ , mimicking the trend from K<sub>2</sub>OsCl<sub>6</sub> to K<sub>2</sub>OsBr<sub>6</sub>.

appear at  $E_{{}^{1}\!A_{1}} - E_{\rm ph}$ , strongly supporting our assignment. The spectral weight of the phonon-annihilation peaks is governed by the Boltzmann factor. Hence peaks at lower energy  $E_{A_1} - E_{ph}$  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, 51]. 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]. In single crystals, this pattern usually is washed out. Exceptions have been observed in quasimolecular crystals such as K<sub>3</sub>NiO<sub>2</sub> with isolated NiO<sub>2</sub> units [50], and the rich optical spectra of K<sub>2</sub>OsCl<sub>6</sub> most probably reflect the weak interactions between well separated OsCl<sub>6</sub> octahedra. A detailed assignment of the sidebands in K<sub>2</sub>OsCl<sub>6</sub> has been discussed previously [57].

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 $t_{2a}$  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.,  $\Gamma_1$  to  $\Gamma_4$ [75]. This peak splits below 45 K, see Fig. 9 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].

To compare the excitation energies found in RIXS and optics, we extract the RIXS peak energies for the intra- $t_{2q}$  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- $t_{2q}$  excitation energy, as mentioned in Sec. III. For the other low-energy RIXS peaks, this yields

| 1                 | 1 ( ) | · · · | 1 ( ) | · · · · |
|-------------------|-------|-------|-------|---------|
| $\Gamma_4(^3T_1)$ | 350   | 383   | 349   | 388     |
| $\Gamma_5(^3T_1)$ | 609   | 608   | 604   | 604     |
| $\Gamma_3(^3T_1)$ | _     | 631   | -     | 632     |
| ${}^{1}T_{2}$     | 1311  | 1289  | 1285  | 1267    |
| $^{1}E$           | _     | 1323  | -     | 1312    |
| ${}^{1}\!A_{1}$   | 2117  | 2123  | -     | 2050    |
| ${}^{5}E$         | 2721  | 2716  | 2391  | 2381    |
| $^{3}E$           | 3428  | 3432  | 3033  | 3042    |

TABLE I. Experimental and calculated excitation energies. The four intra- $t_{2q}$  energies are taken from the optical data, the two  $e_q$ 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  $10Dq = 3.27 \text{ eV} (2.85 \text{ eV}), \zeta = 0.336 \text{ eV}$  $(0.325 \text{ eV}), F^2 = 3.73 \text{ eV}$  (3.90 eV), and  $F^4 = 2.22 \text{ eV}$  (2.01 eV), which corresponds to  $J_H = 0.425 \text{ eV} (0.422 \text{ eV})$ .

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. 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. In the antifluorite halides, a non-cubic crystal field splitting  $\Delta_{CF}$  is driven by tilts and rotary or librational modes of the metal-ligand octahedra [76–79]. 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. 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  $\Delta_{CF}$  of K<sub>2</sub>OsCl<sub>6</sub>. For instance for a small tetragonal field  $|\Delta_{\rm CF}| \ll \zeta$ , one finds  $|\Delta_{\rm CF}| \approx 2\Delta_{\rm exp}$  [30].

### E. Calculation of energy levels of K<sub>2</sub>OsCl<sub>6</sub>

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  $t_{2q}$  and  $e_q$  levels, spin-orbit coupling  $\zeta$ , 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]. Note that  $F^0$ , 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, 61]. Figure 10 displays the behavior as a function of 10 Dq,  $J_H$ , and  $\zeta$ . Starting with  $J_H = \zeta = 0$ , the cubic crystal field yields a  $t_{2q}^4$  ground state and raises the excitation energies of the



FIG. 11. **Measured and calculated RIXS spectra of K**<sub>2</sub>**OsCl**<sub>6</sub>. Solid orange lines: Simulation based on the fit result for the full *d*-shell model, cf. Tab. I. 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  $\zeta$  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  $t_{2a}^3 e_a^1$  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, the width of this  $t_{2q}$ -to- $e_q$  excitation is much larger than observed for the intra- $t_{2g}$  peaks, see Fig. 11. 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 [80–83]. Also for optical data on single crystals of K<sub>2</sub>OsCl<sub>6</sub>, it has been found that the determination of the electronic parameters is difficult [57], 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  $K_2OsCl_6$ , 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. 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 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 K<sub>2</sub>OsCl<sub>6</sub>, it yields  $J_H^{\text{eff}}/\zeta^{\text{eff}} \approx 3/4$ . b) Comparison of the two lowest excitation energies in K<sub>2</sub>OsCl<sub>6</sub> and related  $5d^4$ iridates [32–35]. For all of them,  $J_H^{\text{eff}}/\zeta^{\text{eff}}$  is very similar.

