Resonant inelastic x-ray scattering study of the electronic structure of Cu$_2$O

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A resonant inelastic x-ray scattering study of the electronic structure of the semiconductor cuprous oxide, Cu$_2$O, is reported. When the incident x-ray energy is tuned to the Cu K-absorption edge, large enhancements of the spectral features corresponding to the electronic transitions between the valence band and the conduction band are observed. A feature at 6.5 eV can be well described by an interband transition from occupied states of mostly Cu 3d character to unoccupied states with mixed 3d, 4s and 2p character. In addition, an insulating band gap is observed, and the momentum dependence of the lower bound is measured along the Γ − R direction. This is found to be in good agreement with the valence band dispersion measured with angle-resolved photoemission spectroscopy.

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I. INTRODUCTION

In recent years, resonant inelastic x-ray scattering (RIXS) has been used as a probe of various types of electronic excitations in many condensed matter systems. In these studies, when the incident photon energy is tuned to the x-ray absorption edge of interest, the intensity of certain spectral features is greatly enhanced, sometimes by up to a few orders of magnitude. Initially, soft x-ray photons were used to study the electronic structure in semiconductors and insulators. Recently, RIXS at transition metal K edges has also been gaining interest due to the added benefit of the momentum-resolving capability provided by the short wavelength of the hard x-ray photons. Such transition metal K-edge RIXS is often called indirect RIXS, since the intermediate state does not directly involve 3d photoelectrons, unlike RIXS in the soft x-ray regime (transition metal L-edges), which is therefore referred to as direct.

One of the attractions presented by hard x-ray RIXS is the possibility of its use in studying momentum-resolved electronic structure. In a simple picture of the RIXS cross-section, the momentum-dependent part of the cross-section may be expressed as the joint density of states (JDOS) of the unoccupied and occupied bands for a particular momentum transfer. In other words, the RIXS spectrum can be regarded as measuring interband transitions at a finite momentum transfer, with an appropriate prefactor. Although this viewpoint is probably too simplistic, attempts to develop a linear response theory for the RIXS cross-section based on this approach have been made. For example, in the limit of either very weak or very strong core hole potential, van den Brink and van Veenendaal have shown that the indirect RIXS cross section is a linear combination of the charge response function and the dynamic longitudinal spin density correlation function. This line of approach is quite intriguing, since it suggests that one could use RIXS as a tool for reconstructing electronic structure at the finite momentum transfer.

Despite extensive RIXS investigations of strongly correlated cuprate compounds, little work has been done to date to study conventional semiconductors with well-known electronic structure. This is unfortunate, because investigation of well-characterized materials with a known band structure is essential to formulate quantitative understanding of this new experimental technique. In this paper, we present just such an investigation of semiconducting Cu$_2$O, using the Cu K-edge RIXS technique, and show that the indirect RIXS can measure JDOS of this weakly correlated system.

Cuprous oxide, Cu$_2$O, is a naturally occurring mineral called “cuprite.” It is a direct-gap semiconductor with well-characterized exciton lines, which are often considered as textbook examples of Mott-Wannier type excitons. In particular, Bose-Einstein condensation of the exciton gas has been reported and has drawn much attention over the last two decades. In recent years, however, this material has been drawing renewed interest due to its potential applications in solar energy conver-
sion and catalysis. Considerable attention has also been paid to this material due to the unusual O-Cu-O linear bonding.

Cuprous oxide crystallizes in a cubic structure with space group \( \text{Pn}3\text{m} \). Since Hayashi and Katsuki’s measurement of exciton absorption lines, early experimental work on this material focused mostly on optical absorption studies of the different exciton series, and is reviewed in Refs. 21, 22. Further, the electronic structure of \( \text{Cu}_2\text{O} \) has been studied using various \textit{ab initio} methods, 23-24, 25-26, 27-28, 29-30, 31. These studies suggest that \( \text{Cu}_2\text{O} \) is a semiconductor with direct band gap, although the calculated gap varies widely among the different approaches, and typically disagrees with the experimental value of about 2 eV. (For a comprehensive comparison, see Table 1 in Ref. 31.

