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Thickness effect on the extended-x-ray-absorption-fine-structure amplitude

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The thickness effect, which is caused by inevitable leakage radiation accompanying the desired radiation, can cause significant decreases of extended-x-ray-absorption-fine-structure (EXAFS) amplitude when the sample is thick enough. The effect is illustrated by measurements of the K-edge EXAFS on a series of copper foils of varying thicknesses. Significant distortions in EXAFS amplitudes occur when $\Delta\mu_0 x \geq 1.5$, where $\Delta\mu_0$ is the K-edge step in the absorption coefficient and x is the sample thickness. Therefore, the optimum total sample thickness of $\mu_T x = 2.6$ as determined by statistical considerations will introduce errors in EXAFS amplitudes in concentrated samples due to the thickness effect. The measurements presented here determine the most accurate values of EXAFS amplitude for copper metal which agree well with theory as corrected for the many-body overlap effect.

I. INTRODUCTION

Measurements of the extended-x-ray-absorption fine structure (EXAFS) have been used in recent years to determine the local configuration around a specific atom in various materials.[1] Interatomic distances, types, and number of atoms can be obtained about each type of atom. The interatomic distance is not sensitive to the amplitude of EXAFS, but determining the number of given atoms and the disorder at a distance requires accurate measurement of the amplitude of EXAFS.

Typically it is assumed that the measured EXAFS is correct and discrepancies with theory[2] are assumed to lie with the theory.[3,4] This is true, of course, only if the experimental measurements are correct. Unfortunately, the experimental amplitudes published in the literature have not always been correct. Perhaps the effect which most frequently distorts the measured amplitude of EXAFS is the "thickness effect." This point has been noted earlier[3,5-8] but, because it is still apparently not universally recognized, leading to erroneous statements about the reliability of EXAFS measurements, it is worthwhile to emphasize it further.

This is the case even for copper metal, the material that, because it shows such a clear and large EXAFS and is easily prepared, has attained the position of the "canonical" EXAFS material. For example, in a recent publication[4] a copper sample that was claimed to have $\Delta\mu_0 x = 3.52$ had its EXAFS amplitude reduced a factor of 0.7 by the thickness effect.

It is usually argued on the basis of statistics that the optimum $\mu_T x$ to measure EXAFS is 2.6, where μ_T is the total x-ray absorption coefficient and x is the sample thickness.[9,10] If statistics were the only criterion, this result would be correct, but, as we show in this paper, $\mu_T x = 2.6$ is already thick enough in concentrated samples for a serious error to be introduced in the EXAFS amplitude by the thickness effect. Because of the thickness effect the preferred $\mu_T x$ is around 1.5 for concentrated samples.

We illustrate the problems by investigating copper foils of various thicknesses. The thickness effect is described in Sec. II. The experiments are described in Sec. III and a discussion is presented in Sec. IV. A summary and conclusions are presented in Sec. V.

II. THICKNESS EFFECT

In the ideal case, the amplitude of EXAFS as measured in absorption is independent of the thickness of the samples. But, in practice, there is always some form of leakage and the measured amplitude depends on the thickness of the samples. By leakage is meant that part of the signal that is not attenuated in the sample as much as expected. This could be due to pinholes in the sample, harmonics in the incoming beam, radiation that passes around the sample, or the wings of the monochromatic resolution function containing significant intensity below the absorption-edge energy. Of course, the change will be small if the leakage is small. But the "smallness" of leakage depends on the thickness of the sample.

Let us consider a simple model where there is leakage which is not attenuated by the sample. It is assumed that the only contribution to the absorption coefficient is the edge of interest and all other contributions to μ are subtracted off.

