

# 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 system<sup>1</sup>. 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 5<sup>2</sup>. 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 extensively<sup>3</sup>.

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

## 2. Methods

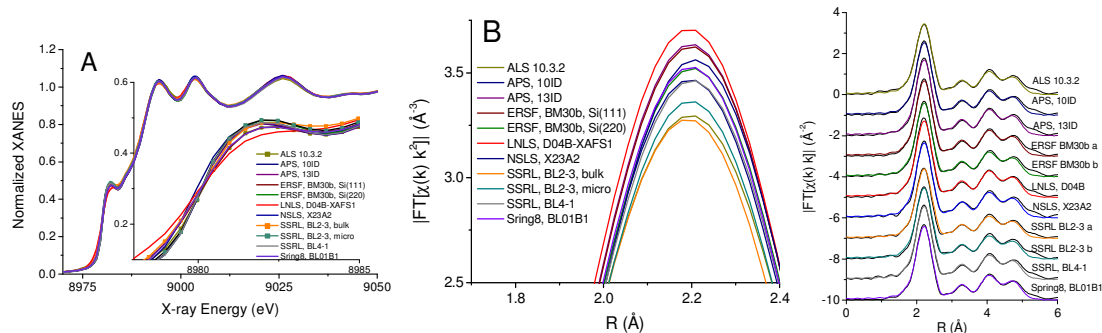
The ambient temperature EXAFS foil spectra were collected at the Advanced Light Source (ALS), Advanced Photon Source (APS), European Synchrotron Radiation Facility (ESRF), Brazilian Synchrotron Light Laboratory (LNLS), National Synchrotron Light Source (NSLS), Stanford Synchrotron Radiation Laboratory (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  $\text{\AA}^{-1}$  and were modeled from 1.5 to 4.7  $\text{\AA}$ . Each spectrum contains 22 independent points. The EXAFS spectra were processed in Athena<sup>8</sup> an interface to IFEFFIT<sup>9</sup>. The model was built from FEFF 7.02<sup>3</sup>. The model was refined to all 11 spectra using a k-weighting of 1, 2, and 3 in the FT using FEFFIT<sup>10</sup>. The use of all three k-weights weakens the correlations between  $S_0^2$  or  $E_i$  and  $\sigma^2$ -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  $\text{\AA}$ . 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 ( $\Delta E_0$ ), 4  $\sigma^2$  values (one for each shell) and an expansion/contraction term ( $\alpha$ ) to describe a change in the path length  $\Delta R = \alpha \cdot R_{\text{eff}}$ .  $R_{\text{eff}}$  is determined from the crystalline structure of Cu. The  $\sigma^2$ -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 ( $\Delta E_0$ ) are  $-2.2 \pm 0.1$  eV for the  $E_i$ -model. The  $\sigma^2$ -values are  $0.0095 \pm 0.0002$ ,  $0.0130 \pm 0.0005$ ,  $0.0133 \pm 0.0003$ , and  $0.0134 \pm 0.0003$   $\text{\AA}^2$  for the first, second, third and fourth shells, respectively for the  $E_i$ -model. The path distance  $R$  was determined through an  $\alpha$  and was found to be  $-0.001 \pm 0.001$  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  $E_i$ -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 reported<sup>2</sup>, 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  $1.04 \pm 0.05$  is the best beamline independent value for Cu-foil given our set of 11 spectra.”

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

The  $S_0^2$ -values for the Pd foil EXAFS spectra varied slightly between 0.83 to  $0.85 \pm 0.04$  with Ei = 0. In the model with  $S_0^2$  refined to the common value of  $0.85 \pm 0.04$ , the Ei-values varied from 0.0 to  $0.2 \pm 1.0$  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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#### **References**

- [1] Rehr, J J, Stern, E A, Martin, R L and Davidson, E R 1978 *Phys. Rev. B* 17 p 560.
- [2] Li, G G, Bridgest, F and Booth, C H 1995 *Phys. Rev. B* 52 p 6332.
- [3] Mustre de Leon, J, Rehr, J J, Zabinsky, S I and Albers, R C 1991 *Phys. Rev. B* 44 p 4146
- [4] Marcus, M A, MacDowell, A A, Celestre, R, Manceau, A, Miller, T, Padmore, H A and Sublett, R E 2004 *J. Synch. Rad.* 11 p 2390247.
- [5] Segre, C U, Leyarovsky, N E, Chapman, L D, Lavender, W M, Plag, P W, King, A S, Kropf, A J, Bunker, B A, Kemner, K M, Dutta, P, Druan, R S and Kaduk, J 2000 *Synchrotron Rad. Inst. CP521* p 419.
- [6] Proux, O, Biquard, X, Lahera, E, Menthonnex, J J, Prat, A, Ulrich, O, Soldo, Y, Trévisson, P, Kapoujyan, G, Perroux, G, Taunier, P, Grand, D, Jeantet, P, Deleglise, M, Roux, J P and Hazemann, J L 2005 *Phys. Scr. T115* p 970.
- [7] Tolentino, H C N, Ramos, A Y, Alves, M C M, Barrea, R A, Tamura, E, Cezar, J C and Watanabe, N 2001 *J. Synchrotron Rad.* 8 p 1040.
- [8] Ravel, B and Newville, M 2005 *J. Synch. Rad.* 12 p 537.
- [9] Newville, M 2001 *J. Synch. Rad.* 8 p 322.
- [10] Stern, E A, Newville, M, Ravel, B, Yacoby, Y and Haskel, D 1995 *Physica B* 209 p 117.