

Extended x-ray absorption fine structure determination of thermal disorder in Cu: Comparison of theory and experiment

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(Received 9 March 1979)

The extended x-ray absorption fine structure (EXAFS) of Cu at temperatures from 10 to 683K has been used to evaluate the EXAFS disorder term and compare it with theory. The change in disorder for different temperatures was extracted from the slopes of $\ln(\chi_1/\chi_2)$ plots and by using a least-squares curve-fitting program. The values of the disorder parameter vs temperature are compared to a pure Debye model without correlation, a Debye model with correlation, and a model incorporating the measured phonon spectrum of Cu. The pure Debye model predicts too large an effect, whereas there is good agreement between the experimental data and either of the other two theories. This indicates that models which account for the correlated motion of the absorbing and scattering atom can give σ values which are in good agreement with those determined experimentally.

INTRODUCTION

The extended x-ray absorption fine structure (EXAFS) has recently become a relatively well-understood and widely used technique for determining many structural parameters associated with the local environment surrounding a specific atomic species. The primary information obtained from EXAFS is the number, kind, and distance of atoms surrounding a given atom. In addition, the disorder due to thermal and static variations can be obtained. In spite of the wide and increasing use of EXAFS, little attention has been given to the study of this parameter.¹

It is the purpose of this paper to discuss methods for determining the disorder using EXAFS data and then to compare the values obtained with models which predict the disorder as a function of temperature. The height and width of the peaks of the Fourier transform were examined and found to be unreliably related to the disorder parameter. Good agreement with theoretical values of the disorder was found when experimental data were analyzed with a least-squares fitting routine and a $\ln(\chi_1/\chi_2)$ vs k^2 technique developed previously.² Copper was used in this study, since it has been previously applied to test theories of EXAFS and because its vibrational properties are well known.

The x-ray absorption data for a 5- μ m Cu foil were measured at the Stanford Synchrotron Radiation Laboratory (SSRL) at four temperatures, 10 ± 1 , 77 ± 1 , 295 ± 2 , and 683 ± 5 K. The normalized EXAFS spectra are shown at the specified temperatures in Fig. 1.

ANALYSIS OF EXAFS DATA

The equation for the EXAFS function, assuming no multiple scattering, is given by

$$\chi(k) = \frac{1}{k} \sum_j \frac{N_j}{r_j^2} F_j(k) \sin[2kr_j + \psi_j(k)] e^{-2\sigma_j^2 k^2}. \quad (1)$$

Here k is the wave vector of the ejected photoelectron, the sum is over shells containing N_j atoms at distance r_j from the absorbing atom, $F_j(k)$ is the backscattering amplitude which depends on the kind of neighboring atom, σ_j^2 is the mean-squared relative displacement of the atoms arising from both static and dynamic disorder, and ψ_j is the k -dependent phase shift containing contributions from both the absorbing and scattering atoms. The quantity σ^2 characterizes the vibrational mo-

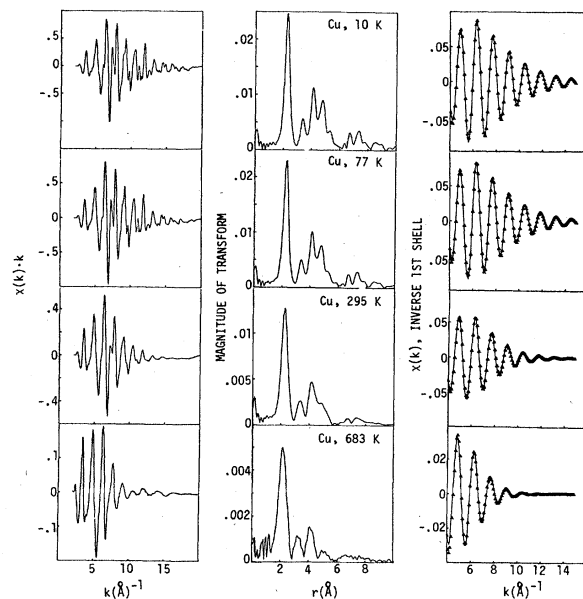


FIG. 1. EXAFS data and least-squares fits to inverse Fourier transforms at four temperatures for Cu.

