

Evaluating covalency using resonant inelastic x-ray scattering spectral weights: Silver fluorides versus cuprates

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We investigate the electronic structure of AgF_2 , AgFBF_4 , AgF , and Ag_2O using x-ray absorption spectroscopy (XAS) and resonant inelastic x-ray scattering (RIXS) at the $\text{Ag } L_3$ edge. XAS results were compared with density functional theory computations of the spectra, allowing an identification of main features and an assessment of the theoretical approximations. Our RIXS measurements reveal that AgF_2 exhibits charge-transfer (CT) excitations and dd excitations, analogous to those observed in La_2CuO_4 . We propose to use the ratio of dd to CT spectral weight as a measure of the covalence of the compounds and provide explicit equations for the weights as a function of the scattering geometry for crystals and powders. The measurements at the metal site L_3 edge and previous measurement in the ligand K edge reveal a striking similarity between the fluoride and cuprate materials, with fluorides somewhat more covalent than cuprates. These findings support the hypothesis that silver fluorides are an excellent platform to mimic the physics of cuprates, providing a promising avenue for exploring high- T_c superconductivity and exotic magnetism in quasi-two-dimensional (AgF_2) and quasi-one-dimensional (AgFBF_4) materials.

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I. INTRODUCTION

In the search for superconducting materials similar to cuprates, a natural route is the replacement of Cu by Ag, as they both belong to the coinage metal group. Despite this chemical similarity, copper and silver have important differences. Because Ag^{2+} is more electronegative than Cu^{2+} , AgO has a negative charge-transfer (CT) energy that ends up in a nonmagnetic charge disproportionated state ($1+/3+$), instead of the desired $4d^9 \text{Ag}^{2+}$. This is in contrast to CuO , which is an antiferromagnetic charge-transfer insulator with the $3d^9$ ground state of Cu^{2+} . The lack of magnetism in AgO can be

addressed by replacing each oxygen with two fluorine atoms, resulting in AgF_2 . The stronger electronegativity of fluorine compensates for the electronegativity of Ag^{2+} and results in the wished spin-1/2 antiferromagnetic charge-transfer insulator that has been proposed [1,2] as an alternative route to high-temperature superconductivity.

Unlike the charged CuO_2 plane of cuprates [Fig. 1(a)], AgF_2 is inherently neutral due to the presence of F^- ions instead of O^{2-} . Consequently, AgF_2 does not need a charge reservoir [Fig. 1(b)] and can be regarded as the “012” equivalent of the 214 stoichiometry found in cuprates like La_2CuO_4 . Indeed, AgF_2 consists of neutral planes stacked one on top of the other, which have the same topology as the CuO_2 planes of cuprates but with much larger buckling [cf. Figs. 1(a) and 1(b)].

The magnetic ground state of AgF_2 has been determined long ago [3]. It is a canted antiferromagnet with a weak ferromagnetic component larger than the analogous phenomena in parent cuprates. This can be understood as due to the larger buckling of planes of AgF_2 and larger spin-orbit coupling leading to a stronger Dzyaloshinskii-Moriya interaction.

The Néel temperature [3] of AgF_2 (163 K) is half that of La_2CuO_4 (325 K) [4], which hints at a moderately large

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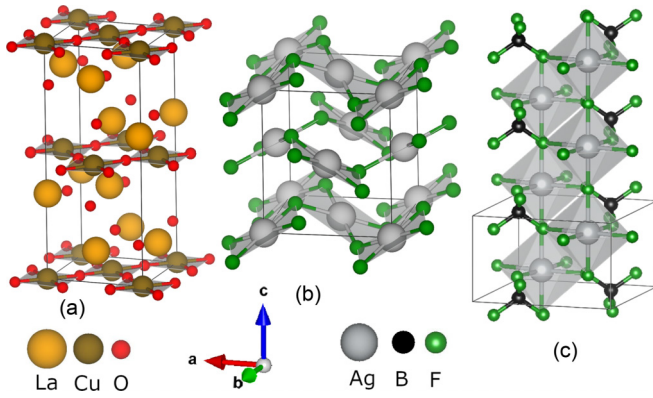


FIG. 1. Crystallographic structures of La_2CuO_4 [panel (a)], AgF_2 [panel (b)] and AgFBF_4 [panel (c)].

antiferromagnetic interaction. Indeed, the antiferromagnetic interaction has been measured with two-magnon Raman scattering and inelastic neutron scattering [1], yielding a value $J = 70$ meV compared to $J = 100\text{--}130$ meV in the Cu-based siblings.

In cuprates, theoretical [5] as well as empirical arguments suggest that spin fluctuations are important for Cooper pairing with a reported positive correlation between T_c and doping for monolayer systems [6–8].

It has been proposed [8] that the antiferromagnetic interaction of AgF_2 could be enhanced by growing a flat layer on appropriate substrates. This, in addition, has the advantage of reducing polaronic tendencies, which could hamper metallicity [9]. This strain engineering approach predicts a maximum superconducting T_c of nearly 200 K. However, it relies on a close analogy between AgF_2 and parent cuprates, which calls for an in-depth comparison.

Although optical measurements are challenging due to the lack of single crystals, strongly compressed powder samples have been produced using explosives, which allowed the recording of optical spectra [10]. The optical absorption shows an onset at 1.75 eV for charge-transfer excitations and a broad peak at 3.4 eV. These energies are somewhat higher than, for example, La_2CuO_4 (LCO), which shows an onset at about 1.6 eV and a peak at 2.2 eV. Hybrid density functional theory (DFT) calculations predicted a charge-transfer parameter $\Delta = 2.7$ eV for AgF_2 [1]. High-energy spectroscopies combined with small cluster exact computations [11] yield a somewhat higher value $\Delta = 3.5\text{--}4.1$ eV.

In addition to optical spectroscopy, Ref. [10] presented the resonant inelastic x-ray scattering (RIXS) spectrum of AgF_2 at the fluorine K edge (682 eV, soft x-rays). The spectrum is dominated by charge-transfer excitations above 3 eV, but also dd excitations around 2 eV are clearly visible due to mixing between the transition metal and the ligand. Moreover, a tail of the elastic peak around 200 meV has been assigned to bimagnon excitations. Interestingly, the spectrum of AgF_2 holds several analogies to that of LCO measured at the O K edge. This is a very encouraging result for attempting to dope and search for superconductivity in AgF_2 . Because the RIXS was performed on the F K edge and on a powder sample, polarization information was not available. Therefore, the assignment of the symmetry of the different dd excitations

could be done only indirectly by comparing the energy with DFT computations.

Besides the potential interest as cuprate analogs [1,2,8,12–14], silver fluorides are interesting because of the possibility to host exotic magnetic phases [15–25]. In this regard, a particularly intriguing system is AgFBF_4 [Fig. 1(c)]. Initially thought to be a metal due to its temperature-independent susceptibility [26], it is now believed to be an excellent realization of the one-dimensional Heisenberg model [18,19] with a superexchange interaction of $J \approx 300$ meV. Ironically, this model can be mapped to a one-dimensional “metallic” system, but in which the fermionic excitations are not electrons but neutral spinon excitations [27].

According to DFT computations [18,19], the strong superexchange in AgFBF_4 is due to partially filled $d_{3z^2-r^2}$ orbitals oriented along the c axis hybridizing with ligand p_z orbitals. Up to now, one of the best realizations of the one-dimensional Heisenberg model is Sr_2CuO_3 , whose spinon spectrum observable in optics can be perfectly fitted with this model [28] with $J = 246$ meV. The spectrum has a logarithmic singularity at $\omega_s = J\pi/2 = 386$ meV, which could be observed in RIXS [29], and the extracted value of J coincides with the theoretical fit of the optical experiments. In the case of AgFBF_4 , which we study here, the value of J predicted by DFT implies a Van Hove singularity in the RIXS spectrum (due to powder average) at $\omega_s = 470$ meV.

For insulating cuprates, the determination of dd excitations [30,31] and the full characterization of the single and multi-magnon spectra [32–35] were made by Cu L_3 RIXS. This is because at the L_3 edge (930 eV), those excitations are accessed directly and not indirectly as at the ligand K edge. Indeed, in 3d transition metals, the $2p \rightarrow 3d$ resonance is particularly intense, providing ideal conditions for RIXS spectroscopy.

Even though AgF_2 is not a new material, advanced spectroscopy studies are scarce, due to its instability and the lack of single crystals. To have a complete comparison of the electronic structure of the AgF_2 and cuprates, it is highly desirable to perform RIXS at the absorption edge of the metal. Unfortunately, the Ag L_3 edge is at 3350 eV (tender x-rays), and the soft and hard x-ray beamlines and high-resolution spectrometers developed for 3d and 5d transition metal L edges are unsuitable.

In order to perform a RIXS measurement at the Ag L_3 edge, we used the ID26 Tender X-ray Emission Spectrometer (TEXS) beamline (ESRF, Grenoble) [36]. Although this beamline is dedicated mainly to high-energy-resolution fluorescence detection and does not have the resolution of present-day experiments at dedicated RIXS beamlines, we show here that RIXS measurements at the Ag L_3 edge are feasible, and clear conclusions about the electronic similarity between silver fluorides and cuprates can be drawn.

The paper is organized as follows. Section II presents the experimental and DFT methods. In Sec. III A, we present silver L_3 ($2p \rightarrow 4d$) x-ray absorption spectroscopy (XAS) measurements of powder samples of AgF_2 and AgFBF_4 (d^9), and, as a reference, AgF and Ag_2O (d^{10}). We compare the spectra with previous literature results, including pure silver, and with DFT computations. The near-edge spectra of the d^9 materials exhibit pre-edge features, indicating the feasibility

of RIXS processes. Indeed, a rich RIXS spectrum was obtained at the Ag L_3 edge for AgF_2 and AgFBF_4 , while AgF and Ag_2O show essentially only fluorescence signals (Sec. III B). In Sec. III D, we compare cuprates and silver fluorides in ligand and metal edges. In Sec. III E, we present a method to determine covalency from spectral weight ratios and apply it to cuprates and silver fluorides. To this aim, Appendix C presents general formulas to compute the powder average of RIXS scattering intensities. Finally, we conclude in Sec. IV.

II. METHODS

A. Sample preparation and handling

AgF_2 and AgFBF_4 polycrystalline samples for the measurements have been freshly prepared. The handling of volatile (anhydrous HF , F_2 , BF_3) and nonvolatile materials, as well as the types of reaction vessels, has been described previously [37].

Preparation of AgF_2 was described in Ref. [10], including the procedure to obtain compact pellets.

AgFBF_4 consisted of nonpelletized powder. For the preparation, AgF_2 was loaded into a fluorinated ethylene propylene reaction vessel in a dry box, and anhydrous HF was condensed onto it at 77 K using a vacuum system. The reaction vessel was then warmed to ambient temperature, and BF_3 was introduced to achieve a total pressure of 4 bar. Additional BF_3 was periodically added to replace the amount consumed. The supernatant solution above the insoluble blue solid was also blue. A small amount of fluorine was added to prevent the formation of AgBF_4 . After three days of extensive stirring at ambient temperature, the anhydrous HF and excess BF_3 were removed under vacuum at room temperature, yielding powdered AgFBF_4 [26].