Let us denote the incoming flux of x rays with energy E by $I_0(E)$ and leakage by $b(E)$. Then the measured I_0 and transmitted intensity I are

$$I_{0m} = I_0(E) + b(E),$$
$$I_m = I(E) + b(E) = I_0(E) e^{-\mu(E)x} + b(E),$$

where $\mu(E)$ is the true absorption coefficient. Then μ', the measured absorption coefficient of the edge, is given by

$$e^{\mu' x} = \frac{I_{0m}}{I_m} = \frac{I_0(E) + b(E)}{I_0(E) e^{-\mu(E)x} + b(E)}.$$

Now with $\alpha(E) = b(E)/I_0(E)$, we can put the above equation in the following form:

$$\mu'(E)x = \ln\left(\frac{1+\alpha(E)}{e^{-\mu(E)x} + \alpha(E)}\right). \tag{1}$$

All primed quantities are measured ones and unprimed are true ones.

Because of EXAFS, $\mu(E)$ has a small variation about $\mu_0(E)$, the smooth background. We expand μx about $\mu_0 x$ in Eq. (1). We now have the following:

$$\mu'(E)x = \ln\left(\frac{1+\alpha(E)}{e^{-\mu_0(E)x} + \alpha(E)}\right) + \frac{\delta\mu(E)x}{1+\alpha(E)e^{\mu_0(E)x}} - \frac{1}{2}\frac{\alpha(E)e^{\mu_0(E)x}}{[1+\alpha(E)e^{\mu_0(E)x}]^2}[\delta\mu(E)x]^2, \tag{2}$$

where the first term is the measured smooth background $\mu_0'(E)x$ and other terms are the measured oscillating EXAFS terms caused by the true EXAFS $\delta\mu x$. In principle, the EXAFS is given by

$$\chi = \frac{\mu - \mu_0}{\mu_0},$$

where usually the variable E is replaced by k, the photoelectron wave number, and μ_0 is the smooth part of the absorption contributed by the edge alone. In practice, χ is normalized by a constant, the edge step $\Delta\mu_0$, rather than by a function $\mu_0(k)$. Thus

$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\Delta\mu_0}, \tag{3}$$

which holds for both measured (with primes) and true (without primes) χ's. From Eqs. (2) and (3), we obtain

$$\chi'(k,x) = \frac{\Delta\mu_0}{\Delta\mu_0'}\frac{\chi(k)}{1+\alpha(k)e^{\mu_0(k)x}} \times \left(1 - \frac{1}{2}\frac{\alpha(k)e^{\mu_0(k)x}}{1+\alpha(k)e^{\mu_0(k)x}}\delta\mu_0 x\chi(k)\right) + \cdots. \tag{4}$$

The dependence of χ' on x is explicitly indicated by denoting the measured values by $\chi'(k,x)$. In case of large leakage and/or very thick samples higher terms are important, but we will not consider such extreme cases here.

From Eq. (4) we can see that the amplitude of EXAFS is reduced to lowest order by a factor of

$$\frac{\chi'(k,x)}{\chi(k)} = \frac{\Delta\mu_0}{\Delta\mu_0'}\frac{1}{1+\alpha(k)e^{\mu_0(k)x}} = \frac{\Delta\mu_0 x}{1+\alpha(k)e^{\mu_0(k)x}}\left[\ln\left(\frac{1+\alpha(k_0)}{e^{-\Delta\mu_0 x}+\alpha(k_0)}\right)\right]^{-1}. \tag{5}$$

Here k_0 is the value at the edge. Note from Eq. (4) that $(\chi'/\chi) \to 1$ as $x \to 0$, i.e., the true value is approached as $\Delta\mu_0 x \to 0$. Approximating $\alpha(k) = \alpha(k_0)$ and $\mu_0(k) = \Delta\mu_0$, we obtain the reduction of EXAFS as a function of $\Delta\mu_0 x$ and α. Plots are given in Fig. 1(a). Also given is the reduction of the measured thickness in Fig. 1(b).