tion of the atoms and is a function of temperature. This quantity can be extracted from the EXAFS data by a variety of methods discussed below, all of which assume a Gaussian disorder distribution. Some analyses assume other forms for the disorder³; these forms will be discussed later. As a first step in the analysis, $\chi(k)$ is Fourier transformed as

$$\phi(r) = \frac{1}{\sqrt{2\pi}} \int_{k_{\min}}^{k_{\max}} k\chi(k)e^{2ikr} dk. \quad (2)$$

The resulting transform, whose magnitude is shown in Fig. 1, is proportional to the convolution of the Fourier transforms of the sine term, the scattering amplitude, and the Debye-Waller term in r space. Pendry⁴ has extracted σ using the Fourier transform by selecting the shells one at a time, and for each shell separately subtracting the calculated contribution of that shell from the measured spectrum. The peak in the Fourier transform was used only as a monitor of the efficiency of subtraction. An indication of the dependence of the magnitude of the transform on the disorder parameter can be seen by taking the Fourier transform ($k=0$ to k) of the Debye-Waller term, which gives⁵

$$\phi^{\text{DW}}(r) = \frac{\exp[-(r-r_j)^2/2\sigma^2]}{8\sigma} \left[\operatorname{erf}\left(\sqrt{2}\sigma k + i\frac{r-r_j}{\sqrt{2}\sigma}\right) + \operatorname{erf}\left(\sqrt{2}\sigma k - i\frac{r-r_j}{\sqrt{2}\sigma}\right) \right], \quad (3)$$

where erf is the error function. The magnitude of the transform at the peak is then

$$\phi^{\text{DW}}(r=r_j) = \frac{\operatorname{erf}(\sqrt{2}\sigma k)}{4\sigma}. \quad (4)$$

The erf has a maximum value at an argument of approximately 1.7 which corresponds to a value of $\sigma=0.06$ Å for a k of 20 Å⁻¹. For values of $\sigma > 0.06$ the magnitude of the peak has approximately a $1/\sigma$ dependence, and for $\sigma < 0.06$ the erf limits the $1/\sigma$ dependence. Figure 2 shows the magnitude (plotted on an arbitrary scale) of the transform of the Debye-Waller term as a function of σ . Note that, when a numerical Fourier transform is made of the full χ equation for a single shell with a form like that of Cu, the dependence for $\sigma > 0.06$ Å is more like $1/\sigma^{3/2}$. This is due to the convolution of the other terms in the χ equation, as was mentioned previously. This σ dependence varies with the form of the scattering amplitude. Since different elements have different forms of F , the σ dependence will not be the same. Thus, making a ratio of the magnitude of the Fourier transform peaks is not a reliable

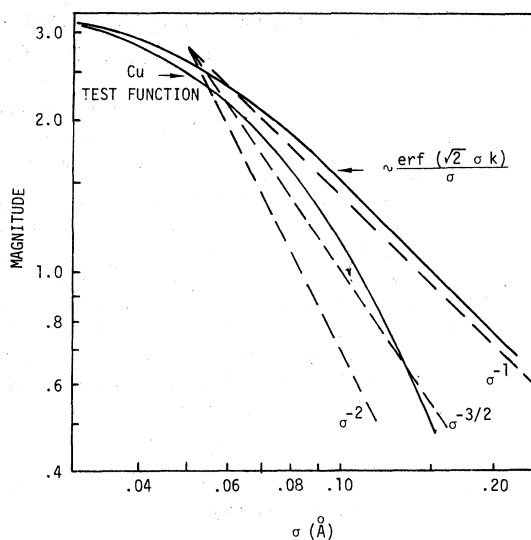


FIG. 2. Dependence of the magnitude of the Fourier transform (for Cu) on the disorder parameter.

method of determining σ (or N) unless the precise σ dependence is known.