Because the samples are very sensitive to moisture, it was necessary to mount them in a specially designed cell closed by a Kapton window. The samples were loaded into the cell and sealed hermetically inside a glove box filled with argon. They were then immediately transferred to the beamline chamber via a load lock. This avoided degradation in the low vacuum (10^{-5} mbar) of the TEXS instrument. Ag_2O and AgF samples were also powder samples.

B. Experimental

The measurements were done at beamline ID26 of ESRF—The European Synchrotron (Grenoble, France) using the TEXS [36]. The spectrometer can host up to 11 cylindrically bent Johansson crystal analyzers arranged in a nondispersive Rowland circle geometry and a 16-wire detector. For the present experiment, we used one Si(220) Johansson crystal with bending radius of the crystal planes of 1004 mm at a horizontal scattering angle around 96° . All the measurements were done with the incoming polarization in the scattering plane (π polarization). The incident beam energy was selected by the Si(111) reflection of a cryogenically cooled double-crystal monochromator. The combined energy bandwidth as measured in the elastic scattering peak from a Cu holder was 0.5 eV. All measurements were performed at $T = 15$ K.

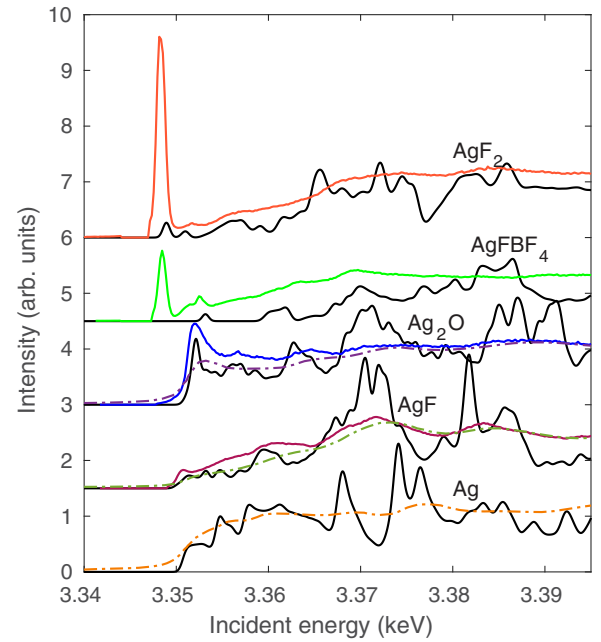


FIG. 2. Absorption spectra of the investigated compounds and silver in the region of the Ag L_3 absorption edge. We show data from the present work (full colored lines) and Ref. [42] (dot-dashed lines). The curves were normalized to 1 at the highest energy measured (3.44 keV) and plotted with a vertical shift of 1.5 (arb. units). We also show the SCH results (black). The intensity of the DFT data was adjusted to ease the comparison with the experiment. The theoretical spectra were shifted by 2 eV to higher energy, except for AgF_2 (+4 eV shift), AgFBF_4 (+11 eV shift), and Ag (−2 eV shift). For the upper two curves, the spectra shown correspond to the antiferromagnetic DFT solution.

We used high-energy-resolution fluorescence-detected (HERFD) XAS. This technique [38–41] consists of measuring the x-ray absorption near-edge structure (XANES) of the incident photons by monitoring the intensity of a fluorescence line, in our case $L\beta_{2,15}$, using a narrow energy resolution. The $L\beta_{2,15}$ line corresponds to the decay $4d \rightarrow 2p_{3/2}$. It should be noted that the fluorescence line used for detection is in the same energy region as the outgoing RIXS photons. The $L\beta_{2,15}$ line was chosen for HERFD-XANES instead of $L\alpha_1$ in order to avoid moving the XES instrument over large angular ranges between XANES and RIXS measurements. As a consequence, the elastic peak appears in the HERFD XANES scans at the energy that was chosen for the emission spectrometer (3346.6 eV). In the XAS spectra shown in Fig. 2, we removed the elastic line from the data for the sake of clarity.

Regarding RIXS, a two-dimensional map is constructed by scanning the energies of both incoming and outgoing photons. Due to the limitation in resolution, the quasielastic line likely has significant inelastic contributions (e.g., from magnetic excitations and phonons). Thus, the energy of our “elastic” feature has a systematic positive error, which implies an underestimation of the reported energy of excitations (on the order of the energy resolution) as discussed below. The count rates in the dd excitations were tens of kilohertz.

Several scans were performed for each sample to check for possible degradation during measurement. In the absence of

TABLE I. Parameters used in the DFT computations. The standard VASP parameters are energy cutoff for the plane-wave basis (ENCUT), parameters for the Monkhorst-Pack (MP) k -point grid, and total number of states (NBAND).

Compound	Lattice constants			ENCUT (eV)	XAS		DOS	
	a (Å)	b (Å)	c (Å)		MP k -point grid	NBAND	MP k -point grid	NBAND
Ag	4.052	4.052	4.052	700	$15 \times 15 \times 15$	1504	$48 \times 48 \times 48$	150
Ag ₂ O	4.716	4.716	4.716	600	$9 \times 9 \times 9$	300	$15 \times 15 \times 15$	150
AgF	4.900	4.900	4.900	700	$13 \times 13 \times 13$	360	$19 \times 19 \times 19$	150
AgF ₂	5.073	5.529	5.813	600	$10 \times 10 \times 10$	500	$16 \times 16 \times 16$	200
AgFBF ₄	6.670	6.670	3.995	600	$9 \times 9 \times 15$	504	$15 \times 15 \times 25$	200

significant changes, the reported spectra are the average over such scans. Despite the low energy resolution, as we shall see, the main structures could be identified and compared to typical spectra in cuprates.

C. DFT computations

We used the Vienna *Ab initio* Simulation Package [43–46] (VASP) to compute the XAS functions of bulk AgF₂ and related compounds using the supercell core-hole (SCH) method [47] with the PBEsol [48] exchange and correlation functional. In the case of d^9 compounds, we repeated the computation in the antiferromagnetic state using the DFT + U corrections with $U = 5$ eV. For the crystal structures, we used the experimental data.

In the following, VASP parameters are indicated by their standard name in capital letters. We used Gaussian smearing with a width given by SIGMA = 0.02 eV, while for the XAS spectrum, the corresponding smearing parameter was set at CH_SIGMA = 0.5 eV. The self-consistent loop was interrupted when the error in the energy was less than EDIFF = 10^{-6} eV. VASP parameters used for the energy cutoff of the plane-wave basis and the Monkhorst-Pack grid are detailed in Table I for each compound, together with the cell dimensions.

In the SCH method, the absorption is computed in the presence of a real-space core hole. To minimize the effect of the periodic images of the core hole, one can perform the computation in a supercell. We checked that for AgF₂ the results were almost identical in the unit cell (four Ag atoms) or in a $2 \times 2 \times 2$ supercell. Therefore, for the fluorides and the oxide, we performed the computation in the unit cell, as we do not expect they would behave differently. For Ag, we found that the elementary cell was not enough, and we used a $2 \times 2 \times 2$ supercell.

A window of about 50 eV above the Fermi level is necessary to compare with the XAS spectra measured. For this, a significant number of unoccupied states had to be added to the calculation. The total number of states, NBAND (occupied plus unoccupied), is also shown in Table I.

Notice that VASP does not include spin-orbit coupling in the $2p$ core hole. Therefore, the L_2 ($j = 1/2$) and L_3 ($j = 3/2$) edges are represented by the same feature in the theory.

For the density of state (DOS) computation, the elementary cell was used in all cases. The plane-wave energy cutoff is kept identical to that used in the XAS simulations. However, the total number of states per k point is substantially reduced, while the number of k points is increased, as summarized in

Table I, to obtain an energy resolution comparable to that of the XAS calculations.

III. RESULTS

A. X-ray absorption spectroscopy

The Ag L_3 absorption edge is due to transitions from the core $2p_{3/2}$ states to $4d$ or $5s$ unoccupied states. Typically, the transition to empty d states leads to pre-edge peaks in x-ray absorption, commonly referred to as “white lines” due to their appearance in old photographic detection.

Figure 2 shows the XAS spectra from the present work for powder samples (full lines) and from previous measurements by Miyamoto *et al.* (dot-dashed lines) [42]. The Ag₂O and AgF spectra are in good agreement with Ref. [42], although our measurements show sharper features and more details, probably because of the different techniques used. Black lines are the theoretical computations in the SCH approximation.

Although the spin-orbit interaction, which splits the L_2 and L_3 edges by 172 eV, is not considered in the calculations, the energy of the theoretical edge is surprisingly close to the experiment for the L_3 edge. A shift in the range -2 to 4 eV was enough to align the theoretical data to the experiments. In Fig. 2, lifetime effects were neglected, yet the theory reproduces gross features of the data. In Appendix A, we show that adding a phenomenological Lorentzian broadening substantially improves the agreement with experiment (Fig. 14).

In the following, we discuss the theory without broadening effects as this allows to make contact with the DOS computations.

1. Ag

The experiment shows no white-line consistent with the $4d^{10}5s$ configuration of pure Ag. The theory describes the overall edge shape quite well (Fig. 2) and exhibits some peaks at 3.368, 3.374, and 3.377 keV that correspond to broad structures observed in the experiment. Naively, one would expect the edge to have a dominant $5s$ character, but the DOS analysis (Fig. 3) shows that there are significant $5p$ and $4d$ contributions due to strong hybridization. In general, the theoretical XAS spectra reflect main structures in the DOS except for the strong s peak at high energy.

2. $4d^{10}$ compounds

AgF data by Miyamoto *et al.* reproduced in Fig. 2 (dot-dashed lines) show no evident pre-edge peak, although a weak structure at 3.352 keV was interpreted as a peak. We

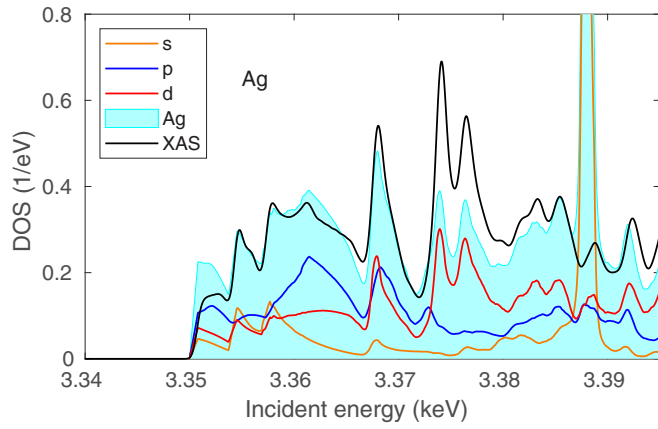


FIG. 3. Ag symmetry projected (orange, blue, red) DOS and total silver DOS (cyan shadowing) compared to the computation of the XAS in the SCH method shown in Fig. 2 (black, intensity in arb. units). To simulate the edge, we show only the unoccupied part of the DOS, and the Fermi energy has been shifted to match the main features of the SCH computation.

do observe a weak excitonic resonance at the edge of the absorption profile, which can be considered a precursor of the white line. We interpret this as due to the mixing of the nominally d^{10} ground state with the d^9s^1 state mediated by the fluorine p orbitals. Similar pre-edge peaks have been observed [49] in Cu_2O with a $3d^{10}$ ground state and in other Ag $4d^{10}$ compounds [42].

