

EDGE SEPARATION USING DAFS

B. RAVEL¹, C.E. BOULDIN¹, H. RENEVIER², J.L. HODEAU² AND J.F. BERAR²

¹ NIST CERAMICS DIVISION, GAITHERSBURG MD (USA)

² LABORATOIRE DE CRISTALLOGRAPHIE, CNRS-UJF, GRENOBLE (FRANCE)

We exploit the crystallographic sensitivity of the diffraction anomalous fine structure (DAFS) measurement to separate the fine structure contributions of different atomic species with closely spaced resonant energies. In BaTiO₃ the Ti K-edge and Ba L_{III} are separated by 281 eV, or about 8.2 inverse angströms, which severely limits the information content of the Ti K-edge signal. Using the site selectivity of DAFS we can separate the two fine structure spectra using an iterative Kramers-Kronig method, thus extending the range of the Ti K-edge spectrum.

Recent x-ray absorption spectroscopy (XAS) studies [1] of the Ti K-near-edge and Ba K-extended spectra of BaTiO₃ demonstrate that the local structure in this material remains disordered even at temperatures well above the transition to a crystallographically cubic phase. The analysis of the Ti K-edge extended spectrum was hindered by the presence of the nearby Ba L_{III} absorption edge at 5247 eV, compared to 4966 eV for the Ti K-edge. This separation of 281 eV, or about 8.2 Å⁻¹, places such a severe limit on the information content of the Ti extended spectrum that meaningful analysis of those data is not possible.

Use of an energy discriminating detector in a fluorescence XAS measurement is precluded by the proximity of the various Ti and Ba fluorescence lines. In this article we present Diffraction Anomalous Fine Structure (DAFS) as a solution to the problem of overlapping edges. DAFS has been used to separate the fine structures of single atomic species in multiple crystallographic sites, for example the Cu in YBa₂Cu₃O₇ [2] and the Fe in BaZnFe₆O₁₁ [3] or at the interfaces of a multi-layer compound [4]. Using similar methodology, we can separate the signals from the Ti and Ba sites in BaTiO₃, thus isolating the Ti K-

edge fine structure spectrum and extending it beyond the 8.2 Å⁻¹ limit of the absorption experiment.

In the DAFS experiment, the variation in energy of the intensity of a diffraction peak is measured in an energy range spanning one or more absorption energies in the sample. The data were taken at the ESRF beamline BM2 on a 1000 Å thick film of BaTiO₃ deposited on sapphire by pulsed laser deposition. The film was found by x-ray diffraction to be oriented with an an axis normal to the surface. In our experiment, we measured the (100) and (200) reflections (Figure 1).

The oscillatory fine structure seen in the data above the absorption energies contains the same local structural information as an XAFS spectrum. This diffracted intensity can be expressed [2] as eq. (1):

$$I(\vec{Q}, E) = \left| \sum_j M_j e^{i\vec{Q}\cdot\vec{R}_j} (f_j^0(\vec{Q}) + f_j'(E) + if_j''(E) + [\Delta f_j''(E)\tilde{\chi}(E)]_j) \right|^2$$

where the sum is over all sites *j* in the unit cell, *M_j* is the thermal factor at site *j*, *f⁰* is the Thomson scattering of the atom at site *j*, and *f'* and *f''* are the energy-dependent atomic anomalous corrections. The final term contains the complex fine structure $\tilde{\chi}$ (of which only the imaginary part is measured in a XAS experiment), as a coefficient of $\Delta f''$, the portion of *f''* being due to the resonant electron.

We extracted the imaginary component of the scattering factor from the spectra of the (100) and (200) reflections. We solved eq. (1) for its real part and

Fig. 1: Measured DAFS spectra of the (100) and (200) reflections from BaTiO₃. The (200) spectrum is displaced upwards for clarity.

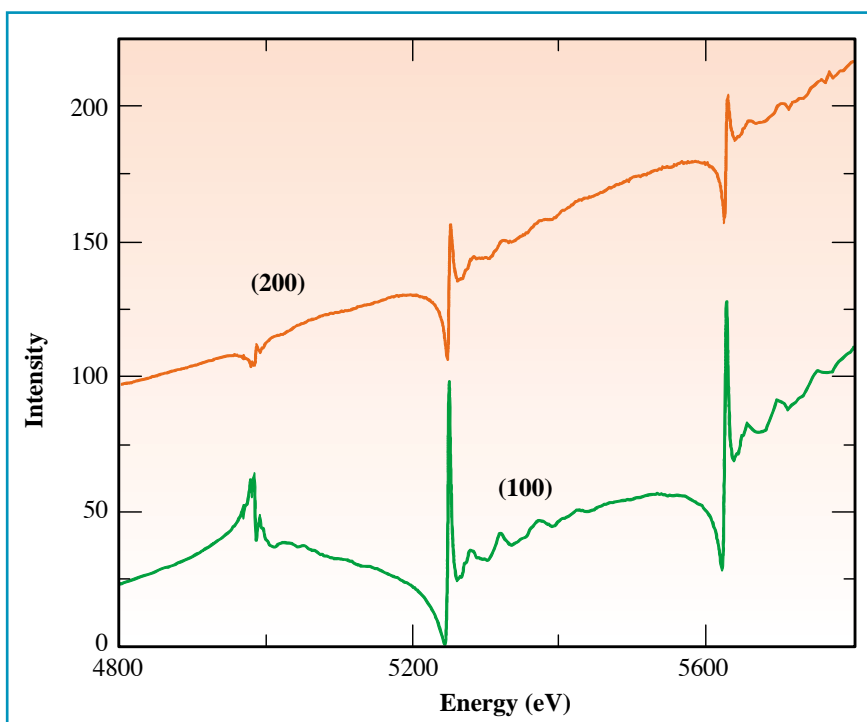




Fig. 2: Extracted $f''(E)$ for the Ti atom. Note the incomplete cancellation of the Ba L_{III} white line at about 5250 eV.

