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## Edge separation using diffraction anomalous fine structure

Bruce Ravel,<sup>a\*</sup> Charles E. Bouldin,<sup>a</sup> Hubert Renevier,<sup>b</sup> Jean-Louis Hodeau<sup>b</sup> and Jean-Francois Berar<sup>b</sup>

<sup>a</sup>NIST, Ceramics Division, Gaithersburg MD, 20899 USA, and <sup>b</sup>Laboratoire de Cristallographie, CNRS, BP 66, 38042 Grenoble Cedex 09 France. E-mail: bruce.ravel@nist.gov

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 BaTiO<sub>3</sub> the Ti K edge and Ba L<sub>III</sub> edges are separated by 281 eV, or about 8.2 Å<sup>-1</sup>, thus severely limiting 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. This technique has application to many rare earth/transition metal compounds, including many magnetic materials of technological significance for which K and L edges overlap in energy.

**Keywords:** DAFS; BaTiO<sub>3</sub>; Site separation.

### 1. The Difficulty of Analyzing BaTiO<sub>3</sub> XAS Data

Recent X-ray absorption spectroscopy (XAS) studies (Ravel *et al.*, 1998) of the Ti K near edge and Ba K extended spectra of BaTiO<sub>3</sub> 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 fine structure was hindered by the presence of the nearby Ba L<sub>III</sub> absorption edge at 5247 eV, compared to 4966 eV for the Ti K edge. This separation is about 8.2 Å<sup>-1</sup> in photoelectron wavenumber. This narrow data range places such a severe limit on the information content of the Ti extended spectrum that meaningful analysis of those data is not possible given the complexity of the BaTiO<sub>3</sub> local structure. Furthermore, the energies of the various fluorescence lines of Ti and Ba preclude the use of an energy discriminating detector in fluorescence mode. The dominant lines are the Ti K<sub>α1</sub> and Ba L<sub>α1</sub>, which are separated by only 45 eV. We were unable to resolve either the Ti K<sub>α1</sub> or K<sub>β1</sub> lines using a Si(Li) detector. This energy separation is near the limit of even the best wavelength dispersive detection, which we have not yet attempted.

In this paper we suggest 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 Cu in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> (Sorensen *et al.*, 1994) and Fe in BaZnFe<sub>8</sub>O<sub>11</sub> (Vacínová *et al.*, 1995) or at the interfaces of a multi-layer compound (Renevier *et al.*, 1997). Using a similar methodology, we can separate the signals from the Ti and Ba sites in BaTiO<sub>3</sub>, thus isolating the Ti K edge fine structure spectrum and extending it beyond the 8.2 Å<sup>-1</sup> limit of the absorption experiment.

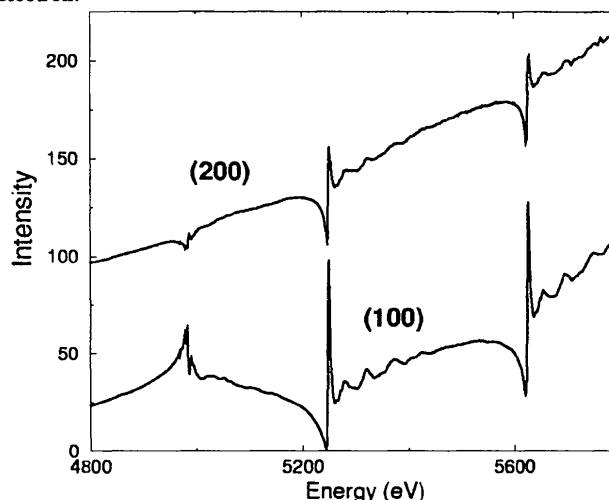
### 2. Using DAFS to Separate Edges

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. Near the absorption edge the complex anomalous correction to the scattering factor of the resonant atom becomes large (Sorensen *et al.*, 1994) compared to the Thomson scattering, resulting in the characteristic cusp shape seen in Fig. 1. These data were taken at ESRF beamline BM-02 on a 1000 Å thick film of BaTiO<sub>3</sub> deposited on sapphire by pulsed laser deposition. The film was found by x-ray diffraction to be oriented with an *a* axis normal to the surface. In our experiment, we measured reflections in the vertical scattering plane. Due to physical limitations to the range of motion of the goniometer and the long wavelength of the incident x-rays (about 2.5 Å around the Ti K edge), we were restricted to the (100), (200), and (300) reflections. The (300) reflection is very weak and will not be considered in this paper.