The SCH computation reveals a gradual increase in intensity from the edge, accompanied by intense structures at high energies (3.36, 3.37, and 3.382 keV), which also corresponds

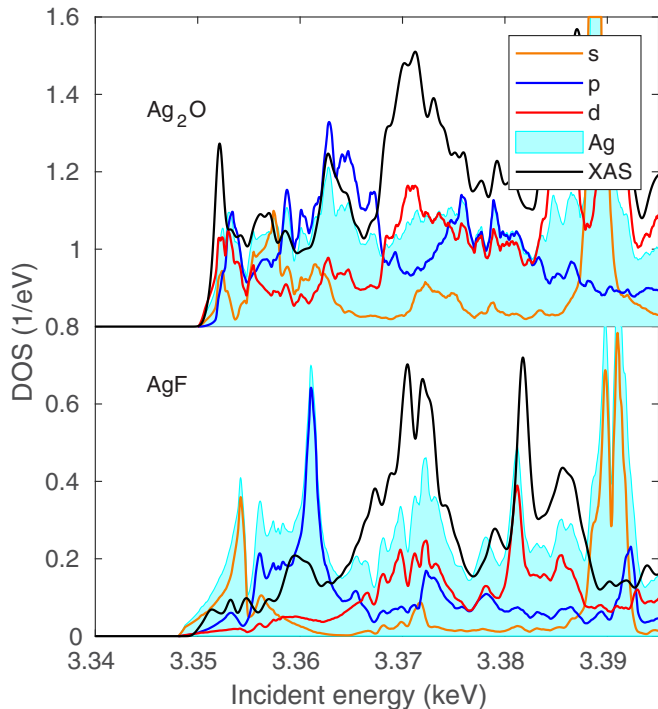


FIG. 4. Same as Fig. 3 for d^{10} compounds. The Ag_2O data have been shifted vertically by 0.8 eV^{-1} .

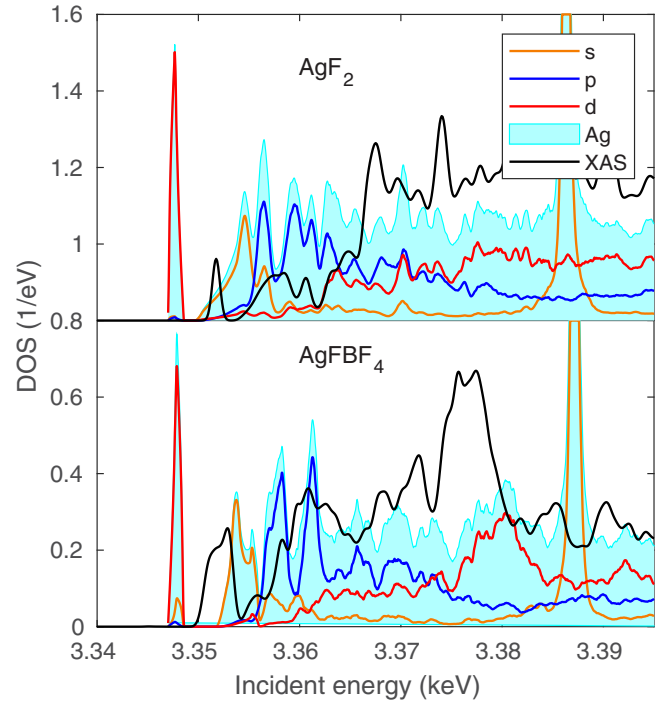


FIG. 5. Same as Fig. 3 for d^9 compounds in a nonmagnetic DFT solution. The AgF_2 data have been shifted vertically by 0.8 eV^{-1} . The leading peak in the DOS has been aligned with the experimental white line.

to broad structures observed in the experiment. We attribute the very weak excitonic resonance to the small density of states at the edge, which has mainly $5s$ character (Fig. 4). In contrast, the DOS in Ag_2O exhibits a steep rise at the edge region, which explains the strong excitonic resonance both in the theory and in the experiment. Also, in this case, the resonance is sharper than the results from Ref. [42] (cf. Fig. 2).

In Ag_2O , the DOS shows a weaker s contribution and more weight of other symmetries due to stronger hybridization.

3. $4d^9$ compounds

The experiment for AgF_2 and AgFBF_4 shows clear white lines at nearly the same energy (3.348 keV), consistent with a d^9 ground state (Fig. 2).

For the theoretical computations, we considered an anti-ferromagnetic state. In this case, we obtain very weak white lines compared with experiments. Despite this deficiency, in the case of AgF_2 the white line and higher-energy structures are located in reasonable agreement with the experimental features (Fig. 2).

The experiment in AgFBF_4 shows two pre-edge features: Besides the narrow white line at 3.348 keV, there is a broader feature at 3.352 keV (Fig. 2). Aligning this with the weak white line in the theory results in a partial match of high-energy structures except for the intense absorption around 3.385 keV. However, the main problem is that the leading white line is not explained.

A hint for the reason for the weak white lines in the theory is obtained by plotting simply the unoccupied DOS without the core hole in a nonmagnetic computation. This yields a

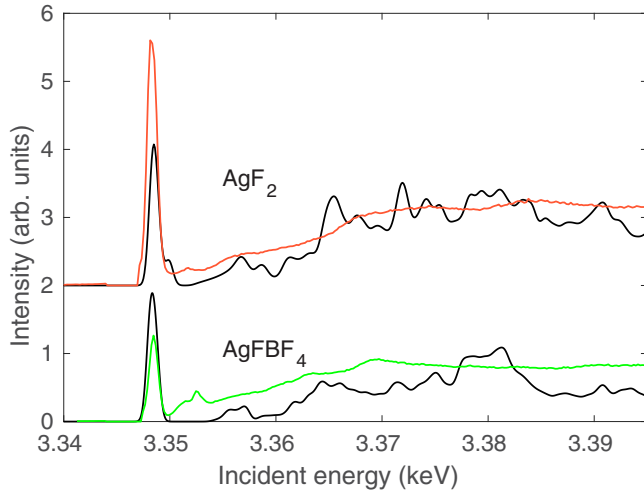


FIG. 6. Comparison of the experimental absorption spectra of the d^9 compounds with the SCH in the presence of $1/2$ core hole in the antiferromagnetic DFT solution. The AgF_2 spectra were plotted with a vertical shift of 2 (arb. units). The theoretical spectra was shift in energy by 3.5 eV (AgF_2) and 5.5 eV (AgFBF_4) to align the white lines.

result similar to the experiment (Fig. 5). Indeed, because $4d$ are narrow and only $1/10$ of the $4d$ DOS is unoccupied, one obtains a narrow feature that mimics the experimental white line. As expected, this is almost purely $4d$ character. The black lines in Fig. 5 show the results of the SCH in the nonmagnetic case, showing again that this approximation yields very weak white lines.

A similar result as the DOS computation but taking into account that matrix element effects can be obtain using the Slater transition state method [50,51]. This amounts to doing the SCH with $1/2$ core hole, which significantly reduces the screening effect and yields a strong white line comparable to the experiment, as shown in Fig. 6. These results underscore the importance of dynamical screening effects [52,53] and their competition with the core-hole lifetime [54], a well-documented phenomenon in resonant emission studies [55,56].

For the Ag L_3 edge, the core-hole lifetime is short, resulting in a Lorentzian broadening (FWHM) of 2.4 eV [57]. The core hole acts as a localized, positively charged impurity that gets screened via particle-hole excitations near the Fermi level. However, excitations with energies below the core hole broadening scale lack sufficient time to fully relax and may be considered “frozen.”

If this dynamical effect dominates, the experimental spectra should resemble the ground-state DOS calculated in the absence (Fig. 5) of a reduced core-hole potential (Fig. 6). Our observations are consistent with this interpretation.

In contrast, the SCH calculation assumes a very long core-hole lifetime, allowing for complete electronic relaxation. In this regime, metallic electrons populate the “impurity” state, which becomes Pauli blocked as a final state, drastically suppressing the white-line intensity. Since this suppression is not observed experimentally, we conclude that the screening time is comparable to, or exceeds, the core-hole lifetime—a behavior characteristic of correlated systems [55,56].

A more accurate computation should consider core-hole lifetime and excitonic effects on an equal footing and is beyond our present scope.

Because of the symmetry of the structures [Figs. 1(b) and 1(c)], the theoretical spectra can be different along different crystalline axes. In Appendix A, we report the polarization dependence of the computed spectra for both compounds.

B. Resonant inelastic x-ray scattering

Figure 7 shows the false color map of the RIXS/fluorescence spectra of AgF and AgF_2 . The dispersive features correspond to fluorescence, while the nondispersive ones are Raman contributions to the RIXS spectra. The former are related to band behavior and can be captured in a joint band DOS computation with appropriate matrix elements as shown in Ref. [58]. The latter are related to localized states, can be captured with cluster computations, and will be our focus.

AgF_2 shows a strong feature at 2 eV of energy loss corresponding to dd transition and a faint structure in the 4–8 eV energy loss range corresponding to charge-transfer excitations (notice the log intensity scale). These assignments are based on previous computations and measurements at the fluorine K edge [10] as discussed in more detail below. In contrast, for AgF, these features are not present; only the elastic line and the dispersive fluorescence feature are visible. This behavior is consistent with the closed-shell nature of AgF in contrast to the open $4d$ shell of AgF_2 . Ag_2O exhibits a map similar to AgF consistent with the d^{10} nature and is not shown. Likewise, the AgFBF_4 map (not shown) resembles AgF_2 reflecting the d^9 ground state.

The black dashed line in panel (b) corresponds to the scan done at constant outgoing photon energy in the HERFD-XAS experiments. Such a scan intercepts a strong dd process, which is the white line identified in Fig. 2. Notice that, strictly speaking, HERFD XAS is not a measurement of the absorption coefficient, but it can be shown to be closely related to it. This is related to the fact that photon absorption is the first step of the RIXS process. Therefore, the same feature can be interpreted in different ways depending on how the scan is done: a dd excitation for a vertical scan in Fig. 7 or an absorption white line for the diagonal scan (constant outgoing photon energy).

For AgF_2 in Fig. 7(b), the maximum RIXS intensity is obtained for an incident photon energy of 3.349 keV. Therefore, in the following, we concentrate on the spectra at this incident energy.

