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Comparison of EXAFS Foil Spectra from Around the World

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Abstract. The EXAFS spectra of Cu and Pd foil from many different beamlines and synchrotrons are compared to address the dependence of the amplitude reduction factor (S_0^2) on beamline specific parameters. Even though S_0^2 is the same parameter as the EXAFS coordination number, the value for S_0^2 is given little attention, and is often unreported. The S_0^2 often differs for the same material due to beamline and sample attributes, such that no importance is given to S_0^2 -values within a general range of 0.7 to 1.1. EXAFS beamlines have evolved such that it should now be feasible to use standard S_0^2 values for all EXAFS measurements of a specific elemental environment. This would allow for the determination of the imaginary energy (Ei) to account for broadening of the EXAFS signal rather than folding these errors into an effective S_0^2 -value. To test this concept, we model 11 Cu-foil and 6 Pd-foil EXAFS spectra from around the world to compare the difference in S_0^2 - and Ei-values.

1. Introduction

The methodology for determining the amplitude reduction factor (S_0^2) is to measure a standard such as simple metal foil in the same detector geometry and with the same beamline parameters as that of the unknown sample. Although S_0^2 -values are the same variable as the EXAFS coordination

number and the later is often the main purpose of an EXAFS study, S_0^2 values often go unmentioned in EXAFS papers as little information can be gained by simply reporting an S_0^2 -value.

S_0^2 is defined as the incomplete overlap between the passive electrons in the ground state and the final (correlated) ionic state of the system¹. In this definition, it is only the absorbing atom properties that contribute to S_0^2 , although the bonding environment can affect the final ionic state and hence the value for S_0^2 . A comparison of EXAFS spectra of approximately 30 reference compounds was performed using FEFF 5². In that comparison, the value for S_0^2 varied significantly for an absorbing atom with different neighboring atom types. For example, S_0^2 values for Cu compounds were found to vary from 0.64 to 0.84. The EXAFS spectra of Cu foil has been studied extensively³.

Calculated or tabulated S_0^2 -values have not been adopted even for a specific bonding environment because of differences in beamline parameters (such as energy resolution, harmonic rejection, detector efficiency) and differences in sample homogeneity and thickness which affect the effective value for S_0^2 . These beamline and sample differences lead to a broadening of the EXAFS signal that can be described by an effective S_0^2 , but should be better described by an imaginary energy shift (Ei). Because of the high correlation of S_0^2 and Ei usually only an effective S_0^2 is determined. EXAFS beamlines have evolved such that it should now be feasible to use standard S_0^2 values for a specific bonding environment, so that the more meaningful Ei-value can be reported.

To test this concept, we compare the Cu and some Pd K-edge EXAFS spectra from 11 different beamlines and 7 different synchrotrons to address the dependence of S_0^2 values on beamline specific parameters. We test whether a single S_0^2 value with independent Ei-values can provide better description of the spectra, with spectral broadening information contained in Ei.

Table 1. Description of Foil Spectra.				
Synchrotron	Beamline	Mono.	Cu Foil Thickness	Contributor
ALS	10.3.2 ⁴	Si(111)	Cu (8 μ)	S. Fakra
	Microprobe, Pre-mono slits 200 μ x 20 μ			
APS	10ID ⁵	Si(111)	Cu (4 μ), Pd(15 μ)	S. R. Bare, S. Chattopadhyay, N. Greenlay, S. D. Kelly,
	Sample slits = 0.8x0.8 mm, harmonic rejection mirror			
APS	5BM	Si(111)	Pd (5 μ)	D. Barton
APS	33BM	Si(111)	Pd(15 μ)	S. R. Bare, N. Greenlay,
APS	13ID	Si(111)	Cu (10 μ)	M. Newville
	vert. slits after mono = 300 μ , 50% detuned			
ESRF	BM30b-FAME ⁶	Si(111)	Cu (7 μ)	G. Pokrovski, O. Proux
	BM30b-FAME	Si(220)	Cu (7 μ)	
	Sagittal focusing, beam size 300 μ m x 100 μ m, harmonic rejection mirror			
LNLS	DO4B-XAFS1 ⁷	Si(111)	Cu (7.5 μ)	G. Azevedo
	DO4B-XAFS2	Si(111)		
	Vert. slits after mono slits = 300 μ			
NSLS	X23A2	Si(311)	Cu (4 μ), Pd(15 μ)	B. Ravel
	Pre-mono slits= 1mm, sample slits = 800 μ ; Harmonic rejection mirror for Cu, Au, Pt			
SSRL/ SPEAR3	BL2-3	Si(111)	Cu (12 μ)	S. Webb
	Microprobe, beam size = 2 μ x 2 μ			
	BL2-3	Si(111)	Cu (12 μ)	
	Bulk, sample slits = 2 x 12 mm; 50% detuned			
SSRL/ SPEAR3	BL4-1	Si(220)	Cu (5 μ)	J. Pena
Spring8	BL01B1	Si(111)	Cu (6 μ)	K. Priolkar

