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Copper K-edge XANES of Cu(I) and Cu(II) oxide mixtures

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Abstract. XAFS at the copper K-edge has been recorded for cuprous oxide and cupric oxide separately and also for a mixture of the two in a specific ratio, at the XAFS beam line at SSRL. The normalized $\mu(E)$ data obtained for the two oxides, i.e., Cu(I) and Cu(II) oxides separately was linearly combined to fit the normalized $\mu(E)$ data of the mixture using the Linear Combination Fitting (LCF) method. The values obtained for the statistical goodness-of-fit parameters, R-factor and chi-square, show that the fit is reasonably good. This procedure yielded the percentage of the oxides in the mixture which was found to be nearly the same as the actual percentage which was used to prepare the mixture. Another method based on the analysis of normalized difference absorption edge spectra has also been used to quantitatively determine the percentage of the two copper species in the mixture. The LCF method is, however, found to be better than the normalized difference absorption edge analysis.

Keywords: Cu K-edge XANES, copper oxide mixture, LCF, Difference spectra

PACS: 78.70.Dm.

1. Introduction

In the process of structural characterization of a sample, containing two or more species of an element in different oxidation states, it becomes important to know the proportion of the different oxidation states in the sample. In another case, a sample containing an element in one oxidation state may get converted partially into another oxidation state due to some reaction and the percentage of the original oxidation state and the converted oxidation state, present in the sample after the reaction, is to be determined. In yet another case, an organometallic complex may contain a metal in different oxidation states at different nuclear sites. Such problems can be solved with the help of X-ray absorption spectroscopy (XAS) because this spectroscopy is a direct probe of the oxidation state and of the local structural and electronic environment of the atom absorbing the X-rays. In the present work, we have chosen Cu(I) oxide and Cu(II) oxide as the two species and have taken their X-ray absorption spectra separately. The two oxides have been mixed in a definite proportion to make a mixture and the X-ray absorption spectra of this sample have also been taken under similar conditions. The data have been analyzed to yield the proportions of the two oxides in the sample by two different methods, namely, linear combination fitting (LCF) [1-9] and normalized difference absorption edge analysis [10-15].

2. Experimental

Commercially available 99.99% pure Cu_2O and CuO powders were mixed in the ratio of 3:1 by weight. Absorption screens were prepared of the finely powdered pure Cu_2O , pure CuO and their mixture. The X-ray absorption spectra were recorded at XAFS beam line of Stanford Synchrotron Radiation Laboratory (SSRL) for these absorption screens. Cu metal foil spectra were recorded simultaneously, for calibration, in each case using three ionization chambers. The data were imported into the XAFS computer software *Athena* [16]. The normalized spectra of Cu metal foil, CuO , Cu_2O and the mixture are shown in figure 1.

3. Data analysis

We have used two methods for extracting the information about the proportion of the CuO and Cu₂O in the mixture, namely, linear combination fitting (LCF) and normalized difference absorption edge analysis. In the LCF method, which has been used by several authors [1-9], the X-ray absorption spectrum is modeled by least squares fitting using a linear combination (LCF) of known species to fit an unknown spectrum. In this method, one determines the proportions of the spectra for selected standards that, when summed, yield the least squares fit to the spectrum for an unknown sample. The underlying principle of this method is the additive nature of the absorption from each species in the sample. It can be applied to XANES, derivative XANES or EXAFS spectra. The total absorption coefficient can be written as a sum of the chemical forms or species. Mathematically, $\text{Model} = \sum_i f_i (\text{STD}_i)$, where Model represents the least square fit to the sample spectrum over a selected energy range, and f_i represents the scaling factors applied to each spectrum of the corresponding standard (STD_i) across the energy range of the fit. The scaling factor obtained from LCF represents the fraction of each standard species within the unknown sample. Linear combination fitting subroutines are available in XAS data analysis program like *Athena* and we have used the same program for the present work. In the present analysis, linear combination fitting (LCF) has been carried out in the normalized $\mu(E)$ spectrum of the mixture, using the reference spectra from -20 eV to 30 eV. The relative weights of the components of mixture are allowed to vary from 0 to 1. However, the absorption edge energies are kept fixed during the analysis.

