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Studies of copper valence states with Cu L_3 x-ray-absorption spectroscopy

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We have used x-ray-absorption spectroscopy to study a series of compounds in which Cu assumes a formal valence between 0 and 3. We find that the shape, the threshold energy, and the intensity of the Cu L_3 absorption edge is strongly influenced by the chemical state of the Cu atoms. We use the Cu 2p x-ray-absorption spectra of a large number of Cu compounds, including sulfides, oxides, La-Sr-Cu-O compounds, a phthalocyanine complex, and various minerals to show that the presence of a strong 2p-3d excitonic transition is a fingerprint of the Cu(d^9) contribution to the ground state. A simple ionic picture is generally inadequate to describe these compounds.

I. INTRODUCTION

The nature of the electronic structure and bonding in Cu compounds is a matter of intrinsic interest which has gained added impetus since the discovery of high-temperature superconductivity in a class of Cu oxides. If Cu compounds were purely ionic then Cu^0, Cu^{I}, $\mathrm{Cu}^{\mathrm{II}}$, and $\mathrm{Cu}^{\mathrm{III}}$ compounds would have the configurations (Ar)$3d^{10}4s^1$, (Ar)$3d^{10}4s^0$, (Ar)$3d^9 4s^0$), and (Ar)$3d^8 4s^0$, respectively. However, Cu belongs to the group-B metallic elements, which are much more electronegative than the group-A metals, i.e., the effective nuclear charge felt by the 4s electrons is larger in elements such as Cu, Zn, etc. than in Na, Ca, etc. As a consequence group-B elements show enhanced affinity for highly polarizable anions[1] and a marked tendency to covalency.[2] Further, as recognized for many decades,[2] the covalency in compounds of the group-B metals increases with increasing valency, i.e., the sharing of electrons between metal and ligand atoms can lead to nonintegral values for the number of electrons on the metal atoms. It should also be noted that inorganic chemists have for several decades known that the $3d^{10}$ configuration of Cu^{I} should not be regarded as inert but that the d electrons are also important for bonding in these compounds.[3] Thus, a discussion of whether Cu is present as Cu^0, Cu^+, Cu^{2+}, or Cu^{3+} in a given compound is rather sterile as it is probably never present in precisely these ionic states. A discussion of whether Cu is monovalent (Cu^{I}), divalent ($\mathrm{Cu}^{\mathrm{II}}$), etc. may be relevant when the partner elements in a compound have variable valence,[3] but most relevant is simply the question of the weights of the Cu configurations d^8, d^9, d^{10}, and $d^{10}4s^1$.

High-energy spectroscopies [x-ray photoelectron spectroscopy (XPS), x-ray-absorption spectroscopy (XAS), Auger-electron spectroscopy (AES), and bremsstrahlung isochromat spectroscopy (BIS)] are well suited to provide information on these points, as proved, for instance, by the breakthroughs obtained in studies of the lanthanides and of transition-metal compounds.[4–12] XAS, in particular, offers several advantages over the other techniques, not only because of its site selectivity, which it shares with XPS core-level studies, but also because of the role of selection rules, which often lead to a simpler theoretical treatment of the data.[12–15] In addition, the surface sensitivity of XAS in the photoyield mode is, to some extent, tunable. We use the total-electron-yield mode which probes a layer some hundreds of angstroms thick, so that the surface cleanliness is less critical, and which gives a strong signal so that measurement times are short. The situation is particularly clearcut for the 2p ($L_{2,3}$) absorption edge of Cu as transitions to the 3d states are possible in $\mathrm{Cu}^{\mathrm{II}}$ (and $\mathrm{Cu}^{\mathrm{III}}$) but not in Cu^{I} compounds. In this paper we underline the potential utility of Cu L_3 XAS for determination of the Cu ground-state configuration and we give some examples of a qualitative exploitation of the technique.

