Anisotropic Anomalous Dispersion in Cuprite, Cu_2O

Klaus Eichhorn
Hamburger Synchrotron-Strahlungs-Labor HASYLAB

Armin H. Kirfel and Karl F. Fischer
Fachrichtung Kristallographie, Fachbereich Physik,
Universität des Saarlandes Saarbrücken

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The paper reports the observation of significant "resonance peaks" in the intensity vs. energy curves around the Cu-K-absorption edge for forbidden reflections in centrosymmetric cubic Cu_2O. A qualitative interpretation is given in terms of an anisotropic anomalous dispersion model based on f', f''-tensors compatible with the symmetry at the Cu-site.

Keywords: Synchrotron radiation; X-ray diffraction; Anomalous dispersion; X-ray absorption edge; Cuprite.

Violations of the "special" extinction rules caused by anisotropic thermal vibrations and/or by bond-induced deformations of the atomic valence shells are well known [1]. In addition, anisotropic behaviour of the anomalous dispersion around K- and L-absorption edges can give rise to observation of "forbidden" reflections, even to those which are invariant against anisotropies of the thermally smeared atomic scattering factor. The availability of synchrotron light with its tunability over a wide energy range enables detailed investigations of this effect.

In conventional X-ray work anomalous dispersion is taken into account by the energy-dependent correction terms f' and f'' [2]. Recent experiments and theoretical studies have shown that f', f'' can *also* vary in reciprocal space due to a local anisotropy of the X-ray susceptibility in the crystal [3, 4]. Consequently, in a limited energy range around an absorption edge the anomalous dispersion is not only an atomic property but it is also affected by the chemical and structural environment of the anomalous scatterer under consideration. Then, the next approximations for describing f' and f'' are second rank tensors, in general $f'(\boldsymbol{h}, E)$ and $f''(\boldsymbol{h}, E)$ at $\boldsymbol{h}$ in reciprocal space, and their analysis is *no more* confined to acentric structures.

Cuprite, Cu_2O, crystallizes in the cubic space group Pn$\bar{3}$m, $a = 4.2696$ Å. Cu, in 2b ($\bar{3}$m, 0, 0, 0), is linearly bonded to two oxygen atoms in 4a ($\bar{4}$3m, 1/4, 1/4, 1/4). This arrangement provides a highly anisotropic Cu-environment, which is reflected in one of the largest known electric field gradients, at the Cu position $|\nabla E_{zz}| = 134 \cdot 10^{20}\ \mathrm{Vm}^{-2}$ [5, 6].

Reflections of parity (eeo) are strictly forbidden for spherically symmetric atoms. However, anisotropic vibration of Cu ($U_{12} \neq 0$) and a quadrupolar deformation of its valence shell [5] give rise to small intensities for (eeo)-reflections. Any anisotropy of f', f'' around the Cu-K-absorption edge will result in an additional contribution to I(eeo) and should be readily observable with an intense tunable X-ray source.

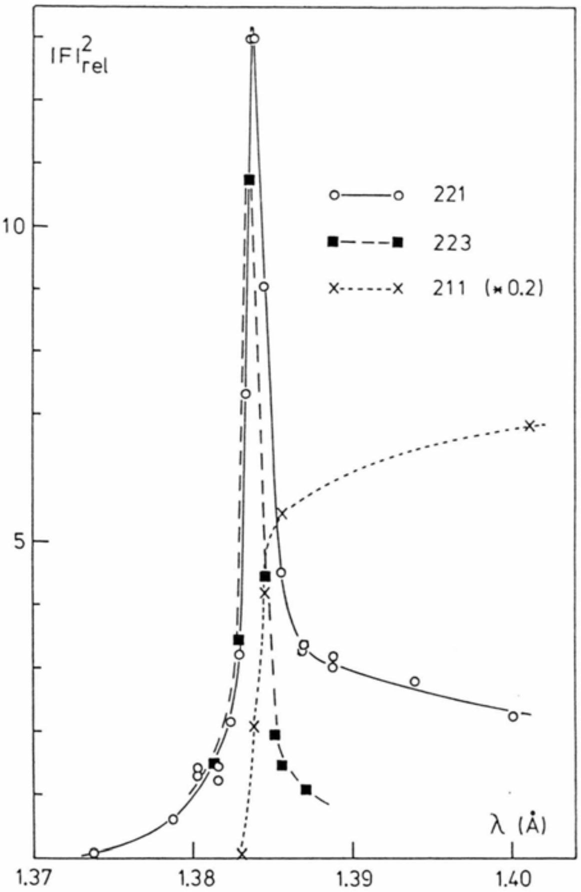

Fig. 1. Observed intensities of reflections (221), (223), and (211) as function of photon energy around the Cu-K-absorption edge (intensity factor for (211) is 0.02 instead of 0.2).