2. Methods

The ambient temperature EXAFS foil spectra were collected at the Advanced Light Source (ALS), Advanced Photon Source (APS), European Synchrotron Radiation Facility (ESRF), Brazilian Synchrotron Light Laboratory (LNLS), National Synchrotron Light Source (NSLS), Stanford Synchrotron Radiation Laboratory (SSRL), and Spring 8 (Spring8). Description is in table 1. The normalized XANES are shown in figure 1A. In general all 11 spectra are similar. In the enlarged region, some broadening of a few of the spectra (LNLS, D04B-XAFS1, SSRL BL2-3 bulk, and Spring8, BL01B1) is apparent. The top of the first shell peak in the magnitude of the Fourier transform

(FT) is shown in figure 1B (figure 1C shows the full FT). Figure 1B shows less than 10% differences in the peak height. The spectra with the smallest peak heights are SSRL, BL23bulk, ALS, 10.3.2, and SSRL, BL23micro. The energy resolution observed in the inset of figure 1A does not always correlate with the first peak height in the FT. For example, LNLS, D04B-XAFS1 has low energy resolution in the pre-edge region but the greatest peak height. Whereas SSRL, BL2-3 bulk has less energy resolution and a smaller peak height.

The Cu K-edge EXAFS spectra were FT from 3 to 13 \AA^{-1} and were modeled from 1.5 to 4.7 \AA . Each spectrum contains 22 independent points. The EXAFS spectra were processed in Athena⁸ an interface to IFEFFIT⁹. The model was built from FEFF 7.02³. The model was refined to all 11 spectra using a k-weighting of 1, 2, and 3 in the FT using FEFFIT¹⁰. The use of all three k-weights weakens the correlations between S_0^2 or E_i and σ^2 -values. The same normalization parameters were used for all spectra and the bkg was found to be un-correlated to the fit parameters (defined as less than 25% correlation). The model includes 4 shells of Cu atoms and all of the paths to 5.3 \AA . Two equally equivalent models were used to describe the measured spectra. Both models are described by 5 common and 2 independent parameters. The common parameters include one energy shift (ΔE_0), 4 σ^2 values (one for each shell) and an expansion/contraction term (α) to describe a change in the path length $\Delta R = \alpha \cdot R_{\text{eff}}$. R_{eff} is determined from the crystalline structure of Cu. The σ^2 -values for multiple scattering paths were constrained to the same value as the single scattering path with the same atom at the largest distance. The first model (S_0^2 -model) varies the S_0^2 -value for each spectrum. The second model (E_i -model) includes one S_0^2 -value and an independent E_i -value for each spectrum. The Pd K-edge spectra were treated similarly but due to limited space the details are not given.

3. Results and Conclusions

The EXAFS fitting results for S_0^2 and E_i are listed in Table 2. The energy shift parameters (ΔE_0) are -2.2 ± 0.1 eV for the E_i -model. The σ^2 -values are 0.0095 ± 0.0002 , 0.0130 ± 0.0005 , 0.0133 ± 0.0003 , and 0.0134 ± 0.0003 \AA^2 for the first, second, third and fourth shells, respectively for the E_i -model. The path distance R was determined through an α and was found to be -0.001 ± 0.001 for E_i -model. The values are similar for the S_0^2 -model. The magnitude of the FTs are shown in figure 1C.

