

Charge-Transfer and *dd* excitations in  $\text{AgF}_2$ 

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Charge-transfer insulators are the parent phase of a large group of today’s unconventional high-temperature superconductors. Here we study experimentally and theoretically the interband excitations of the charge-transfer insulator silver fluoride  $\text{AgF}_2$ , which has been proposed as an excellent analog of oxocuprates. Optical conductivity and resonant inelastic x-ray scattering on  $\text{AgF}_2$  polycrystalline sample show a close similarity with that measured on undoped  $\text{La}_2\text{CuO}_4$ . While the former shows a charge-transfer gap  $\sim 3.4$  eV, larger than in the cuprate, *dd* excitations are nearly at the same energy in the two materials. Density functional theory and exact diagonalization cluster computations of the multiplet spectra show that  $\text{AgF}_2$  is more covalent than the cuprate, in spite of the larger fundamental gap. Furthermore, we show that  $\text{AgF}_2$  is at the verge of a charge-transfer instability. The overall resemblance of our data on  $\text{AgF}_2$  to those published previously on  $\text{La}_2\text{CuO}_4$  suggests that the underlying charge-transfer insulator physics is the same, while  $\text{AgF}_2$  could also benefit from a proximity to a charge density wave phase as in  $\text{BaBiO}_3$ . Therefore, our work provides a compelling support to the future use of fluoroargenates for materials’ engineering of novel high-temperature superconductors.

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## I. INTRODUCTION

Following the discovery of a high- $T_c$  superconductivity in the cuprate oxide (CuO) family, there has been an ongoing search for other systems in which it will be possible to replicate such novel properties. Apart from purely fundamental research into the underlying physics of the unconventional superconducting state, there has also been the goal to find  $T_c$  at higher temperatures.

In most cases, the key players of this approach were elements originating, such as copper, from the transition-metal group of the periodic table, and over time several candidates came into focus such as iridates, nickelates, and vanadates.

The vanadates [1,2] appear to be extremely resilient to external doping [3] unlike the various compounds of the cuprate family. Superconductivity under doping was predicted theoretically in iridates [4], which are isostructural to the cuprates and share several similarities with the properties of the antiferromagnetic (AFM) phase. However, there are some distinct differences compared to the cuprates. First, there is a strong competition between electronic correlations, spin-orbit coupling, and crystal field energy scales in the iridates. Second,  $\text{Sr}_2\text{IrO}_4$  is a Mott insulator [5], while  $\text{La}_2\text{CuO}_4$  is a charge-transfer (CT) insulator. Extensive experimental studies via various doping approaches did not result in any signatures for superconducting properties even upon heavy doping levels, as in the  $\text{La}_{2-x}\text{Sr}_x\text{IrO}_4$  compound [5–7]. Quite interestingly, although  $\text{NdNiO}_3$  has neither the AFM ground state nor the strong covalent bonding commonly found in cuprates, Sr-doped  $\text{NdNiO}_2$  exhibits low-temperature superconductivity in an infinite layer structure as was shown recently [8].

There is, however, another approach to replace copper, and that is by staying in the same column of the periodic table of elements and by choosing silver. It was already clear from the early stages of that paradigm that silver oxide cannot become

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a true charge-transfer insulator because of the high second ionization energy of silver and the fact that oxygen is not a sufficiently electronegative element [9]. As a result, AgO has a negative charge-transfer energy that ends up in the Ag<sup>1+</sup> oxidation state without a magnetic ordering as opposed to its sibling, CuO. Fluorine is more electronegative than oxygen, therefore has deeper  $2p^6$  states, which results in a positive charge-transfer energy. Several fluoroargentates were found to be isoelectronic to their cuprate sibling La<sub>2</sub>CuO<sub>4</sub>. However, previous work showed that their magnetic ground state is not the same as, for example, in the case of Cs<sub>2</sub>AgF<sub>4</sub> [10] and K<sub>2</sub>AgF<sub>4</sub>, both being ferromagnetic [11], with small local structural distortions of the AgF<sub>6</sub> octahedron stabilizing an antiferro orbital ordering [12].

Recent calculations predict that the magnetic ground state of KAgF<sub>3</sub> and AgF<sub>2</sub> is AFM. KAgF<sub>3</sub> has an arrangement of spins within the zigzag chain along the crystallographic *c*-axis direction forming an AFM with a low-temperature Néel transition and a theoretical gap of 0.7 eV [11,13]. However, its quasi-one-dimensional (quasi-1D) magnetic structure cannot be compared directly with the quasi-2D AFM state of the cuprates. On the other hand, AgF<sub>2</sub> has a neutral-plane stacked structure due to the inherent F<sup>-</sup> character (instead of O<sup>2-</sup> in CuO<sub>2</sub>), although with strongly buckled planes. Therefore, AgF<sub>2</sub> is the equivalent “012” (free-of-charge reservoir layer) of the 214 stoichiometry in cuprates [11,14]. The Néel temperature of AgF<sub>2</sub> ( $T_N = 163$  K) is half of that for La<sub>2</sub>CuO<sub>4</sub> ( $T_N = 325$  K). LSDA + U calculations predicted a gap of 1.5–2.5 eV in various forms of AgF<sub>2</sub> [15–17]. Hybrid density functional theory calculations involving orbital character demonstrated the striking resemblance of the electronic structure of AgF<sub>2</sub> and its cuprate analog La<sub>2</sub>CuO<sub>4</sub> [14]. Furthermore it predicted also the exchange energy  $J$  to be about 70 meV in AgF<sub>2</sub> [14,17], half of the  $J$  value in typical cuprate compounds. A one-to-one comparison of the two-magnon excitation in Raman spectroscopy data of AgF<sub>2</sub> and EuBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> confirmed the expected  $J$  of about 70 meV in AgF<sub>2</sub> [14]. Although the charge-transfer gap between the F  $2p$  state and the Ag  $4d$  state was predicted in previous theoretical calculations, a direct experimental verification of the high-energy electronic excitations in AgF<sub>2</sub> is still lacking [11,14]. In that respect, optical spectroscopy is an unprecedented method for determining intraband and interband transitions, which proved to be of most importance in the study of doped charge transfer and Mott insulator systems. Moreover, resonant inelastic x-ray scattering (RIXS) has been exploited in the past decade to study core and valence excitations of cuprates, thus providing novel and exciting observations of electronic  $dd$  and charge-transfer excitations along with collective excitations such as bimagnons [18] and charge density waves [19]. Therefore, not only are the latter two spectroscopy techniques essential in verifying the electronic character of argentates, but they act as a direct tool to do so in order to compare them exclusively with previous theoretical predictions or future and further study of these cupratelike compounds. As we will see, the current study sheds light on previous predictions and gives new insight regarding the charge-transfer physics in argentates.

In this work, we study the high-energy excitations of AgF<sub>2</sub> by combining optical spectroscopy and resonant inelastic x-

ray scattering. The excitation spectrum is compared with cluster computation aided with DFT computation of parameters. We show that the optical conductivity spectrum close to the charge-transfer gap resembles that of the oxocuprates and contradicts previous band-gap estimations in AgF<sub>2</sub>. In addition, we identified several  $dd$  excitations in the RIXS spectra. Our experimental observations are supported by new theoretical calculations of the electronic excitations in AgF<sub>2</sub>. The striking similarity between fluoroargentate and oxocuprates suggests that the former could be a promising candidate for a future high- $T_c$  superconductor. Moreover, a close analysis of our results suggests that AgF<sub>2</sub> is at the border of a charge-transfer instability. Therefore, we suggest that AgF<sub>2</sub> is a novel and interesting test bed for further investigation of strong electronic correlations in quantum materials.

## II. METHODS

### A. Sample preparation

A 10 g batch of polycrystalline AgF<sub>2</sub> has been freshly prepared as described previously [14]. Purity of the obtained sample has been verified using powder x-ray diffraction testing to the presence of minute amounts (approximately 1 wt %) of diamagnetic AgF only.

To obtain a compact specimen of AgF<sub>2</sub> for optical measurements, an explosion compaction procedure was applied as described in Appendix A. Sample cylinder was cut into approximately 2 mm thin hard compact wafers, which were fine polished inside the glove box using diamond paper before performing any optical measurements.

Samples were loaded inside the cryostat chamber using an inert gas-filled glove bag and with an active flow of gas, with a loading period of a few minutes, followed by evacuation of the sample chamber to ultrahigh vacuum (UHV). No visual changes of the sample surface could be seen, testifying the successful loading without any chemical deterioration of the sample.

### B. Optical spectroscopy

The optical response of polished pressed powder AgF<sub>2</sub> samples was measured by combining infrared reflectivity and ellipsometry. The sample was installed in an UHV helium flow cryostat and data was recorded at selected temperatures from room temperature down to 8 K. The cryostat is designed to maintain a high position stability of the mounted sample during cool down. Measurements were obtained using a near normal incident reflectivity setup in a Bruker Vertex 70V Fourier transform infrared (FTIR) spectrometer in the photon energy range of approximately 3.5 meV to 0.6 eV. Calibration spectra were obtained by measuring a gold layer deposited on top of the sample using *in situ* thermal evaporation. In the photon energy range of 0.5–3.5 eV the complex dielectric function was determined using a Woollam VASE® spectroscopic ellipsometer. The ratios of the reflection coefficients for  $p$  and  $s$  polarized light  $\rho = r_p/r_s$ , were measured at incident angles of 61° and 63° (see Appendix B).