The oscillatory fine structures seen above the absorption energies contain the same local structural information as an XAS spectrum. The diffracted intensity is expressed (Sorensen *et al.*, 1994) as

$$I(\mathbf{Q}, E) = \left| \sum_j M_j e^{i\mathbf{Q}\cdot\mathbf{R}_j} \times (f_j^0(\mathbf{Q}) + f_j'(E) + if_j''(E) + [\Delta f''(E)\chi(E)]_j) \right|^2 \quad (1)$$

where the sum is over all sites *j* in the unit cell, *M<sub>j</sub>* is the thermal factor at site *j*, *f<sup>0</sup>* is the Thomson scattering of the atom at site *j*, and *f' + if''* is the atomic portion of the energy dependent anomalous correction. The final term contains the complex fine structure  $\chi$  (of which only the imaginary part is measured in an XAS experiment) as a coefficient of  $\Delta f''$ , the portion of *f''* due to the resonant electron.

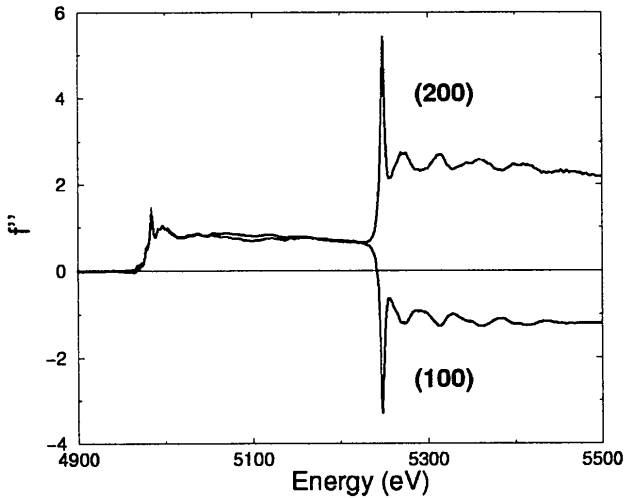


**Figure 1**

Measured DAFS spectra of the (100) and (200) reflections from BaTiO<sub>3</sub>. The (200) spectrum is displaced upwards for clarity. Note that the anomalous correction to the scattering factor causes the (100) spectrum to drop at 5244 eV to about 4% of its value from the beginning of the data range.

Our objective is to extract the imaginary portion *f''(E)* of the scattering factor from the spectra of the (100) and (200) reflections. Because of the positions of the Ti and Ba atoms in the unit cell and the *e<sup>iQ·R<sub>j</sub></sup>* term in the structure factor, the relative phase of the scattering from the Ti and Ba planes shifts by about 180 degrees

between the two reflections. This phase shift is evident in the Ti edge cusps in Fig. 1 which point in opposite directions. Because of this simple phase relationship, the XAS-like fine structure signal due to the titanium atom can be isolated by taking a weighted difference of  $f''(E)$  contribution to Eq. (1) from the two reflections.