In Fig. 8, we show the RIXS spectrum corresponding to a photon energy of 3.349 keV. The inset shows the CT part of the spectrum for different photon energies, confirming that it does not disperse and therefore it is not a fluorescence feature. The vertical lines in the main panel are the results of the exact diagonalization computations from Refs. [10,11] showing the position of one-hole states in an AgF_6 cluster. We write the one-hole states as

$$\begin{aligned} |\psi_d(v)\sigma\rangle &= \alpha_v |d^9, v\sigma\rangle + \beta_v |d^{10}\underline{L}, v\sigma\rangle, \\ |\psi_p(v)\sigma\rangle &= -\beta_v |d^9, v\sigma\rangle + \alpha_v |d^{10}\underline{L}, v\sigma\rangle, \end{aligned} \quad (1)$$

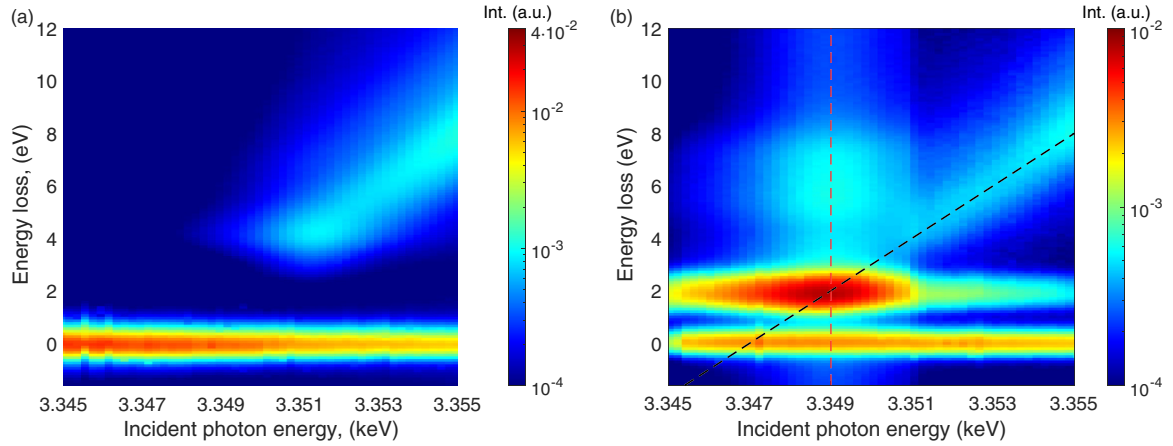


FIG. 7. RIXS/fluorescence intensity maps for AgF [panel (a)] and AgF₂ [panel (b)] powder samples in log scale. The vertical gray dashed line shows the cut in Fig. 8. The oblique black dashed line is the fluorescence scan used for the absorption measurement. Notice the overlap with the strong dd RIXS excitation.

where $\nu = x^2 - y^2, 3z^2 - r^2, xy, yz, zx$ and σ denotes the spin. The states on the right are the ionic configurations, where $|d^{10}\bar{L}, \nu\sigma\rangle$ denotes a d^{10} state with a hole in a linear combination of ligand p orbitals that transforms like one of the d orbitals [10,59]. α_ν and β_ν are real coefficients and without loss of generality we take $\alpha_\nu^2 > \beta_\nu^2$, so $|\psi_d(\nu)\sigma\rangle$ ($|\psi_p(\nu)\sigma\rangle$) has prevalent d^9 ($d^{10}\bar{L}$) character. Each pair ($|\psi_d(\nu)\sigma\rangle, |\psi_p(\nu)\sigma\rangle$) represents a bonding-antibonding combination for one-hole states in D_{4h} symmetry. This is not an exact symmetry in AgF₂, but it can be assumed within the AgF₆ cluster to a good approximation. Reference [10]

reported that deviations from exact D_{4h} symmetry generate small matrix elements coupling different symmetry sectors; however, omitting these contributions does not significantly affect the results.

The ground state has approximate $d_{x^2-y^2}$ symmetry and is represented by the vertical line at zero energy in Fig. 8. The excited states near 2 eV correspond to the states with the hole in orbitals of prevalent Ag d character and different symmetry, as indicated by the labels. Transitions between the ground state and these states are classified as dd transitions. The excited states between 4 and 6 eV have a prevalent hole ligand character, so transitions from the ground state to these states correspond to charge-transfer transitions. Comparison of the cluster computation with the spectrum confirms the peak at 2 eV as the dd excitations and the broad feature at high energy as the CT part.

Figure 9 shows the RIXS spectrum for AgFBF₄. The spectrum shows similar dd and CT features as AgF₂. One difference is that the CT band shows a weak feature at 4 eV

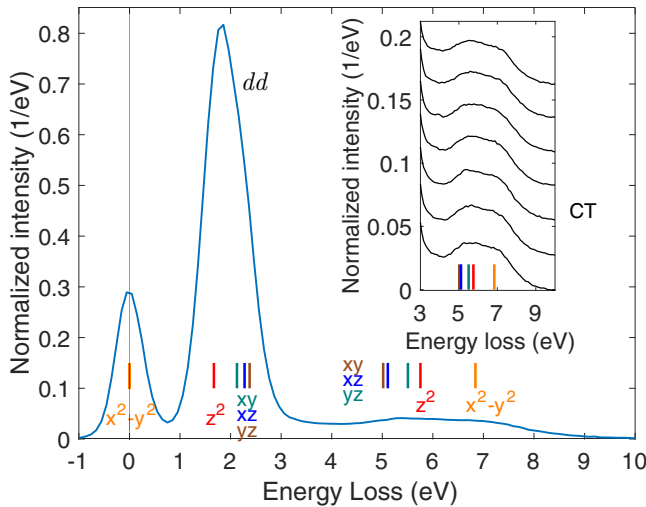


FIG. 8. Ag L_3 RIXS spectrum of powder AgF₂ sample (blue curve)—measured at 3.349 keV incident energy. Colored vertical lines represent bonding and antibonding states for hybridized orbitals between d^9 and $d^{10}\bar{L}$ configurations, following cluster computation done in Ref. [10], with the colors identifying the symmetry of the states ($z^2 \equiv 3z^2 - r^2$). The inset shows the CT part of the spectrum for different incoming photon energies. The lower curve is for an incoming photon energy of 3.3485 keV, and the following curves correspond to steps of 0.2 eV successively shifted by 1.5×10^{-4} (normalized intensity, 1/eV). All the curves are normalized over $dd + CT$ area. A linear background was subtracted.

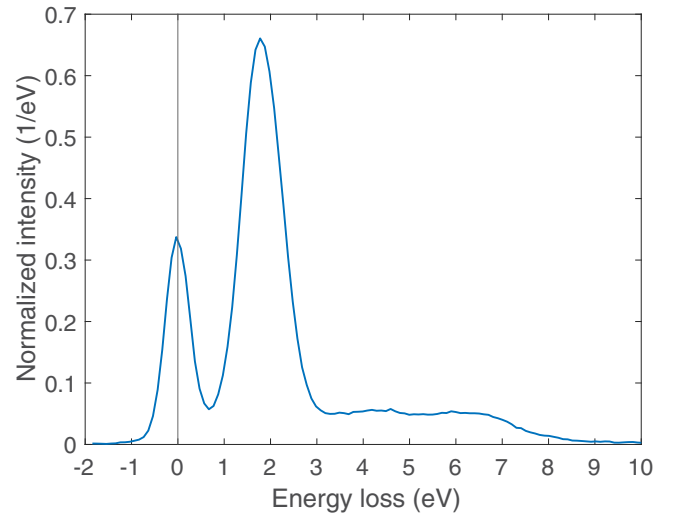


FIG. 9. RIXS spectrum for powder AgFBF₄ sample measured with 3.349 keV incident photon energy. The curve was normalized over $dd + CT$ area. A linear background was subtracted.

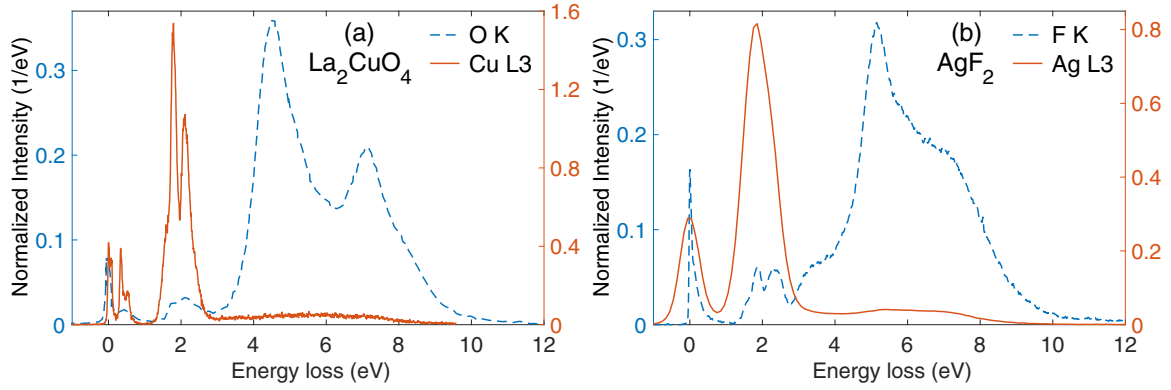


FIG. 10. Comparison between RIXS spectra for La_2CuO_4 [panel (a)] and AgF_2 [panel (b)] measured at both edges (K, L). The AgF_2 $\text{Ag } L_3$ data are the present measurement. The other curves are based on reference data from Ref. [10] (AgF_2 K edge), [60] (LCO K edge), and [61] (LCO L edge). All the curves are normalized over $dd + \text{CT}$ area.

energy loss, where the AgF_2 spectrum shows a minimum (see also the inset of Fig. 11). Also in this case, we have verified that the CT feature exhibits no signs of dispersion (not shown), thereby excluding fluorescence contamination. A cluster computation has not been performed in this case; however, the experimental results indicate similar hybridizations and charge-transfer energies as for AgF_2 (cf. Fig. 8). Due to the sensitivity of the samples to radiation, we cannot exclude the possibility that part of the boron was released as BF_3 and the sample became partially AgF_2 , thereby increasing its similarity to this compound.

C. Observability of spin-flip process

It was suggested long ago that spin-flip processes may be excited in RIXS [62] because of the strong spin-orbit inter-

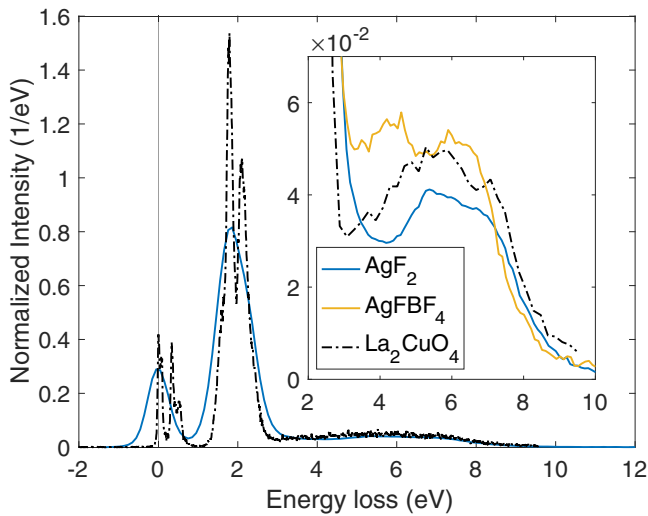


FIG. 11. RIXS $\text{Ag } L_3$ spectrum for AgF_2 powder sample (full line) compared with $\text{Cu } L_3$ spectrum of LCO (dotted-dashed line). The inset shows a zoom of the CT part for AgF_2 and AgFBF_4 compared with LCO. All the curves are normalized over $dd + \text{CT}$ area. The curve for LCO shown in the inset was smoothed with a step of 0.2 eV.

action in the transition metal core hole. It was later shown [63] that for the spin-flip process to be allowed in d^9 systems with a $d_{x^2-y^2}$ hole state (e.g., parent cuprates and AgF_2), the magnetic moment must lie in the basal plane. This is the case in cuprates and also AgF_2 according to early neutron scattering experiments [64].