and  $F^4 = 2.2 \text{ eV}$ , resulting in  $J_H = 0.43 \text{ eV}$ . Note that the value of 10 Dq agrees very well with our simple estimate discussed above. Figure 11 compares the calculated result for direct  $L_3$ -edge RIXS [46] 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. 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  $4d^4$  K<sub>2</sub>RuCl<sub>6</sub>, 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, 41]. For K<sub>2</sub>OsCl<sub>6</sub>, our optical data resolve the vibronic sidebands in the excited states, cf. Fig. 8, 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  $J_H = 0.42 \text{ eV}$  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] yields very similar results. Overall, we find  $J_H/\zeta \approx 1.3$  which puts K<sub>2</sub>OsCl<sub>6</sub> 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  $Rb_2OsBr_6$ . The difference in size and electronegativity between Br and Cl ions alters the crystal-field and charge-transfer excitations. In comparison, the intra- $t_{2g}$  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  $5d^4$  iridate data in Refs. [32–35] 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  $\zeta^{\text{eff}}$  and  $J_H^{\text{eff}} = 3/49 F^2 + 20/441 F^4$  [42]. With  $10 Dq = \infty$ , the Kanamori model restores the degeneracy of  ${}^1T_2$  and  ${}^1E$  around 1.3 eV and of the  $\Gamma_3$  and  $\Gamma_5$  states of J = 2 around 0.6 eV, as mentioned in Sec. IV C. 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].

A fit of the four intra- $t_{2g}$  excitation energies with the  $t_{2g}$ 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. 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  $J_H^{\text{eff}} = 310 \text{ meV}$  and  $\zeta^{\text{eff}} = 399 \text{ meV}$  describes the lowest three peaks of K<sub>2</sub>OsCl<sub>6</sub> 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). For K<sub>2</sub>OsCl<sub>6</sub> with 609 meV/350 meV  $\approx$  1.7, this corroborates  $J_H^{\text{eff}} \gtrsim 3/4$ . Remarkably, very similar values of the ratio E(2)/E(1) have been reported for several  $5d^4$  iridates, see Fig. 12b), highlighting the close relationship of the properties of this series of  $5d^4$ 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**  $K_2$ **OsCl**<sub>6</sub> **and**  $K_2$ **OsBr**<sub>6</sub>**.** The main change is the shift of the Mott gap from 2.2 eV to 1.8 eV. The small offset in the K<sub>2</sub>OsCl<sub>6</sub> data indicates a possible surface issue. Note that we polished this sample with CeO<sub>2</sub> in propanol, while the K<sub>2</sub>OsBr<sub>6</sub> crystal was measured as grown.

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

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

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

for the second excitation energy and hence  $\zeta^{\text{eff}}/\zeta \approx 1.2$  in the  $5d^4$  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. This suggests that the intensity of the lowest RIXS peak depends sensitively on 10 Dqand on the admixture of  $e_q$  character.

## V. RESULTS ON THE BROMIDES

RIXS spectra of K<sub>2</sub>OsCl<sub>6</sub>, K<sub>2</sub>OsBr<sub>6</sub>, and Rb<sub>2</sub>OsBr<sub>6</sub> are compared in Fig. 13. We find a close resemblance of the RIXS data of K<sub>2</sub>OsBr<sub>6</sub> and Rb<sub>2</sub>OsBr<sub>6</sub>, i.e., a very small effect of the A ion. Hence we focus on the comparison of  $K_2OsBr_6$  and K<sub>2</sub>OsCl<sub>6</sub>. The behavior is different above and below 2 eV. In RIXS we find the intra- $t_{2g}$  excitation energies of K<sub>2</sub>OsBr<sub>6</sub> at 0.34, 0.60, and 1.27 eV. Compared to K<sub>2</sub>OsCl<sub>6</sub>, 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 K2OsBr6 with respect to the chloride. More precisely, the peak energies are 2.4 and 3.0 eV for the strongest  $t_{2q}^3 e_q^1$  transitions and 4.0 and 4.9 eV for the charge-transfer excitations  $|5d_{Os}^4 4p_{Br}^6\rangle \rightarrow |5d_{Os}^5 4p_{Br}^5\rangle$ . 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  $\Delta_{CT}$ .

