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A new approach to determining the charge distribution in copper compounds

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Abstract. An analysis of the energy moments of x-ray absorption spectra at the copper K edge has been used to assign characteristic energies for a series of copper compounds with formal valences of +1, +2, and +3. The results indicate that there is a good correlation between the characteristic energies defined in this way for near-edge x-ray absorption spectra and the charge distribution in these copper compounds.

1. Introduction

The valence of copper in oxides pertinent to high-temperature superconductivity has been a key point in discussions during the last year [1–6]. In this paper, we develop a new empirical approach to the relationship between charge distribution and the energy of the K edge for copper compounds. We have measured the Cu K-edge x-ray absorption spectra (XAS) of a series of copper compounds with formal valences of +1, +2, and +3, and then assigned a location for the edge based on energy moment analysis. In this way we obtain a characteristic energy that as a first approximation correlates well with formal Cu valence in a semi-quantitative way.

The energy required to excite a 1 s electron to a delocalised p level varies as the number of electron holes associated with the Cu atom changes. However, these excitations are accompanied by various shake-down processes involving charge transfer from the ligand atoms surrounding the copper atom as it relaxes and fills the 1 s hole that was created during the absorption process. These effects lead to additional features in the near-edge absorption spectra that complicate the interpretation. It is usual to focus attention on particular, more or less well defined, features in order to obtain information about the chemical environment of the Cu atoms in the solid.

We avoid attributing detailed meaning to such isolated, individual features. Instead, we take an overall approach, more akin to the concept of 'valence' in its 'chemical' sense, avoiding the details of spatial charge distribution and electronic hybridisation. In other words, the numerical values we present are more representative of the overall charge density at the copper atom in each compound. Our approach relies on a point of view about XAS similar to that outlined by Gol'danskii as background for understanding chemical shifts in Mössbauer spectra [7]. Recently, another technique based on location of the first maximum in the derivative of the XAS curve has been used to define an energy

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Table 1. The mean characteristic energies and their standard deviations for the 17 copper compounds studied. The mean values are based on 10 different upper limits of integration between 30 and 40 eV in 1 eV steps.

Compound	$\langle S\rangle$ (eV)	σ (eV)	Formal Cu valence
CuBr	1.57	0.08	+1
Cu_2O	3.58	0.14	+1
Cu metal	3.58	0.04	—
CuCl	3.82	0.62	+1
$YBa_2Cu_3O_{6.5}$	6.46	0.17	+2
CuO	6.49	0.14	+2
$CuCl_2$	6.66	0.37	+2
Y_2BaCuO_5	6.90	0.32	+2
$BaCuO_2$	7.11	0.24	+2
$Cu(acetate)_2$	7.18	0.50	+2
CuF_2	7.28	0.43	+2
$CuSO_4$	7.32	0.47	+2
$Cu(NO_3)_2$	7.58	0.30	+2
$YBa_2Cu_3O_{6.9}$	7.66	0.14	+2.27
La_2CuO_4	7.94	0.13	+2
$NaCuO_2$	8.03	0.24	+3
$KCuO_2$	8.25	0.14	+3

for the K edge of +2 and +4 tin compounds [8]. However this method cannot be unambiguously extended to copper compounds with complicated pre-edge structure. The compounds we have selected for the study are listed in table 1. We show that there is a general correlation between the average energy position of the Cu K edge in x-ray absorption and the formal valences that are customarily associated with Cu in these compounds. But, of course, formal valence is only one factor contributing to the charge environment of Cu atoms. Other factors such as coordination numbers and the relative electronegativities strongly influence the actual charge environment in solids.

2. Experimental details

The x-ray absorption spectra have been collected at room temperature, in the transmission mode at beamlines X-18B, and X-11A of NSLS at Brookhaven National Laboratory, and also at CHESS facility of Cornell University. Si(220) crystals are used to monochromatise the synchrotron radiation. The spectral resolution varied between 2 and 3 eV at 8979 eV, depending mainly on the slit size and the source-to-monochromator distance. Cu-metal spectra have been recorded simultaneously to provide an energy calibration between different beamlines, and between separate runs. The inflection point in the first resolved peak of copper metal has been chosen to be the zero of the energy scale. This is relatively easy to locate and reproduce, since the derivative of the spectrum has a sharp peak at that point. The energy calibration is estimated to be better than 0.25 eV. The spectra were collected at 0.5 eV steps in the region of −50, +50 eV of the absorption edge, and data are collected up to 500 to 1000 eV above the absorption edge to facilitate the background removal and normalisation. The thickness of the samples were monitored from the height of the step jump across the absorption edge, and they were kept close to one absorption length which corresponds to approximately 4 μm or 3.5 mg cm^{-2} for copper atoms.