The transitions that make the spin flip possible are the following:

$$|x^2 - y^2 \uparrow_x\rangle \xrightarrow{x E_x} |x \uparrow_x\rangle \xrightarrow{S_z L_z} |y \downarrow_x\rangle \xrightarrow{y E_y} |x^2 - y^2 \downarrow_x\rangle. \quad (2)$$

Here, $|x^2 - y^2 \uparrow_x\rangle$ is a shorthand for the state $|d^9, x^2 - y^2 \uparrow_x\rangle$ defined above but with the spin polarized in the x direction, $x E_x$ represents an electric dipole transition with the photon electric field in the x direction, $|x \uparrow_x\rangle$ represents the d^{10} state with a core hole in a p_x state, and $S_z L_z$ is the spin-orbit coupling with the term $S_z(x\partial_y - y\partial_x)$, which flips both the direction of the spin and the p orbital. The remaining terms follow an analogous notation. The two dipole transitions correspond to the incoming and the outgoing photon electric field, and the chain of transitions illustrates the well-known fact that the two polarizations should be crossed for the spin-flip transition to be allowed [63].

For the case of AgFBF_4 , an important difference according to DFT [18,19,23] is that the ground state has prevalently $d_{3z^2-r^2}$ character with the z axis oriented along the chain, different from parent cuprates and also one-dimensional cuprates such as Sr_2CuO_3 . Long-range order has not been reported, consistent with a spin liquid ground state. We can still expect antiferromagnetic quasi-long-range order to develop with the magnetic moment predominantly in one spatial direction. Adding spin-orbit coupling, we find that at the DFT level, the spin is in the x - y plane. In this case, the chain of transitions that can lead to a spin-flip process reads

$$|3z^2 - r^2 \uparrow_x\rangle \xrightarrow{z E_z} |z \uparrow_x\rangle \xrightarrow{S_y L_y} |x \downarrow_x\rangle \xrightarrow{x E_x} |3z^2 - r^2 \downarrow_x\rangle. \quad (3)$$

This shows that the process is allowed with one polarization in the chain direction and the other polarization perpendicular to it.

Unfortunately, the quasielastic line is too broad in both compounds to disentangle these excitations. Still, the present

considerations set the stage for future studies of magnetic excitations using higher-resolution measurements.

D. The electronic structure of AgF_2 versus La_2CuO_4

Having available data in the Cu L_3 and O K edge in LCO [31,60], and analogous data for the Ag L_3 (this work) and the F K edge [10], we can now make a detailed comparison of the electronic structure of the two compounds.

Figure 10 shows the RIXS spectra in the metal and the ligand edge for LCO [panel (a)] and for AgF_2 [panel (b)]. Despite the much lower resolution of the present Ag L_3 data, the similarity of the spectra in the two materials is striking.

Figure 11 shows a comparison of the data in the L_3 edge of both compounds normalized to the CT + dd total intensity. The dd excitation appears much broader in AgF_2 due to the poorer energy resolution, while the inset shows the surprising similarity of the CT band in AgF_2 , AgFBF_4 , and LCO. This clearly indicates that electronic parameters in these materials are very similar, apart from the following caveat. The main panel shows that the quasielastic peak of AgF_2 likely contains magnetic and phonon excitations, which are visible in high-resolution experiments in LCO but cannot be separated in the present low-resolution experiments. From this comparison, it is clear that the zero of energy determined for AgF_2 , in reality, corresponds to an average between magnetic excitations and the truly elastic line. Therefore, all Ag L_3 spectra should be shifted by some systematic error of the order on the difference between a broadened version of the cuprate data and our elastic peak ~ 0.3 eV. In other words, we estimate that all excitation energy reported for the Ag L_3 edge should be increased by about that amount. However, since the relative weight between elastic and inelastic signals is unknown, and there is no systematic way to estimate this effect, we do not attempt such a correction. Notice that the excitations at the F K edge measured at high resolution and shown in Fig. 10(b) appear systematically at higher energy with respect to the analogous features in the Ag L_3 edge, which we attribute to this effect.

E. Measuring covalency from intensity ratios

Here, we present a method for evaluating the covalency of compounds based on the intensity ratios of their main features. To quantify the relative intensities of different features, we fitted all the spectra with Gaussians as shown in Appendix B (Fig. 16).

Relative spectral weights of the dd and CT excitations are reported in Table II. The quasielastic spectral weight was found to be too sensitive to the experimental conditions and is not included in the analysis. Computed values of dd/CT intensity ratios measured at L_3 edges are similar between Ag compounds and reference LCO data.

The physical content of the relative spectral weights can be understood as follows. The RIXS cross section is given by the Kramers-Heisenberg equation [65,66]. The Ag L_3 core state is quite broad (FWHM = 2.4 eV [57]), which implies a quite short lifetime. To leading order in the ultrashort hole lifetime approximation [60,67–69], we can neglect the state dependence of the energy denominators. Then, the total

TABLE II. Comparison of RIXS integral intensities for dd and CT peaks for powder and single-crystal samples from the present work and integrating previous spectra for the F K edge data of AgF_2 [10] and Cu L_3 and O K RIXS of LCO [31]. Integrals were computed by fitting the different features with Gaussians as shown in Fig. 16. This yields approximately 4% of total weight assigned to the CT band, which overlaps with the dd excitations. Changing the criteria for assignment (e.g., with a sharp cutoff at the minimum intensity) introduces an indeterminacy in the weights of this order. All angles are in radians.

Edge	Compound	Notes	dd	CT
L_3	AgF_2	$\Delta\theta = \pi/2$	79%	21%
	AgFBF_4	$\Delta\theta = \pi/2$	75%	25%
	La_2CuO_4	$\theta' = 0.68$ [61]	73%	27%
K	AgF_2	Ref. [10]	9%	91%
	La_2CuO_4	Ref. [60]	3%	97%

spectral weight of dd excitations (including elastic and spin flip) is proportional to the sum of the matrix elements of Ref. [31],

$$I(dd) = \sum_{\nu\sigma\alpha=\pi,\sigma} |\langle \psi_d(x^2 - y^2) \downarrow | (\hat{\epsilon} \cdot \hat{r}) P_{3/2}(\hat{\epsilon}'_\alpha \cdot \hat{r}) | \psi_d(\nu)\sigma \rangle|^2, \quad (4)$$

with the projector onto the core hole $j = 3/2$ manifold

$$P_{3/2} \equiv \sum_m |d^{10} p_{3/2,m}\rangle \langle d^{10} p_{3/2,m}|$$

and the dipole operator for incoming and outgoing photons written in terms of their polarization vectors, $\epsilon, \epsilon'_\alpha$, which we are assuming to be real vectors. The sum over α is over the possible polarizations of outgoing photons, as they are not discriminated in the experiment.

Because the core hole is on the transition metal, the operators in Eq. (4) act only on the d^9 component of the wave functions [Eq. (1)]. Figure 12(a) shows the energy levels before (left) and after hybridization (right).

Figure 12(b) illustrates the RIXS process. The $|d^9, x^2 - y^2\rangle$ component of the ground-state wave function gets excited by the incoming photon with probability $\alpha_{x^2-y^2}^2$ to an intermediate $|d^{10} p_{3/2,m}\rangle$ state. Then, it emits a photon and gets deexcited to a $|d^9, \nu\sigma\rangle$ with probability α_ν^2 (dd excitation) or to a $|d^{10} \bar{L}, \nu\sigma\rangle$ with probability β_ν^2 (CT excitation).

The intensity can be put as

$$I(dd) = \alpha_{x^2-y^2}^2 \sum_\nu W_\nu \alpha_\nu^2, \quad (5)$$

with the weights computed with the ionic configurations,

$$W_\nu = \sum_{\sigma\alpha} |\langle d^9, x^2 - y^2 \downarrow | (\hat{\epsilon} \cdot \hat{r}) P_{3/2}(\hat{\epsilon}'_\alpha \cdot \hat{r}) | d^9, \nu\sigma \rangle|^2. \quad (6)$$

Similarly, for the CT intensity, substituting $d \rightarrow p$ in the last ket in Eq. (4) we obtain

$$I(CT) = \alpha_{x^2-y^2}^2 \sum_\nu W_\nu \beta_\nu^2. \quad (7)$$

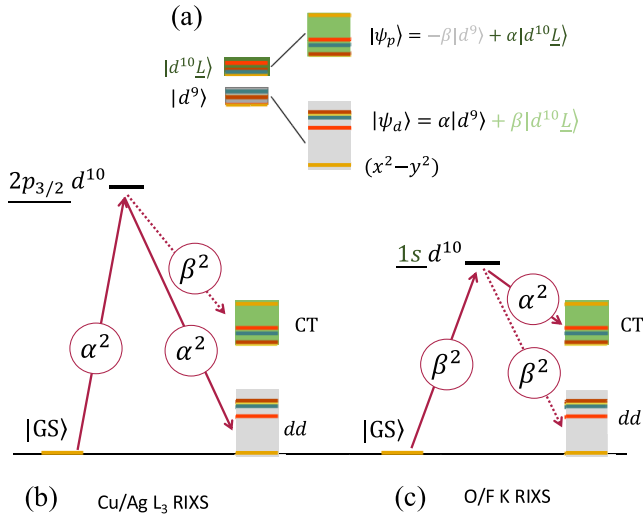


FIG. 12. (a) Ionic levels (left) and hybridized levels (right) according to Eq. (1). The parameters to obtain these levels are the same as in Ref. [10]. The hybridized levels are the same as shown in Fig. 8. (b) Processes involved for the transition metal L_3 -edge RIXS. Circles indicate the probabilities of the transitions due to projection onto the ionic configurations. (c) Same for ligand K -edge RIXS. An underline in labels indicates a hole.

Defining

$$\begin{aligned}\overline{\alpha^2} &\equiv \sum_v w_v \alpha_v^2, \\ \overline{\beta^2} &\equiv \sum_v w_v \beta_v^2, \\ w_v &\equiv \frac{W_v}{W_T}, \\ W_T &\equiv \sum_v W_v,\end{aligned}\quad (8)$$

we find

$$\frac{I(\text{CT})}{I(dd)} = \frac{\overline{\beta^2}}{\overline{\alpha^2}}. \quad (9)$$

Since $\overline{\alpha^2} + \overline{\beta^2} = 1$, we can estimate $\overline{\alpha^2}$, $\overline{\beta^2}$. Because of technical reasons, $I'(dd)$ was determined, excluding the quasielastic part. We can take this into account by correcting the intensity by the corresponding factor:

$$\frac{I(\text{CT})}{I'(dd)} = \frac{\overline{\beta^2}}{\overline{\alpha^2}} \left(\frac{1}{1 - w_{x^2-y^2} \alpha_{x^2-y^2} / \overline{\alpha^2}} \right). \quad (10)$$

The left-hand side is accessible experimentally, while the right-hand side can be computed for different models and different scattering geometries.