Advances in core level spectroscopy techniques developed at synchrotron x-ray sources have made it possible to test some of the earlier predictions concerning the electronic structure of \( \text{Cu}_2\text{O} \). X-ray absorption studies near copper L-edges as well as at the O K-edge have been carried out to elucidate the unoccupied bands. Ghijsen and coworkers carried out both x-ray photoemission spectroscopy (XPS) and bremsstrahlung isochromat spectroscopy (BIS) to probe both valence band and conduction band density of states, respectively. These experimental results could be largely accounted for with the calculated band structure, confirming that \( \text{Cu}_2\text{O} \) is a conventional band insulator with no, or very weak, electron correlation. The top of the valence band is dominated by Cu \( d \) states, while the lowest lying conduction band is primarily of \( d \)-character which hybridizes with Cu 4s and 4p states.

As a result of the renewed interest in this material, there have been several recent studies of the electronic structure of \( \text{Cu}_2\text{O} \) using state-of-the-art electron spectroscopy techniques. Bruneval and coworkers measured the valence band dispersion along the \( \Gamma - R \) direction with the angle resolved photoemission spectroscopy (ARPES), and were able to explain the observed dispersion using a self-consistent \( \text{GW} \) method, while \( \text{O} \) et al. used high-energy ARPES to measure the valence band dispersion along the \( \Gamma - M \) direction. Finally, and of particular interest here, Hu et al. carried out comprehensive soft x-ray (direct) RIXS studies of \( \text{Cu}_2\text{O} \), and have compared their results with a calculation based on JDOS-like interband transitions.

In this paper, we present a detailed study of \( \text{Cu}_2\text{O} \) using indirect RIXS. In particular, we will focus on the energy region near the band gap, and report our measurement of the dispersion relation of the band-gap edge along the \( \Gamma - R \) direction. The observed momentum dependence of the gap edge is consistent with the dispersion of the valence band as observed with ARPES. In addition, we observe another band of excitations at 6.5 eV, which can be explained as interband transitions from the occupied Cu 3d state to the unoccupied state, which is a mixture of Cu 3d, 4s, and O 2p. We contrast this with the soft RIXS data of Hu et al. Taken together, these results suggest that the indirect (Cu K-edge) RIXS is a good probe of electronic structure.

II. EXPERIMENTAL DETAILS

The RIXS experiments were carried out at the Advanced Photon Source on the undulator beamline 9IDB. A double-bounce Si(333) monochromator and a spherical (R=1 m), diced Ge(733) analyzer was used to obtain an overall energy resolution of 0.4 eV (FWHM). We also utilized a high-resolution setup with a Si(444) channel-cut secondary monochromator and a diced Ge(733) analyzer with 2 m radius of curvature. This provides an overall energy resolution of 0.13 eV.

A single crystal sample of \( \text{Cu}_2\text{O} \) was grown using the traveling solvent floating zone method. The details of the crystal growth were reported in Ref. 36. The crystal used in the RIXS measurements came from the same batch as the one used in the optical studies reported in Ref. 37. The as-grown crystal was mechanically polished and etched in order to optimize the surface condition. The crystal was mounted on an aluminum sample holder at room temperature inside an evacuated chamber.

Most of the measurements were carried out near the \( Q = (2,0,1) \) point, which also corresponds to a reciprocal wave vector \( \mathbf{G} \). The reduced momentum transfer \( q \) is defined as \( q = Q - \mathbf{G} \), and is measured from the Brillouin zone center. Note that the \( \text{Cu}_2\text{O} \) structure is composed of an interpenetrating fcc lattice of Cu and a bcc lattice of O. Therefore, \( (h,k,l) \) reflections with unmixed indices \( h+k+l = \text{even} \), will have a weak Bragg peak intensity, following the fcc structure factor, while the reflections with mixed indices, but \( h+k+l = \text{odd} \), such as the \( (2,0,1) \) point, are forbidden. However, Eichhorn and coworkers reported intensity at such positions with the incident energy near the Cu K-edge, due to the anisotropic Cu environment. As a result, the \( q = 0 \) point data were in fact taken at the \( (2,0,0.5) \) position, to reduce the background due to the resonant elastic intensity.