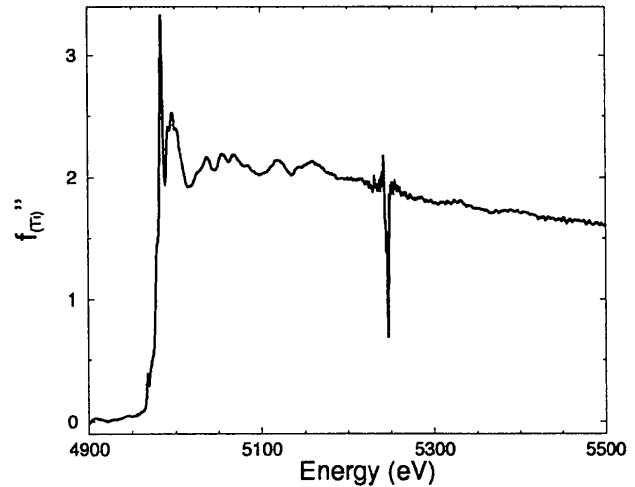


**Figure 2**

$f''(E)$  extracted from the (100) and (200) reflections using the iterative Kramers-Kronig technique. These spectra have been normalized to a Ti edge step of +1.

The initial step in the extraction of the imaginary part of Eq. (1) from the measured intensities is to fit the data using the crystal structure and standards for  $f^0$ ,  $f'$ , and  $f''$  for each of the atoms in the material. For  $f^0$  and the small anomalous correction of oxygen we used tabulated atomic data (Brennan & Cowan, 1992). For the anomalous corrections to the Ti and Ba scattering factors, we used transmission XAS data from a BaTiO<sub>3</sub> fine powder sample to construct initial guesses for  $f''$ . For Ti, we converted the absorption data to  $f''$  using the optical theorem (Cullity, 1978) and matched (Cross *et al.*, 1998) this to tabulated atomic values (Brennan & Cowan, 1992) beyond the Ba L<sub>III</sub> edge. For Ba we converted the data to  $f''$  and matched it before the Ba L<sub>III</sub> edge and at high energy to the tabulated atomic data. We then used a differential Kramers-Kronig algorithm (Cross *et al.*, 1998; Ohta & Ishida, 1988) to generate initial guesses for  $f'$  for Ti and Ba. Using these functions and the room temperature crystal structure (Kwei *et al.*, 1993) of BaTiO<sub>3</sub>, we obtained a best fit of an overall amplitude and a polynomial background to the measured data.

We then subtract the polynomial from the data and use the initial  $f''(E)$  functions to solve for the real part of the anomalous corrections in Eq. (1). We perform a differential Kramers-Kronig transform on that function to obtain a refined value of the imaginary part of the anomalous correction, which we then use to extract a new value of the real part. This process is iterated until convergence. This typically takes about 5 iterations. Fig. 2 shows the final imaginary functions for the two reflections. The use of the iterative Kramers-Kronig method for BaTiO<sub>3</sub> is made possible by the fact that the symmetry of the BaTiO<sub>3</sub> lattice is such that  $\sin(\mathbf{Q} \cdot \mathbf{R}_j) = 0$  for all of the ( $\ell$ 00) reflections and so all of the cross terms in Eq. (1) vanish. The shift in relative phase between the Ti and Ba planes in the two reflections is evident in Fig. 2 as the Ba L<sub>III</sub> steps are oppositely signed when the Ti steps are normalized to +1.



**Figure 3**

Extracted  $f''(E)$  for the Ti atom. Note the incomplete cancellation of the Ba L<sub>III</sub> white line at about 5250 eV.

