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Reliability of structural parameters determined from DAFS data using the iterative dispersion integral algorithm

Julie O. Cross,[a]* W. Tim Elam,[a] Joseph C. Woicik[b] and Larry B. Sorensen[c]

[a]*Naval Research Laboratory, Washington, DC 20375, USA,* [b]*National Institute of Standards and Technology Gaithersburg, MD 20899, USA, and* [c]*University of Washington, Seattle, WA 98195, USA. E-mail: jox@pnc.aps.anl.gov*

The iterative Kramers-Kronig (IKK) dispersion integral algorithm is commonly used to isolate the complex resonant scattering amplitude $\Delta f = f' + if''$ from measured diffraction anomalous fine structure (DAFS) intensity data, where the imaginary part f'' is then analyzed in the same manner as the absorption coefficient μ. We have performed studies using simulated and experimental DAFS data to evaluate the reliability of structural parameters determined from f'' resolved by the IKK algorithm. The results of a few of these experiments are presented here.

Keywords: DAFS; Kramers-Kronig; Analysis.

1. Introduction

Diffraction anomalous fine structure (DAFS) is the oscillatory feature observed in Bragg peak intensities as a function of energy near core electron resonances. The goal of DAFS spectroscopy is to obtain XAFS-like information about the local environment and chemical state of subsets of the resonant atoms selected using the diffraction condition, based on their long-range order. This is accomplished by isolating the real or imaginary part of the complex fine-structure $\chi = \chi' + i\chi''$ from the energy dependence of one or more Bragg peak intensities, and analyzing and interpreting the spectral content similar to XAFS.

Spline-based methods for removing the DC background from DAFS, similar to those used for XAFS background removal, can give satisfactory results (Arčon *et al.*, 1987; Stragier *et al.*, 1992), however, DAFS is an intensity measurement, and therefore the resulting fine-structure function is a mix of χ' and χ''. This has the effect of introducing additional energy-dependent phase shifts into the individual path contributions. Although these phase shifts can be calculated based on the average structure factor, or can be argued as negligible in some cases, they can also be avoided entirely by an alternative method of background removal.

When the symmetry of the crystal is such that the part of the structure due to the resonant atoms satisfies either $\sum \exp(\mathbf{q}\cdot\mathbf{r}) = \sum \cos(\mathbf{q}\cdot\mathbf{r})$ or $i\sum \sin(\mathbf{q}\cdot\mathbf{r})$, the equation for the Bragg peak intensity in the kinematic approximation reduces to a simple quadratic in the anomalous scattering amplitudes. In this situation, since f' and f'' are related causally by dispersion integrals, an iterative algorithm can be used to resolve a self-consistent analytic amplitude $\Delta f = f' + f''$ from the experimentally measured DAFS intensity (Pickering *et al.*, 1993). Since the imaginary part of the resonant scattering amplitude is directly proportional to the total absorption cross-section for synchrotron vertical plane scattering (σ-σ), the analysis of χ obtained from f'' is straightforward.

The iterative Kramers-Kronig (IKK) dispersion integral algorithm has been described in detail elsewhere (Cross, 1996). In this short article we present the results of computer studies using simulated and experimentally measured DAFS data to test the reliability of structural parameters determined using standard XAFS analysis methods on the f'' returned by the IKK method. Overall, we find excellent agreement between structural parameters determined from XAFS μ and from the IKK f''. The largest disagreement between analysis of XAFS and IKK-resolved DAFS is that the amplitude factor S_0^2 is systematically larger for the DAFS than for the XAFS. This appears to be due to the difference between the step height determined by the spline-based AUTOBK background fitting, and the step height in the theoretical background functions used in the IKK algorithm.

2. Experiment

The DAFS from a 2000 Å single crystal film of Cu metal, electrochemically deposited on a mica substrate was collected at NSLS beamline X23A-2, using a Si(311) fixed-exit monochromator and Bragg peak tracking. The diffractometer angles were recalculated at each energy to maintain the Bragg condition. The mosaic width of the crystal was 0.25°, determined from the θ rocking curves, and the variation in the ratio of $I_{\rm peak}$ to $\int I(\theta)d\theta$, measured at 100 eV intervals, was found to be less than 0.8% over the 1200 eV energy range of the scan. The energy dependence of the detectors was measured by scanning the monochromator through the range of the DAFS with no sample in place. The background fluorescence signal was measured by detuning θ by 5° in a θ-2θ scan. Fluorescence XAFS was measured simultaneously with the DAFS using a gas ionization chamber placed normal to the vertical scattering plane at the sample position. Bragg diffraction glitches into the fluorescence chamber were removed individually by hand, and the effect was minimized by collecting data at several values of the goniometer angle ϕ. Self-absorption was neglected in the XAFS since the film thickness was less than 5% of the absorption length. The diffraction data were collected in the vertical scattering plane in order to maintain σ-σ polarization in the DAFS.