Information about σ is also contained in the width of the transform peaks. For a single peak in the Fourier transform, the radial distribution function can be written as

$$\phi(r) = \phi(r_j) \exp[-(r-r_j)^2/2(\sigma_j+w)^2], \quad (5)$$

where $\phi(r_j)$ is the magnitude of the transform at $r=r_j$ and w is the broadening of the transform due to the back-scattering function, the phase dependence, and the transform window function. Assuming the width Δr of the transform at e^{-1} is related to σ and w by

$$\left(\frac{\Delta r}{2}\right)^2 = 2(\sigma+w)^2, \quad (6)$$

then for two temperatures with constant w ,

$$\frac{\Delta r(T_2) - \Delta r(T_1)}{\sqrt{8}} = \sigma(T_2) - \sigma(T_1). \quad (7)$$

Figure 3 shows the results of a numerical transform of a χ test function similar to Cu. The widths of the peaks were measured at e^{-1} for different known input σ 's. As can be seen the difference in widths does not accurately predict the difference in σ 's. This is because the additional width w is not a constant and is dependent on σ , i.e., w and σ are correlated with each other.

The value of σ^2 can be ascertained more accurately by methods which begin by isolating one of the transform peaks and performing an inverse transform (Fourier filtering). This effectively de-

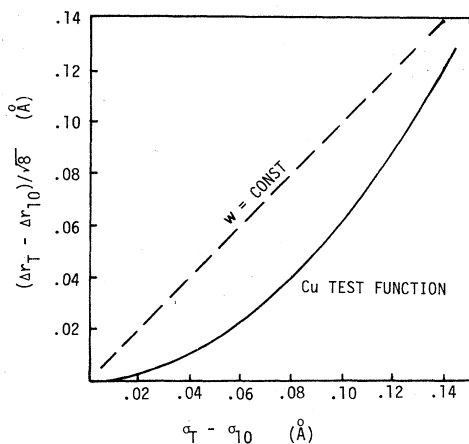


FIG. 3. Dependence of the width of the Fourier transform (for Cu) at e^{-1} on the disorder parameter.

couples the effects of multiple shells. Such inverses for the first shell of Cu are shown in Fig. 1. The natural logarithm of the ratio of the inverse Fourier transforms at 10K and higher temperatures plotted as a function of k^2 (Fig. 4) has a slope² which is proportional to $\Delta\sigma^2$. Analytically this making of a ratio gives

$$\ln \frac{\chi(k, 10K)}{\chi(k, T)} = 2[\sigma^2(T) - \sigma^2(10K)]k^2 + \ln \frac{N(10K)}{N(T)}, \quad (8)$$

which is of the form

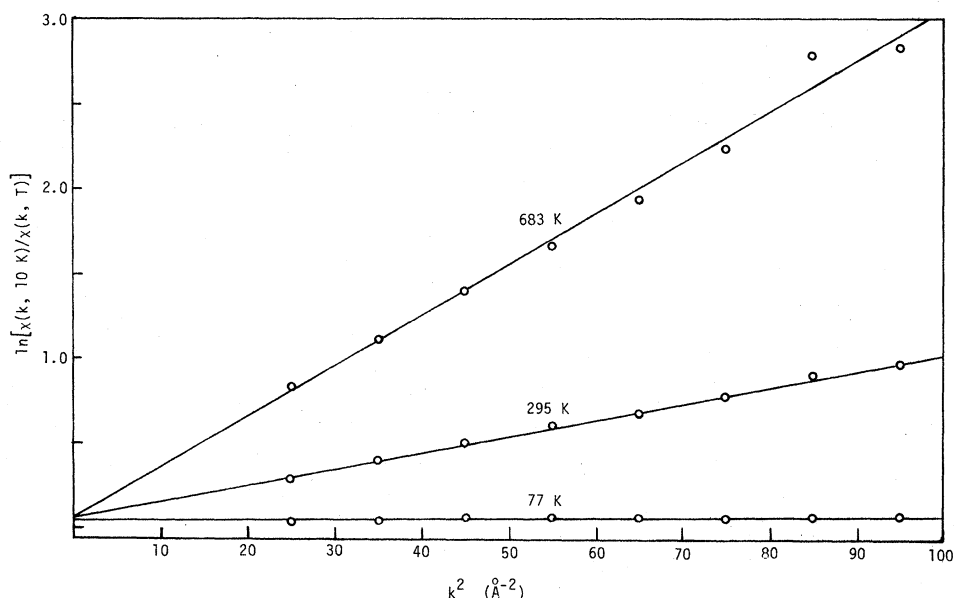


FIG. 4. Plots of the $\ln \chi(10K)/\chi(T)$ vs k^2 for Cu at $T = 683, 295,$ and 77 K.