II. EXPERIMENT

Measurements of the Cu L_2 and L_3 edges were made at the Berliner Elektronspeicherring-Gesellshaft für Synchrotronstrahlung (BESSY) and les Anneux de Collisions de l'Accélérateur Linéaire (ACO) storage rings using synchrotron radiation. The radiation was in both cases monochromatized using double-crystal monochromators equipped with beryl crystals,[16,17] which gave an energy resolution of ~400 meV at the Cu L_3 edges (~932 eV) and absorption spectra were collected in the total-yield mode. The vacuum during the XAS measurements was often as low as 2×10^{-10} torr, but this could only be achieved after bakeout, and in some cases where the compounds were sensitive to heat, the bakeout procedure was omitted and the pressure was $\sim 10^{-9}$ torr. XPS studies were made in ultrahigh vacuum using monochromatized Al $K\alpha$ radiation from a large-solid-angle (0.1 sr) quartz-crystal monochromator custom built by Vacuum Science Workshop. Cu_2O, $CuFeS_2$ (chalcopyrite), CuS (covellite), $Cu_{1.8}S$ (digenite), Cu_2S (chalcocite), Cu_3As (domeykite), and Cu_3AsS_4 (enargite) were natural minerals. For these samples, and Cu metal, a clean surface, as shown by XPS, was prepared by scraping the surface in vacuum. La_2CuO_4 and $La_{1.8}Sr_{0.2}CuO_4$ were sintered disks and were not baked. XPS showed that these samples were free of surface carbon, hydroxide, and other detectable impurities after thorough scraping. The commercial CuO powder samples and ground powder samples of the minerals malachite ($Cu_2[(OH)_2CO_3]$), turquoise ($CuAl_6[OHPO_4]_4 \cdot 3H_2O$) chrysocolla ($CuSiO_3 \cdot nH_2O$), and dioptase [$Cu_3(Si_3O_9) \cdot 3H_2O$] were pressed on to an Al sample holder. XPS showed the presence of some carbon on the CuO surface, but this should not influence the XAS spectra, where the probing depth is larger than in XPS. We had no access to methods to detect loss of water from the minerals which contain water, but include the spectra for completeness. Beam damage is in principle feasible for these samples, but the photon doses are smaller in this experiment than in XPS and no time dependence of the spectra was detected.

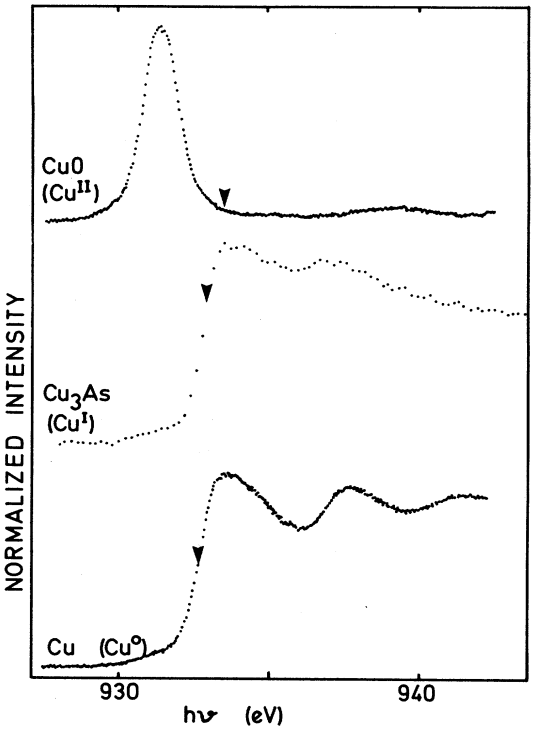

FIG. 1. XAS spectra of Cu, Cu_3As, and CuO at the Cu L_3 edge. The arrows mark the position of the main peak Cu L_3 peak binding energy in XPS, relative to E_F, and the combined error limits for alignment of XPS and XAS energy scales are ~ 0.5 eV. The spectra have been arbitrarily scaled to give the same peak height.

III. RESULTS AND INTERPRETATION

For the present discussion it is sufficient to consider the Cu L_3 edge. Figure 1 shows the Cu L_3 absorption edges of CuO (formally Cu^{II}), Cu_3As (formally Cu^{I}) and Cu metal (formally Cu^0). The relative intensities of the spectra have been normalized to the peak height, after subtraction of a sloping background which was extrapolated from the linear region below the threshold.

