# Crystal Field Effect on the Chemical Shift in Cu $L_{III}$ XANES Spectra of Cu(II) Compounds

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Chemical shifts of the $2p_{3/2} \rightarrow 3d$ peaks in the Cu $L_{III}$ XANES spectra of copper(II) compounds were correlated with the crystal field parameter, $10Dq$, and were understood in terms of the simple crystal field concept.

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X-Ray absorption spectroscopy has been revealed to be a potential tool to derive informations on the electronic and geometrical structure of complex compounds.[1-12] In particular, the white line peaks in $L_{II,III}$ XANES spectra of transition metal compounds have been the topic of several studies[3-12] since the spectra can be influenced by the nature of the d states, which are primarily responsible for the bonding with ligands. For example, we have recently reported that Cu $L_{III}$ XANES analysis is useful for the quantitative estimation of Cu(II) coordination states (tetrahedra and octahedra) in copper-aluminate catalysts.[12] However, in general, the theoretical interpretation of XANES is complicated as a result of the complexity of the phenomena.[1,2] To derive more structural informations from XANES spectra, it is desirable to establish a simple relationship between the XANES feature and the chemical state of X-ray absorbing atom. In this study, an attempt was made to clarify a predominant factor affecting the chemical shift in Cu $L_{III}$ XANES spectra. Cu $L_{III}$ XANES spectra of a series of Cu(II) model compounds are measured, and the shifts of white line peak are compared with the crystal field parameter obtained from UV-VIS spectra and then are interpreted in terms of a simple crystal field theory.

The copper(II) compounds studied in the present study were obtained as follows. CuO, copper(II) acetylacetonate [$Cu(acac)_2$], $CuBr_2$, $CuCl_2 \cdot 2H_2O$, $Cu(OH)_2$ and copper(II) phthalocyanine [Cu(pc)] were purchased commercially. Copper(II) chloride was obtained by the dehydration of the $CuCl_2 \cdot 2H_2O$. Copper(II) containing mixed oxide of stoichiometric spinel ($CuCr_2O_4$, $CuFe_2O_4$ and $CuAl_2O_4$) and copper aluminate with Cu content of 6 wt% were prepared by a coprecipitation method.[12] Cu $L_{III}$ XANES spectra were measured in a mode of total electron yields on BL-7A at UVSOR with a ring energy of 750 MeV and a stored current of 70-220 mA. A double-crystal monochromator equipped with beryl crystals was used, and the absolute energy was calibrated to the Cu $2p_{3/2}$ peak in CuO at 931.3 eV.[7] The intensity of the spectra has not been normalized because of missing of an adequate normalizing procedure. The UV-VIS spectra were measured using UV-VIS spectrometer (JASCO V-750) in a diffuse reflectance mode.

Figure 1 shows the Cu $L_{III}$ XANES spectra of Cu(II) compounds. All the spectra exhibited a large white line feature due to $2p_{3/2} \rightarrow d$ transition. In all the spectra except for $CuAl_2O_4$, a single symmetric absorption peak appeared, which should consistent with the fact that an unoccupied $3d$ level of $d^9$ compounds exists only at the highest $3d$ orbital. Therefore, the absorption peak in the Cu $L_{III}$ XANES spectra is assigned to the transition from the $2p_{3/2}$ to the highest unoccupied $3d$ state, and hence the energy position of these $2p_{3/2} \rightarrow 3d$ transition peak should correspond to the energy difference between $2p_{3/2}$ level and the highest unoccupied $3d$ state. Table 1 summarizes the positions of the peak in the order of increase in the energy. For $CuAl_2O_4$, in which $Cu^{2+}$ cations are distributed in either tetrahe-