In Appendix C, we present a computation of the weights for general geometries and averaged for powder samples. For oriented crystals, we take the x, z plane to be the scattering plane with the incoming ($\hat{k}$) and outgoing ($\hat{k}'$) vectors forming an angles θ and θ' , respectively, with the z axis, i.e., $\hat{k} = (\sin \theta, 0, \cos \theta)$, $\hat{k}' = (\sin \theta', 0, \cos \theta')$. We define $\Delta\theta \equiv \theta - \theta'$. Table III shows the relative weights w_v for specific

TABLE III. Relative weights w_v for different scattering geometries and initial polarizations (pol) appropriate for oriented crystals, and averages for powder samples. Overlines are a reminder that a powder average has been performed.

	Crystal			Powder	
(pol, θ')	$(\pi/\sigma, 0)$	$(\pi, \pi/2)$	$(\sigma, \pi/2)$		
(pol, $\Delta\theta$)				$(\pi/\sigma$ [70], $\bar{0})$	$(\pi, \overline{\pi/2})$
$x^2 - y^2$	0.366	0.079	0.293	0.307	0.136
$3z^2 - r^2$	0.122	0.132	0.195	0.147	0.156
xy	0.366	0.316	0.073	0.217	0.317
xz	0.073	0.158	0.366	0.165	0.196
yz	0.073	0.316	0.073	0.165	0.196

geometries and π, σ incoming polarizations. Normal ($\theta' = 0$) and grazing ($\theta' = \pi/2$) emission provide extreme values of the general weights presented in Table IV.

The more important parameter determining the covalency of the material is the ratio of the hybridization in the $x^2 - y^2$ sector (T_{pd}) to the charge-transfer energy (Δ). The remaining $p-d$ hybridizations are assumed to be proportional to T_{pd} . Figure 13 shows the intensity ratio for different geometries as a function of T_{pd}/Δ for cuprates [panel (a)] and AgF_2 [panel (b)]. Other parameters needed for the computation are the crystal field splittings of the ionic d^9 configurations and the splittings of the symmetrized $d^{10}\bar{L}$ configurations due mainly to the $p-p$ hybridization. In Ref. [59] for cuprates, the first is neglected and the latter is controlled by the parameter T_{pp} . In the plot, we varied T_{pp} in the same proportion as T_{pd} , but our definition of Δ as in Ref. [10] is given by the difference of the averaged multiplet energies. This introduces a small contribution from T_{pp} , which we keep fixed. In analogy, for the case of AgF_2 , we keep the average distance between the two multiplets, Δ , fixed and vary the splitting of the $d^{10}\bar{L}$ orbitals and the T_{pd} term in the same proportion, while keeping the crystal field splitting of the d^9 orbitals fixed. For details of the model and parameters, see Appendix D.

We can now use the experimental ratios to determine the degree of covalency of the compounds parametrized by the ratio T_{pd}/Δ . In the case of the cuprate, we need the curve for the specific geometry of the experiment in an oriented crystal [black line in Fig. 13(a)]. The horizontal black segment indicates the experimental ratio, so the intersection with the curve gives the estimated value of T_{pd}/Δ . The obtained value is close to the values deduced decades ago using high-energy spectroscopies and cluster computations, as indicated by the labeled black points. The labels are the fundamental gap, E_{gap} , of Ref. [59]. Three different parameter sets were proposed in this work, and experimental and theoretical results are closer for the parameter set with the smaller E_{gap} . If one tries to fit the position of the structures, the parameter with the higher E_{gap} is the one that fits best (see Ref. [10]). However, the three parameter sets are close, and the vertical distance between the segment and the curve is on the order of the error due to different criteria to separate CT and dd excitations. Here, the separation is performed with the Gaussian fit of Fig. 16. Given the uncertainties involved, we consider the agreement very

TABLE IV. Weights of transitions from a $|d^9, x^2 - y^2 \downarrow\rangle$ to possible ionic final d states in terms of the incoming (ϵ) and outgoing (ϵ') polarization vectors (first column after the line) and for π and σ incoming polarizations summing over outgoing polarizations. Polarization vectors are assumed to be real. We sum over all spin directions, so the elastic and the spin-flip weights are contained in the first row. The last line is the sum over the columns. For simplicity, the weights are multiplied by the factors indicated in the first row. The absolute weights correspond to the result for states constructed in terms of normalized spherical harmonics and omitting radial wave functions.

ν	$225W_\nu$	$225W_\nu(\pi)/\cos^2\theta$	$225W_\nu(\sigma)$	$375A_\nu$	$375B_\nu$
$x^2 - y^2$	$(\hat{\epsilon}_x\hat{\epsilon}'_y - \hat{\epsilon}'_x\hat{\epsilon}_y)^2 + 4(\hat{\epsilon}'_x\hat{\epsilon}_x + \hat{\epsilon}'_y\hat{\epsilon}_y)^2$	$3 + 2\cos(2\theta')$	$\frac{1}{2}[9 + \cos(2\theta')]$	59/18	23/18
z^2	$\frac{1}{3}[(\hat{\epsilon}'_x\hat{\epsilon}_y)^2 + (\hat{\epsilon}_x\hat{\epsilon}'_y)^2 - 6\hat{\epsilon}'_x\hat{\epsilon}_x\hat{\epsilon}'_y\hat{\epsilon}_y + 4\hat{\epsilon}_x^2[(\hat{\epsilon}'_x)^2 + (\hat{\epsilon}'_y)^2] + 4\hat{\epsilon}_y^2[(\hat{\epsilon}'_x)^2 + (\hat{\epsilon}'_y)^2]]$	$\frac{5}{3}$	$\frac{1}{6}[13 - 3\cos(2\theta')]$	121/54	-1/18
xy	$4(\hat{\epsilon}_x\hat{\epsilon}'_y - \hat{\epsilon}'_x\hat{\epsilon}_y)^2 + (\hat{\epsilon}'_x\hat{\epsilon}_x + \hat{\epsilon}'_y\hat{\epsilon}_y)^2$	$\frac{1}{2}[9 + \cos(2\theta')]$	$3 + 2\cos(2\theta')$	71/18	-13/18
yz	$(\hat{\epsilon}_x^2 + \hat{\epsilon}_y^2)[(\hat{\epsilon}'_y)^2 + (\hat{\epsilon}'_x)^2] + 3(\hat{\epsilon}_y\hat{\epsilon}'_x)^2$	$\frac{1}{2}[3 - \cos(2\theta')]$	$3 - 2\cos(2\theta')$	8/3	-2/9
xz	$(\hat{\epsilon}_x^2 + \hat{\epsilon}_y^2)[(\hat{\epsilon}'_x)^2 + (\hat{\epsilon}'_y)^2] + 3(\hat{\epsilon}_x\hat{\epsilon}'_y)^2$	$\frac{1}{2}[5 - 3\cos(2\theta')]$	1	8/3	-2/9
Total	$\frac{19}{3}\{\hat{\epsilon}_x^2[(\hat{\epsilon}'_x)^2 + (\hat{\epsilon}'_y)^2] + \hat{\epsilon}_y^2[(\hat{\epsilon}'_x)^2 + (\hat{\epsilon}'_y)^2]\} + \frac{22}{3}[(\hat{\epsilon}'_x)^2\hat{\epsilon}_x^2 + (\hat{\epsilon}'_y)^2\hat{\epsilon}_y^2] - 2\hat{\epsilon}'_x\hat{\epsilon}_x\hat{\epsilon}'_y\hat{\epsilon}_y$	$\frac{79}{6} + \frac{1}{2}\cos(2\theta')$	41/3	799/54	1/18

good, which validates this method to obtain the covalency parameter T_{pd}/Δ .

Having established the usefulness of the analysis, we now switch to the case of AgF_2 shown in Fig. 13(b). The horizontal violet line is the intensity ratio for the present experiment, which should intersect with the violet line. The vertical black dashed line indicates the deduced value of T_{pd}/Δ .

In this case, two different parameter sets were proposed from the analysis of F K -edge RIXS, optical spectroscopy [10], and high-energy spectroscopy experiments [11], while a third parameter set can be deduced taking bare DFT values from the Wannier analysis of Ref. [10] and labeled as DFT in Fig. 13(b).

The DFT computations of Ref. [10] suggested a very covalent scenario. In order to fit the position of the RIXS features, the covalency was increased even more, leading to the “local” parameter set showing a small value of E_{gap} . Instead, the gap in the optical conductivity suggested a more ionic picture for unbound particle-hole excitations, leading to the “nonlocal” parameter set. Both scenarios were made compatible by invoking exciton effects, which lower the gap for local particle-hole excitations. The covalency parameter for all three parameter sets is indicated in Fig. 13(b) by the violet points. Intersection with the violet line (powder average) yields the estimated value of the covalency parameter for the present experiment.

The present analysis points to an intermediate value of T_{pd}/Δ but closer to the nonlocal parameter set. This indicates a very similar, but somewhat higher degree of covalency in AgF_2 than in LCO. Notice that the different geometry of the experiments compensates for the higher intensity ratio of the latter.

Qualitatively, in a similar analysis for the K edge of the ligand, one expects the role of α and β to be interchanged as shown schematically in Fig. 12. In addition, one should consider the nonbonding orbitals. Furthermore, in this case, the dispersion of p states becomes important, and modeling beyond a cluster model becomes relevant, which is outside our present scope. In any case, the larger relative weight of the dd transitions in the K edge of AgF_2 with respect to LCO (Table II) suggests that AgF_2 is the more covalent material. However, as discussed in Ref. [10], in this case, also Coulomb intersite matrix elements can influence the intensity.

IV. CONCLUSIONS

We have presented XAS and RIXS measurements on the Ag L_3 edge of three silver fluorides (AgF , AgFBF_4 , AgF_2) and Ag_2O as a reference. The XAS results were compared with DFT computations, which allowed us to identify the origin of the main features in the spectra. The approximation used with a localized frozen core hole worked relatively well for closed-shell systems but strongly underestimated the spectral weight of white lines in d^9 systems. We attributed this problem to the deficient treatment of core hole lifetime effects and an overestimation of the screening of the core hole by the conduction electrons, which calls for more accurate treatments.

The AgF_2 L_3 RIXS results complement previous K -edge RIXS measurements. In addition, we present the RIXS spectrum of AgFBF_4 , which is believed to host a spin-liquid ground state.

The Ag L_3 edge belongs to the tender x-ray range (3.35 keV), making it a challenging experiment in commonly available facilities. In addition, the strong reactivity of silver fluorides and the sensitivity to radiation damage further complicate the measurements. Despite these difficulties, very informative RIXS spectra were obtained.

The K -edge measurements of Ref. [10] already demonstrated a striking similarity between the cuprate and the fluoride electronic structure. The present measurements independently confirm this trend.

Notwithstanding the low resolution available in the present L_3 measurements, the silver fluorides exhibit clear dd and CT features very similar to those in cuprates. The positions of peaks coincided very well with the results of previous cluster computation and the measurements at the K edge [10].

The results were extended to the very interesting one-dimensional quantum antiferromagnet AgFBF_4 . The positions of the dd and CT peaks were located at very similar energies as for AgF_2 , suggesting that the octahedral-like geometry primarily determines the local electronic structure and depends weakly on the global structural details. Unfortunately, a partial sample degradation into AgF_2 could not be excluded. High-resolution studies would be most welcome here because a better characterization of the spectral differences in the spectra would enable verification of the sample integrity.