The spectra of Fig. 1 exhibit important differences related to the different configuration of Cu atoms in the three samples. The L_3 edge of CuO has a strong peak at 931.3 eV. The origin of this feature is now well understood: a Cu 2*p* electron is excited from the 2*p* level to the empty 3*d* bands, but the effect of the Coulomb interaction between the strongly localized 2*p* hole and the rather small Cu 3*d* orbital is to localize the extra 3*d* electron. The final state is thus a "core exciton," in some ways like a Frenkel exciton.[18,19] Similar peaks are expected whenever a core electron is excited into a narrow (*d* or *f*) band and have been found in many rare-earth[14] and transition-metal compounds. The observation that the Cu L_3 XAS peak of CuO is below the XPS binding energy (marked with a vertical arrow) is itself proof that the peak is not a density-of-states feature, although the density of states of CuO does show a sharp peak just above the Fermi level. The intensity of this peak is related to the total amount of Cu 3*d* character in the unoccupied states.

The spectra of "monovalent" Cu in Cu_3As and Cu metal do not show such a peak because the *d* shell is essentially full. The absorption edge is ~ 3 times weaker on an absolute scale[20] because the matrix elements for the 2*p*-4*s* transitions are smaller than those for the 2*p*-3*d* process[21] and the 4*s* bands are broad (although see comments in the next paragraph). Because the 4*s* wave function is more extended than that of the 3*d* orbital, the core-hole potential has much less effect on the spectral shape and the observed XAS of Cu bears a close resemblance to the calculated total density of Cu states[22–25] (although the L_3 absorption only probes *s* and *d* states). Also, the XAS threshold energy is in agreement with the Cu $2p_{3/2}$ binding energy as determined by XPS.

The data in Fig. 1 support the idea that one could use the presence of a sharp peak in the Cu L_3 spectrum, below the XPS threshold, as a measure of the amount of unoccupied Cu 3*d* character in the initial states. However, in answering this question we must be careful to define what we mean by a *d* count. The problem may be illustrated by comparison with Ni. Ni is well known to have approximately 9.4 electrons per atom in the bands with predominantly Ni *d* character, but because of hybridization with the *s* states the 3*d* character in the occupied "*d* band" only adds up to 8.8 electrons per atom.[26] Likewise, for Cu metal where the Cu "3*d* band" itself is clearly full, analysis shows 3*d* character adding up to 9.6 3*d* electrons per Cu atom.[27] The ~ 0.4 3*d* holes of Cu metal must contribute to the intensity of the $L_{2,3}$ edges in Cu. This partly explains why the Cu L_3 edge of bulk copper is much more intense than the structures which occur above the large peak in CuO and which probably result from transitions into 4*s* states not hybridized with Cu 3*d* states. However, it is probably not the whole explanation as the extra intensity extends to high energies above E_F where no $3d$ weight can be expected.

We present in Figs. 2 and 3 spectra from a wide range of Cu compounds. First, we consider Fig. 2 where the spectra of many compounds with nominally monovalent, or zero valent Cu are collected. Few of these bear much resemblance to the spectra of divalent Cu in CuO, while all of the $\mathrm{Cu^{II}}$ compounds shown in Fig. 3 do show a large peak. Note that of all the spectra in Fig. 2, only CuS and $Cu_{1.8}S$ show real intensity below the arrows marking the Cu $2p_{3/2}$ binding energies found by XPS. At least for CuS there is indication from the crystal structure that $\frac{1}{3}$ of the Cu atoms could be described as $\mathrm{Cu^{II}}$ (Ref. 28, p. 907) (the shoulder at $\sim$931 eV in Cu_2S is probably due to CuO impurity). For the rest of the materials the structure in the Cu L_3 edges can probably be explained by structure in the single-particle density of states appropriate to the Cu site and some of these details will be discussed more fully in later publications.

