CHAPTER 5

COPPER K-ABSORPTION EDGE STRUCTURE
5.1. INTRODUCTION

There has been a considerable amount of work done on the X-ray absorption near-edge spectra (XANES) of the high-temperature superconductors with the hope that such measurements will provide detailed information about the electronic structure of the constituent metal ions. The most widely studied ion has been the copper ion $^{1-8}$. Despite such wide interest in the problem and excellent reproducibility of spectra in a given system, there has been no commonly accepted interpretation of the XANES features. The major controversy is in the identification of the ubiquitous feature at about 6 eV above the main absorption peak in the XANES spectra of polycrystalline samples of all the members of the superconducting family of the copper oxides. This feature was first discussed by Alp et al.$^1$ (peak C for example in Figure 5.1a). Considerable theoretical as well as experimental efforts have been expended in resolving this problem. One electron excitation calculations$^1$ (see Figure 5.1a) for $\text{La}_2\text{CuO}_4$ do not show the presence of this feature. Alp et al.$^1$ have suggested that this feature must be associated with the presence of Cu$^{3+}$ ions. Subsequent single crystal studies by Heald et al.$^7$ show two strong absorption features, $B_1$ and $B_2$ (shown in Figure 5.1b) which may be associated with the $1s \rightarrow 4p\pi$ and $1s \rightarrow 4p\sigma$ transitions which have energies in agreement with the calculations of Alp et al.$^1$. The feature C is seen as a shoulder ($B_4$) to the main feature $B_2$ for the polarization parallel to the ab plane. The origin of this feature has not been commented upon. It has been pointed out$^8$ that core-level spectroscopies cannot give information about the valence state when there is a strong configuration mixing between initial and final states. By including such configuration interactions in the Anderson impurity Hamiltonian model, Sarma$^8$ has calculated the XPS core Cu 2p$^{3/2}$ as well as the Cu K-edge XANES spectra and has suggested that the feature C is to be associated with a Cu d$^9$
Figure 5.1: (a) Polycrystalline Cu K-edge XANES of La$_2$CuO$_4$ (from Ref. 1) showing the main features (full line); one electron theory calculation of XANES (dotted line) from Ref. 1; configuration interaction calculation of Sarma (dashed line) from Ref. 8. (b) Single crystal XANES spectra of La$_2$CuO$_4$ for $e_{\pi\pi}$ (full line) and for $e_{\perp\pi}$ (dotted line)
configuration, while the feature B is to be associated with a $d^{10}$ configuration in much the same manner as Cu 2$p_{3/2}$ 933 eV band and 942 eV satellite band in the core-level XPS studies. This study has the merit that it attempts to correlate XPS and XANES features.

The X-ray photoelectron study$^9$$^{11}$ of the superconducting copper oxides have been concentrated on the valence band as well as the core Cu 2$p_{3/2}$ region and the oxygen 1$s$ level. Unlike the XANES studies the XPS studies have the disadvantage that it is highly surface specific. The degree of reproducibility of XPS features have thus been entirely unsatisfactory especially with respect to those associated with oxygen ions because of the possibility of the presence of hydroxyl or carbonate groups by contamination.

A completely different approach is that followed by Lytle et al$^4$ who have interpreted the XANES region in terms of a backscattering model from nearby atoms and identified the higher energy features with different Cu-O bond distances. In this model the features at B, C and D (Figure 5.1a) are related to the distances at 3.5, 2.6 and 1.9 Å respectively. The 2.6 Å distance has been related to the occupation of the copper ions in the La sites in La$_2$CuO$_4$.

One of the major shortcomings in the effort to understand the XANES features is the failure to examine the obvious chemical aspect, namely the examination of other ternary copper oxides which have structural features common to the superconducting family of oxides. The family of copper oxides themselves exhibit a fascinating diversity of structures that have been very systematically studied before the discovery of superconductivity in the copper oxide system by Bednorz and Müller$^{12}$, by the pioneering efforts of Müller-Buschbaum and his coworkers$^{13}$ as well as Raveau and coworkers$^{14,15}$. Sreedhar and Ganguly$^{16}$ and Ganguly et al$^{17}$ have carried out various studies such as magnetic
susceptibility and electron spin resonance on such oxides as part of effort to understand the properties of the non-superconducting copper oxides in relation to the properties of the superconductors. In this Chapter we present the results of our XANES as well as XPS investigations on a series of copper oxides which have structural features common to those of the superconducting family of copper oxides.

5.2 RESULTS AND DISCUSSION
The XANES from the Cu K-edge region of several compounds are shown in Figures 5.2-5. In Figure 5.2, K-edge absorption spectra of copper in Cu, Cu2O, CuO, La2CuO4, YBa2Cu3O7, La1.85Sr0.15CuO4, Tl2Ba2Ca2Cu3O10 and Tl0.2V0.8Sr2(Ca0.8Y0.2)Cu2Oy are presented. Some of the spectra reported here are very similar to those reported earlier in the literature 1-7.

