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Electronic phase separation and dramatic inverse band renormalisation in the mixed valence cuprate LiCu₂O₂

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We measured by ARPES the electronic structure of LiCu_2O_2 , a mixed valence cuprate where planes of formally Cu(I) $(3d^{10})$ ions are sandwiched between layers containing one-dimensional edge-sharing Cu(II) $(3d^9)$ chains. We find that the Cu(I)- and Cu(II)-derived electronic states form separate electronic subsystems, in spite of being coupled by bridging O ions. The valence band, of Cu(I) character, disperses within the charge-transfer gap of the strongly correlated Cu(II) states, displaying an unprecedented 250% broadening of the bandwidth with respect to the predictions of density functional theory. Our observation is at odds with the widely accepted tenet of many-body theory that correlation effects generally yield narrower bands and larger electron masses, and suggests that present-day electronic structure techniques provide an intrinsically inappropriate description of ligand-to-d hybridizations in late transition metal oxides.

Monovalent (Cu(I); $3d^{10}$) and divalent (Cu(II); $3d^9$) copper compounds differ widely in their physical and spectroscopic properties. The former have completely filled Cu 3d states that are well described by band theory and are non-magnetic. The latter are characterized by local spins and strong electronic correlations. These differences are well exemplified by the oxides Cu₂O and CuO [1]. Cu₂O is a non-magnetic band insulator. Its first ionization states have a $3d^9$ configuration, i.e. a single hole in the 3d shell. As a result, density functional theory (DFT) correctly predicts the electron removal spectrum, measured by angle-resolved photoemission (ARPES). The gap between the $3d^9$ ionization states and the $3d^{10}4s$ affinity states is a single-particle gap. In CuO, by contrast, a strong on-site Coulomb repulsion splits the $3d^8$ electron-removal and $3d^{10}$ electron addition states, and ${\rm CuO}$ is an archetypical charge-transfer insulator [2] with an antiferromagnetic ground state. The ARPES spectrum exhibits satellites and is not reproduced in a single-particle picture. The lowest energy excitations, in particular, have mixed $3d^9L$ and $3d^8$ character, where L stands for a ligand (oxygen) hole [3, 4]. Such two-holes states have been thoroughly investigated as the quasiparticle states of the high- T_c cuprates and are still matter of debate [5]. Hubbard or t - J model Hamiltonians predict a tendency towards the formation of local singlet states - dubbed Zhang-Rice singlets (ZRS) - between the Cu $3d_{x^2-u^2}$ and O 2p states, which disperse over a bandwidth determined by the superexchange energy $J \sim 130$ meV.

In this Letter we consider the intriguing case of $LiCu_2O_2$, an intermediate-valence compound where Cu has an average formal Cu valence of 1.5. $LiCu_2O_2$ presents several elements of interest. It contains an equal number of Cu(I) and Cu(II) ions that occupy different structural subunits, but are nonetheless coupled by the hybridization with the same O atoms. Moreover, the dimensionalities of these structural subunits are different: two-dimensional (2D) for Cu(I) and



FIG. 1. (a) Crystal structure, tetragonal unit cell and cleavage plane of LiCu₂O₂. (b) In a Cu(II) plane edge-sharing CuO₄ plaquettes form chains that run along the *b*-axis. (c) Cu(I) ions form a (nearly) square lattice with periodicity *b* (red square). Black rectangles outline the intersection of each plane with the 3D unit cell. (d) Momentum-integrated photoemission spectra of LiCu₂O₂ (blue) and T-CuO (red) from the suppl. material of Ref. 6. E = 0 coincides with the Fermi energy. LiCu₂O₂ shows additional states within the charge transfer gap (arrow).

one-dimensional (1D) for Cu(II). It is hard to predict theoretically how the conflicting characteristics of the two Cu subsystems can be merged into a common electronic structure. Our ARPES results show that the system resolves this conflict by separating the Cu(I) and Cu(II) states, which can then retain their own character. However the resulting electronic structure is highly non-trivial because the experimental bandwidth is *larger* by more than a factor of 2 than the predicted DFT bandwidth. This is a surprising and, to our knowledge, unique observation.