The trivalent copper compounds were freshly synthesised by mixing KO_2 and CuO powders and heating them at 450 °C for 12 h for $KCuO_2$ and by heating NaO and CuO under the same conditions for $NaCuO_2$. These compounds are known to be air sensitive, and care was taken during the handling and the measurements to avoid air contact.

3. Methodology

We define the characteristic energy for an absorption edge as follows. Let $M^{(n)}$ be the nth moment of the energy with respect to absorption cross section $\mu(E)$ in the region of energy between L_0 and L_1

$$M^{(n)} = \int_{L_0}^{L_1} E^{(n)}\mu(E)\,\mathrm{d}E.$$

The mean energy for this portion of the cross section is

$$\langle E\rangle = M^{(1)}/M^{(0)}.$$

Assuming a step function model for the absorption edge with a step height of μ_0, located at position $S > L_0$, we take

$$\mu(E) = 0 \qquad \text{for } E \leqslant S$$

$$\mu(E) = 1 \qquad \text{for } E > S.$$

Then for this simple model $\langle E\rangle = (L_1 + S)/2$. On the basis of this heuristic step function model, we assign $S = 2\langle E\rangle - L_1$ as the characteristic energy for the absorption edge in question.

Here, E is the energy expressed in electron volts relative to the position of the first inflection point of Cu-metal absorption spectrum, as described above. The lower limit L_0 has been chosen to be -5 eV on this energy scale, below which there is no measurable K-edge absorption for the compounds of interest. The upper limit L_1 is chosen in the range of energy where the extended x-ray absorption fine structure (EXAFS) oscillations for various compounds meet each other somewhere between 35 to 100 eV above the absorption edge. A cubic spline interpolation routine was used to smooth the data and remove the background absorption, and the Romberg procedure for numerical integration was then followed.

Table 1 gives for each compound a mean value $\langle S\rangle$ and a standard deviation $\sigma(S)$ for its characteristic energy over a set of ten values corresponding to the upper limit of integration, L_1, ranging from 30 to 40 eV, in steps of 1 eV. The occurrence of EXAFS features at higher energies produces certain periodic variations of $\langle E\rangle$ (L_1) versus L_1, which we have tried to average out.

One might try to improve the physical significance of the characteristic energy by including some EXAFS features in the analysis or by modelling more complicated shapes. However, our calculations using these ideas yielded characteristic energies that are shifted by about 2 eV to higher values in absolute terms, without significantly changing the relative position of the compounds. Moreover, this type of refinement introduces a certain subjectiveness about the values chosen for the width and the height of the additional features, something that the step function heuristic model avoids.

4. Results and discussion

The compounds selected for this study contain examples of several formal valences for Cu as listed in table 1. Moreover, these compounds also contain Cu surrounded by anions or atoms with different electronegativities. We must therefore expect the net charge on Cu to vary with both its formal valence and the nature of its ligands. Indeed, the characteristic energy S for the Cu K-edge XAS, as just defined, varies in a strongly non-linear way with changing formal valence. We suggest that this characteristic energy provides a measure of the total charge environment of the Cu atoms. The XAS characteristic energy may provide the basis for a scale of non-integral valence, that is useful in the same fashion as that in which the Mössbauer isomer shift scale is used to identify a valence ([9]; for a general discussion see [10]).

The numbers presented in table 1 indicate that the mean characteristic energy $\langle S \rangle$ of the Cu K-edge XAS generally moves to higher energies as the formal valence of Cu increases from +1 to +2 to +3. This formal valence system is based on an assigned oxidation state of −2 for oxygen, following the convention of 'assigning the pair of electrons in the valence bonds to the more electronegative atom and then counting the charge on the quasi-ion' [11, 12]. Figure 1 shows the overall variation of characteristic energies with respect to formal valence. For the compounds $YBa_2Cu_3O_{6.5}$ and $YBa_2Cu_3O_{6.9}$ there are two crystallographically distinct sites for Cu. Our integral definition for the characteristic energy yields information about the average charge environment of these sites. Thus in figure 2 the average formal charge of Cu in $YBa_2Cu_3O_{6.9}$ is plotted as 2.27.