We also note that the EXAFS is distorted by the second-order term of Eq. (2). Usually this term is negligible but in thick samples it can be ap-

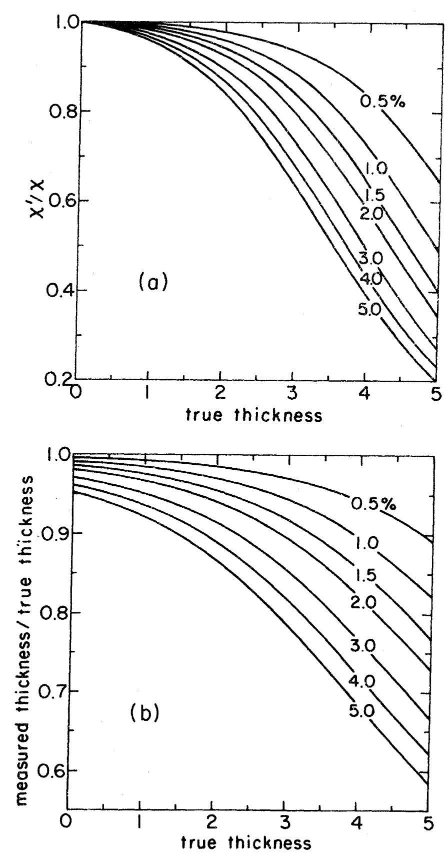

FIG. 1. Amplitude reduction (a) and measured edge step reduction (b) as functions of true edge step thickness $\Delta\mu_0 x$ for various leakage levels α.

preciable. It is a 10% correction when $\alpha = 2\%$ and $\Delta\mu_0 x = 4.0$ for $\chi(k) = 0.1$. Note that the measured thickness $\Delta\mu_0' x$ is only 3.3 and $[\chi'(k, x)]/[\chi(k)] = 0.58$ in this case.

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. Experimental details

Two groups of measurements of EXAFS at the K edge of Cu foils were made. The first group was samples of $\Delta\mu_0' x = 1.6$, 2.9, and 3.3 measured at SSRL (Stanford Synchrotron Radiation Laboratory) on the wiggler beam line No. 4 with an Si(220) double-crystal monochromator; the second was samples of $\Delta\mu_0' x = 0.7$, 0.8, 1.2, 1.6, and 2.0 measured at the University of Washington using a laboratory EXAFS facility to be described below. Both groups include data from a common sample as a standard whose measured thickness $\Delta\mu_0' x = 1.6$. The standard was measured at SSRL and at the University of Washington facility together with other samples. As we will see, the thick samples' $\Delta\mu_0' x$ values require a correction because of the thickness effect. The sample used as a standard ($\Delta\mu_0' x = 1.6$) is made from commercially available Cu foil while the others were prepared by vacuum evaporating ($\sim 4 \times 10^{-6}$ Torr) Cu onto 1-mil thick Kapton strips using an electron gun heater. For thick samples, several sheets of Kapton were used. All measurements reported here were made at room temperature.

The University of Washington EXAFS facility is described briefly. The instrument focuses x rays from a fixed anode x-ray source using a Johann configuration.[11] In the Johann configuration the source, crystal, and detector slit are all on a Rowland circle of 10-in. radius. The crystal is bent to a 20-in. radius. The I_0 and I detectors are placed behind the detector slit and consist of a partially transparent and a fully absorbing gas ionization chamber, respectively. During a scan the apparatus is controlled by a computer and data are recorded on floppy disk. Harmonics which contribute to the leakage, with the attendant thickness-effect distortion, are completely eliminated by running the x-ray tube at a voltage below the harmonics excitation value. In the measurements reported here Ar gas was used in the detectors, an Si(400) crystal was used as the monochromator, and the excitation voltage was 16 kV. The energy resolution is about 5 eV at the copper K edge. The SSRL energy resolution is 1–2 eV.

B. Analysis of data

The data (Fig. 2) were analyzed following standardized procedure.[12] First, $\Delta\mu_0' x$ due to the K edge is obtained by removing the background of other edges using a Victoreen fit. Then the data were normalized by division with the edge step, i.e., $\Delta\mu_0' x$. A smooth background ($\mu_0' x$) is removed using Fourier filtering to give the $\chi'(k)$ of Eq. (3) (Fig. 3), remembering that the prime denotes measured quantities. Here the variable is changed from photoelectron energy E to wave number k by using the relation $k = [0.263(E - E_0)]^{1/2}$, where E is in eV and k in Å^{-1}, and E_0 is chosen to be around the middle of the edge. Great care was taken to assure that the same relative E_0 was chosen for each sample.