3. Computer Simulation

Simulated Cu DAFS spectra were generated using a kinematic structure factor

$$F_{\mathbf{q},E} = \sum_j (f_{0,j} + \Delta f_j)\, e^{i\mathbf{q}\cdot\mathbf{r}_j} \qquad (1)$$

where the sum j is over all of the atoms at positions $\mathbf{r}_j$ in the unit cell, f_0 is the Thomson scattering amplitude, Δf is the resonant scattering amplitude and $\mathbf{q}$ is the photon wavevector transfer. Theoretical Δf, including fine-structure, were calculated using FEFF 7 and a difference KK transform (Cross *et al.*, 1998) using bare-atom atomic background functions Δf_a from tables (Sasaki, 1989). Because the DAFS from each of the Bragg peaks was analyzed separately, the diffraction Debye-Waller factor $\exp(-\frac{1}{2}B_jQ^2)$ was neglected, however, an XAFS Debye-Waller factor σ_j^2 was included in the calculation using a correlated Debye model with $\Theta_D = 315\,K$.

4. Analysis

4.1. Iterative Kramers-Kronig Algorithm

The intensity was first modeled using a parameterization of the kinematic structure factor, omitting the fine structure by substituting the bare-atom Δf_a for Δf. It is useful to rewrite the structure factor Eq. (1) in terms of smooth and resonant parts as In the kinematic (weak) scattering approximation, the intensity is proportional to the squared magnitude of the structure factor

$$\begin{aligned} F_{\mathbf{q},E} &= \sum_j (f_0 + \Delta f_a)_j \, e^{i\mathbf{q}\cdot\mathbf{r}_j} + \sum_{j'} f_{0,j'} e^{i\mathbf{q}\cdot\mathbf{r}_{j'}} \\ &\quad + \sum_{j'} \left(\Delta f_{a,j'} + f''_{0,j'}\chi_{j'}\right) e^{i\mathbf{q}\cdot\mathbf{r}_{j'}} \\ &= |F_0| e^{i\Phi_0} + \Delta F \end{aligned} \tag{2}$$

where the sum j is over the off-resonance atoms and j' over the resonant atoms, f_0 is the Thomson scattering amplitude, Δf_a is the resonant scattering amplitude, and f''_0 is the resonant scattering due to solely to the core electrons.

The Bragg intensity, in terms of Eq. (2), was then rewritten in a form convenient for computer modeling

$$I \propto |F_0|^2 \left[\left(\cos\Phi_0 + \beta f'_w\right)^2 + \left(\sin\Phi_0 + \beta f''_w\right)^2\right] \tag{3}$$

where $\beta = \sum \exp(i\mathbf{q}\cdot\mathbf{r}_j)/|F_0|$, and

$$\Delta f_w = \frac{\sum_{j'} \Delta f_{a,j'} e^{i\mathbf{q}\cdot\mathbf{r}_{j'}}}{\sum_{j'} e^{i\mathbf{q}\cdot\mathbf{r}_{j'}}} \tag{4}$$

In order to use Eq. (3) as a computer model, the non-resonant phase Φ_0 and the magnitude of the non-resonant scattering $|F_0|$ were treated as energy independent over the range or the data. A small additive fitting parameter I_{off} was included in the model to allow for a slope correction

$$\begin{aligned} I_{\text{model}} &= I_0 \left[\left(\cos\Phi_0 + \beta f'_a\right)^2 + \left(\sin\Phi_0 + \beta f''_a\right)^2\right] \times \\ &\quad A_{\mathbf{q},E} L_{\mathbf{q},E} + I_{\text{off}} \end{aligned} \tag{5}$$

where A is the self-absorption coefficient, accounting for attenuation of the diffracted beam as it passes in and out of the sample, L is the energy dependent Lorentz-Polarization correction for σ-σ scattering $1/(E^3 \sin 2\theta)$, and I_0 replaces $|F_0^2|$, since the intensity is known only to an overall scale factor. The model in Eq. (5) has a limited number of adjustable fitting parameters, listed in Table 1, that allowed it change the position and scale of the smooth theoretical structure factor, without affecting the fine-structure.

Table 1
Adjustable fitting parameters used in the IKK method. With the exception of I_{off}, these are energy-independent.