In Figure 5.3, we show the XANES spectra of La2Li0.5Cu0.5O4 and Ba4NaCuO4(CO3)9 and in Figure 5.4 the profiles of K-edges in Nd2CuO4, CuAl2O4, Y2BaCuO5, Y2Cu2O5 and Sr2CuWO4 are given. In Figure 5.5 are shown the K-edges of copper in SrCuO2, MgCu2O3, Ca2CuO3 and CaCu3Ti4O12. Nd2CuO4 has copper ions in a square-planar coordination with the Cu-O distance of ~1.98 Å. The square-planar CuO4 units share corners to form a two-dimensional network in this structure. The main difference from La2CuO4 is that in this compound there are no Cu-O bonds along the c axis. Nd2CuO4 is therefore an ideal model for a pure square-planar array of corner linked CuO4 units. From various studies like X-ray and electron diffraction, magnetic susceptibility, EPR and Li NMR on La2Li0.5BO.5O4 with B = Co, Ni, Cu, it has been concluded that the B ions are in trivalent state including Cu. The most important result has been obtained from the magnetic susceptibility and Li NMR studies. When B = Cu or Co the system is diamagnetic; when B = Ni, the Curie constant is
Figure 5.2: Cu K-edge spectra in copper metal, Cu$_2$O, CuO, La$_2$CuO$_4$, YBa$_2$Cu$_3$O$_{7-\delta}$, La$_{1.85}$Sr$_{0.15}$CuO$_4$, Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ and Tl$_{0.2}$V$_{0.8}$Sr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_y$
Figure 5.3: Cu K-edge spectra in La$_2$Li$_{0.5}$Cu$_{0.5}$O$_4$ and Ba$_4$NaCuO$_4$(CO$_3$)$_2$
Figure 5.4: Cu K-edge spectra in Nd$_2$CuO$_4$, CuAl$_2$O$_4$, Y$_2$BaCuO$_5$, Y$_2$Cu$_2$O$_5$ and Sr$_2$CuWO$_4$
Figure 5.5: Cu K-edge spectra in SrCuO$_2$, MgCu$_2$O$_3$, Ca$_2$CuO$_3$ and CaCu$_3$Ti$_4$O$_{12}$
typical of one unpaired electron as expected for low-spin Ni$^{3+}$ ions ($t_{2g}^6$, $e_g^1$) and the EPR signal characteristic of Li$^{3+}$ ions as in fluorides. The Li NMR does not show any change in the chemical shift on changing B. Since electron diffraction studies show evidence for cation ordering, the constancy of the NMR chemical shift suggests that the Li environment is identical in all the compounds. This could only happen when there are no holes on the oxygen and all the B ions are in the trivalent state. La$_2$Li$_{0.5}$Cu$_{0.5}$O$_4$ is therefore a suitable model for the study of the absorption edge of isolated Cu$^{3+}$ ions. CaCu$_3$Ti$_4$O$_{12}$ has the copper ions located at the A site with twelve oxygen neighbours with three sets of Cu-O distances (1.96x4, 2.78x4 and 3.191x4 Å) so that this compound is ideally suited for testing the model of Lytle et al. The positions of the peaks expected from the ruler of Lytle et al are indicated by arrows in the Figure 5.5.

We see that the XANES of Nd$_2$CuO$_4$ is very similar to that of La$_2$CuO$_4$ and YBa$_2$Cu$_3$O$_7$ shown in Figure 5.2. The XANES of La$_2$Li$_{0.5}$Cu$_{0.5}$O$_4$ is very different and the main absorption peak seems to have shifted by about 3 eV relative to La$_2$CuO$_4$. The spectra of La$_2$Li$_{0.5}$Cu$_{0.5}$O$_4$ bears a striking similarity to the reported spectra of KCuO$_2$ in which the copper ions are expected to be in the trivalent state. In the XANES spectra of CaCu$_3$Ti$_4$O$_{12}$ we do not see any correlation between the features and those expected from the model of Lytle et al.

In Figure 5.4 we show the XANES spectra of CuAl$_2$O$_4$ in which the copper ions are in tetrahedral coordination; Y$_2$BaCuO$_5$ in which the copper ions are in isolated square-pyramidal coordination with the copper-oxygen distance having ~ 2.05 Å; Y$_2$Cu$_2$O$_5$ in which the Cu$^{2+}$ ions have a strong tetrahedral component of distortion; and Sr$_2$CuWO$_6$ in which the copper ions are in isolated octahedral environment. All these compounds have a Curie constant (calculated from the temperature dependence of the magnetic susceptibility at high temperatures)
close to $1.73 \mu B$. In all these compounds the feature C is either absent or is very weak. We note that CuAl$_2$O$_4$ and Y$_2$Cu$_2$O$_5$ show a relatively high intensity of the feature P indicated in Figure 5.1 which is generally associated with a $1s \rightarrow 3d$ transition$^{37}$.