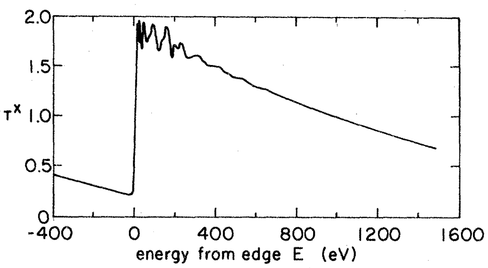

FIG. 2. Raw absorption data for Cu at room temperature taken at SSRL.

This χ is then Fourier transformed with respect to $2kr$ to give an r-space distribution (Fig. 4). In doing so the χ function is weighted with k^3 to compensate for the decrease of χ in high k. The peak near 0 Å is due to imperfect background subtraction but is small enough to introduce negligible overlap at the first true peak and beyond. Putting a window function as indicated in Fig. 4 around the first-neighbor peak in r space, we back-transform it into k space to separate its contribution to the χ data. With this single-shell data we construct an envelope function (Fig. 5). Finally, comparisons were made between samples by taking ratios of the envelope functions.

First, we compared the $\Delta\mu_0' x = 1.6$ copper standard as measured by the two different apparatuses. The ln of the ratio of the amplitudes is shown in Fig. 6. As can be seen, the two results are in good agreement for $4 \leq k \leq 10$. Deviations at high k are due to the amplitude merging into the noise. At small k, the deviation may be due to

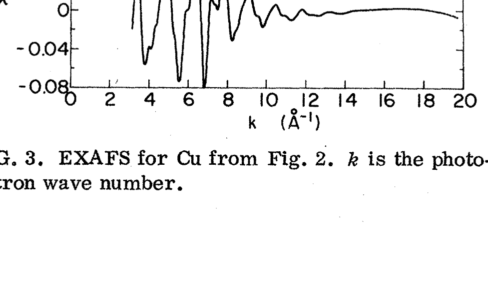

FIG. 3. EXAFS for Cu from Fig. 2. k is the photoelectron wave number.

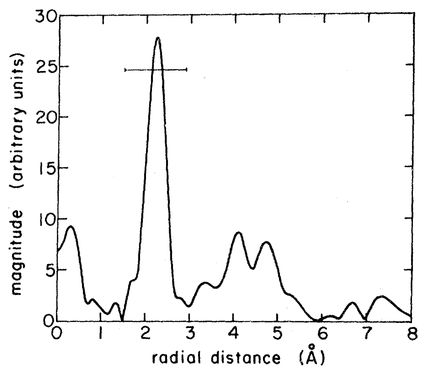

FIG. 4. Magnitude of the Fourier transform of $k^3\chi$ of Fig. 3. Window function used in back transform is shown above the first main peak.

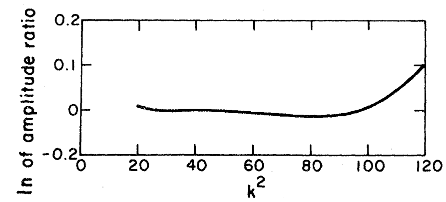

FIG. 6. Natural log of ratio of EXAFS amplitude of standard as measured by two facilities: $\Delta\mu_0' x=1.6$ at SSRL/$\Delta\mu_0' x=1.6$ at University of Washington.

the poorer resolution of the University of Washington data. Another cause may be that we may not have chosen the relative E_0 exactly correctly between the two groups of measurements. However, over the main part of the data range the agreement is good to a few percent. This result proves that the use of two different apparatuses to measure the EXAFS does not introduce significant systematic errors.

Data from the University of Washington are compared with the standard in Fig. 7. The ratios are not as straight as that in Fig. 6. This nonlinearity of the ratios does not appear to be instrumental since the consistency of the measurements in the same sample is within a few percent as indicated in Fig. 6. We believe the nonlinear variations shown in Fig. 7 are mainly due to differences between the evaporated samples and the foil standard. However, the variations are all within 10% and small compared to the variations found in the thickest samples. There appears to be a trend for an increase in EXAFS as the thickness decreases. Results for data taken at SSRL are shown in Fig. 8. Here the decrease in the EXAFS amplitude is very clear. It should be remembered that the ratios are of the measured $\chi'(k,x)$, not the true values.