11

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

In analogy to the discussion of  $K_2OsCl_6$  above, we identify  $\Delta_{CT}^{Br} = 4.0 \text{ eV}$  via the lowest charge-transfer excitation. Furthermore, a fit of the excitation energies using multiplet calculations yield the parameters  $10Dq^{Br} = 2.9 \text{ eV}$ ,  $\zeta^{Br} = 0.33 \text{ eV}$ , and  $J_H^{Br} = 0.42 \text{ eV}$ . Compared to  $K_2OsCl_6$ , the spin-orbit coupling constant is reduced by about 4%, while the change of  $J_H$  is negligible, see Tab. I. 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. 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  $\Delta_{CT}$  indicate a stronger admixture of  $e_g$  and 4p ligand character into the  $t_{2g}$  states. This, in turn, reduces the effective value of  $\zeta$ . However, the large ratio of 10 Dq has only a small effect on  $\zeta$ .

The optical conductivity  $\sigma_1(\omega)$  of K<sub>2</sub>OsBr<sub>6</sub> is depicted in Fig. 14 and in Fig. 7b). 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<sub>2</sub>OsCl<sub>6</sub> 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 <sup>1</sup>A<sub>1</sub> excitation which occurs at 2.1 eV in K<sub>2</sub>OsCl<sub>6</sub>. Along with the Mott gap, also the excitation energy of the exciton is reduced, as already discussed in connection with Fig. 7. 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<sub>2</sub>OsCl<sub>6</sub>, K<sub>2</sub>OsBr<sub>6</sub>, and Rb<sub>2</sub>OsBr<sub>6</sub> with magnetic and spectroscopic methods. These measurements reveal non-magnetic J=0 behavior, as expected for a clean  $5d^4$  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  $OsX_6$  (X = Cl, Br) octahedra, both the  $e_a$  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<sub>2</sub>OsCl<sub>6</sub>. 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 [32–35], 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  $\Delta_{\rm CT}$ . Due to the large size of 10 Dq and  $\Delta_{CT}$  with respect to  $J_H$  and  $\zeta$ , 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  $\zeta$  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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- W. Witczak-Krempa, G. Chen, Y. B. Kim, and L. Balents, *Correlated Quantum Phenomena in the Strong Spin-Orbit Regime*, Annu. Rev. Condens. Matter Phys. 5, 57 (2014).
- [2] J. G. Rau, E. K.-H. Lee, and H.-Y. Kee, *Spin-Orbit Physics Giving Rise to Novel Phases in Correlated Systems: Iridates and Related Materials*, Annu. Rev. Condens. Matter Phys. 7, 195 (2016).
- [3] R. Schaffer, E. K.-H. Lee, B.-J. Yang, and Y. B. Kim, *Recent progress on correlated electron systems with strong spin-orbit coupling*, Rep. Prog. Phys. **79**, 094504 (2016).
- [4] T. Takayama, J. Chaloupka, A. Smerald, G. Khaliullin, and H. Takagi, Spin–Orbit-Entangled Electronic Phases in 4d and 5d

Transition-Metal Compounds, J. Phys. Soc. Jpn. 90, 062001 (2021).

- [5] D. I. Khomskii and S. V. Streltsov, Orbital Effects in Solids: Basics, Recent Progress, and Opportunities, Chem. Rev. 121, 2992 (2021).
- [6] S. M. Winter, A. A. Tsirlin, M. Daghofer, J. van den Brink, Y. Singh, P. Gegenwart, and R. Valentí, *Models and materials for* generalized Kitaev magnetism, J. Phys.: Condens. Matter 29, 493002 (2017).
- [7] G. Cao and P. Schlottmann, *The Challenge of Spin-Orbit-Tuned Ground States in Iridates*, Rep. Prog. Phys. 81, 042502 (2018).