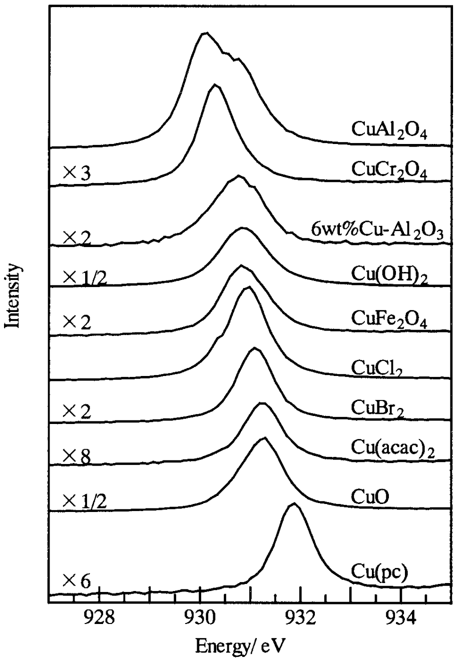

**Figure 1.** Cu $L_{III}$ XANES spectra of a series of divalent Cu compounds.

**Table 1.** Characteristics of Cu $L_{III}$ XANES spectra and $10Dq$ data for Cu(II) compounds

| Compounds | Coordination states | $E^a$/eV | $10Dq^b$/ eV |
|---|---|---|---|
| $CuAl_2O_4$ | $CuO_4$ tetrahedra | 930.1 | 0.8-0.9 |
| | +$CuO_6$ octahedra | 930.8 | 1.4-1.7 |
| $CuCr_2O_4$ | $CuO_4$ tetrahedra | 930.3 | 1.0-1.1 |
| 6wt%Cu-$Al_2O_3$ | $CuO_6$ octahedra | 930.8 | 1.4-1.7 |
| $Cu(OH)_2$ | $CuO_6$ octahedra | 930.8 | 1.7-1.9 |
| $CuFe_2O_4$ | $CuO_6$ octahedra | 930.8 | 1.5-2.0 |
| $CuCl_2$ | $CuCl_6$ octahedra | 931.0 | 1.5-1.6 |
| $CuBr_2$ | $CuBr_6$ octahedra | 931.1 | 1.5-2.1 |
| $Cu(acac)_2$ | $CuO_4$ square plane | 931.2 | 1.9-2.3 |
| CuO | $CuO_4$ square plane | 931.3 | 1.7-2.2 |
| Cu(pc) | $CuN_4$ square plane | 931.9 | 2.2-2.3 |

[a] Positions of $L_{III}$ absorption peak maximum. [b] $10Dq$ was estimated from the d-d band of UV-VIS spectra.

dral and octahedral sites in the ratio of 60/40,[12-14] the XANES spectrum exhibited an absorption maximum at 930.1 eV accompanying a shoulder at about 930.8 eV. In our recent report, these peaks have been assigned to be due to $CuO_4$ tetrahedra and $CuO_6$ octahedra, respectively.[12] The XANES spectrum of $CuCr_2O_4$, which is a model compound of $CuO_4$ tetrahedra,[14] exhibited a peak at 930.3 eV. In the XANES spectra of a compounds of $CuO_6$ octahedra [6wt% Cu-$Al_2O_3$,[12] $Cu(OH)_2$ and $CuFe_2O_4$[14]], the peak positions were 0.5-0.7 eV higher than those for $CuO_4$ tetrahedra. Within octahedral compounds, the peak shifted to higher energy as the electronegativity of the bonding ligand are decreased, in the order O > Cl > Br, which is similar to the results in an earlier report.[3] Further shift of the peak to the higher energy was observed for the compounds with square planer symmetry.

On the basis of crystal-field theory,[15] the crystal-field splitting ($10Dq$) decreases in the order square plane > distorted octahedra > octahedra > tetrahedra (spectrochemical-series). In addition, the degree of Jahn-Teller distortion of octahedra, or, in other word, $10Dq$ decreases in the order $CuBr_2 > CuCl_2 > CuFe_2O_4$.[16] By comparison with our XANES data, it is likely that the order of positive shift in the $2p_{3/2} \rightarrow 3d$ transition peaks corresponds to the crystal field splitting. To obtain the crystal field parameter, UV-VIS spectra of each Cu(II) compounds were measured. $10Dq$ value estimated from the d-d transition peak is included in Table 1. Figure 2 shows a plot of the $L_{III}$ absorption peak energy versus $10Dq$, in which the error bar represents the spread of energy position of the d-d transition peak in UV-VIS spectra. The result clearly indicates that the positive shifts in the $2p_{3/2} \rightarrow 3d$ transition peaks are systematically correlated to the increase in the crystal field splitting. Although the binding energy of $2p_{3/2}$ electron could depend on ligands by the screening effect as generally observed in XPS,[18] this effect is proposed to be negligible in L-edge absorption spectroscopy of transition metal compounds.[5] Whereas, the energy of the outer level, i.e., unoccupied level of the crystal field having 3d character, should increase in the same order as $10Dq$. From the above-mentioned, it is concluded that the crystal field change is a primary factor in determining the chemical shifts in Cu $L_{III}$ XANES spectra; the positive shift in the $2p_{3/2} \rightarrow 3d$ peak energies is attributed to an increase in the unoccupied level of the crystal field, which is due to an increase in the crystal field splitting.

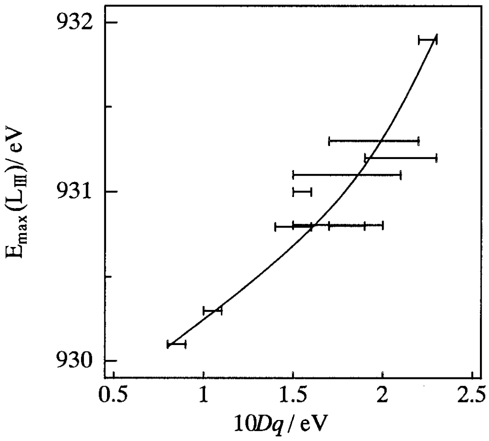

**Figure 2.** Fig. 2 Correlation of the energy position of $2p_{3/2} \rightarrow 3d$ peak in Cu $L_{III}$ XANES spectra with the crystal field splitting ($10Dq$).

In summary, the chemical shifts of the $2p_{3/2} \rightarrow 3d$ transition peaks in the Cu $L_{III}$ XANES spectrum, which systematically correlated to the change in $10Dq$, were understood in terms of the simple crystal field concept. From the observed relationship, Cu $L_{III}$ XANES can now be used to determine the crystal field and coordination states of unknown Cu(II) compounds. Finally, the chemical shift concept obtained in this study will be useful for an improved understanding of Cu L X-ray absorption spectra.

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