



HAL
open science

EXTENDED FINE STRUCTURE OF BRAGG REFLECTIVITY OF COPPER SULPHATE IN THE VICINITY OF COPPER K-EDGE

I. Arçon, A. Kodre, D. Glavič, M. Hribar

► **To cite this version:**

I. Arçon, A. Kodre, D. Glavič, M. Hribar. EXTENDED FINE STRUCTURE OF BRAGG REFLECTIVITY OF COPPER SULPHATE IN THE VICINITY OF COPPER K-EDGE. *Journal de Physique Colloques*, 1987, 48 (C9), pp.C9-1105-C9-1108. <10.1051/jphyscol:19879200>. <jpa-00227318>

HAL Id: jpa-00227318

<https://hal.science/jpa-00227318v1>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

**EXTENDED FINE STRUCTURE OF BRAGG REFLECTIVITY OF COPPER SULPHATE
IN THE VICINITY OF COPPER K-EDGE**

I. ARČON, A. KODRE, D. GLAVIČ and M. HRIBAR

*Department of Physics of FNT and J. Stefan Institute,
E. Kardelj University of Ljubljana, YU-Ljubljana, Yugoslavia*

ABSTRACT - The Bragg reflectivity of a monocrystal of copper sulphate in the energy region around the K edge of copper is examined for an extended fine structure similar to EXAFS. A calculation based on a model of a mosaic crystal shows that the structure is derived from the EXAFS as well as from an analogous effect in the scattering amplitude. The result can be brought to the same form as EXAFS, but with additional phase shifts. In an experimental comparison of the structure to the standard EXAFS of a thin copper sulphate plate the existence of phase shifts is confirmed.

INTRODUCTION

There have been several observations of the EXAFS-like structure in the Bragg reflectivity of crystals on the high-energy side of absorption edges of constituent atoms [1-3]. In mosaic crystals where both the incident and the reflected X-ray beam are mainly attenuated by photoabsorption the effect is apparently related to the EXAFS itself, but a direct comparison has not been reported. Theoretical arguments are given [3-4] that the attenuation of the beam as well as the scattering processes contribute to the structure.

In the present paper explicit results are derived following the path developed in the theoretical treatment of total reflections EXAFS [4]. The effect will be referred to as BREFS (Bragg reflectivity extended fine structure). Analogously to the relative attenuation coefficient in EXAFS, the relative reflectivity is introduced to represent BREFS: this is the oscillatory part of the reflectivity of the crystal normalised to its smooth, slowly varying average. These quantities are usually expressed in k-space, i. e. as function of the photoelectron wavevector.

We measured the BREFS and EXAFS on a crystal of copper sulphate at the copper K edge. The experimental results are used to test the theoretical predictions.

THE MODEL

The integrated coefficient of reflectivity of a mosaic crystal [5] is given by

$$g(\omega) = \frac{N^2 c^3}{2 \omega^3} r_0^2 u(\theta) \frac{|F(\omega)|^2}{\mu(\omega)} \quad (1)$$

where ω denotes the frequency of the scattered wave, r_0 the classical electron radius, N the number of scattering atoms per unit volume and $u(\theta)$ the well known

angular dependence of Bragg reflectivity. The components of the atomic scattering factor are corrected [6] by

$$f^i(\omega) = - \frac{2}{\pi} \int_0^{\infty} \frac{\omega f''(\omega)}{\omega^2 - \omega_0^2} d\omega \quad (2)$$

and the absorption coefficient $\mu(\omega)$ is proportional to the imaginary part of the scattering factor

$$\mu(\omega) = \frac{4}{\omega} \frac{r_0 c N}{\omega} f''(\omega) \quad (3)$$

Its oscillatory part, the relative attenuation coefficient can, in k-space, be decomposed into harmonic contributions of consecutive shells of neighbour atoms:

$$\chi(k) = \frac{(\mu - \mu_0)}{\mu_0} = \sum_i A_i(k) \sin(2kr_i + \Phi_i(k)) \quad (4)$$