- [9] G. Jackeli and G. Khaliullin, Mott Insulators in the Strong Spin-Orbit Coupling Limit: From Heisenberg to a Quantum Compass and Kitaev Models, Phys. Rev. Lett. 102, 017205 (2009).
- [10] M. Hermanns, I. Kimchi, and J. Knolle, *Physics of the Kitaev Model: Fractionalization, Dynamic Correlations, and Material Connections*, Annu. Rev. Condens. Matter Phys. 9, 17 (2018).
- [11] H. Takagi, T. Takayama, G. Jackeli, G. Khaliullin and S. E. Nagler, *Concept and realization of Kitaev quantum spin liquids*, Nat. Rev. Phys. 1, 264 (2019).
- [12] Y. Motome and J. Nasu, *Hunting Majorana Fermions in Kitaev Magnets*, J. Phys. Soc. Jpn. 89, 012002 (2020).
- [13] S. H. Chun, J.-W. Kim, J. Kim, H. Zheng, C. C. Stoumpos, C. D. Malliakas, J. F. Mitchell, K. Mehlawat, Y. Singh, Y. Choi, T. Gog, A. Al-Zein, M. Moretti Sala, M. Krisch, J. Chaloupka, G. Jackeli, G. Khaliullin, and B. J. Kim, *Direct evidence for dominant bond-directional interactions in a honeycomb lattice iridate Na*<sub>2</sub>*IrO*<sub>3</sub>, Nat. Phys. **11**, 462 (2015).
- [14] M. Magnaterra, K. Hopfer, Ch. J. Sahle, M. Moretti Sala, G. Monaco, J. Attig, C. Hickey, I.-M. Pietsch, F. Breitner, P. Gegenwart, M. H. Upton, Jungho Kim, S. Trebst, P. H. M. van Loosdrecht, J. van den Brink, and M. Grüninger, *RIXS observation of bond-directional nearest-neighbor excitations in the Kitaev material Na*<sub>2</sub>*IrO*<sub>3</sub>, arXiv:2301.08340
- [15] A. Revelli, C.C. Loo, D. Kiese, P. Becker, T. Fröhlich, T. Lorenz, M. Moretti Sala, G. Monaco, F.L. Buessen, J. Attig, M. Hermanns, S. V. Streltsov, D. I. Khomskii, J. van den Brink, M. Braden, P.H.M. van Loosdrecht, S. Trebst, A. Paramekanti, and M. Grüninger, *Spin-orbit entangled* j = 1/2 moments in Ba<sub>2</sub>CeIrO<sub>6</sub>: A frustrated fcc quantum magnet, Phys. Rev. B **100**, 085139 (2019).
- [16] A. Revelli, M. Moretti Sala, G. Monaco, P. Becker, L. Bohatý, M. Hermanns, T.C. Koethe, T. Fröhlich, P. Warzanowski, T. Lorenz, S.V. Streltsov, P.H.M. van Loosdrecht, D.I. Khomskii, J. van den Brink, and M. Grüninger, *Resonant inelastic x-ray incarnation of Young's double-slit experiment*, Sci. Adv. 5, eaav4020 (2019).
- [17] A. Revelli, M. Moretti Sala, G. Monaco, M. Magnaterra, J. Attig, L. Peterlini, T. Dey, A. A. Tsirlin, P. Gegenwart, T. Fröhlich, M. Braden, C. Grams, J. Hemberger, P. Becker, P.H.M. van Loosdrecht, D.I. Khomskii, J. van den Brink, M. Hermanns, and M. Grüninger, *Quasimolecular electronic structure of the spin-liquid candidate Ba*<sub>3</sub>*InIr*<sub>2</sub>*O*<sub>9</sub>, Phys. Rev. B **106**, 155107 (2022).
- [18] G. Khaliullin, Excitonic Magnetism in Van Vleck-type d<sup>4</sup> Mott Insulators, Phys. Rev. Lett. 111, 197201 (2013).
- [19] O. N. Meetei, W. S. Cole, M. Randeria, and N. Trivedi, Novel magnetic state in d<sup>4</sup> Mott insulators, Phys. Rev. B 91, 054412 (2015).
- [20] D. I. Khomskii, *Transition metal compounds*, Cambridge University Press (2014).
- [21] A. Akbari and G. Khaliullin, Magnetic Excitations in Spin-Orbit Coupled d<sup>4</sup> Mott Insulator on Square Lattice, Phys. Rev. B 90, 035137 (2014).
- [22] A. Jain, M. Krautloher, J. Porras, G. H. Ryu, D. P. Chen, D. L. Abernathy, J. T. Park, A. Ivanov, J. Chaloupka, G. Khaliullin, B. Keimer, and B. J. Kim, *Higgs mode and its decay in a twodimensional antiferromagnet*, Nat. Phys. **13**, 633 (2017).
- [23] S. Kunkemöller, D. Khomskii, P. Steffens, A. Piovano, A. A. Nugroho, and M. Braden, *Highly Anisotropic Magnon Disper*sion in Ca<sub>2</sub>RuO<sub>4</sub>: Evidence for Strong Spin-Orbit Coupling, Phys. Rev. Lett. **115**, 247201 (2015).