The optical conductivity was calculated directly from the pseudodielectric function using two sets of ellipsometry data at two different angles of incidence. In addition, we

have fitted the ellipsometry parameters,  $\Psi_{\text{ellip}}$  and  $\Delta_{\text{ellip}}$  to the Drude-Lorentz parametrization to obtain boundaries for our confidence in the optical conductivity spectra. We have used the far-IR reflectivity data to obtain the contribution of phonons to the spectra. The fit to the lowest-energy phonon at about  $30 \text{ cm}^{-1}$  along with the fit to the ensemble of all far-infrared (FIR) phonons were used to extrapolate the reflectivity to zero frequency. The frequency and temperature dependence of the real part of the optical conductivity will be discussed in Sec. III.

### C. RIXS

A polycrystalline sample was mounted on a copper sample holder in an inert atmosphere inside a glove box, loaded in a vacuum suitcase, and transferred to the experimental chamber maintained at  $\approx 5 \times 10^{-10}$  mbar. The F K-edge x-ray absorption (XAS) spectrum was collected in the fluorescence yield mode using  $\sigma$  polarization (normal to the scattering plane) at an angle of incidence of  $75^\circ$ . Resonant inelastic x-ray scattering (RIXS) spectra were collected at F K edge with an energy resolution of  $\delta E \approx 0.045 \text{ eV}$  at a scattering angle of  $150^\circ$  at 13 K, at I21-RIXS beam line, Diamond Light Source, United Kingdom [20]. The zero-energy transfer position and energy resolution of the RIXS spectra were determined from subsequent measurements of elastic peaks from an adjacent carbon tape. The RIXS spectrum was collected with  $\pi$  polarization (parallel to the scattering plane) at  $682.2 \text{ eV}$  at an angle of incidence of  $20^\circ$  for 30 min. The RIXS spectrum was fitted with Gaussian line shapes for the elastic peak and phonons, with a damped harmonic oscillator model for the bimagnon, with Gaussian line shapes for the  $dd$  excitations and charge transfer excitation, and a fluorescence model [21] for the emission feature peaking around  $5 \text{ eV}$ . The incident energy map was collected at an angle of incidence of  $20^\circ$  and  $\sigma$  polarization. RIXS spectra comparison after 6 h of x-ray beam exposure showed only a reduction in the overall emission signal, with no noticeable difference in the intensity ratios of the inelastic features (not shown).

### D. Theory

To model the  $\text{AgF}_2$  electronic excitations with Ag in a formally  $d^9$  state, we considered an  $(\text{AgF}_6)^{4-}$  cluster reproducing the local environment of the transition-metal ion as shown in Fig. 1. The one-particle parameters were obtained from unpolarized DFT calculations of the periodic solid using the projector-augmented wave (PAW) method as implemented in VASP [22] within the generalized gradient approximation of Perdew, Burke, and Ernzerhof [23] (PBE) using a mesh of  $8 \times 8 \times 8 k$  points.

The band structure was obtained with the experimental lattice parameters of Ref. [24] and then projected onto maximally localized Wannier functions as implemented in the WANNIER90 code [25]. We used a Wannier basis with five  $d$  orbitals per Ag and three  $p$  orbitals per F. The two planar F-Ag-F bridges deviate slightly from orthogonality ( $93.3^\circ$ ). For the  $d$  orbitals, we took the axes so that the bisectrix of the axes coincides with the bisectrix of the bridges, resulting in

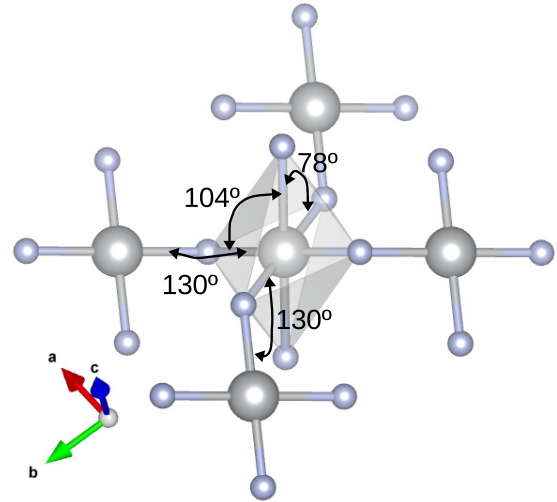


FIG. 1. The central gray octahedron shows the  $\text{AgF}_6$  cluster used in the computations. The surrounding atoms are implicitly taken into account in the definition of diagonal energies. Some key bond angles are indicated for clarity.

axes nearly oriented along AgF bonds. For the  $p$  orbitals we used the local reference frame as in Ref. [14].

The WANNIER90 one-particle Hamiltonian for the solid was truncated to the  $\text{AgF}_6$  cluster yielding a Hamiltonian with five  $d$  orbitals and  $3 \times 6 = 18$   $p$  orbitals. The one-particle Hamiltonian reads

$$\begin{aligned}
 H_{pd} = & \sum_{\nu} \varepsilon_d(\nu) d_{\nu}^{\dagger} d_{\nu} + \sum_m \varepsilon_p(m) p_m^{\dagger} p_m \\
 & + \sum_{\nu m} t_{pd}(\nu, m) d_{\nu}^{\dagger} p_m + \text{H.c.} \\
 & + \sum_{mm'} t_{pp}(m, m') p_m^{\dagger} p_{m'} + \text{H.c.}, \quad (1)
 \end{aligned}$$

where  $\nu, m$  are spin-orbital indexes,  $d_{\nu}^{\dagger}$  creates a hole in the  $d$  orbitals ( $d_{3z^2-r^2}, d_{x^2-y^2}, d_{xy}, d_{xz}, d_{yz}$ ) while  $p_m^{\dagger}$  creates a hole in one of the 18  $p$  orbitals. We considered  $pd$  hopping across the six F-Ag bonds [ $t_{pd}(\nu, m)$ ] and  $pp$  hopping across the 12 F-F bonds forming the edges of the octahedral cage [ $t_{pp}(m, m')$ ]. Spin-orbit coupling was not included, so the spin is conserved.

The symmetry of the octahedra (Fig. 1) is quite low as inversion is the only nontrivial symmetry operation allowed ( $C_i$  point group). Therefore, the five  $d$  levels may have different energies and hybridization matrix elements among them are allowed. Notwithstanding that, we find that with the chosen axes, off-diagonal  $dd$  matrix elements on the Ag site are very small and were neglected.

Some linear combinations of  $p$  orbitals are nonbonding and can be eliminated to reduce the Hilbert space. To this aim, we defined five symmetry adapted orbitals by the following transformation:

$$\tilde{P}_{\nu} = \frac{1}{\sqrt{\tilde{T}_{pd}(\nu)}} \sum_m t_{pd}(\nu, m) p_m$$

TABLE I. Crystal fields and hybridizations obtained from DFT and Wannier computations. All values are in eV. The diagonal energies of  $P$  orbitals in Eq. (2) are determined by  $\varepsilon_P(v) = \Delta + e_P(v)$ . The value for  $\Delta$  obtained this way is  $\Delta_{\text{DFT}} = 1.29$  eV but a different value can be used to study the effect of increased ionicity. The last column are the expressions for the hybridizations in terms of the  $x^2-y^2$  matrix element and for a planar  $D_{4h}$  cluster used by Eskes *et al.* [26].

$v$	AgF <sub>2</sub> ( $C_i$ )			$\varepsilon_d(v)$	La <sub>2</sub> CuO <sub>4</sub> ( $D_{4h}$ )	
	$\varepsilon_d(v)$	$e_P(v)$	$T_{pd}(v)$		$e_P(v)$	$T_{pd}(v)$
$z^2$	-0.25	0.32	1.51	0	$\frac{4}{5}T_{pp}$	$\frac{1}{\sqrt{3}}T_{pd}^a$
$x^2 - y^2$	-0.28	-0.16	2.76	0	$-\frac{6}{5}T_{pp}$	$T_{pd}^a$
$xy$	0.34	-0.05	1.36	0	$\frac{4}{5}T_{pp}$	$\frac{1}{2}T_{pd}^a$
$xz$	0.09	-0.14	1.05	0	$-\frac{1}{5}T_{pp}$	$\frac{1}{2\sqrt{2}}T_{pd}^a$
$yz$	0.10	0.04	1.02	0	$-\frac{1}{5}T_{pp}$	$\frac{1}{2\sqrt{2}}T_{pd}^a$

<sup>a</sup> $(x^2-y^2)$  symmetry.

with

$$\tilde{T}_{pd}(v) = \sqrt{\sum_m |t_{pd}(v, m)|^2}.$$

This defines a set of orbitals with maximum overlap with the  $d$  orbitals. Because of the low symmetry, the resulting orbitals are not orthogonal but are easily orthogonalized, resulting in new operators  $P_v$  and hybridization matrix elements  $T_{pd}(v)$ , which expand the same maximally hybridized subspace. The orthogonalized orbitals (hereafter  $P$  orbitals) have nearly the same symmetry as the original orbitals, so they can still be labeled as  $x^2-y^2$ ,  $xy$ , etc. Furthermore, they have small interorbital  $PP$  and  $Pd$  matrix elements between orbitals of different symmetry. We checked that keeping these matrix elements did not change the results significantly, therefore for simplicity they were also neglected.

