Cu K-absorption edge study of cuprate superconductors†

G SANKAR*, G U KULKARNI and K R KANNAN
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

MS received 28 April 1989

Abstract. Cu K-absorption edges of YBa$_2$Cu$_3$O$_{6.9}$, Tl$_2$CaBa$_2$Cu$_3$O$_4$ and Bi$_2$CaSr$_2$Cu$_2$O$_8$ show similar features. Copper is mainly in the 2+ state in these cuprates suggesting the likely presence of oxygen holes.

Keywords. Superconductivity; layered cuprates.

PACS No. 74.70

K-absorption edge spectroscopy of copper has been employed to investigate the new cuprate superconductors by a few workers. The general conclusion is that there is no Cu$^{3+}$ in YBa$_2$Cu$_3$O$_7$ (Chakraverty et al 1988; Fuggle et al 1988; Rao 1988; Rao et al 1989a). These measurements also show a feature at 21 eV above the absorption edge (taken with respect to the 1s – 3d pre-edge shoulder) which was suspected for sometime to be due to Cu$^{3+}$ by some workers. We have investigated Cu K-edge spectra of cuprate superconductors belonging to different families to see commonalities, if any, and to understand the important features.

YBa$_2$Cu$_3$O$_{6.9}$, Tl$_2$CaBa$_2$Cu$_3$O$_4$ and Bi$_2$CaSr$_2$Cu$_2$O$_8$ were prepared by the procedures described in the literature. Cu K-edge X-ray absorption spectra were recorded using a commercially available X-ray absorption spectrometer (Rigaku, Japan) attached to a 12 kW rotating anode X-ray generator with a copper target and Ge(333) was employed as the monochromatizing crystal. The spectrometer was calibrated using the characteristic emission lines of copper target $K\alpha_1$ or $K\alpha_2$ appearing at 804778 and 802778 keV. The energy resolution at this energy was found to be better than 2 eV. The appropriate amount of powdered samples was sandwiched between adhesive tapes for the Cu K-edge absorption measurement. Measurements were carried out between 8.97 and 9.02 keV in steps of 0.1 eV and repeated several times to confirm the presence of various features appearing in the spectra.

In figure 1 we show the normalized Cu K-edge spectra of the reference materials Cu metal, Cu$_2$O and CuO representing Cu$^0$, Cu$^{1+}$ and Cu$^{2+}$ oxidation states respectively. The spectral features in these systems clearly show expected variation with the oxidation state. In CuO, the pre-edge feature, generally considered to be due to the 1s – 3d transition, appears at 8.982 keV followed by a main peak at 8.997 keV with a shoulder around 8.987 keV. Cu$_2$O, on the other hand, shows a well-defined

† Contribution No 616 from the Solid State and Structural Chemistry Unit.
* To whom correspondence should be addressed.
feature at 8.983 keV due to a symmetry related transition, followed by the main peak. The 8.983 keV feature is characteristic of Cu$^{1+}$ species in oxide systems while the shoulder at 8.987 keV (of CuO) has been used to characterize the Cu$^{2+}$ state (Rao et al 1989b; Tranquada et al 1988).

In figure 2 we show XANES of $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$, $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_{8+\delta}$ and $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{8+\delta}$. All these cuprates show feature at 8.987 keV characteristic of Cu$^{2+}$ as in CuO. The main peak position also clearly suggests that the predominant oxidation state of Cu in these high $T_c$ cuprates is $2^+$. There is no evidence for Cu$^{3+}$ in any of these cuprates. The pre-edge intensity is however slightly different compared to CuO. A systematic investigation of XANES of mixtures of Cu$_2$O and CuO has shown that presence of 50% or more of Cu$_2$O in the mixture is necessary to show the feature due to Cu$^{1+}$ along with that of Cu$^{2+}$. Lower than 50% Cu$_2$O does not show pre-edge feature at 8.983 keV. We are therefore not able to rule out the presence of Cu$^{1+}$ in these cuprate systems. However, the concentration of Cu$^{1+}$ in these cuprates is less than that in Pb$_2$Sr$_2$Ca$_{1-x}$Ln$_x$Cu$_3$O$_{8+\delta}$ where the feature at 8.983 keV due to Cu$^{1+}$ clearly shows up in the K-edge spectrum (Rao et al 1989b). The absence of Cu$^{3+}$ and direct evidence for only Cu$^{2+}$ in these cuprates suggests the presence of oxygen holes (Chakraverty et al 1988; Rao 1988).

Recent reports in the literature have proposed different explanations regarding the appearance of the 21 eV feature (measured with respect to the pre-edge feature). One of the explanations is that this feature is due to Cu occupying the Y site (anti-site). This has been ruled out by an orientation dependence study and also based on configuration interaction calculations (Sarma 1988). A similar feature is seen at 5–6 eV from the main absorption peak in simple transition metal halides (Stern 1982). This has been suggested as due to shake-up satellites associated with the main absorption. Our XANES measurement on simple oxides showed a similar feature at higher energy,
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8.970 8.991 9.012
Energy (KeV)

Figure 2. Normalized Cu K-edge XANES of high Tc superconducting oxides: YBa$_2$Cu$_3$O$_{6.9}$, Tl$_2$CaBa$_2$Cu$_{2+6}$, and Bi$_2$CaSr$_2$Cu$_{2+6}$.

falling well below the EXAFS region which starts from about 40 eV from the absorption edge. This feature probably therefore arises from satellite structure arising from configuration interaction (Sarma 1988).

Acknowledgement

The authors thank Prof C N R Rao for suggesting the problem and guidance. Their thanks are due to the Department of Science and Technology for support of this research.

References