$$y = mk^2 + b, \quad (9)$$

where

$$m = 2\Delta\sigma^2 \text{ and } b = \ln \frac{N(10K)}{N(T)}. \quad (10)$$

Assuming a value of $\sigma^2(10K)$ from theory allows calculation of $\sigma^2(T)$ at higher temperatures. These values of $\sigma(T)$ divided by $\sigma(10K)$ for Cu at four different temperatures are given in Table I and also plotted in Fig. 5. This technique resulted in accurate values of $\Delta\sigma^2$ but $\sigma(10K)$ had to be assumed from theory in order to arrive at absolute σ values.

The inverse transforms can also be used in a least-squares fitting routine to determine σ [as well as other parameters in Eq. (1)]. The least-squares procedure⁶ seeks to minimize the variance S , where

$$S = \sum_{i=1}^n (\chi_i - Y_i)^2. \quad (11)$$

Here Y_i are the Fourier-filtered data and χ_i is the analytical expression given in Eq. (1) which describes Y_i for n data points. Since $\chi(k)$ is not a linear function of the various parameters, a Taylor-series expansion was used which expressed $\chi(k)$ in terms of approximate parameter values, P_j , and parameter adjustments, $\Delta P_j = P_j - P_j'$. When the least-squares condition was applied, a set of simultaneous equations was obtained in terms of ΔP_j , rather than P_j . The equations were solved for the adjustments ΔP_j and the parameters were adjusted by ΔP_j to give a new set of esti-

TABLE I. Disorder values for various models and data extraction techniques.

Temp. <i>T</i> (K)	Debye ^a		Beni-Platzmann ^a		Rehr		Fit ^b		Ratio ^c χ	
	$\sigma(T)$ (Å)	$\frac{\sigma(T)}{\sigma(10K)}$	$\sigma(T)$ (Å)	$\frac{\sigma(T)}{\sigma(10K)}$	$\sigma(T)$ (Å)	$\frac{\sigma(T)}{\sigma(10K)}$	$\sigma(T)$ (Å)	$\frac{\sigma(T)}{\sigma(10K)}$	$\sigma(T)$ (Å)	$\frac{\sigma(T)}{\sigma(10K)}$
10	0.060	1.00	0.056	1.00	0.054	1.00	0.055	1.00	0.054	1.00
77	0.071	1.18	0.060	1.07	0.057	1.06	0.060	1.09	0.057	1.06
295	0.119	1.98	0.095	1.70	0.087	1.61	0.092	1.67	0.088	1.63
683	0.180	3.00	0.141	2.52	0.131	2.43	0.139	2.53	0.135	2.50

^a $\theta_D = 315$ K.

^b $E_0 = 0.0$ eV; $r = 2.556 \pm 0.005$ Å. Amplitude function used was the actual calculated values (Ref. 7)—parametrized functions not used. Mean free path contained in amplitude function. Phase parameters fitted at 10K and transferred to higher temperature. σ , r only fitted parameters at high temperatures.