In Figure 5.5 we show the XANES spectra of SrCuO$_2$, MgCu$_2$O$_3$, Ca$_2$CuO$_3$ and CaCu$_3$Ti$_4$O$_{12}$. In SrCuO$_2$ there are$^{32}$ pairs of edge-shared square-planar CuO$_4$ units forming chains along one direction in a manner similar to that in some of the superconducting family of copper oxides$^{33}$. In MgCu$_2$O$_3$ the structure$^{34}$ has features similar to that of SrCuO$_2$ except that the copper ions are in octahedral coordination with two oxygen ions at $1.94 \text{Å}$, two at $2.01 \text{Å}$ and one each at $2.53$ and $2.76 \text{Å}$. The Cu-O linkage along the chain involves long Cu-O distances. In Ca$_2$CuO$_3$ the square-planar CuO$_4$ units (two oxygen atoms at $1.89 \text{Å}$ and two at $1.96 \text{Å}$) share corners along one direction to form a chain$^{35}$ just as the Cu (I) site ions in$^{36}$ YBa$_2$Cu$_3$O$_7$.

Since the relative intensities of the main and satellite features of the XPS signals from the core levels are prominent, we have recorded the Cu$^{2p_{3/2}}$ XPS spectra of some of the copper compounds studied by XANES. The results are shown in Figure 5.6.

In the forthcoming few paragraphs, we shall briefly review the interpretations of the XANES spectra as discussed in the literature. This has been done for the sake of highlighting the essential features of the various interpretations. The purpose is to focus on the possible identity of the feature C shown in Figure 5.1. As mentioned earlier we will find that not all these interpretations are consistent with one another.

The X-ray K-edge absorption spectra of copper ions show shoulders (see Figure 5.1) on the absorption edge (features B and C) as well as pre-absorption edge feature P. Also there are other features in a range within 50 eV above the absorption threshold (D). The early analysis of these features were based on the
Figure 5.6: XPS Cu$_{2p3/2}$ spectra of CuO and some ternary copper (II) oxides
The assumption that correlation effects are negligible compared to the 1s binding energies and the state to which the 1s electron is excited is atomic in character and localized on the metal ion\(^{38}\). The final state of the ion with atomic number \(Z\) is expected to be similar to that of the corresponding \((Z+1)\) ion with the same charge but having the 1s shell full. Thus atomic spectroscopic splittings may be used for the analyses of the XANES region. In covalent compounds the ligands, however, have a significant influence and introduce additional ligand-to-atom shakedown transitions that are not possible in atomic spectra. Thus when a 1s electron is removed the ground state of the relaxed wavefunction changes from \(d^9\) to \(d^{10}\) with holes introduced on the ligand by a ligand-to-metal charge transfer. Such charge transfer states could have energies around 6-8 eV lower than the main transitions as demonstrated by Bair and Goddard\(^{38}\). The lowering of energy is due to the increased screening of the core hole when an electron is transferred from the ligand to the d shell of the cation.

The assignment of the features especially near the band edge seemed to have been satisfactorily resolved with the introduction of linearly polarized synchrotron radiation for the study of polarization in the XANES transitions in single crystals\(^{39,40}\). Such assignments becomes more facile in compounds of Cu\(^{2+}\) with axial symmetry. The 4p states could be split into 4p\(\sigma\) or 4p\(\pi\) molecular orbital states in such a symmetry and could be of the order of 4-5 eV\(^{42,43}\). The calculations of Alp et al.\(^1\) show that this splitting is of the order of 5eV in La\(_2\)CuO\(_4\). Such splitting cannot account for the feature C. It is because of this fact that Alp et al. attributed the feature at C to the presence of Cu\(^{3+}\) ions. The splitting between the 4p\(\pi\) and 4p\(\sigma\) levels are expected to decrease in clusters with tetrahedral or octahedral symmetries\(^{38}\).

The pre-absorption edge features can then be assigned on the
basis of the conventional interpretation of the XANES region. The pre-absorption edge feature P in Figure 5.1 have been ascribed\textsuperscript{20,37,38} to 1s to 3d transitions which are dipole forbidden but quadrupole allowed. The shoulder on the absorption edge around 7-10 eV relative to the 1s to 3d transition (features A in Figure 5.1 for the single crystal results of Heald \textit{et al.} on La\textsubscript{1.85}Sr\textsubscript{0.15}CuO\textsubscript{4} ) is likely to be due to 1s to 4p\textsuperscript{7,38} shakedown transition. The main peak is therefore to be associated with 1s to 4p transition and is expected to yield information on the p-type unoccupied states. The features B\textsubscript{1} and B\textsubscript{2} could relate to the direct 1s to 4p\textpi and 1s to 4p\sigma transitions.

The relative intensities of the main and shakedown transitions are expected to be in the ratio

$$1:(<3d / L^1>)^2 \quad (5.1)$$

where the term \((<3d / L^1>)\) is the overlap of the ground state 3d orbital with the excited state \(L^1\) ligand orbital with one hole. Such a ratio really implies that there are two distinct states into which transitions can be effected: The one electron excitation which involves the initial state and the other a multielectron excitation which involves the energies in the final state after the shakedown or charge-transfer process.