The resulting Hamiltonian of the  $(\text{AgF}_6)^{4-}$  cluster reads

$$\begin{aligned} H = & \sum_v \varepsilon_d(v) d_v^\dagger d_v + \sum_v \varepsilon_P(v) P_v^\dagger P_v \\ & + \sum_v T_{pd}(v) (d_v^\dagger P_v + P_v^\dagger d_v) \\ & + \sum_{\substack{v_1, v_2 \\ v_3, v_4}} U^{(dd)}(v_1, v_2, v_3, v_4) d_{v_1}^\dagger d_{v_2}^\dagger d_{v_3} d_{v_4}. \end{aligned} \quad (2)$$

Table I shows the one-body parameters deduced from the WANNIER90 computation. Setting  $T_{pd}(x^2 - y^2) = 2.76$  eV, the values of the  $T_{pd}(v)$  matrix elements are in very good agreement with the expressions [26] for a cluster with  $D_{4h}$  symmetry using a Slater-Koster parametrization and assuming  $T_{pd}(xy) = T_{pd}(x^2 - y^2)/2$  (last column of Table I). The symmetrized  $P$  orbitals manifest a more evident deviation of square planar symmetry, and the  $D_{4h}$  expressions for  $e_P(v)$  are not accurate.

We define the charge-transfer parameter  $\Delta = E(d^{10}\underline{L}) - E(d^9)$  where  $\underline{L}$  denotes a hole in the ligand and the energies are average of the indicated multiplets setting  $T_{pd}(v) = 0$ . Interactions with the neighboring atoms are absorbed in the definition of  $\Delta$ . In the case of intracluster excitations in the

insulating phase, we need to consider one hole in the cluster, making the interaction term in Eq. (2) irrelevant. The full Hamiltonian will become relevant for intercluster excitations.

### III. RESULTS

#### A. Optical conductivity

The real part of the optical conductivity,  $\sigma_1$ , of the AgF<sub>2</sub> sample for selected temperatures is shown in Fig. 2. The spectra can be divided into several regimes and their equivalent excitations: far-IR phonons (seen as red sharp peaks), mid-IR absorption (above 0.1 eV), and near-IR to ultraviolet (UV) absorption. The former two low-energy excitations will be discussed in a separate publication. The high-energy spectrum (Fig. 2) can be decomposed into three major excitations. The strongest one is the high-energy absorption centered at about 3.4 eV with an onset at approximately 1.75 eV. This absorption can be associated with a strong interband transition, which sits at energies close to our experimental data range limit.

In addition to the absorption tail of the this excitation, we detect a broad absorption band, which can be roughly decomposed into two modes centered at around 1 eV and 1.7 eV. As the sample is warmed up to room temperature, the 1.7 eV excitation seems to remain almost intact with respect to energy, while the 1 eV excitation seems to soften toward 0.8 eV. The two separate modes can be easily distinguished in the spectra measured at 300 K as shown in Fig. 2. As will be seen below, the excitation at 3.4 eV and the optical mode at 1.7 eV are consistent with a charge-transfer excitation and  $dd$  excitations, respectively, as seen in the RIXS data. We also note a possible spectral weight transfer from the high-energy sector to the subgap excitations as a function of temperature and as shown in Fig. 2. However, the confidence boundary that we have on our optical conductivity data in this range requires a further and more precise experimental investigation of this range to understand this spectral weight interplay as a function of temperature. Further discussion of the optical conductivity spectra and comparison with that of the cuprate analog La<sub>2</sub>CuO<sub>4</sub> (black line) will be given in Sec. IV A.

#### B. X-ray absorption

Figure 3 (top panel) shows the F  $K$ -XAS on AgF<sub>2</sub>. We attribute the edge and the sharp peak marked by the arrow (682 eV) to excitations into Ag  $4d$  orbitals via hybridization with F  $2p$  orbitals, reflecting the narrow UHB in AgF<sub>2</sub> [14]. This is justified by the fact that similar  $p$ - $d$  hybridized peaks have been observed in F  $K$ -XAS of several  $3d$  metal fluorides [30–32]. Further support for this interpretation comes from the similarity with the O  $K$ -XAS on La<sub>2</sub>CuO<sub>4</sub> [29] (black line) to be discussed in Sec. IV B.

The broad absorption structure picking at 689 eV is assigned to Ag  $5s$  and  $5p$  states, which hybridize with F- $2p$  states. These assignments are supported by the DFT computations shown in the bottom panel to be discussed in Sec. IV C.

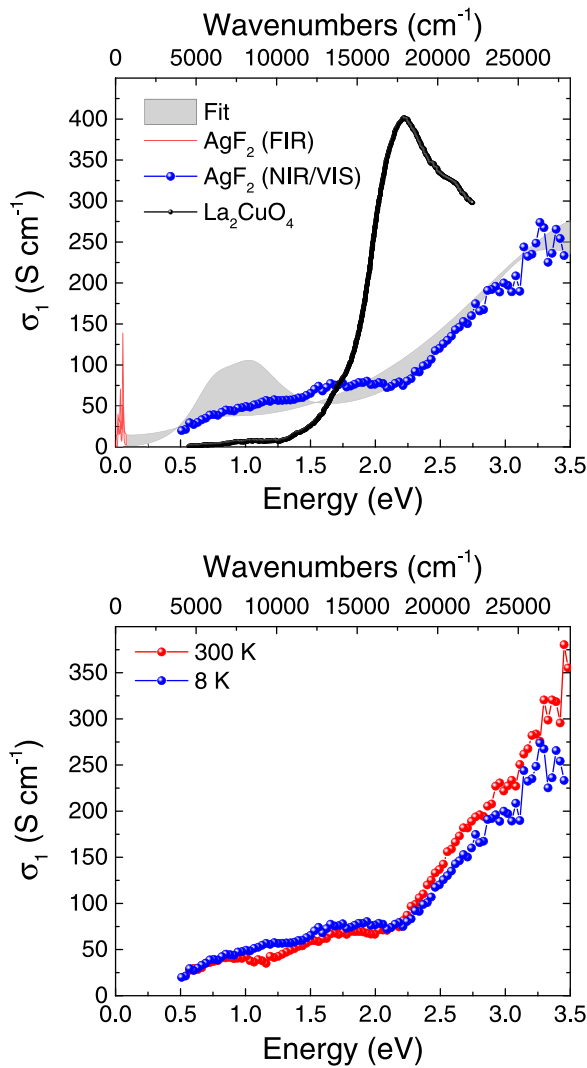


FIG. 2. Real part of optical conductivity for  $\text{AgF}_2$  (this work). The top panel presents  $\sigma_1$  (blue line with circles) as obtained from direct calculation of the pseudodielectric function using ellipsometry parameters  $\Psi_{\text{ellip}}$  and  $\Delta_{\text{ellip}}$  for two angles of incidence as measured at a base temperature of 8 K.  $\sigma_1$  as was obtained by near normal incidence reflectivity measurements in the far infrared is shown in red. The shaded gray area represents the result of a fit to  $\Psi_{\text{ellip}}$  and  $\Delta_{\text{ellip}}$  data separately (see Appendix B), which reflects the confidence boundaries of our model with respect to the experimental data. Our data is compared with optical conductivity data adopted from Falck *et al.* [27,28] on undoped  $\text{La}_2\text{CuO}_4$ . The optical conductivity in the  $\text{AgF}_2$  sample shows an onset at about 1.75 eV with high-energy band transition associated with the charge-transfer gap ( $\Delta_{\text{peak}} \approx 3.4$  eV). The data on  $\text{AgF}_2$  is compared with a charge-transfer excitation peaking at  $\Delta_{\text{peak}} \approx 2.2$  eV with an onset of  $\approx 1.6$  eV in the equivalent oxocuprates compound  $\text{La}_2\text{CuO}_4$ . In addition, the  $\text{AgF}_2$  data shows a low spectral weight subgap absorption suggesting negligible doping as intended [28]. Bottom panel shows a comparison with data at 300 K showing slight modifications of the different excitations in the charge-transfer sector and the subgap sector.

### C. Resonant inelastic x-ray scattering

Upon excitation at the F K edge, a well-resolved RIXS spectrum can be observed (Fig. 4). In the insets of the mid-