The near-edge part of the Cu K-edge absorption spectra for each compound is presented in figure 2. The spectral curves shown have been normalised to unity, representing the height of the 'step jump' at the absorption edge (μ is the linear absorption coefficient and x is the thickness). The mean characteristic energy for each compound is also shown in figure 2.

To understand the physical significance of the mean characteristic energies, $\langle S \rangle$, that are defined in this work, we must consider the initial and the final states associated with the absorption of the Cu K-edge x-radiation. The bulk of this absorption can be described as associated with one-electron transitions from a localised 1 s state to delocalised kp states. Here a kp state refers to a state with wavevector of magnitude k that has p-wave character with respect to the Cu-atom site. In addition to these strongly delocalised kp states, some transient localised Cu np states with $n \geqslant 4$ may also contribute intensity for primarily pre-edge features. Our definition of the characteristic energy in terms of integrals over the observed cross section curves tends to play down the importance of such relatively sharp, localised features. Thus, to understand the changes in $\langle S \rangle$ it is necessary to obtain some measure of the change in the $1s \rightarrow k$p delocalisation energy as a function of chemical environment of the Cu atom.

In the very simplest terms the positive charge on Cu increases as its valence increases. The higher the positive charge on the Cu atom the more energy required to delocalise an electron away from that atom. Therefore, there is a general trend for higher characteristic energies to be associated with increasing valence. In the next level of approximation, we expect that the characteristic energy changes with the relative degree of ionic or covalent nature for the chemical bonding in any particular compound. Thus, although the measured values for characteristic energies of the Cu compounds studied tend to cluster around values typical of each formal valence +1, +2, or +3, the exact value for the position of the absorption edge is determined by the charge environment of the Cu

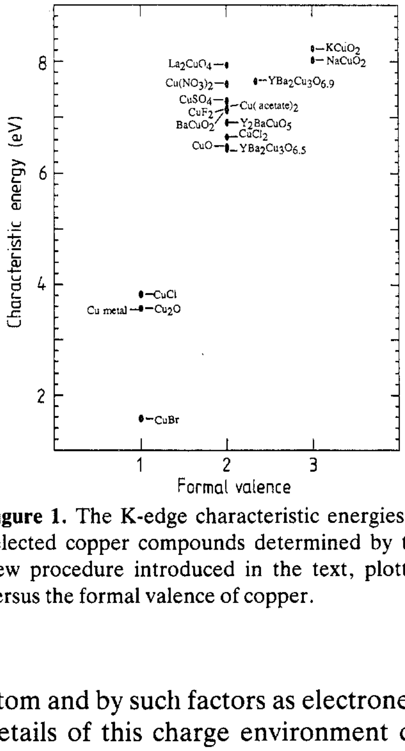

Figure 1. The K-edge characteristic energies of selected copper compounds determined by the new procedure introduced in the text, plotted versus the formal valence of copper.

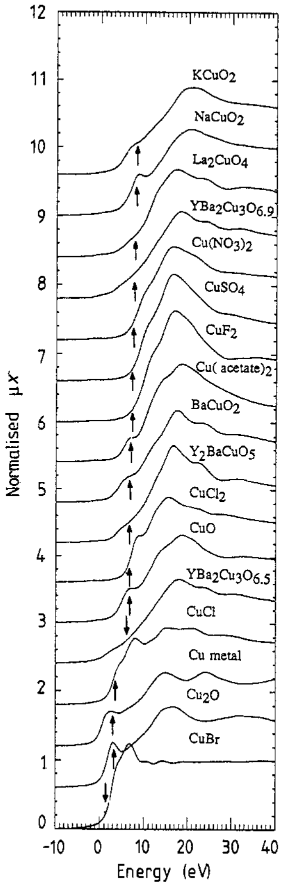

Figure 2. The XANES spectra of the 17 copper compounds studied. Each spectrum is shifted upward by 0.6 normalised units for clarity. The characteristic energy positions are pointed out with arrows for each compound.

atom and by such factors as electronegativities and coordination numbers on which the details of this charge environment depend. More detailed calculations of electronic properties in these compounds should yield charge distributions that can be correlated in detail with the assigned characteristic energies of the Cu K edge.