The main ambiguity lies in the interpretation of the features at higher energies. The next series of transitions should involve the closely spaced 5s, 4d, 5p etc. levels which should lie about 10 eV above the 1s to 4p transition or around 30 eV above the 1s to 3d transition.\textsuperscript{38} Backscattering effects due to other ions not included in the first coordination sphere of the central ion are usually dominant\textsuperscript{1,6} in the region D. Thus an unequivocal identification becomes difficult in this region especially because the relative intensities of the 1s to 5p main and shakedown transitions are difficult to estimate.
The results of Heald et al.\(^7\) (Figure 5.1b) support at least qualitatively the calculations of Alp et al (Figure 5.1a). In these calculations, the feature \(B_1\) in the spectra of Heald et al.\(^7\) (Figure 5.1) is to be attributed to final states composed of \(Cu^{2+}\) axial 4p states (feature A in the calculations of Alp et al.\(^1\) in Figure 5.1a) with weak scattering from oxygen neighbours. Similarly the feature \(B_2\) in the single crystal data may be correlated with the feature B in the calculations associated with the equatorial 4p states.

The shoulders \(B_3\) and \(B_4\) (Figure 5.1b) in the single crystal work of Heald et al.\(^7\) have not been commented upon. In these crystal studies of Kosugi et al.\(^40\) such shoulders are also observed and have been attributed to 1s to 5p\(\pi\) or 5p\(\sigma\) transitions which are expected to show the same kind of anisotropies as the 1s to 4p transitions. The relative position of these 5p energy levels have not been calculated in the case of \(La_{1.85}Sr_{0.15}CuO_4\). In \(CuCl_2\) molecule, Bair and Goddard\(^38\) have calculated the 5p\(\sigma\) level to be about 3.1 eV above the \(n = 4\) level and the 5p\(\pi\) level to be about 1 eV above the 4p\(\sigma\) level. These energy differences are much smaller than that observed with the single crystal of \(La_{1.85}Sr_{0.15}CuO_4\). On the other hand in the configurational-interaction calculations of Kosugi et al.\(^40\) for the Cu K-shell of \([CuCl_4]^{2-}\) ions the deference in energy between the 1s \(\rightarrow\) 4p and 1s \(\rightarrow\) 5p transitions are \(-7.5\) eV which is roughly the separation seen in the case of single-crystal XANES spectrum of \(La_{1.85}Sr_{0.15}CuO_4\).

5.3 XPS and XANES

The difference between XANES and XPS is that the first excited state to which the electron makes a transition by the absorption of a photon of energy \(hv\) is the first unoccupied state above the Fermi level in the case of XANES and that above the
vacuum level in the case of XPS. Both these methods enable one to locate the binding energy of the electrons as referred to the Fermi level. It is important to remember that this binding energy is the difference in energies between the final state with N-1 electrons and an initial state with n electrons: \( B.E. = E_f - E_i \). Consequently it is necessary to obtain a good description of all the possible initial and final states which follow the absorption or photoemission process. The final states reflect the kind of screening processes invoked for the core hole. The binding energies should be identical in two processes provided that the same core hole is studied. Otherwise the separation in energies have to be modified by the differences in the term \( U_{kc} \) which describes the interaction between the core level c and the outer level k. In the case of Ce the configurational mixing deduced from XPS and XANES data from the same core level are identical which suggests that the ratio of the intensities for the fully screened (with ligand to metal charge transfer) and poorly screened processes should be the same in the two processes.

The importance of multielectron excitations involving ligand-to-metal charge transfer process in core-level spectroscopies was first realized in the case of XPS studies. Larsson was among the first to highlight the importance of such processes in accounting for the strong satellites in the core level XPS spectrum of transition metal ions such as \( \text{Cu}^{2+} \). The satellite corresponds to the state assumed in crystal field theory with nine 3d electrons whereas the main peak corresponds to a state with all ten 3d electrons. In this picture the satellite becomes larger when the ligand is more electronegative. In the case of ligand admixture into the final state the relative ratios of the satellite and main peak are expected to be reduced over that in the absence of admixture. Since the ligand-to-metal charge transfer processes are the same in both XPS and XANES, it becomes necessary to assume that the relative intensities of the
shakedown or fully screened configurations as well as the main poorly screened configurations should be the same in both. This is the basic objective of the calculations of Sarma.