III. RESULTS AND DISCUSSION

A. Energy dependence

In Fig. 1 we show representative RIXS scans obtained with different incident photon energies \( (E_i) \) as denoted on the left side of the figure. Each scan is taken at the \( (2,0,0.5) \) position, and plotted as a function of energy loss \( h\omega = E_i - E_f \). In each scan, there is a large zero energy loss peak arising from the quasi-elastic background due to phonons and static disorder. In addition, there is a broad, strong feature on the high energy side of the scan.
FIG. 1: Scattered intensity at $\mathbf{Q} \approx (2 \, 0 \, 1)$, plotted as a function of energy loss, $\hbar \omega$. The scans are shifted vertically for clarity. The incident energy for each scan can be read off from the vertical axis.

The two prominent features are a sharp edge-like RIXS feature around $\hbar \omega \approx 2$ eV, which exhibits a large resonant enhancement at $E_i = 8982.5$ eV. We note that this energy corresponds to the sharp peak in the x-ray absorption spectra (XAS) shown in Fig. 8 of Ref. 38 and Fig. 8 of Ref. 39. Since Cu is found with Cu$^{+}$ valence in Cu$_2$O, this intermediate state energy is shifted down by about 10 eV compared to the Cu$^{2+}$ state in cuprate materials like La$_2$CuO$_4$. The sharp edge-like feature shows quite a narrow resonance behavior around the incident energy of $E_i = 8982.5$ eV.

In general, there are two distinct types of spectral features observed by RIXS: One is a valence electron excitation that appears at fixed energy loss ($\hbar \omega$) regardless of the incident energy, similar to Raman scattering peaks. The sharp edge-like feature at 2 eV corresponds to such an excitation. The other type is due to emission lines arising from radiative transitions between atomic-like states, which are observed at fixed final photon energy ($E_f$). When plotted as a function of energy loss, as shown in Fig. 1, the peak position of the latter features therefore shifts as the incident energy is varied above the edge. The broad feature at higher energy ($\sim 5$ eV) in Fig. 1 corresponds to such a feature.

The sharp edge-like feature shows quite a narrow resonance behavior around the incident energy of $E_i = 8982.5$ eV. We note that this energy corresponds to the sharp peak in the x-ray absorption spectra (XAS) shown in Fig. 8 of Ref. 38 and Fig. 8 of Ref. 39. Since this is the strongest absorption feature, we can associate this incident energy, and the corresponding intermediate state of the resonant inelastic process, with the $1s4p$ state following a $1s \to 4p$ dipole transition, where $1s$ denotes a 1s core hole. Since Cu is found with Cu$^{+}$ valence in Cu$_2$O, this intermediate state energy is shifted down by about 10 eV compared to the Cu$^{2+}$ state in cuprate materials like La$_2$CuO$_4$. Note that the RIXS spectra showed no dependence on the incident photon polarization, presumably due to the cubic symmetry of the sample. We identify this sharp edge-like feature as the $q=0$ band gap, since its energy-loss of $\hbar \omega \approx 2$ eV coincides with the optical gap energy. As we will see in the next section, this identification is corroborated by the momentum dependence of this feature.

In addition to this low energy feature at the band gap, there are higher energy features, which show distinct incident energy dependence. In Fig. 2 we show an intensity map as a function of both incident energy and energy loss again taken at $(2,0.05,1)$. Note that the incident energies used in Fig. 2 are higher than those for the data shown in Fig. 1. One can clearly identify a very broad and strong spectral feature located at around $\hbar \omega \approx 6.5$ eV, which is resonantly enhanced over a wide range of incident energies; most notably around $E_i = 8994$ eV and $E_i = 8999$ eV. In addition, there is a higher energy feature at $\hbar \omega \approx 9 - 10$ eV, and a weak low energy feature located around $\hbar \omega \approx 4$ eV that resonates around $E_i = 8999$ eV. Since the peak positions of the loss features do not change with the incident energy, we chose to examine the $E_i = 9000.5$ eV scan, which exhibit all three features in more detail. These data are shown in Fig. 3.