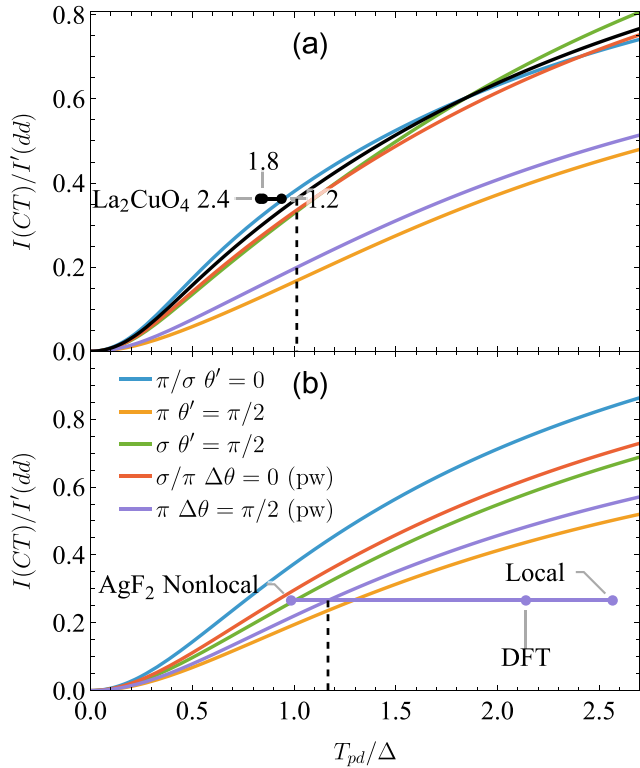


FIG. 13. CT to dd RIXS intensity ratio vs T_{pd}/Δ computed from Eqs. (8) and (10). We show the results relevant for oriented crystal in π/σ polarization for $\theta' = 0$ (light blue) and π and σ incoming polarizations for $\theta' = \pi/2$ (orange and green, respectively). Averages for powder samples (pw) are for π/σ incoming polarization with $\Delta\theta = 0$ (red) and π polarization for $\Delta\theta = 0$ (violet). Notice that powder results for σ polarization are angle independent. (a) Curves computed with LCO parameters with $T_{pp}/T_{pd} = 0.54$ [59]. The horizontal segment is the experimental ratio for LCO in σ incoming polarization and an outgoing angle of $\theta' = 0.68$ (rad). We also show the curve for the same outgoing angle (black). The points indicate different theoretical values of T_{pd}/Δ labeled by the fundamental gap, E_{gap} , in eV from Ref. [59]. (b) Curves computed with AgF₂ parameters from Ref. [10]. The horizontal violet line is the ratio for AgF₂ from the present work. We indicate the value of T_{pd}/Δ estimated in Ref. [10] using DFT and a Wannier analysis (DFT). The points marked “Local” and “Nonlocal” are alternative values of Δ/T_{pd} from Ref. [10]. The vertical dashed lines in panels (a) and (b) indicate the deduced values of T_{pd}/Δ from the present analysis. See text for details.

We argue that the spectral weight ratio between the CT and dd features is a measure of the covalency of the materials. We presented a method to systematically evaluate the degree of covalency for arbitrary geometries in d^9 compounds. The method was validated in cuprates, where parameters are well established, and then applied to silver fluorides. We also presented general formulas to perform the powder average of RIXS spectral intensities for arbitrary scattering matrices and linear polarization.

It is interesting that, for a negative charge-transfer material, the ratio of intensities inverts [71], confirming this ratio as a tool for evaluating covalency.

The degree of covalency of cuprates and silver fluorides appears very similar, with silver fluorides somewhat more covalent than cuprates. One should be cautious that covalency is evaluated in average, summing over all dd and CT excitations. It does not necessarily imply that the covalency of the ground state $x^2 - y^2$ sector is larger in the silver fluorides than in cuprates.

For cuprates, the parameter T_{pd}/Δ estimated here from the RIXS intensity ratios is very similar to well-established values in the literature [59]. For both AgF₂ and LCO, however, it is difficult to fit the peak positions and the intensity ratios with the same parameter set. This may be a problem with the cluster model. Indeed, a similar difficulty was encountered in fitting optical and RIXS experiments in Ref. [10], which was attributed to excitonic effects. It would be interesting to extend the present model to take into account many-body correlations. Furthermore, an analysis of the fluorescence features in line with Ref. [58] could shed light in the role of band behavior on the electronic structure.

Our results also call for a systematic study of spectral weights in RIXS and their dependence on different resonant conditions.

The finding that RIXS experiments are feasible at the Ag L₃ edge of silver fluorides calls for high-resolution spectra enabling the investigation of low-energy excitations as magnons, phonons, and plasmons. Recently available single crystals [72] may allow the characterization of the full momentum dependence of the excitations.

In general, magnetic interactions are expected to increase with covalency. Assuming a magnetic mechanism in a hypothetical metallic silver fluoride should lead to a larger T_c than in cuprates of similar structure, as suggested in theoretical studies [8]. Overall, the strong similarity of the spectra in the two edges strongly supports the idea that, from the electronic structure point of view, AgF₂ is an excellent analog of cuprates. This provides a strong motivation to pursue the synthesis of doped compounds in the search for avenues for high- T_c superconductivity and quantum magnetism.

Note added. Recently, Ref. [73] was posted with an equation equivalent to Eq. (C5).

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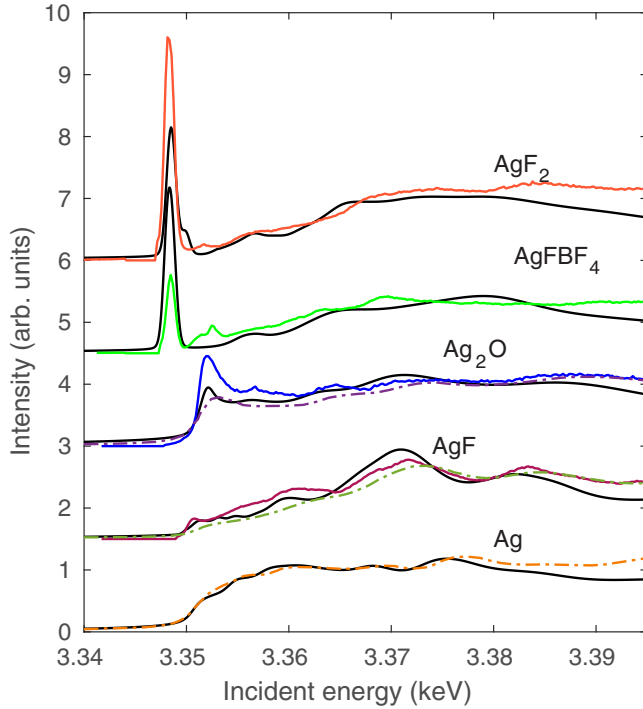


FIG. 14. Same as Figs. 2 and 6 with a Lorentzian broadening. The lower three curves are from Fig. 2 with the same energy shift and the following values of parameters (E_0, Γ_0, S): Ag (3.35 keV, 1eV, 0.2), AgF (3.35 keV, 0, 0.2), and Ag₂O (3.35 keV, 0.1eV, 0.35). The upper two curves are from Fig. 6 with the same energy shifts and the following values of parameters: AgFBF₄ (3.35 keV, 0, 0.3) and AgF₂ (3.353 keV, 0, 0.3).

DATA AVAILABILITY

The data that support the findings of this article are openly available [74].

APPENDIX A: EFFECT OF BROADENING AND ANISOTROPY ON THE THEORETICAL X-RAY ABSORPTION SPECTRA

To explore the effect of a phenomenological finite lifetime broadening, we have convoluted the theoretical spectra of Fig. 2 with a Lorentzian broadening function using a broadening parameter linear in the incident photon energy E . Specifically, the full width at half maximum parameter as a function of energy is written as

$$\Gamma(E) = \Gamma_0 + S \max(E - E_0, 0),$$

where the parameter E_0 is taken near the edge, Γ_0 is an energy-independent broadening, and S is the slope. The resulting spectra are shown in Fig. 14.

We also report in Fig. 15 the dependence of the computed XAS spectra on the orientation of the electric field with respect to the crystalline axes.

Because of the symmetry of the structure [Fig. 1(b)] for AgFBF₄, the XAS spectra are identical for the electric field along the a and b directions and different from the c polarization. We find that the overall form of the absorption has a weak dependence on polarization (cf. Fig. 15) except for the broad feature at 3.356 keV and for the white line. The former is an

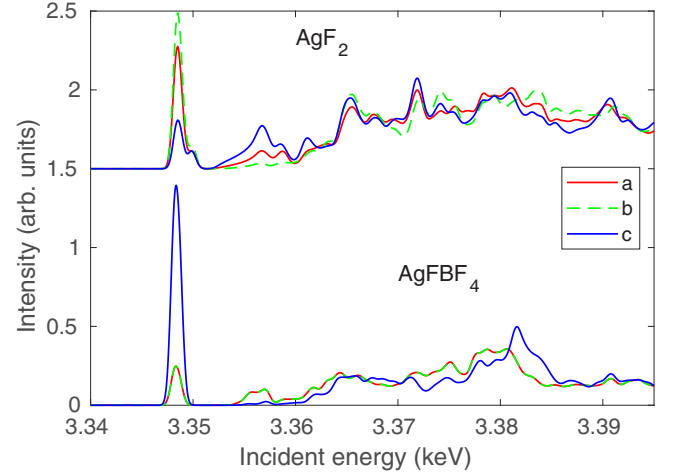


FIG. 15. Dependence of the computed XAS spectra on the direction of the electric field with respect to the crystalline axis for AgF₂ and AgFBF₄ with the same parameters as in Fig. 6. The AgF₂ is shifted vertically by 1.5 arb. units.

order of magnitude more intense for the electric field oriented perpendicular to the chain (a, b) than along the chain direction (c). For the white line, the situation reverses.

For AgF₂, the three directions are nonequivalent. The theoretical white-line intensity shows substantial anisotropy for different polarizations (Fig. 15). A similar feature as the broad pre-edge feature of AgFBF₄ is present in AgF₂ around 3.357 keV, showing also a strong anisotropy in intensity but with the stronger feature when the electric field is along the c axis in Fig. 1. Furthermore, the white line is weakest for the same polarization. This anisotropy is the opposite of what is seen in AgFBF₄, which is consistent with the nature of the ground-state hole found in DFT, which is $d_{3z^2-r^2}$ for AgFBF₄ and $d_{x^2-y^2}$ for AgF₂. These anisotropic effects could be the subject of a future study in oriented single crystals.

APPENDIX B: FITS OF THE RIXS SPECTRA

Figure 16 shows the fit of the RIXS excitation spectra defining the spectral weights shown in Table II.

APPENDIX C: WEIGHTS OF TRANSITIONS

1. Oriented samples

If the outgoing polarization is determined, the sum over polarization should not be done, and the weights read

$$W_v = \sum_{\sigma} |\langle d^9, x^2 - y^2 \downarrow | (\hat{\epsilon} \cdot \hat{r}) P_{3/2}(\hat{\epsilon}' \cdot \hat{r}) | d^9, v\sigma \rangle|^2, \quad (C1)$$

where we assumed real polarization vectors. A more general treatment allowing for circularly polarized radiation has been recently presented in Ref. [75].