Sarma's calculations are derived from the original calculations of Alp et al. As mentioned earlier, these calculations are based on one electron excitation picture in which the state to which the electron is excited is the initial state. Implicit in the calculations of Sarma is the assumption that the most intense features in the calculations of Alp et al are due to multielectron excitations from the 1s to the fully screened configurations 4pσ and 4pπ configurations (d⁰) where the major contribution are from the final states. Sarma then adds on the satellite features of XPS at suitable energies after the normalization of intensities (see Ref.42) to the main peaks of Alp et al. By including lifetime broadening Sarma has been able to reproduce fairly well the experimental features of La₂CuO₄ as shown in Figure 5.1. By doing so Sarma has completely ignored the earlier intensity calculations of say Bair and Goddard or Kosugi et al which identify the main peak with the 1s to 4p transitions. Sarma has not commented on this discrepancy despite the fact that several papers in this area rely heavily on the calculations of Bair and Goddard. The merit of Sarma's interpretation is the remarkably good fit with realistic parameters and also the attempt to correlate XPS and XANES intensities. Another important aspect of this interpretation is that his calculations have shown that the satellite of the 1s to 4pσ main peak should be very small compared to that of the 1s to 4pπ transition. This is actually observed in the later work on single crystals (features B₃ and B₄ in Figure 5.1). However, in such an interpretation it would be difficult to account for the features at lower energies (around 7 eV) which have been attributed to 1s to 4pπ shakedown transition by polarized synchrotron radiation studies on oriented single crystals.
The procedure adopted by Sarma was actually first examined by Stern\textsuperscript{44} who was among the first to propose that the structure on the higher energy side of the main absorption peak in XANES could be related to the satellite peak (what he terms as a shake-up satellite) of the main core level spectra in photoelectron spectroscopy. Stern, however, realized that XPS and XANES intensities need not be similar. The difference in the satellite strengths in XPS and XANES could be attributed to the different excitation energies of the photoelectrons involved; in the former the excitation energy is hundreds of electron volts while in the latter the photoelectron is at the threshold. The highly energetic photoelectron state in the former thus does not play an important role in shielding the core hole compared to the absorption process in which the photoelectron is still located on the metal ion and thus partially shields the core hole from the ligand. The charge transfer processes or final state effects thus become more important in photoelectron spectroscopy. It has also to be noted that at the threshold the core hole potential is turned on adiabatically while at very high energies the sudden approximation becomes valid. This could be interpreted in terms of a more overlap of the photoelectron with initial states at the threshold than at higher energies.

5.4 SCATTERING EFFECTS

As mentioned earlier a completely different interpretation is that due to Lytle et al\textsuperscript{4} who find a simple relation between $E$ and $1/R^2$ where $R$ is the distance of the ligand in various coordination shells from the central cation. In this model the feature at $C$ is to be attributed to a copper-oxygen distance of 2.6 Å. This is typical of the A-O distance in ABO$_3$ pervoskites and from this Lytle et al\textsuperscript{4} suggest that the feature $C$ is to be associated with Cu$^{2+}$ ions at the A sites. This assumption has
been criticized by Heald et al. on the basis of their single crystal work since the feature C is very sensitive to the orientation although no such anisotropy is expected in the Cu-O distances if the copper ions occupy the A sites. However, such an anisotropy is anticipated if the copper ions occupy the Ba sites.

5.5 INTERPRETATION OF PRESENT RESULTS

In the interpretation of the results we resort to qualitative arguments first of all because the resolution of our measurements are not sufficient to warrant such a calculation. It has to be noted, however, that in some cases such as metals the modern techniques using intense synchrotron radiation and the earlier techniques using weaker radiation gave nearly identical results. The resolution obtained by us is sufficient to distinguish between the main features A', B, C and D. The main purpose of this study is to obtain information regarding the origin of the feature C in a systematic manner.

5.5.1 Scattering Models

As mentioned in section 5.4 the anisotropic behaviour of the feature C in the single crystal data of Heald et al. does not unambiguously refute the scattering model of Lytle et al. However, the features near the absorption edge B1 and B2 are seen at the same energies in many single crystal studies of copper complexes and for this reason cannot be simply accounted for by scattering models. We have specifically examined CaCu3Ti4O12 which has Cu ions at the A sites. There three sets of four oxygen ions having Cu-O distances of 3.19, 2.78 and 1.96 A. This is the kind of distance used by Lytle et al. in accounting for spectra of the superconducting compounds. The XANES spectra of CaCu3Ti4O12 should then be very similar to that of La2CuO4. The spectra in Figure 5.3 is, however, slightly different with the
peak positions being far from that predicted from the ruler of Lytle et.al. This seems to demonstrate that the model of Lytle et.al. is inapplicable at least in a straightforward manner. In the following discussion we shall use the scattering model in interpreting our results.

5.5.2 EVIDENCE FOR Cu$^{3+}$ IONS

The comparison of La$_2$CuO$_4$ (Figure 5.2) with La$_2$Li$_{0.5}$Cu$_{0.5}$O$_4$ (Figure 5.3) shows a shift in the main absorption edge by about 4-5 eV. This the kind of shift found in KCuO$_2$ relative to that in the series La$_{2-x}$Sr$_x$CuO$_4$ and hence confirms the observation that a Cu$^{3+}$ ion would have the maximum in the absorption edge at around 20 eV. It is important to note that L$_3$ XANES studies on compounds containing trivalent copper ions reveal the absence of any significant amount of a d$^8$ configuration. It has therefore been postulated that the Cu$^{3+}$ ion is unstable in an oxide matrix and instead a hole is created on the ligand oxygen ions. This aspect has been discussed earlier in connection with the oxidation of Ni$^{2+}$ ions in oxide matrices by Ganguly. One of the conditions for the creation of holes on oxygen seems to be that the energy level of the metal ion in the higher oxidation state should be below that of the anion levels. This seems to be the case for ions such as Cu$^{3+}$ or Ni$^{3+}$. Thus the (Cu-O)$^+$ unit is composed of Cu$^{2+}$ O$^-$ ions. Of importance to this study is our observation that the properties of La$_2$Li$_{0.5}$Cu$_{0.5}$O$_4$ (M = Co, Ni, Cu) are consistent with each other if the copper ions are in the low-spin trivalent Cu$^{3+}$ state. This conclusion is based on several studies including optical spectra, Li NMR, ESR, Raman and infra-red spectra as well as systematics of lattice parameters. The most important of these perhaps, the ESR for M = Ni is typical of Ni$^{3+}$ ion and Li NMR is identical for all M showing the identical environment of the nearest neighbour Li ions which share the same oxygen as the M ions in the ab plane. The $^{57}$Co Mössbaur results of Fontcuberta et
with $\text{La}_2\text{Li}_{0.5}\text{Co}_{0.5}\text{O}_4$ are also consistent with the Co ion in the low spin trivalent state. The L$_3$ XANES results of Bianconi et al$^{49a}$ however show that in $\text{La}_2\text{Li}_{0.5}\text{Co}_{0.5}\text{O}_4$ the hole is on oxygen and not on copper. This apparent contradiction between our results$^{25}$ using conventional techniques and those of Bianconi et al$^{49a}$ using L$_3$ XANES technique is not clear to us yet. We note that the L$_3$ XANES spectra of NaCuO$_2$ as reported by Sarma et al$^{49b}$ is very different from that reported by Bianconi et al$^{49a}$. Unlike the K-edge spectra the technique for obtaining the L$_3$ spectra is surface sensitive$^{49b}$ just as XPS which in the case of superconductors is very irreproducible.