By differentiating Eq.(1) the relation between the small oscillatory parts of $\chi(k)$, $\Delta f'$ and $\Delta f''$ is obtained:

$$\chi_{\rho}(k) = \frac{(\rho - \rho_0)}{\rho_0} = \left[\frac{\partial \ln(\rho)}{\partial f'} \right] \Delta f'(k) + \left[\frac{\partial \ln(\rho)}{\partial f''} \right] \Delta f''(k) \quad (5)$$

The relative reflectivity is expressed by the fine structure of the components of the scattering factor. While $\Delta f''$ is directly proportional to $\chi(k)$, the integral operator defining $\Delta f'$ in Eq.(2) reduces, within the same linear approximation, to a negative derivative of $\Delta f''$ introducing the phase shift of $3\pi/2$. Consequently, BREFS can be expressed as a sum of the same harmonic terms as EXAFS:

$$\chi_{\rho}(k) = g(k) \sum_i A_i(k) \sqrt{1+h^2(k)} \sin(2kr_i + \Phi_i(k) - \text{artg}(h(k))), \quad (6)$$

where

$$g(k) = \frac{(f''^2 - f'^2)}{(f''^2 + f'^2)} \quad (6a)$$

and

$$h(k) = \frac{2 f'' f'}{(f''^2 - f'^2)} \quad (6b)$$

Apart from the small increase of the amplitude, the shell contributions of EXAFS are combined to BREFS with additional phase shifts.

THE EXPERIMENT

A monocrystal of copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) is inserted for the Bragg crystal of the X-ray monochromator with a conventional X-ray tube. A crystal plane with $2d = 0.964$ nm is used and the resolution of 20 eV at the copper K edge (8.980 keV) is achieved in the third order reflection. The reflected beam is analysed by a Ge detector to discriminate the third order from other reflections and from copper fluorescence of the crystal. More than 100 scans of the 500 eV region above the copper K edge are superimposed to extract the structure from the statistical noise.

The relative reflectivity is obtained from the experimental data by subtracting the smooth principal part defined as a best fit third-order polynomial. The result is shown in Fig.1: for clarity, the statistical error is only given for one data point, being constant over the region. For a comparison, the relative attenuation coefficient is shown beside the BREFS: it is the standard EXAFS of a thin copper sulphate platelet measured on the same apparatus with LiF (220) crystal in the first order reflection and in the same resolution and statistics as above.

CONCLUSION

Taking into account the size of the statistical noise, the two sets of experimental data points in Fig.1 run remarkably well in parallel. In copper sulphate [7] the EXAFS spectrum of the copper atom is governed by the contribution from the first shell of oxygen atoms: The sums of Eqs. (4) and (6) are dominated by a single sine term, differing only in its phase. The average size of a phase

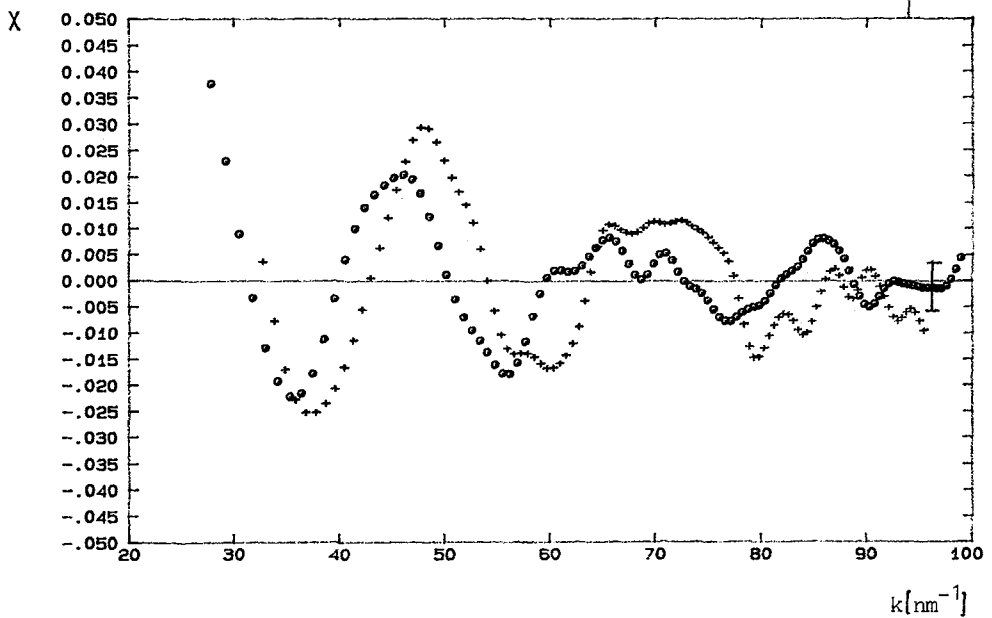


Fig. 1. EXAFS spectrum (+) and the relative Bragg reflectivity (BREFS) (o) at the copper K edge.