- [24] S. Kunkemöller, E. Komleva, S. V. Streltsov, S. Hoffmann, D. I. Khomskii, P. Steffens, Y. Sidis, K. Schmalzl, and M. Braden, *Magnon dispersion in Ca<sub>2</sub>Ru<sub>1-x</sub>Ti<sub>x</sub>O<sub>4</sub>: Impact of spin-orbit coupling and oxygen moments*, Phys. Rev. B **95**, 214408 (2017).
- [25] G. Zhang and E. Pavarini, Mott transition, spin-orbit effects, and magnetism in Ca<sub>2</sub>RuO<sub>4</sub>, Phys. Rev. B 95, 075145 (2017).
- [26] G. Zhang and E. Pavarini, *Higgs mode and stability of xy-orbital ordering in Ca<sub>2</sub>RuO<sub>4</sub>*, Phys. Rev. B 101, 205128 (2020).
- [27] T. Feldmaier, P. Strobel, M. Schmid, P. Hansmann, and M. Daghofer, *Excitonic magnetism at the intersection of spin-orbit coupling and crystal-field splitting*, Phys. Rev. Res. 2, 033201 (2020).
- [28] B. J. Kim and G. Khaliullin, *Resonant inelastic x-ray scattering operators for*  $t_{2g}$  *orbital systems*, Phys. Rev. B **96**, 085108 (2017).
- [29] H. Gretarsson, H. Suzuki, Hoon Kim, K. Ueda, M. Krautloher, B. J. Kim, H. Yavaş, G. Khaliullin, and B. Keimer, *Observation* of spin-orbit excitations and Hund's multiplets in Ca<sub>2</sub>RuO<sub>4</sub>, Phys. Rev. B **100**, 045123 (2019).
- [30] I. Vergara, M. Magnaterra, P. Warzanowski, J. Attig, S. Kunkemöller, D.I. Khomskii, M. Braden, M. Hermanns, and M. Grüninger, *Spin-orbit coupling and crystal-field splitting in Ti-doped Ca*<sub>2</sub>*RuO*<sub>4</sub> *studied by ellipsometry*, Phys. Rev. B 106, 085103 (2022).
- [31] H. Takahashi, H. Suzuki, J. Bertinshaw, S. Bette, C. Mühle, J. Nuss, R. Dinnebier, A. Yaresko, G. Khaliullin, H. Gretarsson, T. Takayama, H. Takagi, and B. Keimer, *Nonmagnetic J = 0 State and Spin-Orbit Excitations in K*<sub>2</sub>*RuCl*<sub>6</sub>, Phys. Rev. Lett. **127**, 227201 (2021).
- [32] B. Yuan, J. P. Clancy, A. M. Cook, C. M. Thompson, J. Greedan, G. Cao, B. C. Jeon, T. W. Noh, M. H. Upton, D. Casa, T. Gog, A. Paramekanti, and Y.-J. Kim, *Determination of Hund's coupling in 5d oxides using resonant inelastic x-ray scattering*, Phys. Rev. B **95**, 235114 (2017).
- [33] M. Kusch, V. M. Katukuri, N. A. Bogdanov, B. Büchner, T. Dey, D. V. Efremov, J. E. Hamann-Borrero, B. H. Kim, M. Krisch, A. Maljuk, M. Moretti Sala, S. Wurmehl, G. Aslan-Cansever, M. Sturza, L. Hozoi, J. van den Brink, and J. Geck, *Observation of heavy spin-orbit excitons propagating in a nonmagnetic background: The case of* (*Ba*,*Sr*)<sub>2</sub>*YIrO*<sub>6</sub>, Phys. Rev. B **97**, 064421 (2018).
- [34] A. Nag, S. Bhowal, A. Chakraborty, M. M. Sala, A. Efimenko, F. Bert, P. K. Biswas, A. D. Hillier, M. Itoh, S. D. Kaushik, V. Siruguri, C. Meneghini, I. Dasgupta, and S. Ray, *Origin of magnetic moments and presence of spin-orbit singlets in Ba*<sub>2</sub>*YIrO*<sub>6</sub>, Phys. Rev. B **98**, 014431 (2018).
- [35] A. A. Aczel, Q. Chen, J. P. Clancy, C. dela Cruz, D. Reig-i-Plessis, G. J. MacDougall, C. J. Pollock, M. H. Upton, T. J. Williams, N. LaManna, J. P. Carlo, J. Beare, G. M. Luke, and H. D. Zhou, *Spin-orbit coupling controlled ground states in the double perovskite iridates A*<sub>2</sub>*BIrO*<sub>6</sub> (*A* = *Ba*, *Sr*; *B* = *Lu*, *Sc*), Phys. Rev. Mater. **6**, 094409 (2022).
- [36] A. Paramekanti, D. J. Singh, B. Yuan, D. Casa, A. Said, Y.-J. Kim, and A. D. Christianson, *Spin-orbit coupled systems in the atomic limit: rhenates, osmates, iridates*, Phys. Rev. B 97, 235119 (2018).
- [37] G. Cao, T. F. Qi, L. Li, J. Terzic, S. J. Yuan, L. E. DeLong, G. Murthy, and R. K. Kaul, *Novel Magnetism of Ir^{5+}(5d^4) Ions in the Double Perovskite Sr<sub>2</sub>YIrO<sub>6</sub>, Phys. Rev. Lett. 112, 056402 (2014).*
- [38] J. Terzic, H. Zheng, F. Ye, H. D. Zhao, P. Schlottmann, L. E. De Long, S. J. Yuan, and G. Cao, *Evidence for a low-temperature magnetic ground state in double-perovskite iri-dates with Ir*<sup>5+</sup>(5d<sup>4</sup>) ions, Phys. Rev. B **96**, 064436 (2017).

