On-site interband excitations in resonant inelastic x-ray scattering from Cu$_2$O

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The electronic structure of cuprite (Cu$_2$O) has been studied by high-resolution x-ray photoemission (XPS), x-ray absorption (XAS), and resonant x-ray emission spectroscopies (XES) supported by band structure calculations using a hybrid exchange approximation to density functional theory. A pronounced loss feature at about 4.5 eV due to on-site interband excitation has been identified in resonant inelastic x-ray scattering from Cu$_2$O close to the $L_3$ (Cu 2$p_{3/2}$) core threshold. Although Cu$_2$O nominally has a filled upper valence band of Cu 3$d$ states and an empty conduction band of Cu 4$s$ states, the band structure calculations show that there is substantial 3$d$ character in the conduction band and that the inelastic loss is dominated by on-site 3$d$ to 3$d$ excitation conforming to the selection rule $\Delta l=0$ rather than 3$d$ to 4$s$ transitions with $\Delta l=-2$. However, unlike in previous work, these transitions do not arise from ligand field splitting of the Cu 3$d$ states but rather from on-site 3$d$-4$s$ hybridization which introduces 3$d$ character into the conduction band. Comparison between XPS, XES, and XAS data shows that Cu $L_3$ XAS is dominated by a core exciton lying 0.65 eV below the bottom of the conduction band and that inelastic scattering is only observed for photon energies below that required to excite the core electron into the conduction band.

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I. INTRODUCTION

There is a growing interest in the development of electronic and optoelectronic devices based on oxides which are transparent in the visible region but which can be doped to induce a high electrical conductivity. Most of the established transparent conducting oxides (TCOs) of this sort are n-type materials.$^1$ This includes the prototype TCOs SnO$_2$, In$_2$O$_3$, and ZnO. It has been proven to be very difficult to develop reproducible strategies for the p-type doping of these materials.$^2$–$^4$ However, exploitation of transparent conducting oxides in devices such as UV diodes will only become possible if suitable wide gap oxides that can be doped p-type can be developed. In the classical n-type TCOs, the top of the valence band is composed of O 2$p$ states and it is not surprising that it is difficult to introduce holes into these bands: in chemical terms, one is attempting to oxidize oxygen. However, in cuprite (Cu$_2$O), the upper valence band states are of dominant Cu 3$d$ atomic character and introduction of holes involves oxidation of 3$d^{10}$ Cu(I) to 3$d^0$ Cu(II). This process is chemically tractable and Cu$_2$O is indeed a p-type semiconductor. The electronic band gap in Cu$_2$O is 2.17 eV (Ref. 5) and is therefore too small for the application in TCO devices. However, the band gaps in many ternary Cu(I) oxides are much bigger than in the parent Cu$_2$O. This has allowed development of new families of p-type conducting ternary Cu(I) oxides that are transparent in the visible region.$^6$–$^{15}$ Cu$_2$O itself has emerged as a p-type host for doping with magnetic ions in order to induce room temperature dilute semiconductor ferromagnetism.$^{14}$–$^{17}$ The recent interest in the functional properties of Cu(I) oxides has prompted us to revisit the electronic structure of Cu$_2$O. The main focus of the present paper is the investigation of the nature of electronic excitations in Cu$_2$O found in resonant inelastic x-ray scattering (RIXS) at the Cu $L_3$ edge. Previous photon excited x-ray emission spectroscopy (XES) studies of Cu$_2$O have been restricted to the Cu $K$ (Refs. 18 and 19) and Cu $M_{3,2}$ (Ref. 20) edges. In both cases, resolution was limited by very pronounced lifetime broadening ($>1.5$ eV) of the core hole and no attempt was made to study resonant x-ray scattering. Elsewhere, electron beam excited Cu $L$ and O $K$ emission spectra were reported many years ago,$^{21}$ but again with poor overall effective resolution and with no possibility to study resonant emission. The discovery of pronounced resonant inelastic x-ray scattering at the Cu $L_3$ edge in the current study prompted reexamination of high-resolution x-ray photoemission spectroscopy (XPS) and x-ray absorption spectroscopy (XAS) spectra of Cu$_2$O. In contrast to previous valence region XPS studies,$^{22,23}$ particular care was taken to establish the position of the Fermi level relative to the valence band edge. This then enabled exploration of the relationship between core level binding energies in XPS and the energies of features in XAS and XES. It is shown that the Cu $L_3$ absorption spectrum$^{24}$–$^{26}$ is dominated by a core-hole exciton that lies 0.65 eV below the bottom of the conduction band. The experimental work is supported by band structure calcula-
ions using a hybrid exchange approximation to density functional theory that gives an accurate first principles description of the bulk band gap. The combined experimental and theoretical study leads to the identification of a general mechanism for inelastic x-ray scattering in Cu(I) compounds.