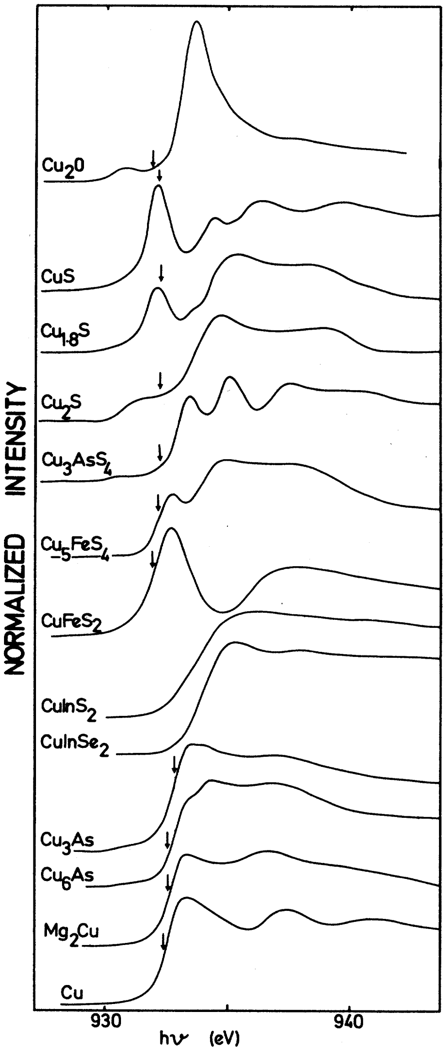

FIG. 2. Cu L_3 XAS spectra of Cu compounds. The spectra have been arbitrarily scaled to give the same peak heights, except for Cu_2O, which was clearly stronger than the other materials. The arrows mark the main XPS L_3 binding energies, as for Fig. 1.

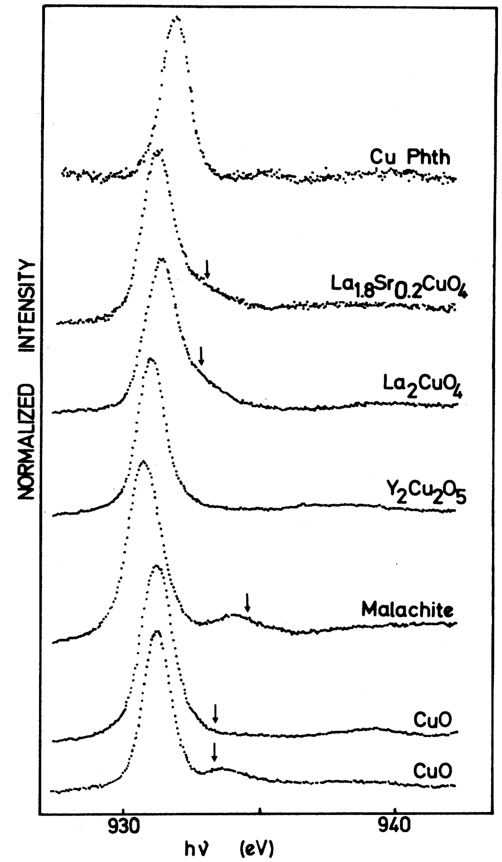

FIG. 3. Cu L_3 XAS spectra of some divalent Cu compounds. Arrows mark the Cu L_3 peak binding energies in XPS, as for Fig. 1.

The spectrum of Cu_2O in Fig. 2 is one of the most complicated to interpret and illustrates very well the dangers of equating a single atomic configuration, d^{10}, with a particular valence, $\mathrm{Cu^{I}}$. The small peak in the spectrum at 931 eV is a spurious feature, attributed to CuO impurities because of its energy and the variation in intensity from sample to sample. The peak at 933.7 eV is asymmetric and is followed by a plateau with weak structure on its high-energy side. Recent augmented-spherical-wave (ASW) band-structure calculations indicate an amount of d character in the unoccupied states that is unusually large for a $\mathrm{Cu^{I}}$ compound and show a sharp peak in the conduction bands.[25] We thus attribute the large intensity of this peak a few electron volts above threshold to the $2p$-$3d$ channel. The amount of unoccupied d character, and hence, the strength of the XAS peak, is certainly related to the unusual structure of Cu_2O in which the Cu is linearly coordinated to only two oxygen nearest neighbors.[29]

Figure 3 gives the Cu L_3 spectra of a number of $\mathrm{Cu^{II}}$ compounds. A strong peak is always observed just below the threshold as defined by the XPS binding energy. In every case we attribute this peak to $2p$-$3d$ character in the excitations which dwarves the $2p$-$4s$ signal. Many of the spectra in Fig. 3 exhibit small peaks and tails on the high-binding-energy side of the main peaks. In some cases these may be attributed to structure in the unoccupied density of states. However, we do not wish to attach undue significance to these peaks because we found small variations in the peaks from one sample to another. An example of this is CuO, itself, where some commercial samples exhibited a small peak at ~934 eV.