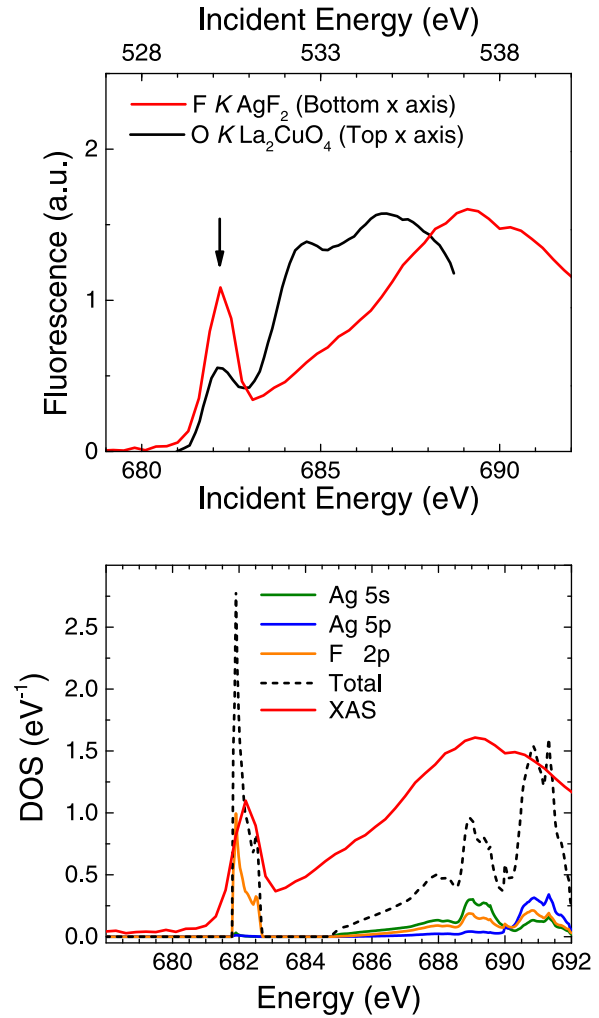


FIG. 3. Top panel: Comparison of F K-XAS on  $\text{AgF}_2$  and O K-XAS on  $\text{La}_2\text{CuO}_4$  [29].  $\text{AgF}_2$  and  $\text{La}_2\text{CuO}_4$  XAS energies correspond to the bottom and the top  $x$  axes, respectively. Bottom panel: Orbital projected unoccupied density of states (DOS) of  $\text{AgF}_2$  from the unpolarized DFT computations. The Fermi level has been shifted to 681.8 eV to facilitate comparison with F K-XAS (red line). The total unoccupied DOS, includes contributions from the shown symmetries above the edge as well as Ag 4d, which will be shown later [Fig. 5(a)]. For the band at the Fermi level, it is nearly equal to the difference of the total and F 2p contribution.

dle panel in Fig. 4, we show that the low-energy part of the  $\text{AgF}_2$  spectrum can be decomposed into an elastic peak (0 eV), phonons (0.041 eV) and their overtones, and a damped bimagnon peak (centered at 0.218 eV). The energy of the assigned bimagnon peak corresponds to that observed in the Raman spectra ( $\sim 3J$ ) [14]. Bimagnons can be probed also with K-edge RIXS. However, to accurately determine the spectral contributions of the phonon progression and the bimagnon peak in  $\text{AgF}_2$ , momentum-resolved RIXS is desirable.

As shown in Fig. 4 (middle panel) a series of excitations at 1.59, 1.86, and 2.33 eV is observed, an assignment which will be substantiated below. At high energies ( $>4$  eV), the RIXS spectrum is dominated by a broad feature with a strong resonance behavior as a function of the incident energy. We

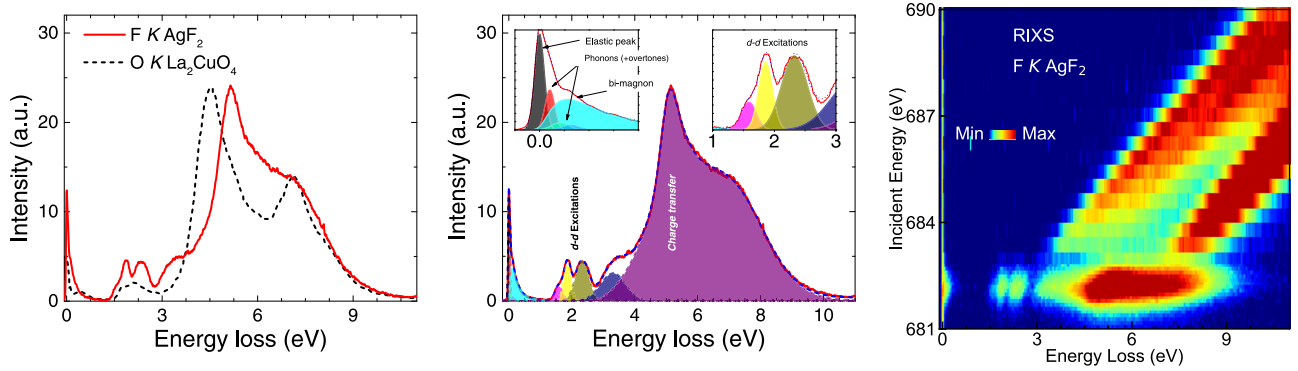


FIG. 4. Left panel: Comparison of F *K*-RIXS on  $\text{AgF}_2$  and O *K*-RIXS on  $\text{La}_2\text{CuO}_4$  [33]. Middle panel: F *K*-RIXS on  $\text{AgF}_2$  fitted with multiple components: black, elastic peak; red, green, and blue, phonons and their overtones; cyan, bimagnon; magenta, yellow, and dark yellow, *dd* excitations; navy and purple, charge-transfer excitations (see text for further description). Insets show the low-energy inelastic features and *dd* excitations with fitted profiles in different colors as noted before. Right panel: F *K*-RIXS incident energy map on  $\text{AgF}_2$  showing Raman and fluorescence features.

attribute the resonance to the excitation of charge-transfer transitions involving an Ag site and its neighboring F's as will be also explained below. Between the *pd* and the *dd* excitations, a peak is observed at 3.32 eV. The energy scale of this peak matches reasonably well with the growing optical conductivity of  $\text{AgF}_2$  shown in Fig. 2. As such, this peak can be assigned to transitions across the charge-transfer gap from an Ag site to more distant F's and provides supporting evidence for the existence of a large fundamental gap in  $\text{AgF}_2$ . In fact, our current experimental observations contradict the previous predictions of the charge-transfer gap as reported in Ref. [14]. Both the *dd* and charge-transfer excitations are discussed in detail below while a further discussion of the comparison with the RIXS data of  $\text{La}_2\text{CuO}_4$  will be given in Sec. IV B.

The map in Fig. 4 (right panel) shows energy-detuned RIXS spectra collected across the F *K*-XAS. Energy-detuned RIXS is very useful for revealing the degree of localization of the excitations. At higher incident photon energies ( $>683$  eV), two fluorescence emission lines arise. We can view the fluorescence RIXS as an incoherent process, that is, the excitation and deexcitation are decoupled from each other. Electrons are excited from F *1s* core level to unoccupied states involving Ag *5s*, Ag *5p*, and F *2p* (cf. Fig. 3, bottom panel). The deexcitation is from the broad valence states to refill the *1s* core hole resulting in a characteristic emission energy. In other words, the energy loss of fluorescence varies linearly with the incident energy. Across the resonance of the UHB peak (682.2 eV), *dd* and charge-transfer excitations resonate at the UHB peak and show an almost fixed energy loss, i.e., Raman-like, indicating the energy loss corresponds to the energy of fixed-number-of-particle excitations (i.e., excitons, particle-hole, etc.). The localized *dd* and charge-transfer excitations are widespread in many transition-metal oxides (including oxocuprates).

## IV. DISCUSSION

### A. Optical conductivity of $\text{AgF}_2$ vs. $\text{La}_2\text{CuO}_4$

We now turn back to the absorption spectrum as seen in the optical conductivity data shown in Fig. 2. Similar behavior

of a high-energy absorption was well studied, in particular in the parent compound  $\text{La}_2\text{CuO}_4$  [27,34]. In that case, a strong peak can be seen in the real part of the optical conductivity at about 2.2 eV [27,34,35] as we demonstrate in Fig. 2. The strong peak at 2.2 eV in  $\text{La}_2\text{CuO}_4$  is associated with the charge-transfer transition between the O *p* band and Cu *d* band and was measured in various parent compounds of the cuprates family [35,36]. Taking into account the resemblance of the experimental data between  $\text{AgF}_2$  and  $\text{La}_2\text{CuO}_4$  with the supporting results of the theoretical analysis and the RIXS data, we associate the strong high-energy absorption in our data to the charge transfer excitation between the F *p* band to the Ag *d* band.

The broad tail down to 1.25 eV in the optical conductivity data of the  $\text{AgF}_2$  sample, is similar but with a much weaker absorption to the tail in the optical conductivity data that was already reported in previous works regarding the cuprates [28,34,35,37–39] and as we reproduce in Fig. 2. Uchida *et al.* [34] demonstrated the appearance of a mid-infrared (MIR) absorption depicted as a subgap peak centered at about 0.5 eV in the real part of the optical conductivity of Sr-doped  $\text{La}_2\text{CuO}_4$ . Falck *et al.* [28] showed that oxygen doping in  $\text{La}_2\text{CuO}_{4+\delta}$  results in a similar MIR absorption, which is dominant in sample with  $\delta = 0.014$  and reduced  $T_N$  of 250 K. On the other hand, in an undoped sample with  $\delta = 0$  and  $T_N = 322$  K the MIR absorption is negligible as can be seen in Ref. [28]. The MIR band, which appears as a peak in the real part of the optical conductivity of doped samples, partially draws spectral weight from a higher energy range, thus diminishes the charge-transfer excitation upon further doping [34]. The intensity of the MIR band is of the order of the charge-transfer excitation in nearly undoped  $\text{La}_2\text{CuO}_4$  and even stronger for intermediate doping levels [28,34]. Since we detect a MIR-NIR absorption band, which is weak compared to that of the charge-transfer excitation, we conclude that the  $\text{AgF}_2$  is practically in its undoped phase, as intended.

### B. $\text{AgF}_2$ vs. $\text{La}_2\text{CuO}_4$ from XAS and RIXS

In Fig. 3 (top panel) we compare F *K*-XAS in  $\text{AgF}_2$  to O *K*-XAS in  $\text{La}_2\text{CuO}_4$  [29]. The peak at the absorption threshold of

$\text{La}_2\text{CuO}_4$  reflects the O  $2p$ -Cu  $3d$  hybridization and originates upon excitation to the upper Hubbard band (UHB) of predominantly  $3d_{x^2-y^2}$  character in this material [29]. The broad structures ranging from  $\sim 531$ – $537$  eV reflect hybridizations between unoccupied O  $2p$  and La  $5d$  and  $4f$  DOS. In  $\text{AgF}_2$  there are no ions playing the role of La, so a different explanation for the broad absorption is needed (see below).