The primitive cubic structure of Cu2O belongs to the space group $O_h^4$ and is based on a body centered cubic array of oxygen ions with Cu ions occupying half the sites between adjacent oxygen ions. The O ions are found at $(0,0,0)$ and $(1/2,1/2,1/2)$ and the Cu ions at $(1/4,1/4,1/4)$, $(3/4,1/4,3/4)$, $(1/4,3/4,1/4)$, and $(3/4,3/4,1/4)$, giving two formula units per cell. The structure can alternatively be described in terms of two interpenetrating anti-SiO2 cristobalite nets. In this structure, the Cu ions occupy sites with linear coordination by two O ions, although due to a staggered arrangement of the three additional Cu ions bonded to these two oxygen ions, the local site symmetry is $D_{3d}$. In addition, the separation between adjacent Cu ions in the two different nets is quite small (~3.02 Å) allowing significant interaction between them. This, in turn, influences the width of the valence band. The O ions are surrounded by four copper ions in a tetrahedral arrangement. The unusual structure is associated with negative thermal expansion.

In the simplest ionic model description, Cu$_2$O is a $d^{10}$ oxide. An upper valence band of filled Cu 3d states sits above a band of filled O 2p states, while the bottom of the conduction band is nominally composed of Cu 4s states with empty Cu 4p states at higher energy. In terms of the linear O–Cu–O units, the Cu 3d$_z^2$ orbitals have $\sigma$-like symmetry, the 3d$_x^2$ and 3d$_y^2$ orbitals have $\pi$-like symmetry, and the 3d$_{xy}$ and 3d$_{xz}$, $3d_{yz}$ orbitals have $\delta$-like symmetry. Thus, O 2p orbitals can mix with Cu 3d$_z^2$ via strong $\sigma$ overlap and with 3d$_x^2$, 3d$_y^2$ via weaker $\pi$ interactions. However, the 3d$_{xy}$, 3d$_{xz}$, and 3d$_{yz}$ orbitals must remain localized on Cu as there are no orbitals on oxygen of the correct $\delta$ symmetry for covalent mixing. Within this description, the lowest energy interband transitions of Cu$_2$O are basically from a filled upper valence band of Cu 3d states (mixed to some extent with O 2p states) into an empty conduction band of Cu 4s states. Interbond excitations are therefore on-site transitions conforming to a change in angular momentum $\Delta l=2$, which makes the transitions allowed in inelastic x-ray Raman scattering where the atomic selection rule is $\Delta l=0, \pm 2$. However, the band calculations show that due to extensive mutual mixing between O 2p, Cu 3d, and Cu 4s states, this simple description must be modified. It transpires that on-site 4s–3d hybridization introduces significant Cu 3d character into the conduction band so that even though Cu$_2$O is nominally a $d^{10}$ oxide, the interband transitions have significant 3d to 3d character and thus satisfy $\Delta l=0$. This allowed channel is mediated exclusively by matrix elements between core Cu 2p states and Cu 3d states and does not involve matrix elements between Cu 2p and Cu 4s states. Since the former are much bigger, the energy loss is dominated by the full and empty Cu 3d partial densities of states.