To understand the origin of these excitations, it is useful to consider the electronic density of states. Using both XPS and BIS techniques, Ghijsen et al. reported valence band and conduction band density of states for Cu$_2$O. The most prominent peak in BIS occurs around
3 eV above the Fermi level, while XPS shows a large peak centered around 3 eV below the Fermi level with shoulders on both sides. The density of states based on these XPS and BIS results are shown schematically in Fig. 2(a). The main peak in the XPS spectra is mainly of Cu d-character (based on the various calculations), while the larger binding energy shoulder, at about 7 eV below the Fermi level, has mainly O 2p character.  

The nature of the low-lying unoccupied states has been attributed to mixed 3d–2p states or to Cu 4s states. Given this picture, it is natural to associate the \( \overline{\omega} \) transition from the 3d to either 3d–2p mixture or 4s. Then the higher energy RIXS feature at 9-10 eV presumably is due to the transition from the occupied O 2p to empty 3d or 4s states.

To make a more quantitative comparison, the hard RIXS scan obtained with \( E_i = 9000.5 \) eV is compared with the calculated spectrum, taken from Ref. 31, in Fig. 3. Hu and coworkers computed the inelastic x-ray scattering intensity due to dipole allowed interband transitions between filled and empty partial density of states. The most dominant loss structure is found around 6.5 eV through the 3d \( \rightarrow 4s/3d \) channels, while there exist weaker features at 4 eV and 10 eV in the other channels (4s \( \rightarrow 4s/3d \)). Since the matrix elements for the K-edge experiments are unknown, we plot simply the dominant 3d \( \rightarrow 4s \) transition (solid line) without any matrix element weighting in Fig. 3. We find it describes the main peak at 6.5 eV remarkably well. Note that neither the peak position nor the core-hole broadening (1.35 eV) has been altered from the calculation in Ref. 31, and only the intensity scale has been changed. On the other hand, the Cu L\(_3\) RIXS spectrum obtained with \( E_i = 933.75 \) eV in Ref. 31 exhibits a very different shape, with an energy loss feature centered around 4.5 eV, as shown in Fig. 3 (open circles). Hu and coworkers used a phenomenological excitonic density of states in order to account for this discrepancy. This was an ad-hoc approach that used the experimental L-edge absorption spectrum (for which there is a 2p core hole in the final state) in place of the calculated occupied DOS. This was labeled the “excitonic DOS”. Although there is no 2p core hole in the L-edge RIXS final state, such excitonic DOS was required to explain experimental observations. Figure 3 shows that no such ad-hoc corrections are required to explain the K-edge RIXS data, which are well reproduced by the theoretical JDOS. Thus, the present comparison suggests that Cu K-edge RIXS (often called indirect RIXS) can measure band structure directly, unlike Cu L\(_3\)-edge RIXS. Note that the additional features observed at 4 eV and 10 eV in the K-edge RIXS could also be explained by the 4s \( \rightarrow 3d \) transition according to the calculation.  

![figure 3](image3.png)

**FIG. 3:** Energy loss scan obtained with \( E_i = 9000.5 \) eV. The momentum is \( \mathbf{Q} \sim (2, 0, 1) \). The open circles are experimental soft x-ray RIXS spectrum from Ref. 31. The solid line is a calculated RIXS spectrum from Ref. 31 scaled to match the current data.  

![figure 4](image4.png)

**FIG. 4:** (a) Schematic representation of experimental density of states (DOS) from Ref. 34. (b) Simplified band structure shown for illustrative purposes as described in the text. The arrows denote possible interband transitions with different momentum transfers. Vertical solid lines are interband transitions. Dashed lines correspond to \( \mathbf{q} = 0 \) transitions. (c) Momentum dependence of the joint density of states (JDOS) arising from the band structure shown in (b). Note that the magnitude of the momentum dependence of the lower bound of the interband transition continuum (thick solid line) mimics that of the valence band.
B. Momentum dependence

We now turn to the 2 eV feature. With the incident energy fixed at $E_i = 8982.5$ eV, we studied the momentum dependence of the sharp edge feature observed at 2 eV (Fig. 1). In Fig. 5 we plot the RIXS spectra obtained at $Q$ positions along the $\Gamma - R$ line, that is, with $q$ along the (1,1,1) direction. We plot only a narrow frequency range, in order to emphasize the evolution of the lowest energy excitation as a function of momentum transfer. (Note that there appears to be a small peak at $h\omega \sim 1 - 1.5$ eV. However, this feature is present in all scans and has no $E_i$ dependence, nor is it observed in the high resolution data, as shown in the inset of Fig. 6. Thus, it is most likely due to an experimental artifact, and we do not discuss it further.)