The other method used by us, i.e., the normalized difference absorption edge analysis, has been outlined by Kau. *et al.* This method is based on the characteristic features due to 1s-4p electric dipole allowed transitions in the copper K-edge spectra (figure 1). Cu(I) compounds exhibit a low energy peak maximum at ~ 8984 eV, while Cu(II) compounds exhibit only a broad low energy tail in the region below 8985 eV. Thus, the appearance of a peak below 8985 eV indicates the presence of Cu(I) in the sample [10]. In Cu(II) compounds the peak is shifted to ~ 8987 eV and appears as a shoulder. This shoulder and an intense band at 8994-9002 indicates the existence of Cu(II) species [8]. In order to quantitatively estimate the amount of Cu₂O present, the procedure involves subtraction of normalized absorption edge spectrum of CuO from that of Cu₂O. This results in characteristic derivative shaped signal with a positive peak at 8983-8984 eV and a broad negative feature at 8990-9000 eV. The energy and shape of the positive peak can provide insight into the type of Cu present and the height of the peak allows quantitation of the amount of cuprous ion present. Normalized

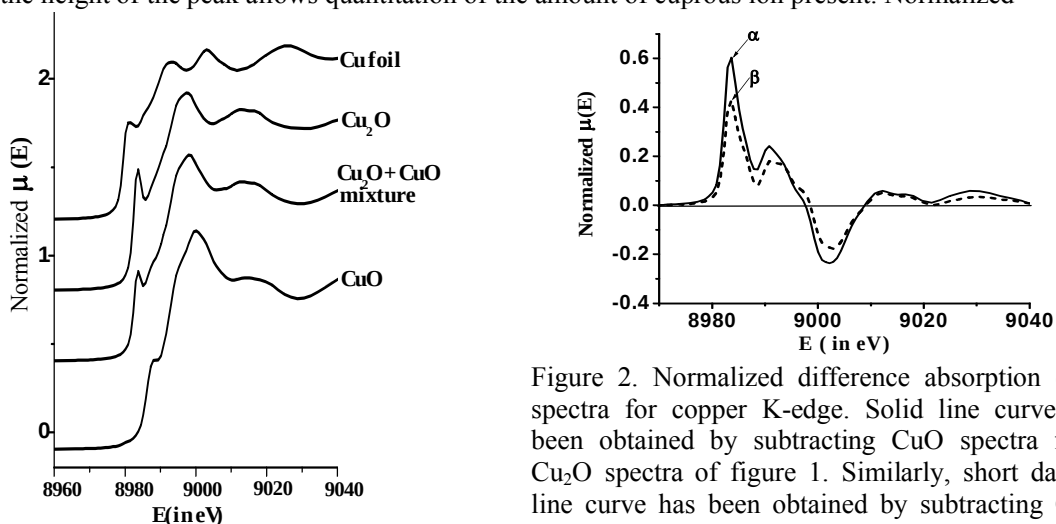


Figure 1. Normalized copper K-edge XANES spectra for Cu metal foil, CuO, Cu₂O and a mixture of Cu₂O+CuO in the ratio 3:1 by weight.

Figure 2. Normalized difference absorption edge spectra for copper K-edge. Solid line curve has been obtained by subtracting CuO spectra from Cu₂O spectra of figure 1. Similarly, short dashed line curve has been obtained by subtracting CuO spectra from the spectra of mixture of Cu₂O + CuO of figure 1. The ratio of the height of positive peak β to that of peak α gives the proportion of Cu(I) in the mixture.

difference absorption edge spectra for copper K-edge is shown in figure 2. In this figure the height of the positive peak (α) corresponds to 100% Cu_2O and 0% CuO . The quantity of Cu_2O present in the mixture can then be estimated from the height of the positive peak (β) in the normalized difference absorption edge spectra of the mixture and CuO .

4. Results and Discussions

The results of LC fitting are shown in figure 3. This figure also shows the fractions of the Cu_2O and CuO making up the fitted spectra. The percentage of Cu_2O and CuO in the mixture, as determined from LCF method is 73% and 27% respectively with an error of $\pm 2\%$, while the values obtained from normalized difference absorption edge analysis are 71% and 29% with an error of $\pm 5\%$. In the case of LCF method, the values obtained for the statistical goodness-of-fit parameters, R-factor and chi-square, are 0.000166 and 0.02309 respectively. The goodness-of-fit can also be seen from the little difference between the experimental data and LC fitted data plotted as difference curve in figure 3. It may be remembered that the mixture was prepared by mixing Cu_2O and CuO in the ratio of 3:1 by weight. Hence, both the methods used by us have yielded correct results within the limits of experimental error. However, we find that the LCF method is better than the normalized difference absorption edge analysis because the error is less in LCF than the other method.