II. ELECTRONIC STRUCTURE CALCULATIONS

The calculations presented have been performed using the CRYSTAL06 software. Electronic exchange and correlation were approximated using the hybrid exchange formalism which has previously been demonstrated to provide a reliable description of the ground state electronic structure in copper oxides and, of particular relevance to the current study, of the nature and value of the band gap in a wide variety of materials. The most significant numerical approximation is the expansion of the crystalline orbitals in a basis set consisting of a linear combination of atom centered Gaussian orbitals. High quality all-electron basis sets used in previous studies were adopted to describe the Cu and O ions and the outermost exponents re-optimized in situ. This resulted in the use of a quadruple valence set for the Cu ion of structure 864111-D31 with outer sp exponents (in $a_0^2$) of 1.582, 0.559, and 0.15 and outer d exponent of 0.430. The triple valence O basis set, 84111D, had outer sp exponents of 0.425 and 0.125 with a d exponent of 0.5. The Coulomb and exchange series were truncated using overlap criteria documented elsewhere (strict tolerances of 7 7 7 7 14 were adopted) and the exchange correlation potentials and energy were integrated numerically on an atom centered grid of points containing approximated 2500 symmetry irreducible points per atom (the XLGRID option). Finally, $k$-space integration was performed on a Pack–Monkhorst grid defined by a shrinking factor of 8 which contained 59 symmetry irreducible points.

III. EXPERIMENT

Cu$_2$O was prepared by decomposing CuO under flowing Ar at 900 °C. The high purity powder sample was pressed into disks between tungsten carbide dies and further sintered under Ar at 900 °C to give robust ceramic disks. Phase purity was confirmed by x-ray powder diffraction.

High-resolution x-ray photoemission spectra were measured in a Scienta ESCA 300 spectrometer. This incorporates a rotating anode Al $K\alpha$ (h$v=1486.6$ eV) x-ray source, a seven crystal x-ray monochromator, and a 300 mm mean radius spherical sector electron energy analyzer with parallel electron detection system. The x-ray source was run with 200 mA emission current and 14 kV anode bias, while the analyzer operated at 150 eV pass energy with 0.8 mm slits. The Gaussian convolution of the analyzer resolution with a linewidth of 260 meV for the x-ray source gives an effective instrument resolution of 350 meV. Spectra were measured in normal emission. The Cu$_2$O sample was cleaned by a surface science recipe which involved bombardment with Ar ions, followed by annealing in order to heal ion beam damage. Following bombardment with 2.5 kV Ar ions for 15 min followed by annealing in UHV ($5 \times 10^{-9}$ mbar) at first 550 °C and then 650 °C for 1 h, the O 1s core line assumed a narrow profile (full width at half maximum height of 0.66 eV) with a symmetric shape and a without high binding energy shoulder due to surface adsorbates. In addition, satellites due to CuO were eliminated from Cu 2p core level spectra. Finally, the Cu 2p to O 1s intensity ratio after correction for atomic sensitivity factors assumed a value of 1.54, which is within the range found for ordered single crystal Cu$_2$O(100) surfaces with Cu terminated reconstructions. The C 1s to O 1s intensity ratio was reduced to below 1/100. Binding
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energies are referenced to the Fermi energy of a silver sample regularly used to calibrate the spectrometer.

X-ray absorption and emission spectra were measured at beamline 7.0.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. This beamline is equipped with a spherical grating monochromator. Emission spectra were recorded using a Nordgren-type grazing-incidence spherical grating spectrometer. For resonant emission experiments, the beamline was set to have an energy resolution of 500 meV at the O K edge and 1 eV at the Cu L3 edge, and the emission spectrometer was set to have a resolution of 350 meV for O K and 750 meV for Cu L3 edge spectra. Absorption spectra were measured in total fluorescence yield and total electron yield modes. For the absorption measurements, the beamline resolution was set to 200 meV for the O K edge and to 1 eV for the Cu L3 edge. The absorption spectra were normalized to a reference current from a clean gold mesh positioned in the path of the photon beam. The spectra were normalized to a reference current from a clean gold mesh positioned in the path of the photon beam. The consistency of the calibrations in XPS and XES is demonstrated by the fact that the peak maximum in nonresonant Cu L3 XES (corresponding to the position of the peak maximum in the Cu 3d partial density of states relative to the Cu 2p(3/2) core hole) is at 929.4 ± 0.2 eV, while the separation between the Cu 2p(3/2) core level and valence band peak maxima (the latter again corresponding to the position of the peak maximum in the Cu 3d partial density of states) in XPS is 929.5 ± 0.1 eV.