I_0	The overall amplitude is proportional to the squared magnitude of the non-resonant structure factor $\|F_0\|^2$;
Φ_0	The overall phase of the non-resonant scattering amplitude from $F_0 = \|F_0\|e^{i\Phi_0}$;
β	$\beta = \alpha/\|F_0\|^2$ is the ratio of amplitude of the resonant scatterers to the squared magnitude of the non-resonant structure factor;
δE_0	The difference in the position of the step between f''_{theory} and f''_w.
I_{off}	An offset correction that allows the fit to correct for any background in the data not removed by the instrument corrections; I_{off} is of the form $a_1 + a_2 E$. For IKK on Cu metal, a_2 was set to zero making I_{off} energy independent.

Once the intensity background was fit using the bare-atom amplitudes, Eq. (5) was iteratively solved as a quadratic in f' and KK transformed to obtain f''.

4.2. IKK DAFS Background Removal

The DAFS background was removed using the real and imaginary parts of the bare-atom resonant scattering amplitudes

$$\chi' = \frac{f' - f'_a}{f''_0} \quad \text{or} \quad \chi'' = \frac{f'' - f''_a}{f''_0} \tag{6}$$

where the step-height normalization f''_0 is due solely to the excited core electrons. Since XAFS and DAFS functions are normalized to the step height in μ or Δf at E_0, not to the background line shape, and f'' differs from μ by a factor of $1/E$, Eq. (6) were multiplied by a factor of E_0/E.

4.3. Spline Background Removal

For evaluation of the DAFS spline background removal, the structure factor was separated into a smooth part F_s, which included the bare-atom contribution Δf_a from the resonant atoms, and a fine-structure part. The intensity was defined

$$\begin{aligned} I &\propto \left| \sum_j \left[f_0 + f'_a + i f''_a\right]_j e^{i\mathbf{q}\cdot\mathbf{r}_j} e^{-M_j} + \right. \\ &\quad \left. f''_0 \sum_r \left[\chi' + i\chi''\right]_r e^{i\mathbf{q}\cdot\mathbf{r}_r} e^{-M_r} \right|^2 \\ &= \left|F_s + f''_0 \alpha\chi_w\right|^2, \end{aligned} \tag{7}$$

Analogous to spline background removal in XAFS, we defined a fine structure function

$$\begin{aligned} \overline{\chi} &= \frac{I - |F_s|^2}{2|F_s| f''_0} \\ &= (\cos\Phi_s \mathrm{Re}[\alpha\chi_w] + \sin\Phi_s \mathrm{Im}[\alpha\chi_w]) + \frac{f''_0}{|F_s|}|\alpha\chi_w|^2 \end{aligned} \tag{8}$$

where $\cos\Phi_s = \mathrm{Re}[F_s]/|F_s|$ and $\sin\Phi_s = \mathrm{Im}[F_s]/|F_s|$. A spline fit to DAFS data closely approximates the function $|F_s|$. To avoid a factor of π phase shifts in the Fourier analysis, the sign of $\overline{\chi}$ was multiplied by -1 since the cusp in Cu DAFS points downward. DAFS with an upward pointing cusp does not require this correction.

4.4. Fine Structure Analysis

Following the procedure described in (Newville, 1995), the first shell signal of $\tilde{\chi}(R)$ was fit using path files from FEFF, calculated based on the fcc Cu structure with a lattice parameter of 2.565 Å. The first twelve significant backscattering paths were used in a fit with total four variable parameters: (1) overall amplitude S_0^2; (2) Debye temperature Θ_D; (3) energy shift E_0; and (4) linear expansion coefficient α, where the change in effective path length is given by $\Delta R = \alpha R_{\text{eff}}$.

5. Results

Table 2 shows the structural parameters determined by Fourier analysis of IKK-isolated χ' and χ'' using FEFFIT on the simulated

DAFS data. Within the uncertainties estimated for the fit, structural information is preserved by the IKK algorithm. Table 3 compares structural parameters determined by analysis of the fluorescence XAFS and the IKK and spline isolated DAFS from the Cu (111) film described above. The amplitude factor the amplitude factor S_0^2 is systematically larger for the DAFS than for the XAFS, due to differences between the step height determined by spline-based background fitting, and the step height in the theoretical background functions used in the IKK algorithm. The error bars determined by FEFFIT for the DAFS data are systematically larger due to the presence of a large low-R background in the IKK χ''. This occurs because the theoretical functions used as background in the IKK algorithm lack the flexibility of the spline used by AUTOBK (Stern, 1996) and many other XAFS background removal algorithms.