As an additional comparison, O  $K$ -RIXS spectrum of  $\text{La}_2\text{CuO}_4$  is also presented in Fig. 4 (left panel). The low-energy excitations around 2 eV resemble the well-known  $dd$  excitations of cuprates [33]. The bimagnon excitation at 0.218 eV of the  $\text{AgF}_2$  sample is similar to that which is observed in the O  $K$ -RIXS on  $\text{La}_2\text{CuO}_4$  in the MIR region [33]. Therefore, the RIXS data of  $\text{AgF}_2$  and  $\text{La}_2\text{CuO}_4$  shows an overall remarkable similarity, which facilitates the assignment of the different features noted above and further supports the claim that silver fluorides are excellent cuprate analogs. Additional information can be learned from the comparison of cluster calculation results between the two families, which will be presented in Sec. IV D.

### C. Comparison with density functional theory computations

#### 1. X-ray absorption

In the x-ray absorption process, a core electron is excited to the unoccupied F states. Thus, the F-projected unoccupied DOS from DFT provides a first approximation to the spectra. Figure 3 (bottom panel) shows that there is a good match with the main structures observed. As anticipated, the DFT computations show that the broad absorption can be assigned to Ag  $5s$  and  $5p$  states. Notice that the F  $2p$  projected DOS has large intensity at the position of both,  $5s$  and  $5p$  states, which testify for the strong hybridization.

The peak near 682 eV is, as explained above, attributed to the upper Hubbard band states, which have mainly Ag- $4d$  character but are strongly mixed with F- $2p$  states. The weight of the  $4d$  states in this region is approximately given by the difference between the total and the F- $2p$  DOS, which is somewhat larger than the F- $2p$  weight and again indicates strong hybridization.

#### 2. Assignment of $dd$ transitions

Figure 5 (top panel) shows the local DOS from DFT computations, projected on the different  $d$ -orbital symmetry in the nonmagnetic (metallic) solution with the abscissa origin now set at the Fermi energy. Due to the stronger hybridization compared to other symmetries (cf. Table I), the antibonding  $d_{x^2-y^2}$  band is half-filled and is well separated from the other (filled)  $d$  bands. Figure 5(b) shows the joint DOS between the unoccupied  $d_{x^2-y^2}$  and occupied orbitals of the other symmetries, representing  $dd$  transitions with a constant matrix element. Averaging over the four possible final states (black line), one obtains a line shape surprisingly similar in position and overall shape to the  $dd$  RIXS spectra, despite neglecting matrix element effects. The theoretical line shape is broader than the experiment, which can be attributed to correlation-induced band narrowing effects absent in DFT. Neglecting minor differences, this analysis allows assigning the lower shoulder to transitions of the  $d_{x^2-y^2}$  hole to  $z^2$  orbitals, the

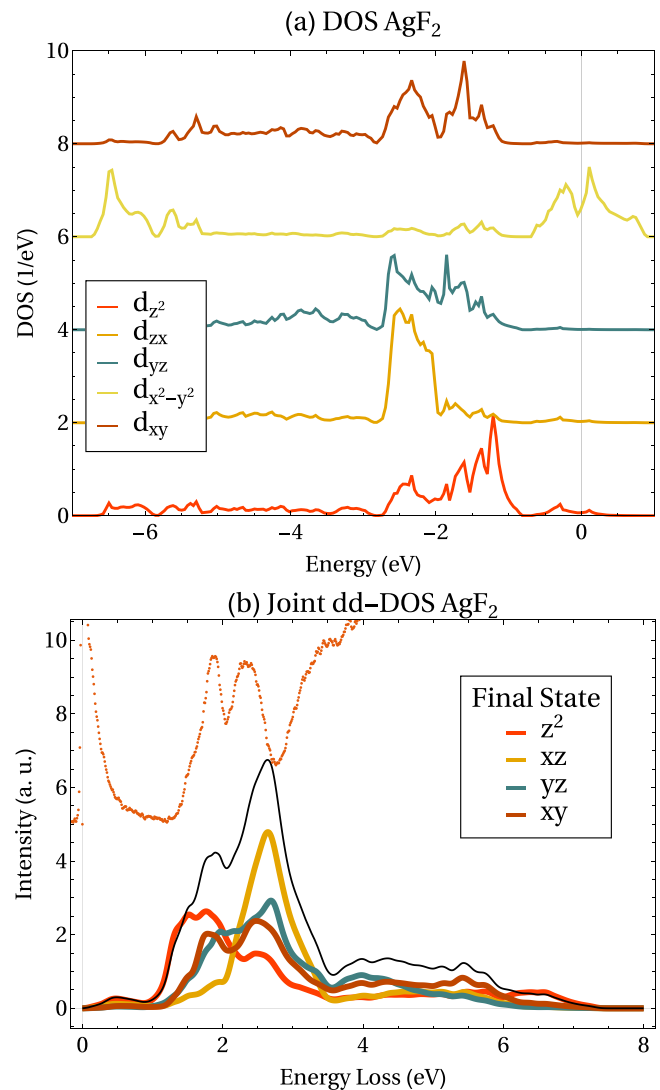


FIG. 5. (a) DOS of  $\text{AgF}_2$  projected on Ag  $d$  orbitals from the unpolarized DFT computations. (curves have been shifted by 2 eV for clarity). The Fermi level is at zero energy. (b) Joint DOS between the unoccupied DOS of  $d_{x^2-y^2}$  character and occupied DOS of different character representing  $dd$  transitions of a hole from the half-filled  $d_{x^2-y^2}$  to a final state (labeled by the final state) character. The thin black line is the average of the different contributions. The dotted line is the experimental RIXS data.

higher peak to transitions to mainly  $xz$  orbitals and the intermediate band to a mixed character. Such assignments are in general good agreement with previous works regarding fluoroargentates [40–44]. Notice, however, that in our work the peaks tend to have a mixed symmetry, which can be attributed to the influence of the ligand orbitals, which depart strongly from  $D_{4h}$  symmetry as discussed in Sec. II D.

Being the compound an insulator, it may appear natural to describe it with a DFT +  $U$  method [45] and an antiferromagnetic ground state as a starting point. Instead, our computation of  $dd$  transitions neglects the Hubbard  $U$ . This is not important here because  $dd$  excitations are charge neutral, i.e., an electron is taken from one-orbital and put in another orbital so that the Hubbard  $U$  does not play an important role.

The nonmagnetic computation, includes only shifts due to the ligand and crystal fields, which are the relevant ones. Instead, a DFT +  $U$  computation would include an additional large  $U$  shift from the outset in a mean-field manner, spoiling the agreement.

#### D. Comparison with cluster computations

An alternative description of the excitations, which emphasizes the local character, can be obtained with the cluster model presented in Sec. II D. Figure 6 shows the energy levels of the one-hole configuration of the cluster for  $\text{AgF}_2$  and a cuprate [26]. The dashed lines on the left (right) of each panel are the  $d^9$  ( $d^{10}\bar{L}$ ) configurations. Each left-right pair of a given symmetry produces a bonding and antibonding level upon hybridization shown with the full lines. Notice that because we are showing hole energies, the bonding (antibonding) states are at high (low) energies. Energies are measured with respect to the  $x^2-y^2$  ground state, so the vertical scale represents the energy of transitions to the different excited states. In addition, following Ref. [46] the energy of the ground state has been lowered by  $J$ , the magnetic stabilization energy due to the interaction with the neighbors. We have added one time  $J$  and not  $2J$  since we have broken bonds with the neighbors while Ref. [46] considered a cluster with five Cu's and excited ferromagnetic alignment of spins.

The first striking difference between cuprates and  $\text{AgF}_2$  is that the  $d^{10}\bar{L}$  configurations have much smaller splittings in the fluoride [cf. Figs. 6(a), 6(b)]. This is in part a consequence of smaller F-F hoppings [14]. Optimized  $p$  Wannier orbitals have large crystal fields splittings parametrized by  $\varepsilon_p(m)$  in Eq. (1), but they get averaged out when projected on the  $d$ -symmetrized states. Notice that in the case of cuprates,  $T_{pp}$  lowers the energy of the  $x^2-y^2$  ligand orbital while the hybridization with the  $d_{x^2-y^2}$  rises it, resulting in a bonding  $x^2-y^2$  orbital at 4.8 eV slightly above the  $yz$  and  $xz$  orbitals. In the case of  $\text{AgF}_2$ , the lowering effect of  $T_{pp}$  is almost absent, so the  $x^2-y^2$  bonding orbital is at much higher energies. The crossing with the other bonding levels as covalency is increased can be visualized in the Tanabe-Sugano diagram of Fig. 6(c) (top yellow line).

##### 1. $dd$ transitions

As a reference, we first discuss the case of cuprates for which we used one of the parameter sets considered by Eskes *et al.* for CuO in Ref. [26] and reproduced in Table II (labeled as Local in the  $\text{La}_2\text{CuO}_4$  sector). The parameter  $\Delta$  corresponds to the value quoted by Eskes *et al.* using a slightly different definition, namely,  $\Delta - T_{pp}/5 = 2.2$  eV. From Fig. 6(b) we see that this set of parameters gives a quite good estimate of  $dd$  transition energies. As a bonus, this analysis suggests that the main structure seen in RIXS near 5 eV is a charge transfer transition from the ground state of mainly  $d_{x^2-y^2}$  character to a hole in a combination of ligand orbitals with  $yz$  or  $xz$  symmetry. This is the lowest-energy  $pd$  transition within the cluster so its referred to as a local charge-transfer transition.