IV. DISCUSSION

The thickness effect, as discussed in Sec. II, has the feature that the true value for the EXAFS is approached as $\Delta\mu_0' x \to 0$, i.e., $\chi'(k,x)/\chi'(k,x_s)$ plotted as a function of $\Delta\mu_0' x$ extrapolates to $\chi(k)/\chi'(k,x_s)$ as $x\to 0$. Here the thickness of the $\Delta\mu_0' x = 1.6$ sample is denoted by x_s. Such a plot is presented in Fig. 9. In estimating the ratio the average in the range of $20 \leqslant k^2 \leqslant 100$ was employed. This range was chosen because the results in Fig. 6 indicate that the instrumental and noise uncertainties are negligible therein. The uncertainty of the points in Fig. 9 are estimated from the variation about the average in this range. It is noted that the $\Delta\mu_0' x = 1.6$ sample has an EXAFS which is ~6% low. The distortion increas-

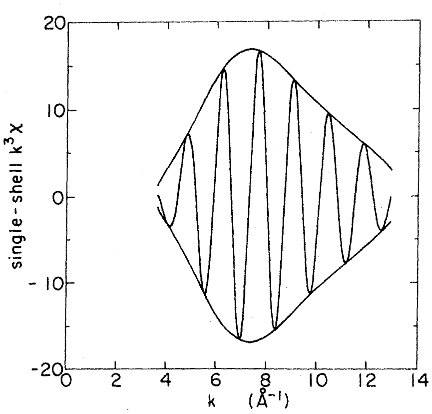

FIG. 5. Single- (first-) shell contribution to EXAFS for Cu. χ is weighted by k^3.

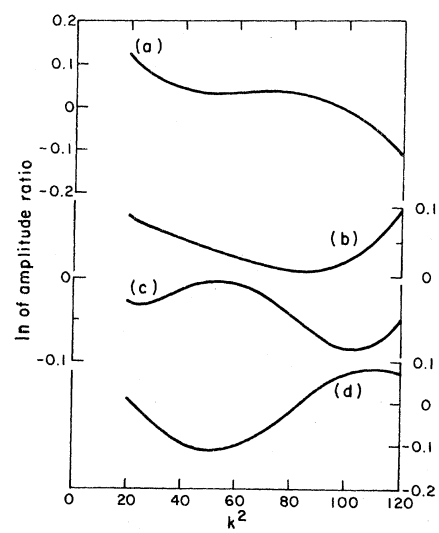

FIG. 7. Natural log of ratios of EXAFS amplitudes of various samples to standard ($\Delta\mu_0' x=1.6$), all measured at the University of Washington facility: (a) $\Delta\mu_0' x=0.7$, (b) $\Delta\mu_0' x=0.8$, (c) $\Delta\mu_0' x=1.2$, (d) $\Delta\mu_0' x=2.0$.

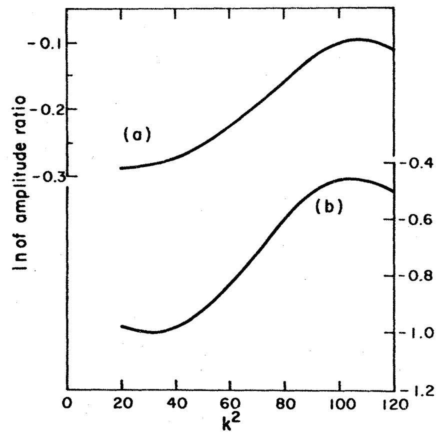

FIG. 8. Natural log of ratios of EXAFS amplitudes of thick samples to standard ($\Delta\mu_0'x=1.6$), all measured at SSRL: (a) $\Delta\mu_0'x=2.9$, (b) $\Delta\mu_0'x=3.3$