- [39] S. Fuchs, T. Dey, G. Aslan-Cansever, A. Maljuk, S. Wurmehl,
  B. Büchner, and V. Kataev, Unraveling the Nature of Magnetism of the 5d<sup>4</sup> Double Perovskite Ba<sub>2</sub>YIrO<sub>6</sub>, Phys. Rev. Lett. 120, 237204 (2018).
- [40] N. R. Davies, C. V. Topping, H. Jacobsen, A. J. Princep, F. K. K. Kirschner, M. C. Rahn, M. Bristow, J. G. Vale, I. da Silva, P. J. Baker, Ch. J. Sahle, Y.-F. Guo, D.-Y. Yan, Y.-G. Shi, S. J. Blundell, D. F. McMorrow, and A. T. Boothroyd, *Evidence for a J*eff = 0 ground state and defect-induced spin glass behavior in the pyrochlore osmate Y<sub>2</sub>Os<sub>2</sub>O<sub>7</sub>, Phys. Rev. B **99**, 174442 (2019).
- [41] N. Iwahara and S. Shikano, Vibronic excitations in resonant inelastic x-ray scattering spectra of K<sub>2</sub>RuCl<sub>6</sub>, Phys. Rev. Res. 5, 023051 (2023).
- [42] A. Georges, Luca de'Medici, and J. Mravlje, *Strong Correlations from Hund's Coupling*, Ann. Rev. Condens. Matt. Phys. 4, 137 (2013).
- [43] J. E. Fergusson and P. F. Heveldt, *The influence of*  $\pi$ *-bonding and steric factors on hexahalogeno-metallates*, Aust. J. Chem., **27**, 661 (1974).
- [44] R. L. Armstrong, D. Mintz, B. M. Powell, and W. J. L. Buyers, *Ferrorotative transition in the antifluorite crystal K<sub>2</sub>OsCl<sub>6</sub>*, Phys. Rev. B **17**, 1260 (1978).
- [45] M. Saura-Múzquiz, M. Avdeev, H. E. A. Brand, and B. J. Kennedy, *Structural and Magnetic Properties of Some Vacancy-Ordered Osmium Halide Perovskites*, Inorg. Chem. **61**, 15961 (2022).
- [46] L. J. P. Ament, M. van Veenendaal, T. P. Devereaux, J. P. Hill, and J. van den Brink, *Resonant inelastic x-ray scattering studies* of elementary excitations, Rev. Mod. Phys. 83, 705 (2011).
- [47] A. Gössling, R. Schmitz, H. Roth, M.W. Haverkort, T. Lorenz, J.A. Mydosh, E. Müller-Hartmann, and M. Grüninger, *Mott-Hubbard exciton in the optical conductivity of YTiO<sub>3</sub> and SmTiO<sub>3</sub>*, Phys. Rev. B 78, 075122 (2008).
- [48] J. Reul, A. A. Nugroho, T. T. M. Palstra, and M. Grüninger, Probing orbital fluctuations in RVO<sub>3</sub> (R = Y, Gd, or Ce) by ellipsometry, Phys. Rev. B 86, 125128 (2012).
- [49] B. Henderson and G. F. Imbusch, Optical spectroscopy of inorganic solids, Oxford (1989).
- [50] B. N. Figgis and M. A. Hitchman, *Ligand Field Theory and its Applications*, Wiley (1999).
- [51] R. Rückamp, E. Benckiser, M. W. Haverkort, H. Roth, T. Lorenz, A. Freimuth, L. Jongen, A. Möller, G. Meyer, P. Reutler, B. Büchner, A. Revcolevschi, S.-W. Cheong, C. Sekar, G. Krabbes, and M. Grüninger, *Optical study of orbital excitations in transition-metal oxides*, New J. Phys. 7, 144 (2005).
- [52] E. Benckiser, R. Rückamp, T. Möller, T. Taetz, A. Möller, A. A. Nugroho, T. T. M. Palstra, G. S. Uhrig, and M. Grüninger, *Collective orbital excitations in orbitally ordered YVO<sub>3</sub> and HoVO<sub>3</sub>*, New J. Phys. **10**, 053027 (2008).
- [53] E. Benckiser, L. Fels, G. Ghiringhelli, M. Moretti Sala, T. Schmitt, J. Schlappa, V. N. Strocov, N. Mufti, G. R. Blake, A. A. Nugroho, T. T. M. Palstra, M. W. Haverkort, K. Wohlfeld, and M. Grüninger, *Orbital superexchange and crystal field simultaneously at play in YVO<sub>3</sub>: Resonant inelastic x-ray scattering at the V L edge and the O K edge*, Phys. Rev. B 88, 205115 (2013).
- [54] B. W. Lebert, S. Kim, V. Bisogni, I. Jarrige, A. M. Barbour, and Y.-J. Kim, *Resonant inelastic x-ray scattering study of α-RuCl<sub>3</sub>: a progress report*, J. Phys.: Condens. Matter **32**, 144001 (2020).
- [55] P. Warzanowski, N. Borgwardt, K. Hopfer, J. Attig, T. C. Koethe, P. Becker, V. Tsurkan, A. Loidl, M. Hermanns, P. H. M. van Loosdrecht, and M. Grüninger, *Multiple spin-orbit ex-*