The position and ordering of  $dd$  transitions predicted in Ref. [26] and partially reproduced in Fig. 6(b) was studied with the advent of RIXS two decades latter. A detailed

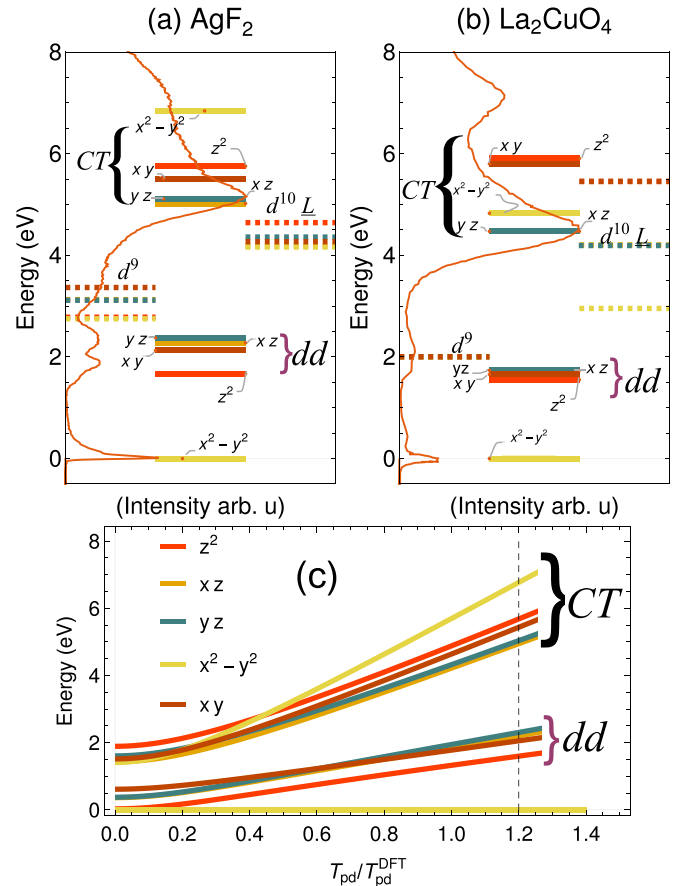


FIG. 6. Energy level diagram for one hole states in the clusters considered for (a)  $\text{AgF}_2$  with  $\Delta = 1.29$  eV and parameters from Table I with a 20% increase of the  $T_{pd}$  matrix elements and  $J = 70$  meV as stabilization energy [46]. (b)  $\text{La}_2\text{CuO}_4$  with  $\Delta = 2.45$  eV and  $J = 130$  meV. Dashed lines correspond to energies before hybridization in the  $d^9$  configuration (left) and  $d^{10}\bar{L}$  (right). Hybridization yields bonding and antibonding states (full lines). The ground state corresponds to the half-filled antibonding  $d_{x^2-y^2}$ , which was placed at zero energy so the vertical scale represent energies of transitions to states of majority  $d^9$  character (i.e.,  $dd$  transitions) around 2 eV and  $d^{10}\bar{L}$  (i.e., charge-transfer transitions) at higher energy. RIXS spectra has been superposed for comparison. (c) shows the Tanabe-Sugano diagram for  $dd$  (lower lines set) and charge-transfer transitions (higher lines set). The position of excited states is measured with respect to the  $x^2-y^2$  ground state and are plotted as a function of the renormalization of the  $T_{pd}$  matrix element with respect to the DFT value. The vertical line at  $T_{pd}/T_{pd}^{DFT} = 1.2$  represents the value that was taken in our analysis to fit the experimental data. The magnetic stabilization energy of the  $d_{x^2-y^2}$  state mentioned in the text has been omitted.

analysis [47] of the angular dependence of RIXS matrix elements confirmed the ordering and provided a refinement of the energies. Using a more ionic parameters set with a larger fundamental gap (last column in Table II) do not produce a satisfactory agreement. We will come later to this important point. Notice that the parameters in Fig. 6(a) have been adjusted ad hoc to fit the experiment while no such adjustment has been done for Fig. 6(b), which yields a slightly less accurate agreement for  $dd$  excitations.



TABLE II. Comparison of parameter sets appropriate for local and nonlocal excitations and resulting fundamental gap for  $\text{AgF}_2$  and  $\text{La}_2\text{CuO}_4$ . We also show the numbers of holes in the transition metal  $n_d$ .  $\text{La}_2\text{CuO}_4$  parameter sets are taken from Ref. [26].

	$\text{AgF}_2 (C_i)$		$\text{La}_2\text{CuO}_4 (D_{4h})$	
	Local	Nonlocal	Local	Nonlocal
$\Delta$	1.29	2.8	2.45	2.95
$T_{pd}^a$	3.31	2.76	2.3	2.5
$T_{pp}$	0.11 <sup>b</sup>	0.11 <sup>b</sup>	1.25	1.0
$F^0$	6.48	6.48	6.81	7.31
$F^2$	8.19	8.19	11.41	11.41
$F^4$	6.80	6.80	7.31	7.31
$E_{\text{gap}}$	1.54	2.25	1.27	1.8
$n_d$	0.60	0.73 <sup>c</sup>	0.60	0.66

<sup>a</sup> $(x^2-y^2)$  symmetry.

<sup>b</sup>For  $\text{AgF}_2$  we used crystal field parameters from Table I. For comparison we defined an effective  $T_{pp} = [e_P(xz) + e_P(yz)]/2 - e_P(x^2 - y^2)$ .

<sup>c</sup>Since the charge balance is determined by local transitions the physical value should be considered as the one computed with  $\Delta$  in the Local column.

For  $\text{AgF}_2$ , we found that DFT parameters of Table I give a first ansatz for the position of RIXS structures including the DFT value for the charge-transfer parameter,  $\Delta_{\text{DFT}} = 1.29$  eV. However, this parameter set underestimates the energy of the  $dd$  transitions, which can be corrected by increasing the  $T_{pd}$  matrix elements by 20% as shown in the Tanabe-Sugano diagram of Figs. 6(c) and 6(a). In this way, the energies of the  $dd$  transitions match the experimental ones but, due to the low symmetry of the cluster, the lines should be understood as averages of the structures shown in Fig. 5(b) and a one-to-one correspondence of peaks and  $dd$  lines is oversimplified. On the other hand, this analysis suggests that also for the fluoride, the main peak in RIXS near 5 eV can be assigned to the local charge-transfer transition with a final state consisting in a hole in an orbital with  $xz$  or  $yz$  symmetry and mainly F character [cf. Fig. 6(a)].

The increase of  $T_{pd}$  should not be taken too seriously as it may just reflect longer-range hopping process from the  $d_{x^2-y^2}$  and nonmagnetic stabilization terms of the  $x^2-y^2$  ground state due to intercluster interactions beyond the magnetic correction introduced above. More importantly, increasing  $\Delta$  with respect to the DFT value (i.e., increasing the ionicity) monotonously decreases the energy of  $dd$  transitions (i.e., worsening the agreement). We conclude that the description of  $dd$  transitions requires a quite covalent ground state in  $\text{AgF}_2$ . This is confirmed by the previous analysis of the joint DOS in Fig. 5, which is based on the same DFT computation.

## 2. Optical transitions

We now compare our theoretical analysis with the optical transitions. For a clean insulator, optical excitations measure the direct gap of the material. More precisely, the optical absorption may or may not show sharp transitions corresponding to particle-hole bound states (excitons), but should show an edge to a continuum of states. The threshold of the continuum

corresponds to the minimum energy to separate an electron and a hole at an infinite distance and zero total momentum and defines the fundamental gap. We refer to these charge-transfer transitions as nonlocal. From the optical experiments, we obtained lower and higher bounds for the fundamental gap using two different methods: (i) a linear extrapolation of the edge giving a lower bound and (ii) a fit with a sharp edge broadened with a Gaussian distribution giving a higher bound. We estimate  $E_{\text{gap}} = 1.8 \pm 0.1$  eV for  $\text{La}_2\text{CuO}_4$  and  $E_{\text{gap}} = 2.2 \pm 0.3$  eV for  $\text{AgF}_2$ .

Neglecting the band formation effects, we can estimate the fundamental gap as the minimum energy to extract an electron from one cluster and add it to another cluster, i.e.,  $E_{\text{gap}} \equiv E_0(N+1) + E_0(N-1) - 2E_0(N)$ . This energy corresponds also to the effective  $U_{\text{eff}}$  in a one-band model, which for cuprates provides a good description of the main charge-transfer absorption band in optics [48].  $E_0(N-1)$  corresponds to the ground state of the two-hole multiplet ( $d^8 + d^9\bar{L}$ ), which is the Zhang-Rice state. The  $N+1$  configuration corresponds to the filled shell so there is no multiplet but a unique state ( $d^{10}$ ).

