Excitation-energy dependence of L_{2,3} X-ray spectra of Cu metal and its oxides

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The L_{2,3} X-ray emission spectra of Cu metal and its oxides (Cu_{2}O and CuO) have been measured by using monochromatic synchrotron radiation. From the analysis of spectra recorded at different excitation energies, the L_{2}/L_{3} X-ray emission intensity ratio, i.e., I(L_{2})/I(L_{3}) is discussed. The intensity ratio, I(L_{2})/I(L_{3}) is found to show significant enhancements for the compound materials such as Cu_{2}O and CuO, at resonance energy. At non-resonant high energy, I(L_{2})/I(L_{3}) for CuO is observed to be higher than those for Cu and Cu_{2}O. These tendencies are explained to be resonant or non-resonant excitation/deexcitation processes and absorption coefficients, including the chemical bonding effects.

1. Introduction

Cu metal and its oxides have been recently attracted consider- able attention for the study of the electronic structure of copper oxides based on the superconducting matters. The Cu L X-ray emission spectra for these materials have been measured for studying on the electronic structure of the core levels and valence bands and the effects of chemical binding on the satellite structures of the main peak of Cu L_{2,3} X-ray emission using usual electron or X-ray sources (Barnole et al., 1990; Sugiuara, 1994; Kawai, 2001).

Nowadays, with the advent of recent synchrotron radiation (SR) sources, studies on excitation-energy dependence of X-ray emission spectra have become possible. L_{2,3} X-ray emission spectra of Cu metal excited with monochromatic SR were presented by Wassdahl et al. (1990). They measured energy dependence of L_{2,3} emission spectra of Cu metal and discussed the satellite structure in Cu L X-ray spectra due to M-shell vacancies produced before the decay of 2p holes. It is shown that these additional vacancies are produced by Coster–Kronig (C–K) processes, but to a large extent by shake-up/shake-off. Then, energy dependence study of Cu L_{2,3} satellites was presented and discussed by Magnuson et al. (1997). They interpreted and confirmed the satellite spectra of Cu L_{3} X-ray emission in the previously accepted picture of initial-state satellite, produced either by shake-up/shake-off during the excitation or as a result of C–K decay of inner hole states.

Assuming that the L_{2} and L_{3} ionization probability is proportional to the number of electrons, i.e., multiplicity of the core hole states, we obtain that the L_{2}/L_{3} intensity ratio, i.e., the I(L_{2})/I(L_{3}) intensity ratio in L_{2,3} X-ray emission is \frac{1}{2}. It was first noticed by Skinner et al. (1954) that the I(L_{2})/I(L_{3}) intensity ratio of pure 3d-metals is much less than the predicted value of \frac{1}{2}, which is attributed to C–K processes. The results of L_{2,3} X-ray emission spectra measurements and theoretical calculations of the relative intensity ratio I(L_{2})/I(L_{3}) for the entire series of 3d transition metals were presented by Kurnaev et al. (2005). They observed a large reduction in the I(L_{2})/I(L_{3}) ratio of the emission intensities from the value of \frac{1}{2} given by L_{2}/L_{3} degeneracy of the core hole states and showed that this effect is primarily to the non-radiative L_{2,3}M_{4,5} C–K transitions in solids, which is stronger than in free atoms.

Changes in the L_{2,3} X-ray emission spectra with oxidation of the 3d transition metals have been measured using electron excitation by Fischer (1965). It was found that relative intensity ratio I(L_{2})/I(L_{3}) significantly depends on the incident electron energies and the target materials, where I(L_{2})/I(L_{3}) decreases with increase of excitation energy and increases considerably for the Cu oxides as compared to Cu metal. This intensity ratio was found to be sensitive to the chemical bonding, which enabled us to determine the oxidation state of 3d elements in various chemical compounds and minerals using commercial electron-probe microanalysis (Armstrong, 1999), conventional X-ray fluorescence spectroscopy (Kawai, 2001) and ion-beam microanalysis (Kawatsura et al., 2002).