In summary, a new procedure for assigning a characteristic energy for the Cu K x-ray absorption edge based on a moment analysis of the measured near-edge absorption spectra has been developed. We have demonstrated that these characteristic energies shift consistently toward higher energies with increasing formal Cu valence in a series of 17 Cu compounds for which we have measured and analysed K-edge spectra. The strongly non-linear nature of this correlation between characteristic energy and formal valence is due to the importance of other factors such as coordination number and relative electronegativites in determining the actual charge environment of the Cu atoms in a solid material.

The relative location of the characteristic energy in superconducting Cu oxides on this scale should be helpful in assigning valence to Cu atoms in these important compounds. This procedure can also be extended to other x-ray absorption edges and to other absorbing atoms. The present analysis leads to better and more reliable correlations between x-ray absorption near-edge structure (XANES) features and the idea of a valence for the absorbing atoms.

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References

[1] Alp E E, Shenoy G K, Hinks D G, Capone D W, Soderholm L, Schüttler H-B, Guo J, Ellis D E, Montano P A and Ramanathan M 1987 *Phys. Rev.* B **35** 7199
Alp E E, Soderholm L, Shenoy G K, Hinks D G, Veal B W and Montano P A 1988 *Physica* B **150** 74
Alp E E, Shenoy G K, Soderholm L, Goodman G L, Hinks D G, Veal B W, Montano P A and Ellis D E 1988 *Mater. Res. Soc. Symp. Proc.* **99** 177
Soderholm L, Alp E E, Beno M A, Morss L R, Shenoy G K and Goodman G L 1988 *High Temperature Superconducting Materials* ed. W E Hatfield and J H Miller Jr (New York: Dekker) p 167
[2] Oyanagi H, Ihara H, Matsubara T, Matsushita T, Hirabayashi M, Tokumoto M, Murata K, Terada N, Senzaki K, Yao T, Iwasaki H and Kimura Y 1987 *Japan. J. Appl. Phys.* **26** L1233, L488, L638
[3] Steiner P, Kinsinger V, Sander I, Siegwart B, Hüfner S, Politis C, Hoppe R and Müller H P 1987 *Z. Phys.* B **67** 497
Steiner P, Hüfner S, Kinsinger V, Sander I, Siegwart B, Schmitt H, Schulz R, Junk S, Schwitzgebel G, Gold A, Politis C, Müller H P, Hoppe R, Kemmler-Sack S and Kunz C 1988 *Z. Phys.* B **69** 449
[4] Tranquada J M, Heald S M, Moodenbaugh A and Suenaga M 1987 *Phys. Rev.* B **35** 7187
Heald S, Tranquada H M, Moodenbaugh A R and Xu Youwen 1988 *Phys. Rev.* B **38** 761
[5] Bianconi A, Castellano A C, DeSantis M, Politis C, Marcelli A, Mobilio S and Savoia A 1987 *Z. Phys.* B **67** 307
Bianconi A, Budnick J, Demazeau G, Flank A M, Fontaine A, Lagarde P, Jegoduez J, Revcolevski A, Marcelli A and Verdauguer M 1988 *Physica* C **153–155** 117
[6] Nücker N, Fink J, Fuggle J C, Durham P J and Temmerman W M 1988 *Physica* C **153–155** 119
Fuggle J C, Weijs P J W, Schoorl R, Sawatzky G A, Fink J, Nücker N, Durham P J and Temmerman W M 1988 *Phys. Rev.* B **37** 123
[7] Gol'danskii V I 1964 *Chemical Applications of Mössbauer Spectroscopy* (Princeton, NJ: van Nostrand) p 27
[8] Meitzner G, Via G H, Lytle F W, Fung S C and Sinfelt J H 1988 *J. Phys. Chem.* **92** 2925
[9] Dunlap B D 1987 *Mössbauer Spectroscopy Applied to Inorganic Chemistry* vol 2, ed. G J Long (New York: Plenum) p 481
[10] Shenoy G K and Wagner F E (ed.) 1978 *Mössbauer Isomer Shifts* (Amsterdam: North-Holland)
[11] Douglas B E and McDaniel D H 1965 *Concepts and Models of Inorganic Chemistry* (New York: Blaisdell) pp 42–5
[12] Kjekshus A and Rakke T 1974 *Struct. Bonding* **19** 45–83