To compute the fundamental gap, we solved the many-body problem in the cluster using Lanczos exact diagonalization as implemented in the QUANTY package [49]. The Coulomb interaction in Eq. (2) was parametrized in terms of Slater integrals. For Cu we used the values corresponding to the Racah parameters of Ref. [26]. For Ag we took the values corresponding to the Racah parameters of Ref. [9] for  $F^2$  and  $F^4$  and took  $F^0$  to be larger in view of the reduced screening expected in a fluoride with respect to an oxide [14]. Table II shows the resulting fundamental gap for the various parameters chosen. Both for  $\text{AgF}_2$  and  $\text{La}_2\text{CuO}_4$  the parameters that fit well the  $dd$  transitions (labeled Local) correspond to  $E_{\text{gap}}$  smaller than the one measured with optics. The effect is much stronger in  $\text{AgF}_2$ , which requires a quite small charge-transfer parameter to fit the  $dd$  transitions and yet has a larger experimental  $E_{\text{gap}}$  than cuprates. Notice that a small  $\Delta$  does not imply that the local charge-transfer transitions are at small energy. Indeed, the local  $\Delta$  represents the difference in energy between the levels before hybridization (difference between left and right multiplets with dashed lines in the top panels of Fig. 6). Instead, the local charge-transfer transition energies are set by the difference between hybridized levels (full lines in Fig. 6).

## 3. Nearest-neighbor repulsion and valence instability

We argue that the difference in  $\Delta$  needed to fit optics (labeled Nonlocal) and RIXS (Local) reflects interactions beyond the on-site ones considered in Eq. (2). In particular, adding a nearest-neighbor repulsion between  $p$  and  $d$  orbitals,  $U_{pd}$ , renormalizes  $\Delta$  in a different way for local (intracluster) and nonlocal (intercluster) charge-transfer excitations as shown schematically in Fig. 7. In the ionic limit, the effective  $\Delta$  for local excitations ( $d^9 \rightarrow d^{10}\bar{L}$ ) is  $\Delta^{\text{loc}} = \Delta_0 + U_{pd}$  while it enters as  $\Delta^{\text{nl}} = \Delta_0 + 2U_{pd}$  in the nonlocal excitations that define the fundamental gap. Here we define the difference of one-hole diagonal energies in the absence of Coulomb interactions,  $\Delta_0 = \bar{\epsilon}_p^0 - \bar{\epsilon}_d^0$  and bar indicates average over the multiplet. Taking the difference of the first and second col-

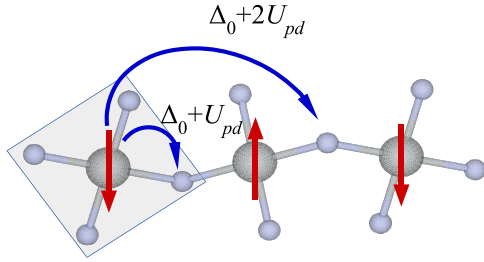


FIG. 7. Charge-transfer processes within the  $\text{AgF}_6$  cluster (gray region) and to a distant fluorine.

umn  $\Delta$  for each material, this implies a  $U_{pd} \approx 0.5 \pm 0.2$  eV for cuprates (consistent with the accepted value) and  $U_{pd} \approx 1.5 \pm 0.5$  eV for  $\text{AgF}_2$ , a value much larger than in cuprates.

In general,  $U_{pd}$  matrix elements will be orbital dependent, so our estimate above should be considered as a multiplet average. Coming back to the original  $p$  operators, the Hamiltonian for the nearest-neighbor Coulomb repulsion in one Ag-F bond can be written as

$$H_{\text{bond}} = \sum_{v,m} U_{pd}(v,m) d_v^\dagger d_v p_m^\dagger p_m.$$

We expect that also off-diagonal terms will be present, in particular

$$H'_{\text{bond}} = \sum_{v \neq \mu, m} W_{pd}(v, \mu, m) d_v^\dagger d_\mu p_m^\dagger p_m + \text{H.c.}$$

in which a hole in a  $p$  orbital induces a  $dd$  transition. This last operator naturally explains the RIXS activity for  $dd$  transitions at the ligand K edge and can be used to evaluate the cross section. We expect that  $U_{pd}$  and  $W_{pd}$  have a similar material dependence so the larger RIXS activity for  $dd$  transitions in  $\text{AgF}_2$  with respect to the cuprates [cf. Figs. 6(a) and 6(b) in Fig. 6] is an indirect confirmation of the large intersite interactions.

So far we have used DFT to obtain spectral responses as it is customary done (Figs. 3 and 5). In general, these comparisons should be taken with a grain of salt as Kohn-Sham DFT [50] is a theory, which aims to find an auxiliary noninteracting system with the same density as the interacting system, and it is not warrant that the spectral functions of the auxiliary system will match the interacting ones. In the two cases above, correlations either not play an important role or tend to cancel, which partially explain the success.

The situation is different for the fundamental gap. The band structure of hybrid DFT computations [14] shows a smaller gap for  $\text{AgF}_2$  than for  $\text{La}_2\text{CuO}_4$  despite the fundamental gap in optics appears to have the opposite behavior. This should not be taken as a deficiency of DFT as this gap is just the gap of the auxiliary system constrained to be smaller to match the charge distribution of the interacting system. In other words, it is a measure of the strong covalency of the interacting system, not of its gap. Indeed, model computations [51] show that the Kohn-Sham gap in exact DFT is determined by the energy cost of neutral (i.e., local) excitations ( $\Delta_0 + U_{pd}$  in our case) and not the nonlocal ones determining the fundamental gap  $\Delta_0 + 2U_{pd}$ . This gives further support to our finding that the DFT value for  $\Delta$  has the right magnitude for describing

neutral (local) transitions reconciling strong covalency [52] in the ground state with a large fundamental gap.

The large value of  $U_{pd} \approx 1.5 \pm 0.5$  eV for  $\text{AgF}_2$  poses a stability problem as it implies  $\Delta_0 \approx -0.2 \pm 0.8$ , which would make  $\text{AgF}_2$  a negative charge transfer system as  $\text{AgO}$ . Taken literally and in the ionic limit, holes should populate the ligands as it occurs in formally  $d^9$ , silver oxide [9]. This can be avoided if one assumes that also intra- and intersite F-F Coulomb repulsions are present, which can stabilize the  $d^9$  state. At present, the indeterminacies are too large, and it could be that  $\Delta_0$  is small but positive. In any case, our results point to  $\text{AgF}_2$  being close to a charge-transfer instability. In this regard, it is very suggestive that besides the magnetic brown  $\alpha$ - $\text{AgF}_2$  considered in this study, a metastable red-brown diamagnetic  $\beta$  phase has been reported [53], which has been interpreted in terms of a disproportionated (charge density wave) ground state. Although the structure of the  $\beta$  phase is not known, DFT computations [54,55] find a CDW polymorph very close in energy with respect to the usual antiferromagnetic phase, which also points to  $\text{AgF}_2$  being at the verge of a charge-transfer instability.

## V. CONCLUSIONS

We have measured the optical conductivity and resonant inelastic x-ray scattering spectra of  $\text{AgF}_2$  to study its electronic excitations. We observe a charge transfer excitation between the F  $p$  bands and the Ag  $d$  bands peaking at about 3.4 eV in both optical conductivity and RIXS spectra. We resolve several  $dd$  excitations at 1.59, 1.86, and 2.33 eV from the RIXS spectra. We performed DFT and cluster calculations of the electronic structure, which allowed us to identify  $dd$  excitations and local charge-transfer transitions at high energy and a nonlocal charge-transfer transition determining the optical gap.

Using DFT and cluster computations, we provided estimates of the fundamental electronic parameters of this emerging quantum material, which are essential for future theoretical studies. The similarity between our data and that of the charge transfer insulator  $\text{La}_2\text{CuO}_4$  is striking, but the subtle differences encode very interesting new physics. In particular,  $\text{AgF}_2$  is predicted to be close to a charge-transfer instability due to a quite large value of  $U_{pd}$ . Interestingly, this parameter has been considered essential in some theories of cuprates [56] so a material with an enhanced  $U_{pd}$  can provide key clues to its role in determining the physics of cuprates.

The superconductivity in cuprates appears close to an insulating magnetic phase, while the same phenomenon in doped  $\text{BaBiO}_3$  appears in proximity to the insulating CDW phase. Moreover, CDW instability along with a positive but small charge transfer energy have been realized in a recent study on K-doped  $\text{BaSbO}_3$  [57] where the superconducting transition was shown to be higher than that of the same doping level in K-doped  $\text{BaBiO}_3$ . It is further postulated that the enhancement of  $T_c$  stems from the strong covalency of the metal-ligand bond, which is extremely relevant to our conclusions in view of the current results on  $\text{AgF}_2$ . Therefore, we expect a bright future in the search for doped [58] and hopefully superconducting [59] phases of  $\text{AgF}_2$  that seems to combine both instabilities in the same material.

TABLE III. Explosives used for consecutive explosive compaction with their densities and detonation velocities, *D*.

Type	Explosive	Density [g/cm <sup>3</sup> ]	<i>D</i> [m/s]
A	Ammonal 2% (98% ammonium nitrate + 2% aluminum powder)	0.77	2600
B	Emulsion explosive (EmEx, mostly ammonium nitrate + fuel oil + water)	1.17	5300
C	Emulsion explosive (EmEx) + 20% 1,3,5-trinitro-1,3,5-triazinane (RDX)	1.25	5700

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### APPENDIX A: SAMPLE PREPARATION PROCEDURE

A few-gram sample of AgF<sub>2</sub> has been placed inside of a 99.99% Cu container (Fig. 8), pressed manually using a copper cylinder, and the upper plug has been hammered into the container for even better compactness. All operations were carried out inside an argon-filled glove box.