IV. RESULTS AND DISCUSSION

A. Electronic density of states

The full and partial densities of states derived from the band structure calculations are shown in Fig. 1. The occupied full and empty densities of states are in broad general agreement with the previous work although with exception of the semiempirical calculations of Robertson and the self-interaction corrected local density approximation (LDA) calculation of Filippetti and Fiorentini, the present calculations reproduce the experimental band gap and valence bandwidth much better than previously (Table I). In particular, earlier density functional calculations underestimated the bulk band gap, whereas a Hartree–Fock calculation dramatically overestimated the gap. The failure of these well-established methods is well known and has been discussed in many previous publications. The hybrid method used in the present work introduces an element of the Hartree–Fock exchange into the density functional Hamiltonian and has been shown to give accurate predictions of bulk band gaps for a wide range of materials.

![FIG. 1. (Color online) Full and partial densities of states for Cu2O derived from band structure calculations.](image-url)
should be antibonding and involve mixing between the \( \sigma \)-like Cu 3d\(_{\alpha}\) orbitals and an appropriately symmetrized linear combination of \( \sigma \)-like O 2p orbitals. By contrast, the band \( a \) contains \( \delta \)-like Cu 3d\(_{\alpha-\beta}\) and Cu 3d\(_{\chi}\) states which cannot mix with O 2p states, as well as the Cu 3d\(_{\alpha}\) and Cu 3d\(_{\beta}\) states which can only mix with O 2p states via weak \( \pi \)-type overlap. These qualitative ideas are in agreement with the conclusions of Marksteiner et al., who performed a projection of the Cu 3d partial density of states into local \( \sigma \), \( \pi \), and \( \delta \) components. This earlier work showed that \( \sigma \)-like Cu 3d\(_{\alpha}\) character was found in band \( b \) and in band \( x \) at the top and bottom of the valence band, respectively. In addition, Marksteiner et al. found that there was also a significant contribution from Cu 3d\(_{\alpha}\) states at the bottom of band \( a \) in \( \alpha'\)\( \alpha''\), which lies between the main O 2p and Cu 3d valence bands. Turning back to the discussion of our own calculations, we find that in contrast to the simple ionic model description which treats Cu\(^+\) as a \( 3d^{10}\alpha^{\delta}\)\( \delta^0\) cation, significant Cu 4s character is found in the valence band. Three pronounced maxima are found in the Cu 4s occupied partial density of states at energies corresponding to the peaks \( b \), \( a''\), and \( x \). Two of these maxima (those in \( b \) and \( a''\)) in the Cu 4s partial density of states therefore coincide with the maxima in the Cu 3d partial density of states, indicating that there is pronounced on-site 3d-4s hybridization. This finding is in agreement with qualitative ideas first developed by Orgel that rationalized the linear coordination found for Cu(I) compounds in terms of on-site Cu 3d–Cu 4s mixing. These conclusions are also in accord with very recent LDA+U calculations and angle resolved photoemission measurements which found evidence for a state with mixed Cu 3d and Cu 4s character between the main band of Cu 3d states and the O 2p band. The overall width of the Cu 3d part of the valence band in Cu\(_2\)O is found to be about 4.0 eV in our calculations. This is significantly greater than the value of 2.8 eV for SrCu\(_2\)O\(_2\) found in a recent calculation using the same hybrid Hamiltonian approach adopted here. This is despite the fact that the next neighbor coordination of Cu by two O ions in a linear arrangement in SrCu\(_2\)O\(_2\) is similar to that in Cu\(_2\)O and the Cu-O bond lengths have almost identical values of 1.85 \( \text{Å} \) (Cu\(_2\)O) and 1.84 \( \text{Å} \) (SrCu\(_2\)O\(_2\)). The main difference between the two oxides is in the dimensionality of next-nearest neighbor interactions between the Cu 3d\(^{10}\) shells. In Cu\(_2\)O, each Cu ion has 12 next-nearest Cu neighbors (6 of which belong to the interpenetrating framework) in a three-dimensional arrangement with a Cu-Cu separation of 3.01 \( \text{Å} \). In SrCu\(_2\)O\(_2\), by contrast, there are only two next-nearest Cu neighbors in a linear two-dimensional arrangement, although with a reduced Cu-Cu separation of 2.74 \( \text{Å} \). The smaller Cu 3d bandwidth in SrCu\(_2\)O\(_2\) and the associated increase in the band gap reflect this difference.