 $LiCu_2O_2$ is an insulating multiferroic material with a complex helimagnetic spin structure and spontaneous electric polarization along the crystal c-axis [7–11]. Magnetism is determined by competing low energy ($\sim 10 \text{ meV}$) ferromagnetic and antiferromagnetic superexchange interactions, mediated both by basal and apical oxygen atoms and leading to a series of magnetic and structural phase transitions below $\sim 25~{
m K}$ [12, 13]. Its orthorhombic structure (a = 5.72 Å, b = 2.86 Å, c = 12.40 Å) [14, 15] is shown in Fig. 1 (a). Two mirror images of a trilayer unit are stacked along the c-axis, offset by 0.24a. The external layers of each trilayer contain 1D chains of edge-sharing Cu(II)O₄ plaquettes running along the *b*-axis and separated by rows of Li⁺ ions, as shown in Fig 1 (b). The inner layer is a (nearly) square lattice of Cu(I) ions with periodicity b = a/2 (Fig. 1(c)). Owing to the non-symmetric positions of the O atoms above and below the plane, there is a slight distortion and an alternation of short (0.98 b) and long (1.02 b) Cu-Cu distances along the *a*-axis. The actual in-plane unit cell is therefore rectangular and coincides with the projection of the 3D unit cell. The weak coupling between adjacent trilayers determines the natural cleavage plane. Previous ARPES investigations tentatively assigned dispersing spectral features to states with strong Cu(II) character [16, 17], despite inconsistencies with LSDA+U [19] and cluster perturbation calculations [20]. Here we show that a broad survey of momentum space reveals a different, more subtle scenario.

We performed ARPES experiments at the μ ARPES endstation of beam line 7 of the Advanced Light Source. Millimeter-sized single crystals of LiCu₂O₂, grown as described elsewhere [14], were mounted on a cryostat, cleaved in UHV (10^{-10} mbar) and characterized by LEED. We observed single- and twinned-domain regions, with spin chains oriented perpendicular to each other. Single-domain regions were selected by the focused $100 \times 50 \,\mu\text{m}$ x-ray beam spot for ARPES. The energy and momentum resolution of the Scienta R4000 hemispherical analyzer were 30 meV and 0.01 Å^{-1} . The horizontal scattering plane contained the polarization vector of the light and the entrance slit of the analyzer, which was parallel to the chain *b*-axis. We varied k_a , the wave vector component perpendicular to the chains, by rotating the sample around the b-axis. Photon energy dependent ARPES measurements (see Suppl. Mat. [21]) showed a negligible dispersion along the c-axis. Unless otherwise specified, we collected data with 118 eV photons and at 150 K to avoid sample charging.

We performed band structure calculations within densityfunctional theory (DFT) using the QUANTUM ESPRESSO



FIG. 2. (a) Constant energy ARPES map measured at E = -1.75 eV. The red square outlines the BZ of the undistorted Cu(I) plane. The black rectangle is the Brillouin Zone (BZ) corresponding to the actual rectangular unit cell. High-symmetry points are indicated. The triangle is the contour along which the calculated bands are plotted in Fig. 4.

package [22, 23]. The crystal structure and atomic positions were taken from Ref. 15. For the exchange-correlation functional, we adopted the generalized-gradient approximation (GGA) by Perdew, Burke and Ernzerhof [24]. We prepared the Troullier-Martins norm-conserving pseudopotentials [25] in the Kleinman-Bylander representation [26] for Li, Cu and O atoms. Nonlinear core corrections [27] were applied to the pseudopotentials for Li and Cu atoms. The cutoff energy of the plane wave expansion for the wave functions was set to 90 Ry, and we employed $8 \times 8 \times 6$ k points. The atomic-like Wannier functions for Cu 3d and O 2p orbitals were constructed from the whole dp manifold [28, 29].