While performing LCF we have started with the fitting range from -20 eV to 30 eV and varied the higher limit in the steps of 10 eV upto 100 eV. We have found that the percentage of Cu_2O present as determined from the LC fitting does not vary. We have further varied the higher limit in the steps of 100 eV upto 400 eV and still no change in the result was noticed. Hence, in our case the LCF has been found to be successful not only in XANES region but also in EXAFS region. In this regard, it is worth mentioning that Wang *et.al.* [17] have shown that in the Principal Component Analysis (PCA) method also, EXAFS range can be used instead of XANES, if the absorbing atom is spectroscopically silent.

In figures 4 and 5, are shown (solid line) the $\chi(k)$ and $|\chi(R)|$ spectra of the mixture, respectively,

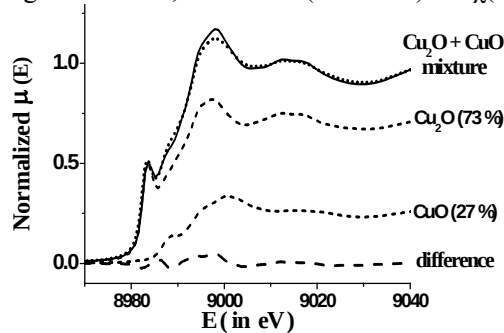


Figure 3. Results of the LCF for copper K-edge XANES spectra of mixture of Cu_2O and CuO . Solid and dotted lines denote experimental and LC fit data respectively. Fractions of Cu_2O and CuO making up the fitted spectra are shown by short dashed line. The goodness-of-fit between experimental data and the LC fit data can be seen from the little difference between the two data, plotted as dashed line curve.

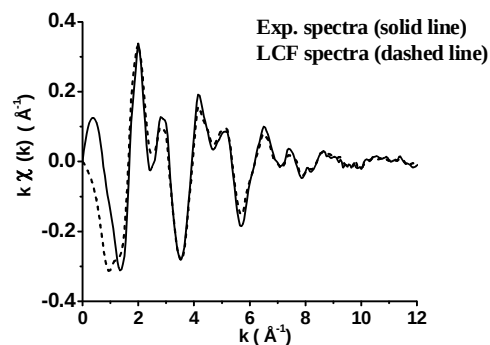


Figure 4. k^1 -weighted $\chi(k)$ spectra of the mixture of Cu_2O and CuO . The $\chi(k)$ data is obtained from experimental $\mu(E)$ data (solid line) and from $\mu(E)$ data obtained after LC fitting (dashed line).

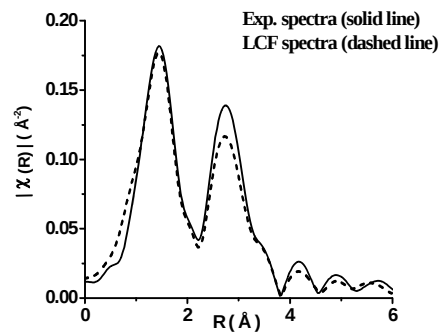


Figure 5. Fourier transform of the $\chi(k)$ spectra shown in figure 4.

as obtained from the experimental $\mu(E)$ spectra. From the $\mu(E)$ spectra obtained after LCF procedure, the $\chi(k)$ and $|\chi(R)|$ spectra have been obtained and are also shown in figures 4 and 5 by dashed line. It can be seen from these figures that the agreement between the spectra in both k and R spaces is found to be good. It may be mentioned here that no attempt has been made to analyze the EXAFS spectra of the mixture.

The commonly used method for the analysis of mixtures is principal component analysis (PCA) method which provides a statistical basis for choosing the number of standards to be included in the fitting [17-20]. It is a valuable complementary tool for LCF as it helps to avoid an excessive number of standards in a fit. The other X-ray spectroscopic methods in use are residual phase analysis (RPA), multiple dataset (MDS) fit method, target transformation method [21] and derivative spectra methods [22]. In the present work as the standards to be used for analysis were known, LCF method proved to be quite successful and better than the normalized difference absorption edge analysis. The LCF method is also useful in the case where more than two components are present in the sample [8]. However, the LCF method needs a more complete investigation in oxide based materials and a detailed study is being planned.

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