

**Experiment title:**

Valence Selective Diffraction on a Cu(I)-Cu(II) Mixed Valence Compound

Experiment number:
CH-68**Beamline:**

ID 11

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9

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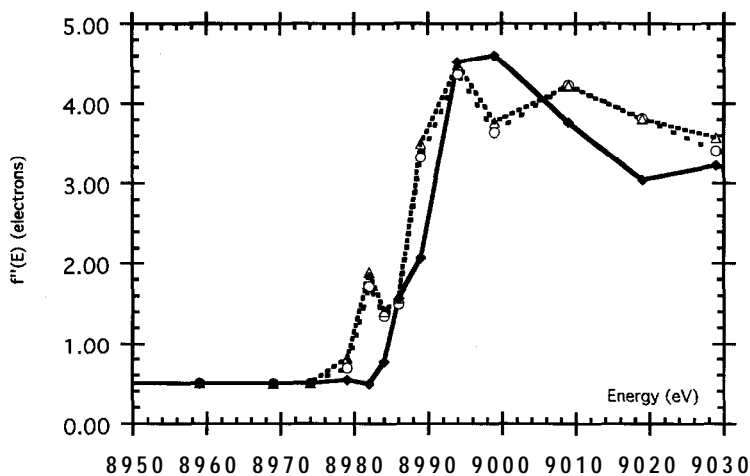
Report: Valence selective diffraction takes advantage of the anomalous scattering effects near an X-ray absorption edge. It has been used in the past decade to obtain information on the chemical shift in X-ray absorption edges and allow extraction of site-specific absorption spectra from mixed valence compounds ([1] and references therein). The compound chosen for the present study, aquobis(en)copper(II)di(cyanocuprate(I)), differs from other compounds hitherto investigated, by having two crystallographically different Cu(I) sites in addition to one Cu(II) and thus provides a possibility for internal check of consistency. Crystal data: monoclinic, Cc, a=14.774, b=7.749, c=14.272 Å, β=112.39°, chemical formula: $\text{Cu}_3\text{ON}_8\text{C}_8\text{H}_{18}$, Z=4. The Cu(I) sites have distorted tetrahedral geometry, the Cu(II) has a square bipyramidal coordination. The atomic scattering factor is written: $f(\theta, \lambda) = f_0(\sin\theta/\lambda) + f'(\lambda) + if''(\lambda)$ where f' and f'' vary considerably near an absorption edge. The noncentrosymmetric space group allows refinement of f'' (E) for the first time as well as f'(E), where E is the photon energy.

The experiment was conducted at the Materials Science Beamline at ESRF, using an oscillation setup and an imaging plate detector. The Fuji plates were read with a Molecular Dynamics scanner, spatial resolution 200 pm. A vertically unfocussed beam was used to obtain optimum energy resolution (1.3 eV at 8.979 keV (1.38 Å), the Cu K-edge). Sample to detector distance was 82 mm, yielding a resolution of $(\sin\theta/\lambda)_{\text{max}} =$

0.4 \AA^{-1} . The oscillation range was 12° with a 2° overlap interval, the crystal mosaicity was $0.6''$. Number of reflections pr. image was in the range 50-70. A total of 16 energies were collected, from 8.879 keV to 9.029 keV, with three complete data sets. The data were processed with FIT2D [2] and Denzo [3]. A total of 3756 observed reflections were used for least-squares refinement with MXD [4]. This program allows simultaneous refinement of atomic parameters, as well as $f'(E)$ and $f''(E)$, and absorption correction. The refinement of 167 parameters leads to $R(F^2)=8.2\%$, $wR(F^2)=11.4\%$. The resulting values of $f''(E)$ is shown in Figure 1. Through the optical theorem, $f''(E)$ is directly related to the absorption: $\mu(E)=\text{constant}\cdot f''(E)/E$.

Figure 1.

The anomalous scattering factor $f''(E)$ for each of the three Cu sites. Cu(I) sites: open circles and triangles, dashed curves. Cu(II) site: closed diamond, solid curve



From the figure it is evident, that the two individually refined $f''(E)$ curves for the Cu(I) sites are identical within experimental uncertainty ($\text{esd} \approx 0.2$ electrons) and significantly different from the $f''(E)$ for the Cu(II) site. The cusp at the edge on the Cu(I) curves is observed in absorption spectra of Cu(I) compounds and metallic Cu(0), but is for square planar Cu(II) complexes dependent on beam polarisation with respect to the plane and is therefore less pronounced. There are indications of a white line for the Cu(II) spectrum, but not for Cu(I), in agreement with literature. The chemical shift is estimated to 3-5 eV. The experiment has thus been successful in establishing a difference in X-ray absorption spectra due to differences in chemical environment.

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1. Gao, Frost Jensen, Pressprich, Coppens, Dupuis, Marquez. *J. Am. Chem. Soc.* 114, 9214 (1992).
2. Hammersley, ESRF. *FIT2D program* for 2D fitting and corrections of detector distortions. (1987-96).
3. Otwinowski. Yale University. *Denzo program* for 2D integration. Gewirth. *HKL manual.* (1993-95).
4. Wolfers. *J. Appl. Cryst.* 23, 554 (1990).