Explosive compaction has been performed using three distinct types of explosives; their composition and results of measurements of the detonation velocity are presented in Table III. Consecutive explosions were carried out using the same container, but changing only parts 5 and 9 each time (cf. Fig. 8), due to their severe shock deformation.

Samples were undergoing explosive compaction in the following way:

- (i) one sample underwent only type A explosion,
- (ii) one sample underwent consecutive type A and B explosions,
- (iii) one sample underwent consecutive type A, B, and C explosions.

Data on high-pressure behavior of silver fluorides up to 40 GPa [16] were used to calculate the compression shock

curve of the crystalline AgF<sub>2</sub>. The equation of state of a multicomponent medium (solid-gas) [60] was used to describe the physical properties of the porous AgF<sub>2</sub> samples loaded by a shock wave. To estimate the temperature in the shock-compressed sample, the dependence of specific heat on temperature for AgF<sub>2</sub> [14] was extrapolated to high temperatures. It was assumed that the entire energy of the shock compression of a porous sample is converted into heat, which causes the sample temperature to rise. The initial density of the samples was 3.14 g/cm<sup>3</sup>. It was estimated that during the type A explosion, the maximum pressure in the sample was ca.

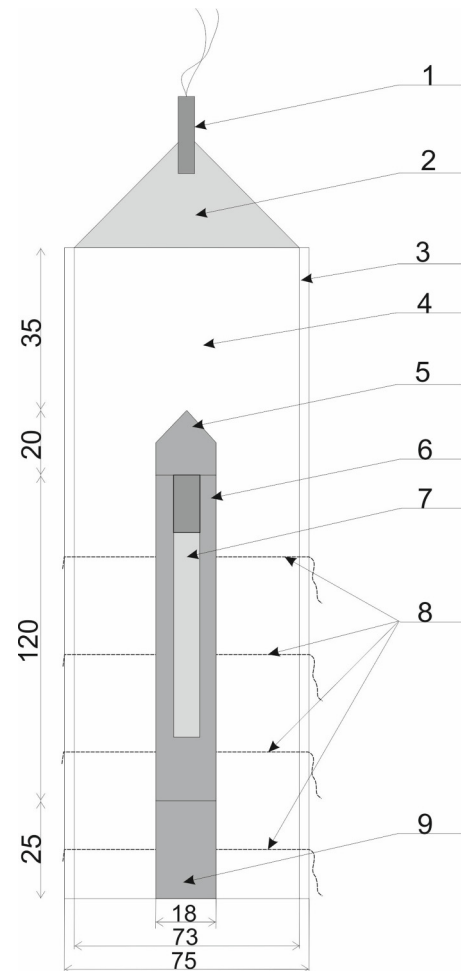


FIG. 8. Experimental setup for explosive compaction. 1 - electric detonator, 2 - plane wave generator, 3 - PVC tube, 4 - explosive, 5 - upper plug together with conical hat, 6 - container with compacted sample, 7 - compacted sample, 8 - short circuit sensors for measuring the detonation velocity, 9 - momentum trap. Dimensions are given in mm on the left-hand side.

11 GPa, the maximum temperature was approximately 1500 °C and the density after loading was 5.1 g/cm<sup>3</sup>. The explosion B in procedure (ii) resulted in substantially increased maximum pressure (63 GPa), but the temperature reached only 2100 K. The density of the samples after the loading B was 5.4 g/cm<sup>3</sup>. In the type C explosion [procedure (iii)], the estimated pressure was 73 GPa and the temperature was 2000 K. Since the copper container did not explode, it was presumed that the pressure increase has substantially hindered the thermal decomposition of AgF<sub>2</sub> with the release of F<sub>2</sub> gas. Copper container was cut into pieces in an inert gas atmosphere. Indeed, visual inspection of the sample indicated that thermal decomposition and partial erosion of the container occurred only in the part of the sample adjacent to the container inner wall, while the inside of the sample cylinder was dark brown as typical for AgF<sub>2</sub>. X-ray diffraction analysis revealed that the samples undergoing the procedure (iii) were nearly pure AgF<sub>2</sub>, and the apparent density of the sample was approximately 95% of the crystallographic density; a small fraction of the sample might be amorphous.

#### APPENDIX B: ELLIPSOMETRY DATA

We measured the complex dielectric function using a Woollam VASE® spectroscopic ellipsometer in the energy range from 0.55–3.5 eV. The reflectivity ratio for *p* and *s* polarization is defined as

$$r_p/r_s = \rho = \tan(\Psi_{\text{ellip}})e^{i\Delta_{\text{ellip}}},$$

where  $\Psi_{\text{ellip}}$  and  $\Delta_{\text{ellip}}$  are the parametric amplitude and phase difference components of the complex reflectivity  $\rho$ . We measured the  $r_p/r_s$  ratios at incident angles  $\theta$  of 61° and 63° at selected temperatures of 300 K, 250 K, 226 K, 200 K, 176 K, 150 K, 100 K, 50 K, and 8 K. The corresponding  $\Psi_{\text{ellip}}(\omega)$  and  $\Delta_{\text{ellip}}(\omega)$  spectra for two angles of incidence measured at the lowest temperature are displayed in Fig. 9.

We fitted  $\Psi_{\text{ellip}}(\omega)$  at two different angles of incidence (AOI) simultaneously following a similar but a separate fit to the  $\Delta_{\text{ellip}}(\omega)$  spectra at two different angles of incidence using a Drude-Lorentz parametrization of  $\epsilon(\omega)$ . For the powder-pressed sample of AgF<sub>2</sub>, we have used an isotropic model for  $\epsilon(\omega)$ . The confidence boundaries presented in Fig. 2 of the main text represent the possible range of  $\sigma_1$  values between the two limits, i.e., a fit to  $\Psi_{\text{ellip}}$  data (2 AOI) and a fit to  $\Delta_{\text{ellip}}$  data (2 AOI), thus reflecting our error bar for the reported results. A simultaneous fit to both  $\Psi_{\text{ellip}}$  and  $\Delta_{\text{ellip}}$  was not possible to obtain under the use of a simple one-layer model of  $\epsilon(\omega)$  for the AgF<sub>2</sub> sample. We assume that the discrepancy is due to the polycrystalline nature of the sample. Nevertheless, the impact of this discrepancy is mostly shown around the

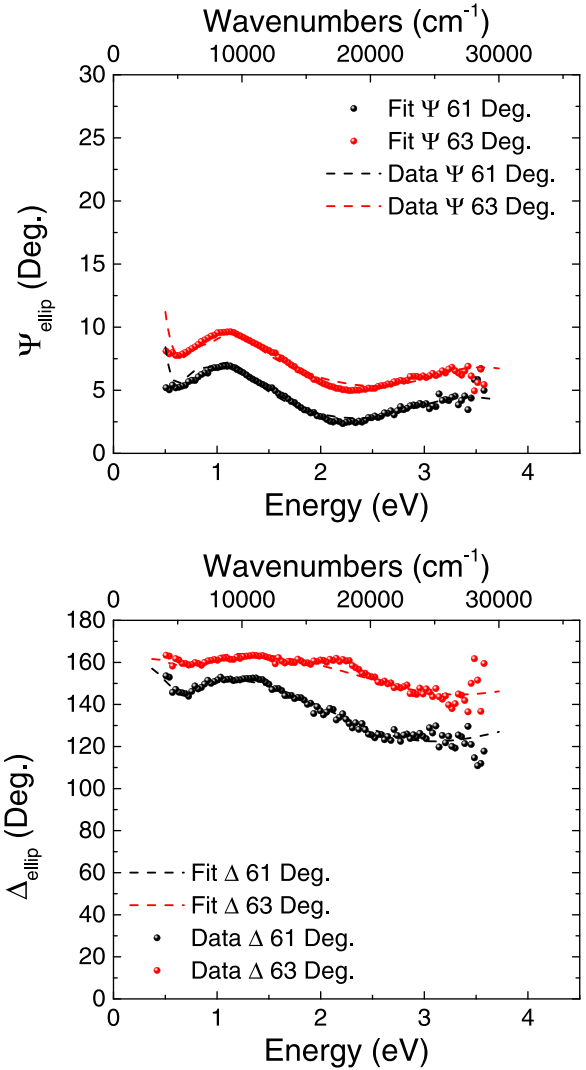


FIG. 9. The ellipsometric parameters  $\Psi_{\text{ellip}}$  and  $\Delta_{\text{ellip}}$  as measured at temperature of 8 K for AOI of 61 (black spheres) and 63 (red spheres) degrees. The corresponding model fit as explained in the Appendix is shown in dashed lines.

1 eV absorption while the charge-transfer excitation is robust for both analysis procedures.

To extract the optical conductivity directly from the  $r_p/r_s$  ratio, we have used the following pseudodielectric function:

$$\epsilon_{ps} = \sin^2(\theta) \left[ 1 + \tan^2(\theta) \left( \frac{1 - \rho}{1 + \rho} \right)^2 \right],$$

where  $\sigma = -iv2\pi c\epsilon_0(\epsilon_{ps} - 1)$  is the optical conductivity in units of S/cm as shown in Fig. 2 for the real part. Here  $\nu$  are wave numbers in cm<sup>-1</sup>,  $c$  is the speed of light in vacuum in m/s and  $\epsilon_0$  is the vacuum permittivity in F/m.

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