5.5.3 1s $\rightarrow$ 3d Transition

The pre-absorption edge feature, P, is usually attributed to the 1s $\rightarrow$ 3d transition. Since the tetrahedral coordination does not have inversion symmetry the ligand field breaks the spherical symmetry of atom potential. As a result the dipole selection rule is relaxed and the quadrupole transition strength increases. In accordance with this the copper ions in octahedral coordination such as in MgCu$_2$O$_3$, Sr$_2$CuWO$_6$, or even in square-pyramidal coordination as in Y$_2$BaCuO$_5$ show very little pre-edge absorption feature. Only in CuAl$_2$O$_4$ or Y$_2$Cu$_2$O$_5$ where the nearest neighbour coordination shell does not have an inversion symmetry do we find a strong pre-edge absorption feature. Thus as per expectation (see section 5.2), the pre-absorption feature, P, can be truly attributed to the 1s to 3d transition.

5.5.4 COMPARISON OF XPS AND XANES

The results of Sarma highlighted the point (see section 5.3) that the XANES intensity near the feature C could be related to the intensity of the poorly screened configuration in the XPS such as the feature at 942 eV in the Cu 2p$_{3/2}$ region. We find in
our studies that the compounds such as CuAl$_2$O$_4$, Y$_2$Cu$_2$O$_5$, Y$_2$BaCuO$_5$, Sr$_2$CuWO$_6$ in which the copper ions are either isolated or do not have strong nearest neighbour antiferromagnetic interaction strengths, do not show any feature corresponding to the feature C although these compounds show a very high satellite intensity in the XPS (Figure 5.6). The main absorption peak shows very little difference in energies in these compounds so that it is unlikely that the satellite feature has been absorbed into the main band. It is also interesting to note that the spectra obtained with Y$_2$BaCuO$_5$ in which the copper ions are in isolated five-fold square-pyramidal coordination just as the Cu (II) ions in YBa$_2$Cu$_3$O$_7$ are almost identical to those calculated for the first coordination shell for the latter ions. In these calculations only one-electron excitation is assumed. We therefore do not see any direct correlation between the intensity of the feature C in these compounds with that of the XPS intensities as suggested by the calculations of Sarma$^8$ and first examined by Stern$^{44}$.

From the above discussion we may come to the following conclusions regarding feature C:

i) The feature C is unlikely to be due to one-electron excitation process involving main 1s $\rightarrow$ 5p$\sigma$ or 5p$\pi$ transitions since in such an one-electron picture it should be seen in both isolated copper ions (with no Cu-O-Cu interactions) as in Sr$_2$CuWO$_6$, Y$_2$BaCuO$_5$ etc., as well as in other compounds such as Ca$_2$CuO$_3$, SrCuO$_2$ etc., which have extended 180$^\circ$ Cu-O-Cu interactions.

ii) Within our experimental resolution the feature C does not seem to correspond to the poorly screened configuration 3d$^{1}L^{0}$ at least not in the sense suggested by Stern$^{44}$ or Sarma$^8$ (see section 5.2) in which the main peak corresponds to the fully screened d$^{0}L^{1}$ configuration. The calculations of Sarma suggest that this separation should be $\sim$ 7 eV and should have been if it had been present with the same relative intensities as in the
As discussed earlier (section 5.2) the feature C does not seem to be due to scattering effects as proposed by Lytle et al.\(^4\).