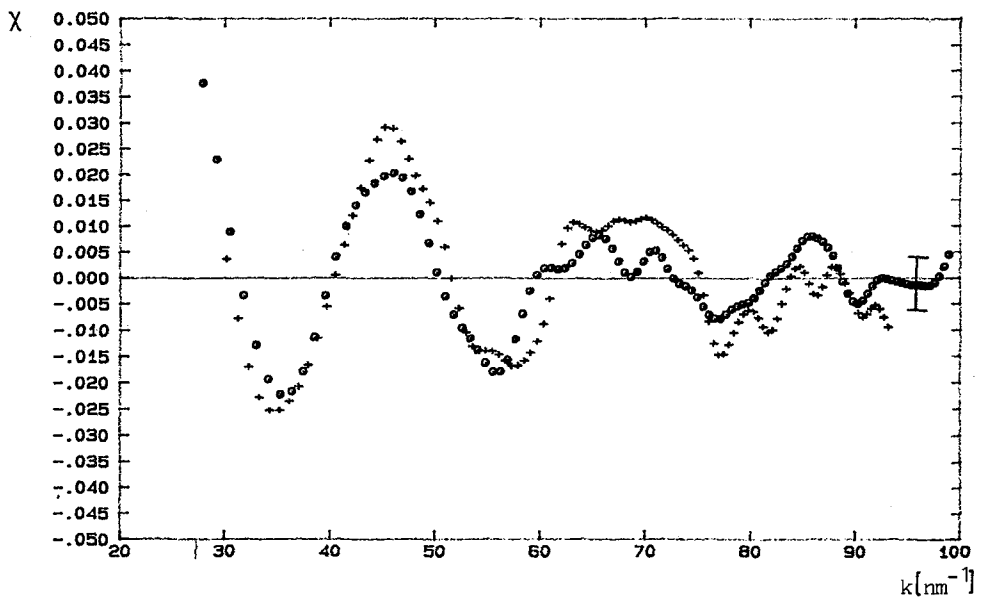


Fig. 2. EXAFS spectrum (+) transformed according to Eq. 6, compared to the BREFS (o).

shift, as can be estimated from the plot, is also in accord with the theoretical value of -0.38 rad (Eq. 6b).

To make the test more stringent, we transformed the experimental EXAFS spectrum with the help of Eq. (6) and with the phase shift calculated from scattering factor tables [8], into the BREFS spectrum. In the calculation the value of 25.0 is adopted for f_0 , the normal dispersion part of f^* , to take into account the scattering angle of 40 degrees. The result, together with the experimental BREFS is shown in Fig. 2.

It should be noted that the absolute value of the Fourier transform, as routinely used to interpret EXAFS spectra, destroys the phase information. Thus, BREFS and EXAFS are largely equivalent when transformed to r -space.

REFERENCES

1. S. I. SALEM, V. L. HALL: J. Phys. F, 10, (1980) 1627
2. V. PONOMAREV, A. TURUTIN: ŽTK 2, (1984) 391.
3. V. PONOMAREV, A. TURUTIN: Vesti. Mosk. Univ. 2, (1984) 92.
4. G. MARTENS, P. RABE: J Phys. 14, (1981) 1523.
5. R. W. JAMES: The Optical Principles of the Diffraction of X-rays, G.Bell, London (1950).
6. T. KAWAMURA, T. FUKAMACHI: Jap. J. Appl. Phys. Suppl. 17-2, (1978) 224.
7. R. W. JOINER: Chem. Phys. Lett. 1, (1980) 162.
8. S. SASAKI: Anomalous Scattering Factors for Synchrotron Radiation Users, National Lab. for High Energy Phys., JAPAN (1984).