Turning now to the empty density of states in Cu\(_2\)O, it can be seen in Fig. 1 that Cu 4s and Cu 3d states make the strongest contributions to the bottom of the conduction band. At higher energy, the Cu 4p contribution becomes dominant. In addition, there is a significant O 2p contribution to the conduction band.

### B. X-ray photoemission and nonresonant x-ray emission spectra

Experimental valence band x-ray photoemission spectra of Cu\(_2\)O are shown in Fig. 2 along with O K and Cu L\(_1\) x-ray emission spectra excited under nonresonant conditions well
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above the core threshold. The photoemission spectrum is compared to the density of states from the band structure calculations with the differing partial contributions to the total density of states weighted in proportion to one electron ionization cross section computed at $h\nu=1486.6$ eV. At this energy, the one electron cross section for ionization of Cu 3d states is a factor of 20 bigger than the cross section for ionization of O 2p states. The overall cross section weighted density of states is therefore dominated by the Cu 3d partial density of states. The experimental spectrum is in agreement with the calculation both in terms of the overall shape of the spectral profiles and in terms of the relative intensities of the upper and lower parts of the valence band. In particular, much of the intensity in the O 2p region in the lower half of the valence band is a direct reflection of covalent mixing of Cu 3d character into the lower valence band states. However, there is a small but significant contribution to the intensity in this region from the O 2p states themselves. Conversely, the O K shell x-ray emission spectrum is a direct measure of the O 2p partial density of states. The lower valence band states are the strongest spectral features, but again due to covalency, there is significant intensity in the upper valence band region. In agreement with the calculations, there is, however, little intensity in the region of the most tightly bound Cu 3d states which dominate the x-ray photoemission spectrum. This reflects the fact that these states have local $\delta$ character and cannot therefore mix with O 2p states. Finally, the Cu L3 emission spectrum is a probe of the Cu 3d partial density of states but without any O 2p contribution. The spectral profile is similar to the x-ray photoemission spectrum although with poorer resolution. However, it is noticeable that the lower valence band structure is slightly weaker relative to the Cu 3d maximum than in x-ray photoemission. This is because the O 2p partial density of states makes a small contribution to x-ray photoemission intensity but not to Cu L2,3 x-ray emission.

C. X-ray absorption spectra and core lines in x-ray photoemission

O K and Cu L2,3 x-ray absorption spectra are shown in Fig. 3. Both spectra contain a strong and relatively narrow peak close to the absorption threshold with maxima at 532.4 and 933.7(5) eV, respectively. These energies are in excellent agreement with the corresponding values of 933.7 and 532.5 eV found by Grioni et al. The O K shell absorption spectrum basically mimics the unoccupied O 2p partial density of states. However, the strikingly asymmetric line shape in the threshold peak of the Cu L3 spectrum is not reproduced by the band structure calculations. The spectrum can be regarded as a superposition of an excitonic component at threshold with structure at higher energy that is associated with the empty density of states.

It is interesting to consider the energies of the absorption maxima above threshold in relation to the associated core level binding energies. The O 1s and Cu 2p$^{3/2}$ XPS core level spectra are shown in Fig. 4. The full widths at half maximum heights for these core lines are 0.66 and 1.32 eV, respectively, very much lower than in previous work. The line-widths are, however, bigger than the resolution of the XPS
system and probably represent the intrinsic linewidths determined by phonon and lifetime broadening. The O 1s binding energy is found to be 530.5 eV and the Cu 2p3/2 binding energy 932.6 eV. These binding energies are both in good agreement with previous work23 and are referenced to the Fermi level. Given that the band gap is 2.2 eV, there is little change in the spectra with varying photon energy, and in all cases, the spectra seem to be dominated by the occupied O 2p partial density of states. By contrast, there is a clear variation in the energy of spectral emission structure with exciting photon energy in the range between $h\nu = 931.50$ eV and $h\nu = 933.75$ eV for the Cu L3 emission spectra shown in Fig. 7. When the spectra are transposed onto an energy loss scale, it is seen that a feature at a constant energy loss of 4.5 eV appears over the photon energy range 931.5 eV < $h\nu$ < 933.75 eV. Above 933.75 eV, the spectra evolve toward the nonresonant spectrum previously discussed, with the appearance of distinct shoulders on both the low and high energy sides of the main peak.