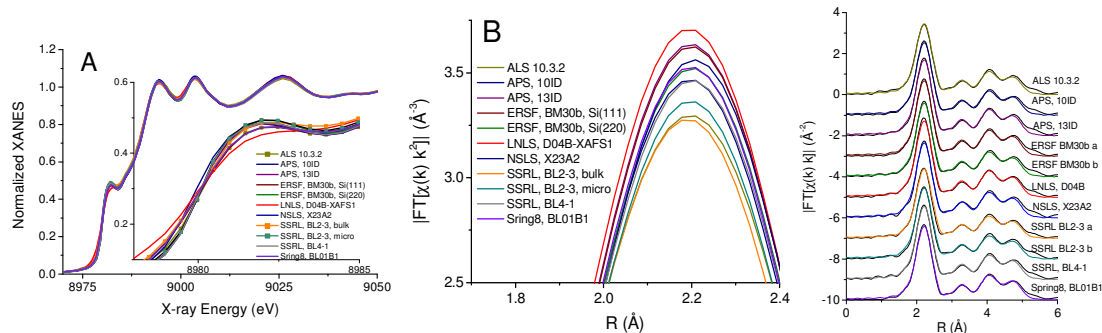


Figure 1. A) Normalized Cu K-edge EXAFS spectra. Inset shows an enlarged view of edge region. B) Magnitude of FT of first shell peak. C) Magnitude of FT (black) and Ei-Model (colored).

For the Cu foil spectra, the S_0^2 -model is statistically equivalent to the E_i -model. The S_0^2 -model shows consistent S_0^2 -values from synchrotrons around the world, with values between 0.93 and 1.04. These values are larger than previously reported², the difference in S_0^2 -values may be caused in part by using theoretical models from FEFF 7.02 rather than FEFF 5. The Cu spectra with smaller EXAFS amplitude in the magnitude of the FT first shell peak, as shown in Figure 1B, have smaller S_0^2 values in the S_0^2 -model and larger E_i -values in the E_i -model. Even so, we are impressed by the level of agreement between the different beamlines. It is interesting to note that the data set with the poorest energy resolution in the XANES region (LNLS, D04B-XAFS1) has one of the largest peaks in the magnitude of the Fourier transform and hence a large S_0^2 -value and small E_i -value. This is not intuitive as other data sets with slightly poorer resolution in the XANES region also have smaller S_0^2 -

values and larger Ei-values as expected. These models illustrate that the single S_0^2 value of 1.04 ± 0.05 is the best beamline independent value for Cu-foil given our set of 11 spectra.”

Table 2. Cu Foil EXAFS parameters.		
	S_0^2-model (Ei = 0)	Ei-model ($S_0^2 = 1.04 \pm 0.05$)
Cu Foil Data Set	S_0^2	Ei (eV)
ALS, 10.3.2	0.93 ± 0.02	0.9 ± 0.3
APS, 10ID	0.97 ± 0.03	0.5 ± 0.3
APS, 13ID	1.02 ± 0.03	0.1 ± 0.3
ERSF, BM30b, Si(111)	1.02 ± 0.03	0.1 ± 0.3
ERSF, BM30b, Si(220)	0.98 ± 0.03	0.4 ± 0.3
LNLS, DO4B-XAFS1	1.04 ± 0.04	0.0 ± 0.4
NLSL, X23A2	1.00 ± 0.02	0.2 ± 0.3
SSRL, BL23, bulk	0.91 ± 0.02	1.0 ± 0.3
SSRL, BL23, micro	0.94 ± 0.06	0.8 ± 0.6
SSRL, BL41	0.97 ± 0.02	0.5 ± 0.3
Spring 8, BL01B1	0.98 ± 0.04	0.4 ± 0.4

The S_0^2 -values for the Pd foil EXAFS spectra varied slightly between 0.83 to 0.85 ± 0.04 with Ei = 0. In the model with S_0^2 refined to the common value of 0.85 ± 0.04 , the Ei-values varied from 0.0 to 0.2 ± 1.0 eV. The variation in the amplitude of the first shell peak in the magnitude of the Fourier transform of the Pd foil spectra were very similar as expected for such a slight variation in S_0^2 .

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