Figure 1 (d) shows the momentum-integrated photoemission spectra of LiCu₂O₂ and of tetragonal CuO (T-CuO), a Cu(II) charge transfer insulator. Both spectra display the characteristic signatures of Cu(II) compounds, namely a manifold of Cu-derived d^8 states around -12 eV and a prominent Oderived $d^9 \underline{L}$ band around -4 eV. However LiCu₂O₂ also exhibits an additional feature, indicated by an arrow, above the top of the $d^9 \underline{L}$ band, i.e. within the charge-transfer gap. These are the lowest-ionization states of LiCu₂O₂ and they have no counterpart in the insulating Cu(II) cuprates. The origin of these states is revealed by their momentum dependence.

Figure 2 shows an ARPES constant energy map collected at -1.75 eV, or 1.1 eV below the valence band maximum, over a large (k_a, k_b) area in reciprocal space. We observe prominent circular contours centered at the Γ point and at $(2m\pi/b; 2n\pi/b)$, with m, n integers. Weaker replicas of these contours are also visible, shifted by π/b along k_a . The main contours reveal an isotropic band in the (ab) plane. Moreover, they follow the periodicity of the square $b \times b$ unit cell of the undistorted Cu(I) plane (red square in Fig. 1 (c)), whose



FIG. 3. ARPES intensity maps measured along various high symmetry lines in the 2D Brillouin zone: (a-c) parallel to the k_b axis; (e,f) parallel to the k_a axis; (d) gives a schematic overview to (a). E = 0 coincides with the Fermi energy.

Brillouin zone (BZ) is outlined by red squares in Fig. 2. The shifted replicas reveal a backfolding of the main contours at the border of the rectangular BZ (primed labels) corresponding to the actual rectangular unit cell of the distorted Cu(I) plane. These observations strongly suggest that, contrary to previous interpretations, the first ionization states in $LiCu_2O_2$ involve Cu(I) atoms from the planes rather than Cu(II) atoms from the 1D chains.

This conclusion is supported by E vs. k ARPES intensity maps measured along high-symmetry lines, shown in Fig. 3. The maps in the first row correspond to three lines parallel to the k_b axis: through the Γ point (a), along the boundary of the rectangular BZ (b), and along the boundary of the square BZ (c). The maps in the bottom row correspond to two lines parallel to the k_a axis: through the Γ point (e) and along the common boundary of the rectangular and square BZs (f). Figure 3 (a) reveals two cosine-like dispersions (sketched in d). The first (red in d), more intense, with an extrapolated minimum at Γ at $-3.9 \,\text{eV}$, the second (blue in d) weaker and narrower, both with maxima at X at $-0.65 \,\text{eV}$. The same cosinelike dispersions are observed in Fig. 3 (c) but the narrow one is now the more intense. These are the bands that give rise to the circular contours of Fig. 2: the main one centered at Γ and the backfolded (or shadow) one at $(0, \pi/b)$. Main and shadow bands coalesce in panel (b) along the S'X'S' line, equidistant from the two centers. Figure 3 (e) illustrates quite clearly the backfolding of the main band at the rectangular BZ boundary X', and the resulting out-of-phase oscillation. The large intensity ratio of the main and backfolded bands indicates that the superlattice potential generated by the distortion

of the Cu(I) square lattice is a relatively small perturbation of the square lattice potential [30]. In summary, the valence band of LiCu₂O₂ is a ~ 3.25 eV-wide cosine band with minimum at Γ and maxima at the *M* points, and it originates from the 2D Cu(I) subsystem. The $d^9\underline{L}$ contribution from the chains is also visible in the maps of Fig. 3 as a narrow band around -2.5 eV, with a ~ 0.6 eV dispersion along the *b*-axis (black in d). Albeit smaller, the 0.3 eV dispersion in the *a* direction indicates a non-negligible perpendicular coupling of the chains, which cannot therefore be considered as a truly 1D system.