As noted earlier the feature C is to be associated with the feature B\(_4\) in the single crystal work of Heald et al\(^7\) (Figure 5.1b). In order to understand the single crystal results of these authors it is necessary to understand first of all the chemical systematics in other single crystal work. To our knowledge the only work of these kind is carried out by Smith et al\(^3\)\(^9\). In this study these authors examined the X-ray absorption spectra of a series of single crystals of copper with various ligands. The important results emerging from this study is that for the polarization parallel to the plane the same two features (B\(_2\) and B\(_4\)) are seen. The separation in energy between these two features are independent of the nature of the ligand and is close to that in Figure 5.1b. The actual energies are, however, sensitive to the nature of the ligand. For the lower energy peak (to be identified as B\(_2\) hereafter) the energy changes from 8994 eV in the case of ionic Cl\(^-\) to 9001 eV with the more covalent trimethylimidazole in which the ligation is through nitrogen. \(\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4\) the energy of B\(_2\) is \(\sim\) 8997 eV which would indicate that the oxygen ligand is less covalently bound than the nitrogen ligand as is to be expected. The ratio, R\(_2\), of the intensities B\(_2\)/B\(_4\) increases with increasing covalency. R\(_2\) is much larger in the superconducting copper oxides.

When the beam polarization is perpendicular to the plane, Smith et al\(^3\)\(^9\) find that there are two sharp peaks which may be attributed to highly localized electrons of copper ions. The energies of these two resonances (\(\sim\) 8986 eV and \(\sim\) 8993 eV) are rather insensitive to the nature of the ligand. They correspond closely to the positions of the A and B\(_1\) peaks in single crystals of \(\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4\) (Figure 5.1b) and \(\text{Nd}_2\text{CuO}_4\) (Figure 5.3). The low energy feature is therefore referred to as A and the higher
energy feature as $B_1$. The sharpness of these features increases as ligand interaction decreases. The ratio of the intensities of feature A to $B_1$ is rather insensitive to the nature of the ligand when the $d_{z^2}$ electrons are localized on copper but becomes rather reduced when these electrons are delocalized over the axial ligands by $\pi$ bonding. We find that the feature A is quite sharply defined in the powder spectra of $\text{Nd}_2\text{CuO}_4$ (Figure 5.4) in which there is no axial ligation relative to that of $\text{La}_2\text{CuO}_4$. The feature A is barely discernible in the powder spectra of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. The decrease in intensity of the feature A on going from $\text{Nd}_2\text{CuO}_4$ to $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ is in agreement with the increasing conductivity and hence increasing delocalization.

We may identify the conditions for observing feature C (and A) in the powder spectra if we assume that in systems with long range $180^\circ\text{Cu-O-Cu}$ interactions there is considerably more delocalization of the electrons over that in which the copper ions are isolated as in $\text{Y}_2\text{BaCuO}_5$ or $\text{Sr}_2\text{CuWO}_6$, or do not have $180^\circ\text{Cu-O-Cu}$ interactions, as in $\text{Y}_2\text{Cu}_2\text{O}_5$ or $\text{CuAl}_2\text{O}_4$. The more covalent nature of those compounds with $180^\circ\text{Cu-O-Cu}$ interactions is seen in the magnetic susceptibility studies. All these compounds have a low susceptibility indicative of high antiferromagnetic ordering temperatures and hence transfer integral or covalency. Those without such interactions show well defined Curie - Weiss type of behaviour with the Curie constant being close to that of copper ions in ionic compounds. From the single crystal studies of Smith et al we would then expect $B_2$ feature shifted to higher energies in the more covalent compounds with delocalized $180^\circ\text{Cu-O-Cu}$ interactions (more covalent) compared to those without such interaction. The associated higher energy satellite feature $B_4$ (feature C in Figure 5.1a) would then become more prominent. The results of Lytle et al (Figure 7 of ref.4) are consistent with such an interpretation where the main peak feature is seen to shift to higher energies on going from $\text{CuTiO}_3$.
to copper phthalocyanine.

The feature A is not conspicuous in powder spectra of the more ionic compounds (Figure 5.5). In compounds such as $Y_2Cu_2O_5$ and $CuAl_2O_4$ the tetrahedral environment could completely change the nature and energies of the resonances. However, in $Sr_2CuWO_6$ and even in $Y_2BaCuO_5$ the square-planar coordination around the isolated copper ions is more prominent. The distortion of the octahedra in the former (c/a ratio $= 1.16$) is considerably less than that in $La_2CuO_4$ (c/a ratio $= ~1.26$). In $Y_2BaCuO_5$ the axial to basal ratio in the square-pyramidal coordination is also $~1.17$. This is consistent with the observation of Lytle et al$^4$ that the feature A becomes more prominent as the environment becomes more square-planar in nature (see Figure 7 of ref. 4). Thus the prominence of the feature A is to be attributed to the relative shifts of the energies of the resonances associated with beam polarization perpendicular or parallel to the square-planar coordinated ligands.

It is difficult at this stage to assign the electronic transitions unequivocally to the features especially in the absence of high resolution data and in the absence of rigorous theoretical calculations. However, we shall make some general qualitative remarks regarding the possible assignments in the following paragraphs.