Kramers-Kronig transform this to obtain a new value for its imaginary part [5]. The steps of solving eq. (1) and transforming are iterated to convergence. A weighed sum of the f'' spectra are then made to yield the isolated Ti f'' spectrum shown in Figure 2. A method developed for isolating χ'' from the XAS μ [6] was applied directly to the Ti f'' spectrum. The extracted χ'' function is shown in Figure 3 along with a FEFF [7] simulation using previously-determined structural parameters [1]. The incomplete cancellation of the Ba white line results in a problem in the data which resembles a monochromator glitch. Despite this, measurable Ti fine structure signal is seen in χ between 9 and 10 \AA^{-1} .

Using DAFS to separate the fine structures of overlapping absorption edges is a novel approach to this problem which does not require the use of energy discriminating detectors. We have shown that it yields data that is analyzable beyond the second absorption edge energy. There are many transition metal/rare-earth compounds of technological interest which are composed of atoms with overlapping edges. We plan to test our method on one such material, $\text{Gd}_3\text{Fe}_5\text{O}_{12}$, a material used in microwave wave guides. In that case, the Fe K and the Gd L_{III} are separated by only 130 eV and their major fluorescence lines are separated by about 100 eV. ■

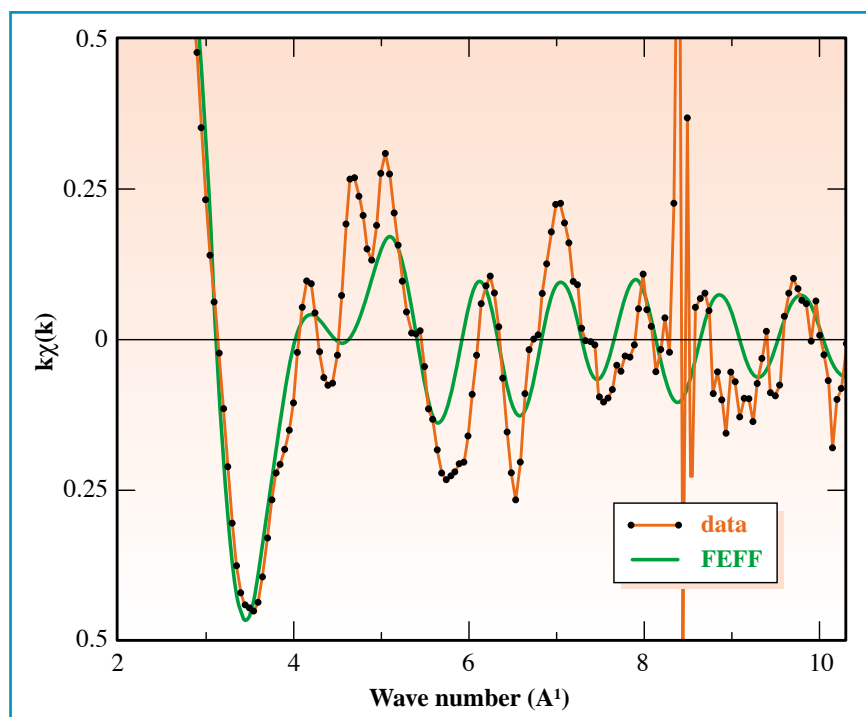
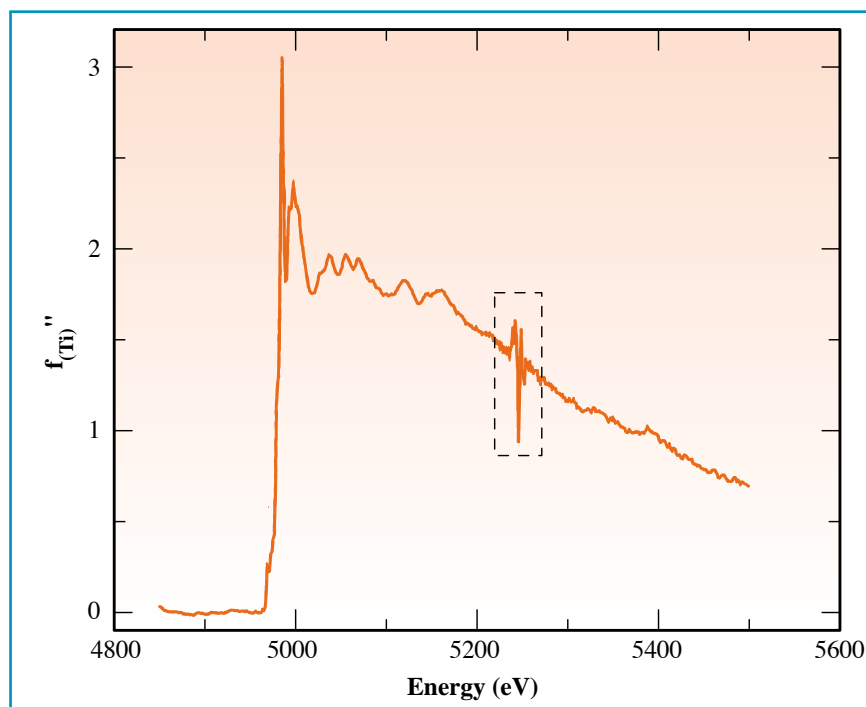


Fig. 3: χ'' for the Ti atom compared to a simulation using FEFF [7]. The large feature around 8.5 \AA^{-1} is due to the incomplete cancellation of the Ba L_{III} white line.

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