citons and the electronic structure of  $\alpha$ -RuCl<sub>3</sub>, Phys. Rev. Res. **2**, 042007(R) (2020).

- [56] H. Suzuki, H. Liu, J. Bertinshaw, K. Ueda, H. Kim, S. Laha, D. Weber, Z. Yang, L. Wang, H. Takahashi, K. Fürsich, M. Minola, B. V. Lotsch, B. J. Kim, H. Yavaş, M. Daghofer, J. Chaloupka, G. Khaliullin, H. Gretarsson, and B. Keimer, *Proximate ferromagnetic state in the Kitaev model material α-RuCl*<sub>3</sub>, Nat. Commun. **12**, 4512 (2021).
- [57] B. A. Kozikowski and T. A. Keiderling, Intraconfigurational absorption spectroscopy of Os<sup>4+</sup> ion in K<sub>2</sub>SnCl<sub>6</sub> and K<sub>2</sub>OsCl<sub>6</sub> crystals, J. Phys. Chem. 87, 4630 (1983).
- [58] A. Bertin, L. Kiefer, and M. Braden, private communication.
- [59] G. A. Bain and J. F. Berry, *Diamagnetic Corrections and Pas*cal's Constants, J. Chem. Educ. 85, 532 (2008).
- [60] M. W. Haverkort, M. Zwierzcki, and O. K. Andersen, *Multiplet ligand-field theory using Wannier orbitals*, Phys. Rev. B 85, 165113 (2012).
- [61] M. W. Haverkort, Quanty for core level spectroscopy excitons, resonances and band excitations in time and frequency domain, J. Phys.: Conf. Ser. 712, 012001 (2016).
- [62] S. Huotari, G. Vankó, F. Albergamo, C. Ponchut, H. Graafsma, C. Henriquet, R. Verbeni, and G. Monaco, *Improving the performance of high-resolution x-ray spectrometers with positionsensitive pixel detectors*, J. Sync. Radiation 12, 467 (2005).
- [63] S. Huotari, F. Albergamo, G. Vankó, R. Verbeni, and G. Monaco, *Resonant inelastic hard x-ray scattering with diced analyzer crystals and position-sensitive detectors*, Rev. Sci. Instr. 77, 053102 (2006).
- [64] M. Moretti Sala, C. Henriquet, L. Simonelli, R. Verbeni, and G. Monaco, *High energy-resolution set-up for Ir*  $L_3$  *edge RIXS experiments*, J. Elec. Spec. Rel. Phen. **188**, 150 (2013).
- [65] M. Moretti Sala, K. Martel, C. Henriquet, A. Al Zein, L. Simonelli, Ch.J. Sahle, H. Gonzalez, M.-C. Lagier, C. Ponchut, S. Huotari, R. Verbeni, M. Krisch, and G. Monaco, A highenergy-resolution resonant inelastic X-ray scattering spectrometer at ID20 of the European Synchrotron Radiation Facility, J. Synchrotron Rad. 25, 580 (2018).
- [66] P. J. E. M. van der Linden, M. Moretti Sala, C. Henriquet, M. Rossi, K. Ohgushi, F. Fauth, L. Simonelli, C. Marini, E. Fraga, C. Murray, J. Potter, and M. Krisch, *A compact and versatile dynamic flow cryostat for photon science*, Rev. Sci. Instr. 87, 115103 (2016).
- [67] M. Minola, G. Dellea, H. Gretarsson, Y. Y. Peng, Y. Lu, J. Porras, T. Loew, F. Yakhou, N. B. Brookes, Y. B. Huang, J. Pelliciari, T. Schmitt, G. Ghiringhelli, B. Keimer, L. Braicovich, and M. Le Tacon, Supplementary Information for *Collective nature* of spin excitations in superconducting cuprates probed by resonant inelastic x-ray scattering, Phys. Rev. Lett. **114**, 217003 (2015).
- [68] D. Reig-i-Plessis, T. A. Johnson, K. Lu, Q. Chen, J. P. C. Ruff, M. H. Upton, T. J. Williams, S. Calder, H. D. Zhou, J. P. Clancy, A. A. Aczel, and G. J. MacDougall, *Structural, electronic, and magnetic properties of nearly ideal J*<sub>eff</sub> = 1/2 *iridium halides*, Phys. Rev. Mater. 4, 124407 (2020).
- [69] A. Paramekanti, D. D. Maharaj, and B. D. Gaulin, *Octupolar order in d-orbital Mott insulators*, Phys. Rev. B 101, 054439 (2020).
- [70] S. W. Lovesey and D. D. Khalyavin, *Lone octupole and bulk magnetism in osmate* 5d<sup>2</sup> *double perovskites*, Phys. Rev. B 102, 064407 (2020).
- [71] G. Khaliullin, D. Churchill, P. P. Stavropoulos, and H.-Y. Kee, Exchange interactions, Jahn-Teller coupling, and multipole orders in pseudospin one-half 5d<sup>2</sup> Mott insulators, Phys. Rev. Research 3, 033163 (2021).