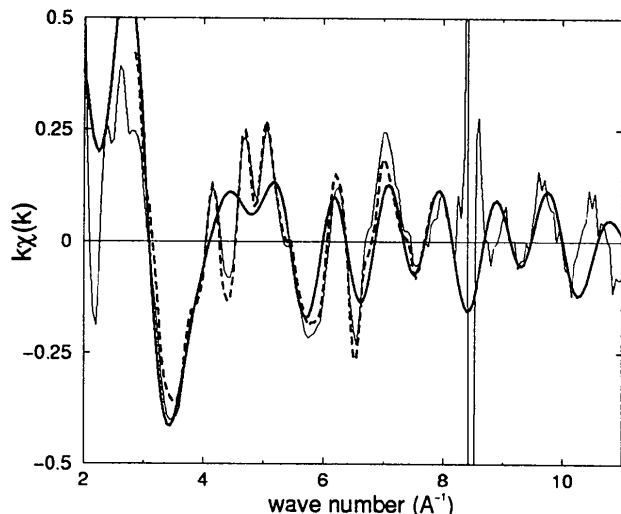
The spectra in Fig. 2 are added together, resulting in the isolated Ti  $f''(E)$  spectrum shown in Fig. 3. This addition of spectra requires two parameters. One is a relative weight — the (100) spectrum was weighted by  $\sim 1.2$  relative to the (200) spectrum. The other parameter is an energy dependent  $E_0$  shift to account for the small difference in tracking of the monochromator between scans. This energy discrepancy was about 1 eV at the Ba L<sub>III</sub> edge between scans aligned at the Ti edge. The criteria for choosing these parameters is that the Ba L<sub>III</sub> white line is minimized and that the background  $f''_0(E)$  is continuous through the Ba L<sub>III</sub> edge energy. With this data set, the Ba white line cancels incompletely, resulting in the large feature around 5250 eV which resembles the effect of a monochromator glitch. Despite this, measurable oscillations in the Ti spectrum remain beyond the Ba L<sub>III</sub> edge energy.

Because of the optical theorem relating  $f''$  and  $\mu$ , the functional form of the spectrum in Fig. 3 can be expressed as

$$f''(E) = f''_0(E) \cdot [1 + \chi''(E)] \quad (2)$$

Therefore, a method developed for isolating  $\chi$  from  $\mu$  (Newville *et al.*, 1993) can be applied directly to this spectrum. The extracted  $\chi(k)$  function is shown in Fig. 4 along with a FEFF simulation using previously determined structural parameters (Ravel *et al.*, 1998). The  $\chi(k)$  shown in Fig. 4 is the average of the four scans obtained from the four possible combinations of scans given that we measured two scans at each reflection.

These data demonstrate the objective of this paper. Specifically, we have shown that DAFS can be used to extract  $\chi(k)$  even beyond the energy of an overlapping absorption edge. Before  $8 \text{ \AA}^{-1}$ , this  $\chi(k)$  spectrum is comparable to that measured by XAS. Between 9 and  $10 \text{ \AA}^{-1}$  there is clearly Ti signal. Unfortunately the incomplete cancellation of the Ba L<sub>III</sub> white line introduces considerable noise to these data. Although analyzable, the data presented here are not of comparable quality to a good XAS experiment. Obtaining data for which the edge region of the higher energy edge cancels correctly is the most important improvement necessary for this technique.



**Figure 4**

$\chi(k)$  for the Ti atom extracted from the DAFS data (thin solid line) compared to a simulation using FEFF (thick solid line) (Zabinsky *et al.*, 1995) and to  $\chi(k)$  out to  $7.8 \text{ \AA}^{-1}$  from transmission XAFS (dashed line). The large feature near  $8.5 \text{ \AA}^{-1}$  is due to the incomplete cancellation of the Ba  $L_{III}$  white line.

### 3. Conclusion

We have presented a novel approach to the problem of overlapping absorption edges which does not require the use of an energy discriminating detector. We have shown that it yields data that, although not comparable to the highest quality XAS data, is analyzable beyond the second absorption edge energy.  $\text{BaTiO}_3$  is a difficult material for this method due to the relatively large separation of the edges. Because of that, the Ti fine structure is quite small compared to the Ba edge step. We anticipate that this method will be *more* successful for a material with more closely spaced absorption edges because the fine structure from the lower energy

edge will be larger compared to the higher energy edge step than in  $\text{BaTiO}_3$ . There are pairs of transition metal and rare earth atoms with overlapping edges and fluorescence lines which would challenge even the resolution of a wavelength dispersive detector. We plan to test our method on a transition metal/rare earth compound material.

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