In the present experiment, we have measured excitation-energy dependence of Cu L_{2,3} X-ray emission spectra of Cu, Cu_{2}O and CuO using SR to study the effects of chemical bonding in the excitation and deexcitation processes inner-shell electrons of Cu metal and its oxides.
2. Experimental

The experiments were performed at beam lines 8.0.1 and 6.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory in USA. The Cu foil sample (99.99% purified) was commercially obtained. The Cu2O and CuO sintered samples were also commercially obtained, which were 99.9% purified ones. The spectral measurements in the Cu L region of these materials were performed at the beam line 8.0.1 for X-ray emission and fluorescence yield X-ray absorption (XYF) and at the beam line 6.3.1 for total-electron yield (TEY) X-ray absorption. The base pressure was lower than 3 × 10⁻⁷ Pa. The resolution of the monochromator of the beam line was ~0.5 eV. The incident photon flux was continuously monitored using a gold mesh in front of the sample to normalize the X-ray emission spectra. The X-ray absorption measurements were performed to determine the L2 and L3 threshold energies for three sample materials of Cu, Cu2O and CuO, respectively.

3. Results and discussion

Fig. 1 displays experimental L2,3 emission spectra excited resonantly (Fig. 1(a) and (b)) and non-resonantly (Fig. 1(c)). The spectra shown in Fig. 1(a)–(c) were measured on L3 edge, L2 edge and at 990 eV above the L2 edge, respectively. In order to compare the intensity ratio \( I(\text{L}_3)/I(\text{L}_2) \), all spectra are normalized to \( I(\text{L}_3) = 1.0 \), respectively. Fig. 1(a) shows Cu L2,3 X-ray emission spectra of Cu, Cu2O and CuO excited at the L3 edge energies of 932.65, 932.41 and 930.30 eV, respectively, which are determined by the X-ray absorption measurements for these three materials. Only one main peak appears at about 930 eV in each spectrum of the different materials, which is attributed to the Cu L1,2 X-ray line. The widths and peak positions of these L1,2 X-ray lines are almost same.

Fig. 1(b) shows Cu L2,3 X-ray emission spectra of Cu, Cu2O and CuO excited at the L2 edge energies of 952.65, 952.65 and 950.36 eV, respectively, which are also determined by the same manner as mentioned above. In this case, two peaks appear in each spectrum of the different materials. The main peak at 930 eV is also attributed to the Cu L1,2 X-ray line and the other peak at about 950 eV is attributed to the Cu L1,2 X-ray line. For CuO, a satellite structure is observed at high-energy side of the main L1,2 line, while the spectra of Cu and Cu2O have no clear satellite structures. The measured spectra show that the intensity ratio \( I(\text{L}_3)/I(\text{L}_2) \) for CuO is 0.51, much higher than those for Cu2O and Cu, 0.27 and 0.15, respectively. So the ratio for Cu2O is about twice as high as that for Cu.

Fig. 1(c) shows Cu L2,3 X-ray emission spectra excited at 990 eV. Two peaks appear in each spectrum of the different materials, similarly as shown in Fig. 1(b). The main peak at 930 eV is attributed to the Cu L1,2 X-ray line and the other peak at about 950 eV is attributed to the Cu L1,2 X-ray line. For CuO, a satellite structure is again observed at high-energy side of the main L1,2 line, while the spectra of Cu and Cu2O have no clear satellite structures. It is considered that the L2 edge main peak corresponds to the 2p⁵3d⁹ → 2p⁶3d⁸ transition due to the charge transfer effect and the high-energy satellite to the 2p⁵3d⁹ → 2p⁶3d⁸ transition in CuO.

However, it is found that the intensity ratio \( I(\text{L}_2)/I(\text{L}_3) \) is different from that observed at L2 edge excitation shown in Fig. 1(b). The ratios for Cu metal and for Cu2O are 0.17 and 0.18, respectively, and that for CuO is 0.31 much higher than those for Cu and CuO. The only difference of spectra in Fig. 1(c) from Fig. 1(b) is that Cu 2p levels of Cu, Cu2O and CuO are excited non-resonantly by 990 eV photon energy between the L1 and the L2 edge energy.

