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Study of x-ray K-absorption edge in copper compounds

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Abstract. X-ray K-absorption edges in the compounds $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, CuS , CuO and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ have been studied using a Cauchois-type x-ray spectrograph. Peaks observed in the edges have been assigned to the electronic transitions $1s \rightarrow 4s$ and $1s \rightarrow 4p$. The observed energies of the peaks have been compared with the spectroscopic energy levels of the $Z + 1$ ion.

1. Introduction

The study of x-ray absorption edges provides valuable information regarding the electronic structure in various compounds. Several workers including Beeman and Friedman (1939), Hanson and Knight (1956), Agarwal and Verma (1968), Ballal and Mande (1976, 1977), Kawata and Maeda (1978), Prasad *et al* (1977) and Murugesan *et al* (1980) have studied the copper K-absorption edge in compounds and complexes of copper. In the present paper we report the shape of the copper K-absorption edge in the compounds CuO , CuS , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The shapes have been explained on the basis of the $Z + 1$ analogy.

2. Experimental

A Philips sealed x-ray tube with tungsten target was employed as the source of radiation. It was operated at 13 kV and 10 mA. A Cauchois-type bent-crystal spectrograph of diameter 40 cm was used to photograph the spectra. The spectrograph was equipped with well-tested mica crystal whose (100) planes were used as reflecting planes, giving a dispersion of $12.5 \text{ X units mm}^{-1}$. The spectra were obtained on Agfa x-ray photographic films. The samples under study were obtained from E Merck, Darmstadt, Germany. The absorbing screens were prepared by pressing uniformly the fine powder of the samples between two cellophane tapes fixed on an aluminium frame. The optimum thickness of absorber and exposure time for each sample were determined after many trials. Microphotometer records of the spectra were obtained with a magnification $\times 50$ on the MD 100 (Carl Zeiss, West Germany) microphotometer. Measurements on the microphotometer were made using L lines of tungsten as reference. The errors in the measurement as obtained, statistically, lie within $\pm 0.5 \text{ eV}$.

3. Results

The shape of the K-absorption edges of copper in the compounds $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, CuS , CuO and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are given in figure 1. These curves, obtained after eliminating the fluctuations due to grain size and other spurious effects, have been drawn by averaging the results of a very large number of microphotometer traces, recorded, in turns from several spectra obtained for each sample. These curves represent the absorption coefficient as a function of energy.

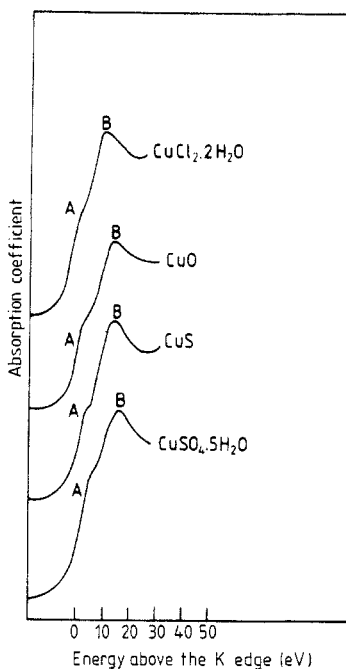


Figure 1. X-ray absorption spectra near the copper K edge of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, CuO , CuS and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

We have observed two peaks A and B in the K edge of compounds. The energy value of the copper K-absorption edge in metallic copper was used as the zero point of a new energy scale for the present compounds. The energy value is 8980.85 eV as measured by us. Our measured value agrees fairly well with 8980.35 eV given by Bearden (1967).

4. Discussion

The well known $Z + 1$ analogy (Shore and Menzel 1968) can be used in order to understand the peaks, A and B. The analogy is useful as it can reveal the energy position of excited states. In this analogy it has been assumed that for inner shell excitation the one-electron model is good for the first approximation. In the x-ray absorption process the hole created due to the absorption of the x-ray photon in the 1s level can be simulated by adding one positive charge to the nuclear charge of the absorbing ion. The number of electrons in valence orbitals should be increased by one. Therefore, the final energies

of the excited levels of an ion having atomic number Z can be taken as that of an ion having atomic number $Z + 1$. We further assume that the first excited states are atomic in character and strongly localised on the absorbing ion. According to Shulman *et al* (1976) this assumption is most relevant to the ionic compounds particularly in the energy region 40 eV of the absorption threshold. According to them the transitions are one-electron in character i.e.

$$[1s^2 2s^2 2p^6 3s^2 3p^6] 3d^n (L, S) \rightarrow [1s^2 2s^2 2p^6 3s^2 3p^6] 3d^{n-1} n'l' (L', S).$$

During a transition, the orbital quantum number L changes, but the spin quantum number S does not change. Furthermore, Shulman *et al* have also shown that the multiplet state of the unfilled d shell, $d^n(L, S)$ does not change in the transition as the transitions are for a single electron. We have used the atomic spectroscopic tables (Moore 1952) of the element $Z + 1$ to calculate the final state energies of the fully relaxed ion.

In the present work the Cu^{2+} excited states $1s^1 2s^2 2p^6 3s^2 3p^6 3d^9 nl$ have been compared with the excited states $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 n'l'$ of Zn^{2+} . The separation between the peaks A and B as can be seen from table 1 varies from 7.35 to 8 eV. The atomic

Table 1. Energy positions of peaks A and B.

Compound	Peak A $1s \rightarrow 4s$ (eV)	Peak B $1s \rightarrow 4p$ (eV)	Experimental ($4s-4p$) (eV)	($4s-4p$) [†] Zn^{2+} ion (eV)	($4s-4p$) [†] Cu^{2+} ion (eV)
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	8986.85	8994.85	8.00		
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	8987.00	8994.60	7.60		
CuO	8987.35	8994.85	7.50	7.90 [†]	7.30 [†]
CuS	8987.85	8995.20	7.35		

[†] This value is taken from Moore's (1952) table.

tables (Moore 1952) for the free Zn^{2+} ion give a 7.9 eV separation of the $4s-4p$ orbitals. It can be seen from the table that the separation of the $4s-4p$ orbitals for the compound $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ agrees fairly well with that of Zn^{2+} . However, the separation for the compounds CuS, CuO and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is lower than that of Zn^{2+} . According to Shulman *et al* this is to be expected as CuS, CuO and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are not highly ionic compounds. We have also given in table 1 the separation of the $4s-4p$ orbitals for the free Cu^{2+} ion. This value is less than that for the compounds under study. Since the compounds under study are not highly ionic, the value for the separation of the $4s-4p$ orbitals should have been less than that of Cu^{2+} . Considering the experimental inaccuracies that may be involved in the determination of A and B, we may attribute the weak peak A due to the forbidden transition $1s \rightarrow 4s$ and the strong peak B to the allowed transition $1s \rightarrow 4p$. According to Shulman *et al* the forbidden transition $1s \rightarrow 4s$ is possible due to vibronic mixing of $4s$ orbitals with $4p$ orbitals.

The peak A cannot be assigned to the $1s \rightarrow 3d$ transition because in that case the separation between the peaks A and B must be of the order of 16.3 eV. (Separation of the $3d$ and $4p$ orbitals for Zn^{2+} is 16.3 eV.)

We might mention here that we have not observed the weak peak due to the forbidden transition $1s \rightarrow 3d$. Perhaps this peak might have been suppressed in the background of

the x-ray film. The present studies show that the $Z + 1$ analogy can be successfully applied to reveal the energy positions of the excited states.

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