Table 2

Comparison between initial values and model fitting parameters for the fits to mocked-up Cu χ'. The first row shows the initial values used to generate the mocked-up data. The second row is the result of a self-test using FEFFIT to fit to the raw FEFFIT-generated χ. The third and fourth columns are the results of fitting the analytic χ' and χ'' after core-hole broadening and application of the difference KK transform. Four adjustable parameters were used: amplitude S_0^2, Debye temperature Θ_D, edge shift ΔE_0, and linear expansion coefficient α. The last column shows the first neighbor path length based on the best fit value of α. Note that S_0^2 for the test functions is systematically low due to convolution with a 2 eV Lorentzian. Uncertainties were determined by FEFFIT.

	S_0^2	Θ_D (K)	ΔE_0 (eV)	d_0 (Å)
Input parameters used to generate test functions				
χ''	0.890±0.00	315±0	0.00 ±0.00	2.565 ±0.000
FEFFIT *self-test (uncertainties could not be estimated)*				
χ''	0.890±x.x	315±x	0.00 ±x.x	2.5650±x.x
Fits to analytic test functions				
χ'	0.836±0.013	313±2	-0.002±0.15	2.565 ±0.001
χ''	0.838±0.010	313±2	-0.020±0.12	2.564 ±0.001
Fits to IKK χ'' from mocked-up Cu (111) and (222) DAFS				
χ''_{111}	0.819±0.013	310±2	0.268±0.15	2.564 ±0.001
χ''_{222}	0.838±0.013	309±2	-0.392±0.14	2.564 ±0.001

Table 3

FEFFIT results for Cu XAFS, IKK DAFS χ' and χ'' and spline DAFS. Four parameters were used in the Levenberg-Marquardt minimization: amplitude S_0^2; Debye temperature Θ_D; edge shift ΔE_0; and linear expansion coefficient α. The last column gives the value of the distance of closest approach, which can be compared to the nominal value of 2.557 Å.

	S_0^2	Θ_D (K)	E_0 (eV)	d_0 (Å)
XAFS	0.911±0.08	311±17	2.7 ±0.8	2.576±0.005
χ'	1.139±0.21	270±21	-0.47±1.9	2.550±0.013
χ''	1.128±0.22	271±23	-0.16±1.9	2.552±0.013
$\overline{\chi}$	1.309±0.07	284±7	3.3 ±0.5	2.559±0.010

6. Conclusion

Overall, we find excellent agreement between structural parameters determined from XAFS μ and from the IKK f'', however there is an inherent difficulty with the IKK algorithm that the conjugate pair f' and f'' that best fits the measured DAFS is not unique, but depends on the the quality of the data and on the theoretical functions used for Δf_a. If the fit to the smooth part of the DAFS intensity background is good, then the iterative part of the algorithm generally produces very accurate results. For this reason, it is recommended to use the average structure factor to guess the phase Φ_0, even though the IKK can nominally be performed with no *a priori* knowledge of the unit cell.

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References

Arčon, I., Kodre, A., Glavič, D. & Hribar, M. (1987). *J. Phys. C (Paris)*, **9**, 1105–1108. *Supplement n°12.*

Cross, J. O. (1996). Analysis of Diffraction Anomalous Fine Structure. *Ph.D. dissertation, University of Washington.*

Cross, J. O., Newville, M., Rehr, J. J., Sorensen, L. B., Bouldin, C. E., Watson, G. M., Gouder, T. & Lander, G. H. (1998). Phys. Rev. B, *58, in press.*

Newville, M. (1995). Local Thermodynamic Measurements of Dilute Binary Alloys Using XAFS. *Ph.D. dissertation, University of Washington.*

Pickering, I. J., Sansone, M., Marsch, J. & George, G. N. (1993). J. Am. Chem. Soc. *115, 6302–6311.*

Sasaki, S. (1989). Numerical Tables of Anomalous Scattering Factors Calculated by the Cromer and Liberman's Method. *Tech. Rep. KEK Report 88-14. National Laboratory for High Energy Physics.*

Stern, E. A., (1996). Information about the UWXAFS *package, including* AUTOBK, FEFFIT *and* ATOMS, *and the* UWXAFS *project can be obtained through the world wide web site at* `http://krazy.phys.washington.edu/`. *Those interested in acquiring the* UWXAFS *codes are directed to contact Professor E.A. Stern at the University of Washington.*

Stragier, H., Cross, J. O., Rehr, J. J., Sorensen, L. B., Bouldin, C. E. & Woicik, J. C. (1992). Phys. Rev. Lett. *69, 3064–3067.*

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