The loss structure near to threshold is interpreted in terms of interband excitations in Cu2O. Following Kotani and Shin25 and Jiménez-Mier et al.,56 the intensity of inelastically scattered photons at energy $\omega$ for incident energy $\Omega$ may be written in terms of filled and empty partial densities of states $\rho_m$ and $\rho_n$,

$$F(\Omega, \omega) \propto \sum_{m,n} \langle \phi_{Cu 2p} | t | \phi_m \rangle \langle \phi_n | t | \phi_{Cu 2p} \rangle + \int \rho_m(\varepsilon) \rho_n(\varepsilon + \Omega - \omega) \frac{1}{(\varepsilon - \varepsilon_{Cu 2p} - \omega)^2 + \Gamma^2} d\varepsilon,$$

(1)

where $t$ is a dipole operator acting between Cu 2p core states.
and valence and conduction band states $\phi_m$ and $\phi_n$ of appropriate symmetry and $\Gamma$ represents the broadening due to the core hole. Since both Cu $2p$ to Cu $3d$ and Cu $2p$ to Cu $4s$ matrix elements are nonzero, the summation should include the four possible convolutions between the occupied and empty Cu $3d$ and $4s$ partial densities of states corresponding to the allowed channels in electronic Raman scattering where $\Delta l = 0$ or $\Delta l = \pm 2$, i.e., the summation should include the integrals involving $\rho_{\text{Cu} \, 3d} \rho_{\text{Cu} \, 3d}$, $\rho_{\text{Cu} \, 3d} \rho_{\text{Cu} \, 4d \, 4s}$, $\rho_{4s} \rho_{\text{Cu} \, 3d}$, and $\rho_{\text{Cu} \, 4s} \rho_{\text{Cu} \, 4s}$. We have evaluated the four energy-weighted convolutions given in expression (1) and these are shown in Fig. 8. Finally, we computed a theoretical RIXS by weighting squares of matrix elements involving Cu $4s$ states by a factor of $1/10$ as compared to those involving Cu $3d$ states. The results of this computation are also shown in Fig. 8 along with an experimental loss spectrum. Although the basic shape of the computed spectral profile is similar to that observed experimentally, the maximum in the experimental spectrum is about almost 2 eV lower in energy than calculated. We attribute this discrepancy to excitonic effects. In fact, the shift in the emission spectrum is very close to the shift in the absorption spectrum associated with the core-hole potential. This observation has prompted us to adopt an ad hoc procedure for calculation of the inelastic loss spectrum in which the empty density of states from the band structure calculation in Eq. (1) is replaced by what we might call an excitonic density of states derived from experimental x-ray absorption spectrum. As shown in Fig. 8 with this approach, there is better agreement between observed and calculated spectra. Proper justification of the procedure is, however, problematic: the excitonic nature of the L shell x-ray absorption spectrum depends on the presence of the Cu $2p$ core hole, but in the RIXS final state, there is obviously no core hole. In general, RIXS spectra have, in the past, been found to be relatively insensitive to core-hole ef-

FIG. 6. O K x-ray emission spectra of Cu$_2$O excited over a range of photon energies close to threshold. The emission features show little change with changing photon energy.