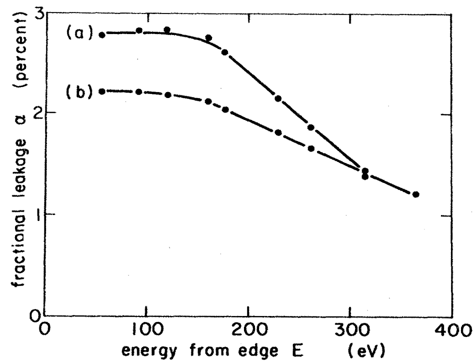

FIG. 10. The leakage $\alpha(k)$ for samples with (a) $\Delta\mu_0'x=3.3$, $\Delta\mu_0x=4.6$, (b) $\Delta\mu_0'x=2.9$, $\Delta\mu_0x=3.3$.

es with thickness and quite large errors are introduced by the thickest samples employed.

With the true value of $\chi(k)$ determined, we can use the model in Sec. II to determine $\alpha(k)$ and the correct values of $\Delta\mu_0x$ for the thickest samples. The results are given in Fig. 10. In obtaining these results we know from our analysis $\chi'(k,x)/\chi(k)$ and $\Delta\mu_0x$ while we need to know μ_0x, as required by Eq. (5). Our method of measurement of μ, both at SSRL and the University of Washington, monitors I_0 by using a partially transparent ionization chamber. In this case $\Delta\mu_0x$ can be determined from the edge step, but $\mu_0(k)x$ cannot be obtained accurately because the fraction of I_0 sensed by the initial ionization chamber varies with energy, making the pre-edge background subtraction unreliable. However, we obtained $\mu_0(k)$ past the copper K edge using tabulated results,[13] and from our knowledge of $\Delta\mu_0x$ and the tabulated value of $\Delta\mu_0$ we found μ_0x.

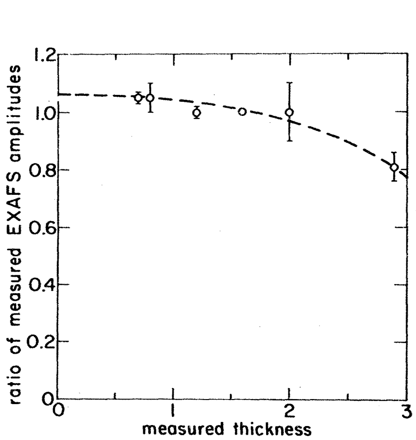

FIG. 9. Ratio of measured EXAFS amplitude as a function of measured edge step thickness $\Delta\mu_0'x$.

The fact that the $\alpha(k)$ is not the same among the various samples is to be expected since they were measured under different conditions and one would not expect the $\alpha(k)$ to remain constant. In addition, the model makes the extreme assumption that the background $b(k)$ is not attenuated by the sample whatsoever. In reality some attenuation is expected which would then make $\alpha(k)$ decrease with increasing thickness.

We next consider the causes of leakage. Firstly, there may be harmonics which pass through the monochromator. In our laboratory EXAFS this leakage was eliminated by running the x-ray tube at a low enough excitation voltage. At SSRL the harmonics can be reduced by detuning the two-crystal monochromator. Secondly, a nonuniform sample causes leakage. This can be avoided by careful preparation of the sample. Thirdly, there may be stray x rays which scatter into the I detector without passing through the sample. These can be removed by proper shielding. Lastly, there is the monochromator resolution function which has a tail overlapping the lower-energy region below the edges. This portion is not attenuated as much as is the center energy and for thick samples may give a significant background.[5] The tail is inherent in the measurement and it has the property of becoming smaller as k increases and less of the tail remains below the edge. By careful arrangement it is possible to eliminate all contributions except for the monochromator resolution tail. Thus even in the best of situations a thickness effect persists. The only way to minimize the thickness effect is to use thin enough samples. The effect is largest for concentrated samples. In fact, as can be noted from Eq. (4), the important criterion is that $\alpha e^{\Delta\mu_0x}\ll 1$. This can be satisfied by making $\Delta\mu_0x$ small enough. In the case of concentrated samples, as for Cu metal, this is accomplished by making x small enough (less than $\Delta\mu_0x$

≈ 1.5). However, for dilute samples $\Delta\mu_0 x$ may be already small enough even when x is the statistically optimum value for the total sample of $\mu_T x = 2.6$ because of the small value of $\Delta\mu_0$. The only safe way to ascertain that there is no thickness effect is to vary x and experimentally determine the limit as $x \to 0$.