Forbidden reflections from a natural Cuprite crystal ($5.2 \times 5.4 \times 6.6\ \mathrm{mm}^3$) have been investigated at room temperature on the Two-Axis-Diffractometer at HASYLAB/DESY [7]. The scattering plane was horizontal and parallel to the polarization plane of the incident beam. The photon energy was calibrated by an absorption spectrum taken on a 0.75 μm Cu foil. The intensities of two "forbidden" reflections, (221) and (223), and of the "allowed" (211) reflection were monitored at a series of photon energies around the Cu-K-absorption edge. (211) is a so called "oxygen" reflection which carries no information about the spherical part of the Cu electron density distribution. The intensities of the "forbidden" (221) and (223), Fig. 1, show impressive "resonance peaks" as function of energy, which *cannot* be ex-

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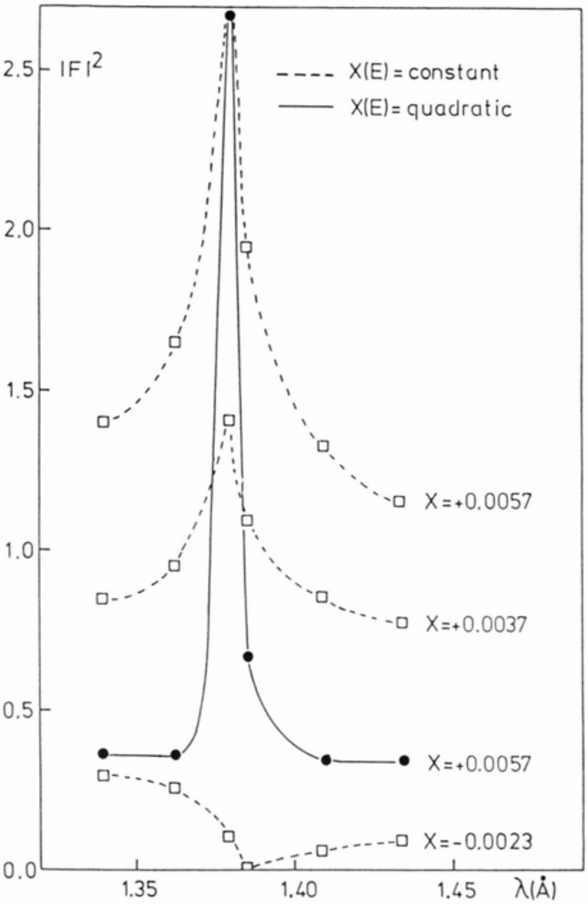

Fig. 2. Calculated intensities for (221) as function of photon energy. Solid line $X(E) = X_0[1 - |E - E_c|^{1/2}]$, broken lines $X(E) = \text{const}$.

plained in terms of scalar f', f'' correction factors. No significant changes were observed for the intensity of the "allowed" (211) apart from the expected absorption effect.

In order to explain these observations qualitatively we have modelled anisotropic f', f'' by introducing an artificial anisotropic temperature factor for the K-shell with components U_{11}(Cu) and U_{12}(Cu) + X. Values $f'(\boldsymbol{h} = 0)$ and $f''(\boldsymbol{h} = 0)$ were taken from the measured Cu absorption spectra. This convolution with a Gaussian combined with an energy dependence, $X = X(E)$, of the anisotropy term gave a qualitative agreement between calculated and observed intensities $I_{221}(E)$ of the "resonance peak" (Fig. 2). This figure shows that X *must* be energy-dependent since the calculated intensity curves for constant X-values follow essentially the comparatively wide $f'(E)$ dispersion curve. In addition, there is a clear correlation of the calculated intensity curves with the sign of X. To fit the observations, X must be positive, rendering an anomalous dispersion "ellipsoid" elongated along [111]. This shape corresponds with that of the deformation potential distribution around Cu, whereas the thermal vibration of Cu is largest normal to the threefold axis ($U_{12} < 0$).

We conclude from the present results that we have observed directly the effect of anisotropic anomalous scattering in a *centrosymmetric* cubic structure as predicted by Dmitrienko [8]. Of course, there are anisotropic anomalous dispersion contributions to the intensities of all reflections. However, the effect will be difficult to detect in "normal" reflections due to the large contribution from the total electron density. Therefore, Forbidden Reflection near Edge Diffraction ("FRED") is of special interest, and more detailed studies of such reflections can yield information about the resonance behaviour *and* about the way the crystal field determines the anisotropy of f', f''. Resonance scattering may provide a local probe to the environment of the anomalous scatterer, and one may infer that this applies also to adsorbates on surfaces and to other two-dimensionally ordered systems.

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