Table IV shows the weights for the transitions from the $x^2 - y^2 \downarrow$ state to the possible d states for fixed linear polarizations.

It is convenient to define a complex scattering tensor,

$$T_{ij}^{v\sigma} = \langle d^9, x^2 - y^2 \downarrow | \hat{r}_i P_{3/2} \hat{r}_j | d^9, v\sigma \rangle. \quad (C2)$$

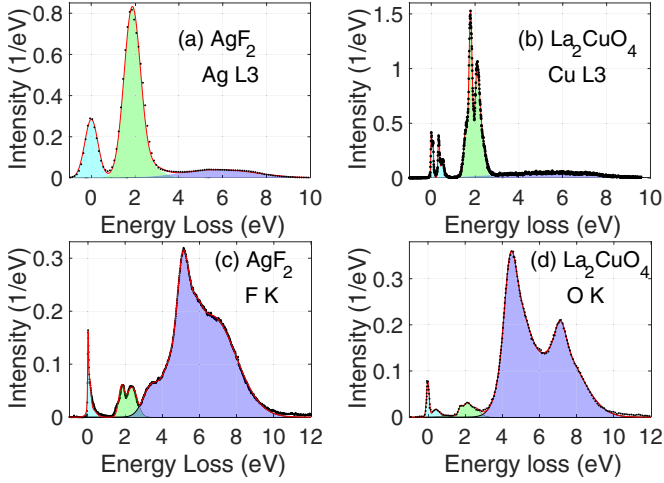


FIG. 16. Fits of elastic, dd , and CT peaks by several Gaussians for metal and ligand edges of AgF_2 and La_2CuO_4 . Correspondent areas on the graphs are marked by various colors (light blue for quasielastic peak, green for dd excitations, and violet for CT). Panel (a) presents the results of the current experiment, while panels (b)–(d) are based on the previously measured data. All the curves and fits are normalized over $dd + \text{CT}$ area.

The weight can be written as

$$W_v = \sum_{\sigma} |\hat{\epsilon}_i T_{ij}^{\nu\sigma} \hat{\epsilon}'_j|^2, \quad (\text{C3})$$

where the sum over repeated indices is understood.

If the outgoing polarization is not measured, one needs to sum over transverse polarizations $\alpha = \pi, \sigma$, which can be taken care of by introducing the projector into the transverse outgoing polarizations P'_{ij} :

$$W_v = \sum_{\sigma\alpha} |\hat{\epsilon}_i T_{ij}^{\nu\sigma} \hat{\epsilon}'_{\alpha j}|^2 = \sum_{\sigma} \hat{\epsilon}_i T_{ik}^{\nu\sigma} P'_{kl} (T_{jl}^{\nu\sigma})^* \hat{\epsilon}_j, \quad (\text{C4})$$

with $P'_{ij} \equiv \sum_{\alpha} \hat{\epsilon}'_{\alpha i} \hat{\epsilon}'_{\alpha j} = \delta_{ij} - \hat{k}_i \hat{k}_j$ and $\hat{k}_i$ is the outgoing wave vector versor. Table IV and Fig. 17 show the weights for general polarizations and in the case of incoming π, σ polarizations [$W_v(\pi/\sigma)$] and for $\hat{k}$ ($\hat{k}'$) in the x, z plane and forming an angle θ (θ') with the z axis i.e., $\hat{k} = (\sin \theta, 0, \cos \theta)$, $\hat{k}' = (\sin \theta', 0, \cos \theta')$. Interestingly, the sum of all weights is independent of the angles in the case of initial σ polarization and has a very weak dependence on the outgoing angle in the case of π incident polarization (keeping a $\cos^2 \theta$ dependence).

2. Symmetry constraints

For $\theta = \theta' = 0$, any plane perpendicular to $\hat{k}$ can be considered as the scattering plane and therefore σ and π polarizations become equivalent. Indeed, one can verify that in this case, the two corresponding columns in Table IV coincide, as also shown in Fig. 17 at the origin. Irrespectively of the polarization, also the xy and the $x^2 - y^2$ polarization should be equal for $\theta' = 0$ as the orbitals are related by a $\pi/4$ rotation around the z axis.

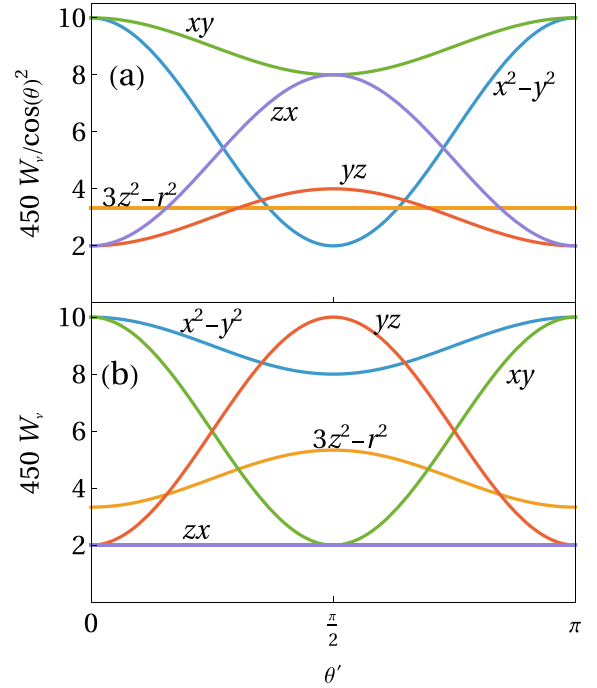


FIG. 17. Weight of the transitions for different final states as a function of the outgoing scattering angle θ' for π [panel (a)] and σ [panel (b)] incoming polarizations.

3. Arbitrarily oriented samples and powder average

The tensors $T_{ij}^{\nu\sigma}$ are given in the crystal reference frame. For an arbitrary orientation of the crystal, we can define a rotated tensor,

$$T_{ab}^{\nu\sigma}(R) = R_{ai} T_{ij}^{\nu\sigma} R_{bj},$$

where the rotation matrix R depends on the Euler angles α, β, γ . Replacing in Eq. (C4) yields the result for a crystal with an arbitrary orientation. For a powder, we need to integrate over all possible orientations,

$$\langle W_v \rangle = \sum_{\sigma} \int dR \hat{\epsilon}_a R_{ai} T_{ik}^{\nu\sigma} R_{bk} P'_{bc} R_{cl} (T_{jl}^{\nu\sigma})^* R_{dj} \hat{\epsilon}_d,$$

with the Haar measure defined as

$$\int dR \equiv \frac{1}{8\pi^2} \int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \int_0^{2\pi} d\gamma \sin \beta.$$

The integrals can be done for a generic scattering matrix $T^{\nu\sigma}$,

$$\begin{aligned} \langle W_v \rangle &= \frac{1}{60} \sum_{\sigma} \{ 14 \text{Tr}(T^{\nu\sigma} T^{\nu\sigma\dagger}) - \text{Tr}(T^{\nu\sigma} T^{\nu\sigma*}) - |\text{Tr} T^{\nu\sigma}|^2 \\ &\quad + [3|\text{Tr} T^{\nu\sigma}|^2 + 3\text{Tr}(T^{\nu\sigma} T^{\nu\sigma*}) - 2\text{Tr}(T^{\nu\sigma} T^{\nu\sigma\dagger})] S \} \\ &= A_v + B_v S \end{aligned} \quad (\text{C5})$$

with $S = \cos[2(\theta - \theta')]$ for incoming π polarization and $S = 1$ for incoming σ polarization. Table IV shows the constants A_v and B_v in the present case.

Numerical weights for notable polarizations applicable for oriented crystals and powders are given in Table III.

TABLE V. Crystal fields and hybridizations used for AgF_2 and LCO. All values are in eV. The diagonal energies of P orbitals in Eq. (D1) are determined by $\varepsilon_p^\nu = \Delta + e_p^\nu$ with the reference value $\Delta_{\text{AgF}_2} = 1.29$ eV corresponding to the “Local” parameter set of Ref. [10]. The last column shows the expressions for the hybridizations in terms of, T_{pd} , the $x^2 - y^2$ matrix element for a planar D_{4h} cluster used by Eskes *et al.* [59]. Columns with an asterisk are the parameters that were rescaled in the same proportion to vary the degree of covalency in Fig. 17.

ν	ε_d^ν	AgF_2 $e_p^{*\nu}$	$T_{pd}^{*\nu}$	ε_d^ν	La_2CuO_4 $e_p^{*\nu}$	$T_{pd}^{*\nu}$
$x^2 - y^2$	-0.28	-0.16	2.76	0	$-\frac{6}{5}T_{pp}$	T_{pd}
$3z^2 - r^2$	-0.25	0.32	1.51	0	$\frac{4}{5}T_{pp}$	$\frac{1}{\sqrt{3}}T_{pd}$
xy	0.34	-0.05	1.36	0	$\frac{4}{5}T_{pp}$	$\frac{1}{2}T_{pd}$
xz	0.09	-0.14	1.05	0	$-\frac{1}{5}T_{pp}$	$\frac{1}{2\sqrt{2}}T_{pd}$
yz	0.10	0.04	1.02	0	$-\frac{1}{5}T_{pp}$	$\frac{1}{2\sqrt{2}}T_{pd}$

APPENDIX D: MODEL AND PARAMETERS

For the calculations, we consider a cluster with a central metal atom and four neighboring ligands in the case of LCO and six ligands in the case of AgF_2 . In the case of LCO, we

neglect the apical oxygen atoms, which, as shown in Ref. [59], is a good first approximation. This provides a reference model with a minimal parameter set. Considering the Hamiltonian in terms of holes and in the case of one hole, interactions are irrelevant and the Hamiltonian separates into five 2×2 problems, one for each sector,

$$H = \sum_{\nu\sigma} \varepsilon_d^\nu d_{\nu\sigma}^\dagger d_{\nu\sigma} + \sum_{\nu} \varepsilon_p^\nu P_{\nu\sigma}^\dagger P_{\nu\sigma} + \sum_{\nu\sigma} T_{pd}^\nu (d_{\nu\sigma}^\dagger P_{\nu\sigma} + P_{\nu\sigma}^\dagger d_{\nu\sigma}). \quad (\text{D1})$$

Here, $d_{\nu\sigma}^\dagger$ creates a hole in the d orbitals ($\nu = x^2 - y^2, 3z^2 - r^2, xy, xz, yz$) with spin σ , while $P_{\nu\sigma}^\dagger$ creates a hole in a linear combination of the p orbitals of the ligand (referred to as a P orbital), which transform like one of the d orbitals. For details, see Refs. [10,11,59]. Diagonal energies and hybridizations in the Hamiltonian are specified in Table V. We define $T_{pd} \equiv T_{pd}^{x^2-y^2}$.

Cuprate parameters are from Ref. [59] as explained in the main text. These authors neglect the crystal field splitting of the d^9 configuration. The splitting of the $d^{10}\underline{L}$ is entirely due to T_{pp} . Table V shows the parameters used in the computations. Columns with an asterisk indicate parameters rescaled in the same proportion as T_{pd}/Δ to draw Fig. 13.

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