We note first of all that the calculations of Alp et al are in good agreement with the later single crystal work, as far as the energies are concerned. These calculations are based on the one-electron theory for the interpretation of near edge structure in which the main transition is to be associated with 1s to continuum (positive energy) p states. This corresponds to the initial state in the one-electron excitation model. Thus, the feature $B_1$ and $B_2$ would correspond to the main 1s to 4p transitions, respectively. The other features could be derived from multi-electron excitation. The lower energy feature, A,
would then correspond to the shakedown process of Bair and Goddard\textsuperscript{38}. In the calculations of Smith \textit{et al}\textsuperscript{39} this is attributed to a bound-a-bound transition localized on copper which should correspond to the fully screened d\textsuperscript{0} (hereafter the superscript will refer to the number of holes) configuration that is familiar in multielectron processes as in XPS. By the same token the feature C or B\textsubscript{4} should correspond to the poorly screened "shakeup" multielectron d\textsuperscript{1} L\textsuperscript{0} transition of the corresponding 1s to 4p\textsigma transition. In such an interpretation the intensity of the "shakeup" feature C or B\textsubscript{4} is expected to decrease with increasing covalency as actually observed in the single crystal studies of Smith \textit{et al}\textsuperscript{39}. The shift to higher energies of the 1s to 4p transitions with increasing covalency is consistent with the antibonding nature of the unoccupied one-electron 4p level obtained from molecular orbital calculations\textsuperscript{18}.

It is not clear, however, why the "shakedown" transition should be associated only with the 1s to 4p\textpi transition and the "shakeup" transition only with the 1s to 4p\textsigma transition. If both single electron and multielectron excitations were simultaneously allowed one would have expected each main transition to be accompanied by these two satellites. The later should become important at higher energies relative to the energies associated with former. The relative intensities of the satellite features cannot be obtained therefore in a straightforward manner from XPS studies using analogous of Eqn.5.1 for example. Evidence for two satellites associated with a main transition may be found in the XANES of some of the single crystals. Thus the feature B\textsubscript{3} on the higher energy side of B\textsubscript{1} in result of Heald \textit{et al}\textsuperscript{7} (Figure 5.1) could correspond to the "shakeup" satellite. Smith \textit{et al}\textsuperscript{39} find a three peak structure for the polarization parallel to the plane in some of the complexes (see Figure 3 of ref 39) and believe that there could be some real intensity (not associated with
artifacts) to the lower energy feature.

The absence or relatively lower intensities of the "shakeup" satellite for B$_4$ may be attributed to the weak non-bonding nature of ligation perpendicular to the plane. The dominance of the feature B$_3$ in La$_{1.85}$Sr$_{0.15}$CuO$_4$ (Figure 5.1b) is then consistent with either holes on the axial oxygens or with a change from d$_{x^2-y^2}$ to d$_{z^2-r^2}$ orbitals. Bianconi et al. have proposed from Cu L$_3$ X-ray absorption spectra of single crystals of YBa$_2$Cu$_3$O$_7$-$\delta$ that such a reordering of orbitals could take place. The calculations of Alp et al. also show such change. Another factor that could be important is that the probability of multielectron excitations becomes diminished when the electrical conductivity increases. This is suggested by the results of Grunes et al. who pointed out that for most metals the one-electron excitation calculations are sufficient to account for most of the features in metals but breaks down completely when applied to insulating oxides. It is interesting to note that in La$_2$Li$_{0.5}$Cu$_{0.5}$O$_4$ (Figure 5.3) the feature A is rather prominent and appears at 7 eV just as in the other Cu$^{2+}$ compounds. One would have anticipated a shift to higher energy because of the higher oxidation state. This emphasizes the non-bonding character of the axial ligands. The dominant intensity of the band at 20 eV is because of the characteristic "trivalent" character.

We find the above model attractive because of the simple manner by which we may account for all the features. All of the ingredients in the above model have been considered at one stage or another but have not been assembled together in this manner. The main difficulty with this model is that the energies separating the satellite features do not correspond to those found in XPS.

In a sense we could modify the above picture and associate the main transition as the d$^1$ hole (d$^9$ electron) configuration
and the satellites as due to $d^0$ (lower energy "shakedown") or $d^2$ (higher energy "shakeup") configurations of copper in much the same manner as the configurations included in the problem of Ce. The $d^0$ configurations ($Cu^+$) is known to be stabilized in axial symmetry and dominates the axial beam polarization features while $d^2$ ($Cu^{3+}$) is known to be stabilized in square-planar geometry and therefore dominates for beam polarizations parallel to the plane. Since the feature C is close in energy to that of trivalent ions, it could support such a conjecture.

In this work, a large number of copper oxides with different structural features have been investigated through XANES studies in order to understand the XANES features reported for the superconducting compounds. The results obtained with polycrystalline samples have been compared with other single crystal work on copper complexes as well as the superconductors. The various models used so far to interpret the XANES features have been reviewed. The importance of one-electron and multi-electron excitations have been examined.

The present study has therefore been useful in delineating the conditions for the observation of the feature which is observed in all the superconducting copper oxides at about 20 ev. This feature is to be associated with the presence of extended $180^\circ$ Cu-O-Cu interactions between corner-linked square-planar $CuO_4$ units.

Scattering models have been specifically examined using suitable model compounds and found to be unsuccessful in explaining the XANES features. The best explanation seems to associate the features with both single-electron and multi-electron excitations picture.
REFERENCES