- [72] S. Voleti, A. Haldar, and A. Paramekanti, Octupolar order and Ising quantum criticality tuned by strain and dimensionality: Application to d-orbital Mott insulators, Phys. Rev. B 104, 174431 (2021).
- [73] L. V. Pourovskii, D. F. Mosca, and C. Franchini, *Ferro-octupolar order and low-energy excitations in d<sup>2</sup> double per-ovskites of osmium*, Phys. Rev. Lett. **127**, 237201 (2021).
- [74] A. Rayyan, D. Churchill, and H.-Y. Kee, *Field-induced Kitaev multipolar liquid in spin-orbit coupled d<sup>2</sup> honeycomb Mott insulators*, Phys. Rev. B **107**, L020408 (2023).
- [75] H. Homborg, Absorptions- und elektronische Raman-Spektren von Intrakonfigurationsübergängen der Hexahalogenokomplexe von  $Os^{IV}$  (X = CI, I) und  $Ir^{IV}$  (X = CI, Br), Z. anorg. allg. Chem. **493**, 121 (1982).
- [76] D. Mintz, R. L. Armstrong, B. M. Powell, and W. J. L. Buyers, Soft rotary mode in the antifluorite crystal K<sub>2</sub>OsCl<sub>6</sub>, Phys. Rev. B 19, 448 (1979).
- [77] G. P. O'Leary and R. G. Wheeler, *Phase Transitions and Soft Librational Modes in Cubic Crystals*, Phys. Rev. B 1, 4409 (1970).
- [78] N. Khan, D. Prishchenko, M. H. Upton, V. G. Mazurenko, and A. A. Tsirlin, *Towards cubic symmetry for Ir<sup>4+</sup>: Structure*

and magnetism of the antifluorite  $K_2 IrBr_6$ , Phys. Rev. B 103, 125158 (2021).

- [79] A. Bertin, T. Dey, D. Brüning, D. Gorkov, K. Jenni, A. Krause, P. Becker, L. Bohatý, D. Khomskii, M. Braden, and T. Lorenz, *Interplay of weak ferromagnetism, ferroelasticity and shape-memory effects in the spin-orbit coupled antiferromagnet K*<sub>2</sub>*ReCl*<sub>6</sub>, arXiv:2207.11101
- [80] B. A. Kozikowski and T. A. Keiderling, Intraconfigurational absorption and magnetic circular dichroism spectra of Os<sup>4+</sup> in Cs<sub>2</sub>ZrCl<sub>6</sub> and in Cs<sub>2</sub>ZrBr<sub>6</sub>, Mol. Phys. **40**, 477 (1980).
- [81] H. U. Rahman, Analysis of the Magnetic Susceptibility of K<sub>2</sub>OsCl<sub>6</sub>, Phys. Rev. B 3, 729 (1971).
- [82] P. B. Dorain, H. H. Patterson, and P. C. Jordan, *Optical Spectra of Os*<sup>4+</sup> in Single Cubic Crystals at 4.2°K, J. Chem. Phys. 49, 3845 (1968).
- [83] S. B. Piepho, J. R. Dickinson, J. A. Spencern, and P. N. Schatz, *High resolution absorption and magnetic circular dichroism spectra of Cs*<sub>2</sub>*ZrCl*<sub>6</sub>: *Os*<sup>4+</sup>, Mol. Phys. **24**, 609 (1972).