FIG. 7. Upper panel: Cu $L_3$ x-ray emission spectra of Cu$_2$O excited over a range of photon energies close to the threshold. The emission features show strong variation in energy for exciting photon energies closest to the thresholds between 931.50 and 934.75 eV. Lower panel: emission spectra as above but presented on an energy loss scale.
FIG. 8. (Color online) Upper panel. Computed terms for the four dipole allowed channels included in the summation in Eq. (1). Lower panel. Dashed line: computed inelastic x-ray scattering spectrum, which is obtained by appropriately weighting the four channels shown above. Solid line: computed inelastic scattering spectrum using “excitonic” density of states. In all cases, the simulated spectra have been broadened by a Gaussian with full width at half maximum height of 1.35 eV to include the effects of broadening of the core hole. Dotted line: experimental energy loss spectrum excited at $h\nu = 933.75$ eV.

fecteds for simple materials such as graphite and $c$- and $h$-BN, where the main effect is to produce a redistribution of spectral weight.\textsuperscript{57–61} On the other hand, electron-valence hole interactions in the final state are known to enhance spectral weight at higher emission energies, i.e., at lower loss energies, as is observed here. The valence electron exciton binding energy in Cu$_2$O is only about 0.14 eV.\textsuperscript{62,63} However, the influence of final state exciton binding on the RIXS spectra may be amplified by localization of the conduction band electron by the core hole in the intermediate state.\textsuperscript{55} A fuller treatment of this problem will be presented elsewhere.

It is finally interesting to note that the lowest photon energy for which there is no longer evidence of loss structure is 934.75 eV, which is sufficient to promote an $L_1$ electron into the conduction band. In other words, the range of photon energies under which inelastic x-ray scattering is observed is all in the excitonic regime, as shown schematically in Fig. 5. It is also significant that O $K$ excitation does not give a true core exciton and that no energy loss structure can be identified at the O $K$ edge.

V. CONCLUDING REMARKS

First principles calculations on Cu$_2$O using a hybrid exchange approximation to density functional theory show that there is pronounced mixing between Cu 3$d$ and O 2$p$ states and that along with strong on-site hybridization between Cu 3$d_{2}$ and Cu 4$s$ states, this mixing introduces significant Cu 3$d$ character into the conduction band of this oxide. Valence level photoemission spectroscopy in combination with O $K$ shell and Cu $L$ shell x-ray emission spectra confirms that there is indeed pronounced cation-anion hybridization.

Well-defined features are observed at a loss energy of 4.5 eV in resonant inelastic scattering close to the Cu 2$p$ core threshold. To date, most previous experimental works on resonant inelastic x-ray scattering of Cu compounds at the $L$ edge have concentrated on open shell Cu(II) species,\textsuperscript{64} including CuO (Ref. 65) and layered cuprates such as La$_2$CuO$_4$,\textsuperscript{65–67} Sr$_2$CuO$_2$Cl$_2$,\textsuperscript{67} Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$\textsuperscript{67} and Tl$_2$Ba$_2$CaCu$_2$O$_{8+\delta}$.\textsuperscript{68} Here, the loss structure is typically found between 1.5 and 2.0 eV to low energy of the incident photon energy and can be understood in terms of localized excitations within the 3$d$ manifold of energy levels, which are split by the ligand field.\textsuperscript{61,67} The excitations found in the present work are at much higher loss energy and cannot be associated with ligand field excitations in the conventional sense because Cu$_2$O is a closed shell material. In the ionic limit, the interband excitations we have observed could be described as 3$d$ to 4$s$ transitions. However, on-site Cu 3$d_{2}$–Cu 4$s$ hybridization introduces significant Cu 3$d$ character into the conduction band and the much bigger dipole matrix elements between core Cu 2$p$ states and Cu 3$d$ states as compared to Cu 2$p$ to Cu 4$s$ matrix elements means that the observed inelastic scattering is dominated by a convolution between the full and empty Cu 3$d$ partial density of states. Similar structure to that found here for Cu$_2$O has been observed in RIX spectra of CuAlO$_2$ (Ref. 69) where a pronounced energy loss feature is found at 5.4 eV for excitation energies close to the $L_1$ core threshold. CuAlO$_2$ is another Cu(I) compound with linear coordination of Cu by two oxygen nearest neighbors. The similarity between the loss spectra of the two materials suggests that on-site interband excitations may be a general feature of RIX spectra of Cu(I) 3$d$ materials.

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1For example, for a discussion of n-type doping in In$_2$O$_3$, see, C. G. Granqvist and A. Hultåker, Thin Solid Films 411, 1 (2002).


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