The results presented here show that the EXAFS for the $\Delta\mu_0 x = 1.6$ sample was ~6% below the true value. This sample was the copper sample employed in a previous publication[3] to compare the measured EXAFS with theoretical values. Correcting the measurements for the thickness effect as determined here, a comparison with theory is shown in Fig. 11. The amplitude ratio $F^{\text{expt}}/F^{\text{theor}}$ is the value of the single-particle calculation of Teo and Lee[2] divided into the corrected measured value. The many-body-overlap prediction of this ratio at high k is the horizontal line denoted by S_0^2. After correcting for the thickness effect there is now reasonable agreement at high k between the measured values and the single-particle calculation for the many-body-overlap effect.

A recent publication[4] also compared measured copper K-edge EXAFS to the theoretical calculations. The ratio was found to be 0.485, about 0.7 of the true value. The sample employed in this measurement had a measured $\Delta\mu_0' x = 3.52$, a value large enough to have an appreciable thickness effect. Correcting for the thickness effect we find the actual value of $\Delta\mu_0 x = 4$. The thickness-effect correction in this case is smaller than those reported here, presumably because the focused beam line which was used in the measurements has a smaller α. This may be due to the complete lack of harmonics in the focused line. The focusing mirror does not reflect the high energy corresponding to the harmonics. This example emphasized the fact that the magnitude of the thickness effect is a characteristic of the particular system utilized in the measurement and varies from system to system.

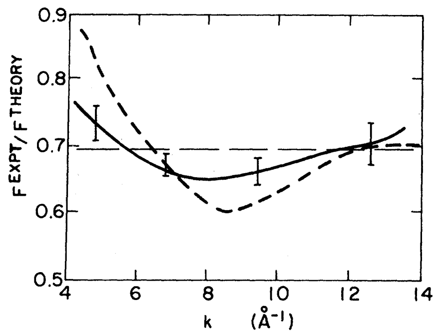

FIG. 11. Ratio of experimental backscattering amplitude for Cu to the theoretical value after correcting the results of Ref. 3 by the thickness effect (~6%). The Debye-Waller factor has been compensated for. The solid curve corresponds to an inner potential which gives the same phase at $k=0$ for theory and experiment. The dashed curve is for an inner potential which matches the slope of the experimental and theoretical phases. Also plotted as the horizontal dashed line is the many-body atomic overlap factor S_0^2.

V. SUMMARY AND CONCLUSIONS

It has been shown by measurements of the copper K-edge EXAFS on a series of metal samples of varying thicknesses that the EXAFS amplitudes are significantly perturbed by the "thickness effect" for commonly used thicknesses. In particular, the total thickness of $\mu_T x = 2.6$, which optimizes the signal for statistical noise, is found for copper metal to have a significant thickness effect leading to a measured EXAFS amplitude appreciably decreased from the true value. The thickness effect occurs because the transmitted beam detector senses some leakage radiation which is not attenuated as greatly as is the radiation at the center of the resolution function of the monochromator. There are various possible sources of this leakage radiation but even in the best shielded arrangement an inherent source remains, namely, the low-energy tail of the monchromator resolution function below the edge energy.

In practice, to ascertain whether the thickness effect is insignificant, measurements of EXAFS must be made as a function of thickness. If the EXAFS does not change significantly as the thickness is varied, the effect is negligible. In practice, one must be suspicious of any EXAFS measurement made on samples whose $\Delta\mu_0 x > 1.5$ unless explicit tests have been made for the thickness effect. In general, the thickness effect is expected to be more important for concentrated samples than for dilute samples which would never attain the value of $\Delta\mu_0 x > 1.5$.

After correcting for the thickness effect we present the most accurate EXAFS amplitude for copper metal and compare it in Fig. 11 with the calculation of Teo and Lee. The measurement is smaller than the calculated values at high k by the amount predicted by the many-body-overlap effect.

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