It is known that the relative intensity \( I(\text{L}_2)/I(\text{L}_3) \) significantly depends on the target materials (probably their oxidation number). It should be noted that the spectra shown in Fig. 1(b) were measured on L3 threshold energy, which means that electrons in L3 level (electrons at 2p1/2 state) are resonantly excited to the 3d or 2s states of Cu, Cu2O and CuO. These materials have one 4s-hole, two 4s-hole and two 4s- plus one 3d-hole configurations in a simple model, respectively. The measured spectra shown Fig. 1(b) reflect the electron configuration of each material. \( I(\text{L}_2)/I(\text{L}_3) \) for CuO (two 4s holes) is about twice higher than that for Cu metal (one 4s hole). The ratio for CuO is much higher than those for the other targets and the ratio for Cu2O is higher than that for Cu metal. It is known that the resonance transition from 2p1/2 to the 3d state is much stronger than that from 2p3/2 to the 4s state.

We show another possibility of the source of intensity ratio difference between metallic and ionic compounds. The CuO L2,3 absorption spectrum measured by the TEY method has sharp resonance lines due to 2p→3d absorption, though the TEY spectra are not given here. Consequently, the absorption coefficients at lower and higher vicinity of L1,2 line could be small and thus the L1,2 line, i.e., \( I(\text{L}_2) \) is rather strong for CuO. On the other hand, the

![Fig. 1](https://example.com/image1.png)
Armstrong (1999). Support some conclusions for Cu and Cu oxides given by as a function of Cu concentration. Our experimental results may Cu L2 edge and above the L2 edge. It is also revealed that ability (Martensson and Johansson, 1983; Sorensen et al., 1991; thus Auger electron emission or Coster–Kronig transition probably resulting in a difference in the effective fluorescence yield and after ionization could be affected by the bonding environment, of the outer shell electron remained in an excited state or states Armstrong, 1999). It is noticed that in the metallic copper, evidence of Cu L2,3 X-ray emission spectra of Cu, Cu2O and CuO. The oxidation-state dependence and the excitation-energy dependence. I experimental results for intensity ratio of I(L2)/I(L3) at the vicinity of the energy of L1 line have finite values for Cu and Cu2O. This is also the reason that I(L2)/I(L3) for CuO is higher than that for Cu2O and the ratio for Cu2O is higher than that for Cu metal. Similar results were reported by the electron excitation method that I(L2)/I(L3) increases monotonically for Cu, Cu2O and CuO with oxidation state increasing from Cu0 to Cu+ to Cu2+. (Armstrong, 1999). In this case, these differences have been attributed to the differential self-absorption by L2,3 and L1 lines as a function of Cu concentration. Our experimental results may support some conclusions for Cu and Cu oxides given by Armstrong (1999).

It has been also shown that the intensity I(L2) is weaker for small band-gap materials, such as metals and covalent compounds and strong for ionic compounds for Cu from the experimental evidence (Kawai, 2001). Fig. 1(c) shows that I(L2)/I(L3) for Cu metal and Cu2O is almost equal and that for CuO is much higher than those for Cu and Cu2O. It is explained that the lifetime of the outer shell electron remained in an excited state or states after ionization could be affected by the bonding environment, resulting in a difference in the effective fluorescence yield and thus Auger electron emission or Coster–Kronig transition probability (Martensson and Johansson, 1983; Sorensen et al., 1991; Armstrong, 1999). It is noticed that in the metallic copper, probably in covalent copper compounds, the L2L3M4,5 C–K transitions are possible, cut off in free Cu atoms (Sorensen et al., 1991; Kawai, 2001). It is suggested that the L2L3M4,5 C–K transitions are energetically forbidden, probably in CuO. Present experimental results for intensity ratio of I(L2)/I(L3) at 990 eV excitation energy are consistent with the previous considerations. We have reported the first measurement that have shown the oxidation-state dependence and the excitation-energy dependence of Cu L2,3 X-ray emission spectra of Cu, Cu2O and CuO. The study reveals the difference of the intensity ratio I(L2)/I(L3) at the Cu L2 edge and above the L2 edge. It is also revealed that I(L2)/I(L3) for CuO and CuO is larger than that for Cu, at resonance energy. At non-resonant high energy, I(L2)/I(L3) for CuO shows higher than those for Cu and CuO. These facts are explained to be resonant or non-resonant excitation/deexcitation processes and absorption coefficients, including the chemical bonding effects.

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