^c $\Delta\sigma^2$ determined from slope of ratio $\ln[\chi(k, 10K)/\chi(k, T)]$. At 10K it was assumed that $\sigma = 0.054$ Å.

mates. The procedure was then repeated with the new estimates P'_j , and so on until the new solution differed from the last by less than 1%. For the results reported here the calculated tabular values of $F(k)$ from Teo and Lee⁷ were used and not the parametrized values.⁸ This gave a better fit to the data at low k values. An overall amplitude A multiplier of $F(k)$ was free to vary, and the best fit was obtained when $A \cong 0.60$. The necessity for this term has been discussed.⁹ Also a mean-free-path value was not explicitly incorporated into the solution, since this term is implicit in the $F(k)$ values used. The parametrized⁸ values for the phase shift ψ were used as an initial estimate and varied to give the best fit to the data at 10 K using the known value of $R = 2.556$ Å. The expression for ψ was

$$\psi(k) = p_0 + p_1 k + p_2 k^2 + p^3/k^3. \quad (12)$$

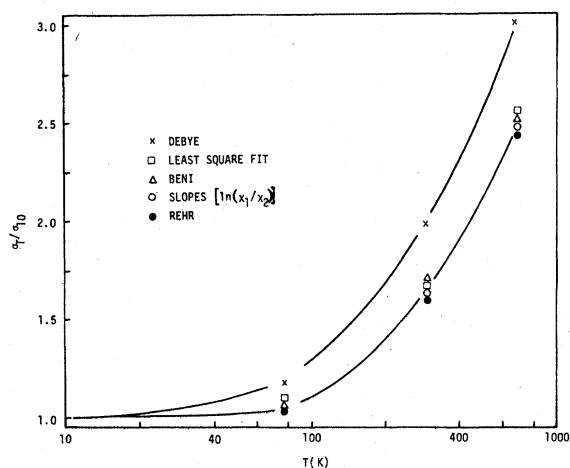


FIG. 5. Comparison of experimentally determined values of the disorder parameter with theoretical values.

Sigma was also free to vary and converged on a value of 0.055 Å at 10K. As discussed later, this value is in good agreement with theory. The phase shift and A parameters obtained were then transferred to the higher-temperature data where only σ and r were allowed to vary. The value of r remained essentially constant at a value of 2.556 ± 0.005 Å. The reason for small, negative changes in r with increasing σ has been discussed by Eisenberger and Brown.¹⁰ The least-square values of σ and $\sigma(T)/\sigma(10K)$ obtained are listed in Table I and are shown plotted in Fig. 5.

It should be noted that care must be exercised in using the least-square-fitting techniques. For example, if the parametrized amplitude functions⁸ are used rather than the tabular calculated values,⁷ differences in the resultant fitted σ may vary by 20% and lead to different apparent temperature dependences.

COMPARISON OF EXPERIMENT AND THEORY

The values of $\sigma(T)/\sigma(10K)$ plotted as a function of temperature for the σ 's extracted from the inverse transforms using the ratio technique and the least-square technique are shown in Fig. 5 compared to calculated values from a pure Debye model with no correlation,¹¹ the Debye model with correlation of Beni and Platzmann,¹ and the theory of Rehr *et al.*¹² Tabularized values are given in Table I.

The pure Debye values indicate a greater temperature dependence than that measured by the EXAFS disorder parameter. This occurs because the EXAFS σ is a measurement of mean relative displacement between two atoms along r_j whose motions are partially correlated, whereas the Debye theory predicts the total mean displacement of an atom along r_j . The expression used to cal-

culate the Debye mean-squared displacement was

$$\sigma_D^2 = 2 \langle \mu_x^2 \rangle = \frac{6\hbar}{m\omega_D} \left[\frac{1}{4} + \left(\frac{T}{\theta_D} \right)^2 D_1 \right], \quad (13)$$

where

$$D_n = \int_0^{\theta_D/T} \frac{x^n}{e^x - 1} dx \quad (14)$$

and

$$\omega_D = \frac{\theta_D k_B}{\hbar}. \quad (15)$$

In the above ω_D and θ_D are the Debye frequency and temperature, respectively, while k_B is Boltzmann's constant and T is the temperature. A temperature-independent value of $\theta_D = 315\text{K}$ was used in the analysis of the data reported here.