The lowest energy excitation across the band gap shows quite a dramatic momentum dependence. In order to show the dispersion of this excitation graphically, we plot the intensity as a function of $h\omega$ and $q$ in Fig. 6. The intensity scale is shown on the right hand side, and is described in the figure caption. The boundary between the high intensity region and the background forms a sinusoidal dispersion relation of the form $h\omega \approx 2.15 - 0.25 \cos(2\pi q)$, as shown as the white dashed line in Fig. 6.

If one adopts the simple view that the RIXS spectrum in a weakly correlated system is proportional to the JDOS at a given momentum transfer, then the observed dispersion in Fig. 6 should reflect the momentum dependence of the lower bound for inter-band transitions. In order to understand this, let’s consider a simple sinusoidal conduction and valence band, with a direct gap located at the $\Gamma$ position. An idealized representation of such a band structure is shown in Fig. 4(b) as a function of electron momentum $k$ along the $\Gamma - R$ direction. Here the valence band dispersion $E_v(k)$ is taken from the recent angle-resolved photoemission (ARPES) data, while the conduction band dispersion $E_c(k)$ is taken from the calculation in Ref. 30.

Finite $q$ interband transitions can be represented as vectors connecting two points on the $E_v$ and $E_c$ curves as shown in Fig. 4(b). The frequency and momentum of a particular transition satisfies $h\omega(q) = E_c(k_p) - E_v(k_h)$ and $q = k_p - k_h$, where $k_p$ and $k_h$ are particle and hole momentum, respectively. Examples of the $q = 0$ transition are shown in solid lines, while the dotted line represents examples of the $q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ transition. Integrating over all possible $k_p$ and $k_h$ combinations, one can obtain the $q$-dependence of inter-band transitions along the (111) direction. This is shown for this simplified band structure in Fig. 4(c). Since the conduction bandwidth is much larger than the valence bandwidth in this case, the lower bound of inter-band transitions is dominated by the valence band. In other words, the lower bound transitions involve exciting electrons from all $k_h$ positions of the valence band to the bottom of the conduction band ($k_p = 0$), since it takes more energy to excite electrons into finite $k_p$ states in conduction band. Therefore, we expect the dispersion of the valence band to be similar to the dispersion of the gap observed in our RIXS measurements. This expectation is borne out by the recent ARPES studies by Bruneval et al. and Onsten et al. In particular, the valence band dispersion along the $\Gamma - R$ direction was reported in Ref. 30, which has the valence band maximum at the $\Gamma$ position and bandwidth of about 0.6 eV as shown in Fig. 4(b). This is very similar to the bandwidth 0.5 eV observed in Fig. 6. Though, we should note that the picture considered in Fig. 4(b) is an over-simplification in one dimension, and in order to make a quantitative comparison, one would have to take into account the full three dimensional band structure.

IV. CONCLUSIONS

A resonant inelastic x-ray scattering (RIXS) study of the electronic structure of cuprous oxide, Cu$_2$O, is reported. By tuning the incident x-ray photon energy to the Cu K-absorption edge, resonantly enhanced electronic transitions are observed. Comparison with Cu L$_3$-edge RIXS spectrum and a calculation based on band-structure density-of-states clearly illustrates that the indirect RIXS spectrum of Cu$_2$O obtained at the Cu K-edge can be explained simply by interband transitions.
Our main result is that the indirect RIXS cross-section seems to be described by interband transitions from the occupied valence band to the unoccupied conduction band. This gives credence to theoretical efforts to connect the RIXS cross-section with the charge correlation function and also allows one to use indirect RIXS to investigate the electronic structure of materials. This last point is an important one, since RIXS has many advantages over other electron spectroscopy techniques, such as bulk-sensitivity, element-sensitivity, and momentum-resolving capability.

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**FIG. 6**: (Color Online) Intensity colormap as a function of energy and momentum transfer. The intensity scale in counts per second is shown on the right hand side of the main figure. Intensity of 10 counts per second or higher is shown in brown.
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