Our first-principles DFT band structure supports this scenario for the electronic structure. However, as discussed below, good agreement with the experiment is achieved if the energy scale in the calculation is *expanded* by 250%, a surprising and unique observation. Figure 4 shows the calculated bands superimposed on ARPES intensity maps, for the triangular contour of the irreducible BZ of the undistorted Cu(I) square lattice (Fig. 2). Four hybrid bands primarily composed of Cu(II) d_{xy} ($= d_{x^2-y^2}$ in the reference frame of one plaquette), O p_x and O p_y orbitals – the states forming the ZRS in the 2D cuprates – are seen to cross E_F . These states do not have a counterpart in the data because the large Cu(II) d_{xy} onsite Coulomb repulsion pushes them well above E_F . (see [21] for a dynamical mean field theory calculation within the Hubbard I approximation [18]). Similar conclusions were reached by Zatsepin et al. [19] based on LDA+U calculations for a hypothetical ferromagnetic phase. Below -0.6 eV we find a broad manifold of hybrid states of different character. The orbital-projections (panel b-d) show that these states mainly derive from the hybridization of Cu(I) d_{z^2} orbitals with the



FIG. 4. (a) ARPES intensity map of LiCu₂O₂ along the triangular contour of Fig. 2. (b-d) Calculated DFT band structure after a 250 % expansion of the energy scale, superposed on ARPES. The panels show projections onto: (b) the Cu(I) d_{z^2} -orbital; (c,d) the p_z orbital of O atoms on opposite sides of the Cu(I) plane. The size of the symbols is proportional to the respective orbital components.

 p_z orbitals of O atoms located above and below the Cu ion (more details are available in [21]). The expanded DFT/GGA bands are in excellent agreement with the measured valence band dispersion.

The huge upward renormalization of the bandwidth is a puzzling and, to the best of our knowledge, unique observation. It is especially surprising because DFT calculations of band structures typically underestimate quasiparticles masses and overestimate bandwidths. It is also surprising because many-body effects are generally believed to be weak in completely filled bands such as the 3d band of Cu(I)-based materials. Neither the accepted interpretation of ARPES nor present theoretical understanding provide a simple explanation for our results. On the experimental side the surface sensitivity of ARPES has often been called into question in the intrepretation of data from strongly correlated materials. However, in this case we can exclude the surface as the likely origin of the discrepancy. On one hand we see no evidence of a structural or electronic surface transition. On the other hand, known surface effects such as a lower atomic coordination and a reduced screening, always result in narrower bands. On the theoretical side one could invoke the deficiency of DFT to give accurate low-energy Hamiltonians for correlated materials. Such limitations have been discussed recently, and models beyond LDA/GGA based on screened exchange [31] or many-body perturbation theory [32, 33] have been proposed. Indeed, screened exchange corrections do increase the bandwidth, but are usually compensated by correlations [31]. We see no indication that in the present compound only the exchange widening should be present. Moreover the giant value of the renormalization makes this explanation unrealistic. We also notice that the large discrepancy between theory and experiment is not removed when correlations are treated within the DFT+U framework. Ferromagnetic GGA+U calculations

(not shown) yield a slight increase of the bandwidth, suggesting that magnetic fluctuations might play a role in widening the bandwidth, but do not remove the discrepancy.

We have also calculated the band structure of an artificial $LiCu_2O_2$ system, where the hybridization between the Cu(II) d and O p_z -states was selectively suppressed. This leads indeed to a significant enhancement of the bandwidth (see [21] for details), even though still not enough to explain the experimental results. These observations suggest that at least part of the problem of DFT-GGA might reside in an inappropriate description (more specifically, an overestimation) of the coupling between O-p and Cu(II)-d, leading to a reduction of the bandwidth through interference effects. An overestimation of the d - p hybridization by DFT-GGA is quite generally observed in oxides, but the effect seems to be particularly strong in $LiCu_2O_2$. One may speculate possible culprits to be the Cu-d to O-p interaction U_{pd} and/or a rearrangement of the charge density of the Cu(II) states following the Mott localisation. It is a challenge for future theory to model how strong correlations on the Cu(II) d-shell and ligand-to-d interactions modify the electronic structure of the O-psubsystem, and to reproduce the unexpected band widening. Obviously, understanding this interplay and the related quite fundamental deficiency of DFT-LDA might also eventually help to elucidate the electronic structure of other copper oxides.

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