The calculation of Beni and Platzmann¹ accounts for the correlated motion of the central absorbing atom and surrounding scattering atoms. As seen in Fig. 5, this calculation gives a good agreement with the experimentally extracted EXAFS values. The Beni-Platzmann calculation for the mean-squared relative displacement is expressed as

$$\langle \Delta_j^2 \rangle = \frac{6\hbar}{m\omega_D} \left[\frac{1}{4} + \left(\frac{T}{\theta_D} \right)^2 D_1 \right] - \frac{6\hbar}{m\omega_D} \left\{ \frac{1 - \cos(q_D r_j)}{2(q_D r_j)^2} + \left(\frac{T}{\theta_D} \right)^2 \left[D_1 - \frac{1}{3!} \left(q_D r_j \frac{T}{\theta_D} \right)^2 D_3 + \frac{1}{5!} \left(q_D r_j \frac{T}{\theta_D} \right)^4 D_5 - \dots \right] \right\}. \quad (16)$$

In this expression $q_D (= \omega_D/V)$ is the Debye wave vector. The first term on the right is simply twice the mean-squared displacement, and the second is twice the displacement correlation function.

The result of the calculation of Rehr *et al.*¹² is also shown in Fig. 5. This calculation accounts for correlated motion of the absorbing and scattering atoms as does the Beni-Platzmann calculation. However, the actual phonon spectrum from neutron-diffraction measurements was used rather than the Debye spectrum. Disorder due to colinear atoms for first and second neighbors was accounted for, while contributions due to atoms lying perpendicular to the colinear atoms were ignored.

DISCUSSION AND SUMMARY

As stated previously, all of the above-discussed techniques of ascertaining the disorder assume a Gaussian form, which results in acceptable agreement with our estimate of σ from theory. Although no actual disorder function is purely Gaussian, this approximation is adequate for isotropic materials within a useful range of σ . Evidence of an asymmetric pair-distribution function is given by an apparent reduction in r (as determined by EXAFS) with increasing disorder. An accuracy of 0.01 \AA in r can be maintained in isotropic systems if σ^2/R and $\sigma^2/L < 0.01 \text{ \AA}$, where L is the electron mean free path.¹⁰ For cases affected by anharmonicity, the Gaussian form for disorder can be replaced by a more accurate pair-distribution function $p(r)$. Techniques have been discussed which extract the pair-distribution function from EXAFS.

In a technique presented by Hayes,³ a function constructed to reproduce $p(r)$ is convolved in r space with a peak function derived from a model system. The resultant complex function is compared with the Fourier transform of the measured EXAFS, and the constructed $p(r)$ is varied for best fit. This method requires knowledge of the EXAFS over a broad range of k . Information about the leading edge of $p(r)$ is contained at high k values while the trailing features are contained at low k , since k and r can be thought of as reciprocal variables. The difficulty of imprecise EXAFS at low k due to edge effects leads to an inherent uncertainty in $p(r)$ at large r .

The disorder term for anharmonic systems could also be constructed in k space by comparing a χ having the constructed disorder function with the experimental χ . This technique would not require comparing forms which had been convolved in r space.

The mean-squared relative displacements for Cu obtained from EXAFS measurements assuming Gaussian disorder agree well with values predicted by models which account for the correlated motion of the central absorbing and scattering atoms. Even at low temperatures in Cu there is an appreciable degree of correlated motion between neighboring atoms. At higher temperatures the amount of correlated motion increases. Either the Beni-Platzmann¹ theory, which uses a Debye phonon spectrum, or the theory of Rehr *et al.*,² which uses an actual measured phonon spectrum, can satisfactorily account for the experimental data. The results shown here are for the first coordination shell. The second and higher shells have larger disorder values, since the

correlated motion is reduced. In fact we would expect the disorder to approach the uncorrelated mean-square displacement as higher coordination shells are analyzed.⁴

Care must be used in the extraction of disorder values from EXAFS data. The height and width of peaks in the Fourier transform lead to σ values which are not accurate unless a precise σ dependence is known. The use of Fourier filtering to isolate single-shell data for making a ratio or for least-squares-fitting techniques does give σ val-

ues which are in good agreement with those predicted by theories which account for the correlated motion of the absorbing and scattering atoms.

ACKNOWLEDGMENTS

We are grateful for beam time at Stanford Synchrotron Radiation Laboratory funded by the NSF. Our research was supported by NSF Grants Nos. DMR 77-12919 and CHE 76-11255.

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