For CuO, $Y_2Cu_2O_5$, La_2CuO_4, and malachite, as well as for turquoise, chrysocolla, and dioptase the formal Cu valence derived from the stoichiometry is clearly 2 and we would expect a strong contribution of the Cu d^9 configuration to the ground state, even if some of the minerals probably lose some of their water of crystallization in the vacuum. This expectation is reflected in the intensity of the observed peaks (only a representative sample is shown in Fig. 3, but all showed the strong peak). Note, however, that even in CuO the number of Cu 3d electrons has been estimated from XPS satellite intensities to be as high as 9.3.[9,30] Without a satisfactory method of absolute normalization of the spectra, and a standard for which we have absolutely reliable values for the number of Cu 3d holes in the ground state, we can only say that these spectra indicate a large and probably majority contribution of the Cu $3d^9$ configuration to the ground state. The same is true of Cu in Cu-phtalocyanine (CuPc) which has been the subject of some debate[31–33] and will be further discussed elsewhere. The formal oxidation number of Cu in $La_{1.85}Sr_{0.15}CuO_4$ is larger than 2 but we see no evidence for a Cu d^8 contribution to the ground state in this spectrum. (See, e.g., Refs. 34–36 for further discussion of this point.)

IV. CONCLUDING REMARKS

We have reported the L_3 XAS spectra of a large number of compounds in which Cu has an oxidation number of 0, 1, 2, or 3. We always find a sharp peak in the spectra when the oxidation number of the Cu is 2 or more. We attribute the sharp peak to transitions with largely $2p \rightarrow 3d$ character. Because the peak is always found below the threshold as defined by XPS, we do not believe it can be explained by density-of-states (DOS) effects alone (although we would expect divalent Cu to have a high density of unoccupied Cu 3d states just above E_F). In principle, the strength of this peak could be used as a monitor of the amount of Cu 3d character in the unoccupied states. We note that the strength of the L_3 edges in Cu^0 and Cu^I compounds is too great to be explained by $2p \rightarrow 4s$ transitions alone and we attribute part of the intensity of these edges to Cu 3d character in the unoccupied states as a result of 3d-4s hybridization. This is particularly true for Cu_2O, where the extra intensity is all very close to threshold. In other materials, such as Cu, unexplained intensity continues to much higher energies and cannot all be accounted for by Cu 3d character in the unoccupied states. However, the case of Cu_2O illustrates very clearly that the atomic configuration labels Cu d^9, Cu d^{10}, and Cu d^{10} 4s should not be applied too literally to Cu^0, Cu^I, and Cu^{II} compounds.

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[20] We have not yet been able to devise a reliable, absolute normalization procedure for XAS in the total-yield mode. The signal is dependent not only on known factors, such as the number of photons transmitted by the monochromator and the atomic concentration of copper, but also on intricate, material-dependent details of the cascade processes following core-hole creation and the escape depths of electrons of a multitude of different kinetic energies. Even the pre-edge background is due to absorption from all the atomic species present so that it is necessary to rely on independent measurements and assumptions regarding the atomic cross sections (e.g., for O) and the solid-state effects. Moreover, the measured edge-background ratio for given material depends on the experimental conditions (e.g., angle between sample normal and the detector, rocking-curve adjustments in the monochromator, etc.). The value quoted for the relative intensity is an average estimate from several measurements in which the measurement conditions (angles, etc.) are kept similar. It is obtained by scaling Cu II and Cu or Cu I spectra to the same intensity over background several electron volts above the edge. A similar value is obtained by scaling the Cu and CuO spectra in the same preedge background intensity, after a correction is made for O absorption in CuO and after edge and/or background variations in different measurements are averaged out. Given the inaccuracies in both methods, not too much importance should be attached in the exact number, which just expresses the fact that I (white line) > I(step) >> I(2p-4s in CuII).

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