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# Extended X-Ray–Absorbtion Fine-Structure Beats: A New Method to Determine Differences in Bond Lengths

G. Martens, P. Rabe, N. Schwentner, and A. Werner
*Institut für Experimentalphysik, Universität Kiel, Kiel, Germany*

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The superposition of two scattering shells produces beats in the envelope function of the extended x-ray–absorption fine-structure spectrum and a modulation in the scattering phases. From the $k$ values of the extrema in the envelope function and from the inflection points of the phases the separation of these shells can be calculated without knowledge of the scattering phases of the single shells. A resolution in $R$ space up to 0.02 Å can be obtained even in cases where methods used so far are not able to resolve the scattering shells.

Absorption spectra of polyatomic systems show a modulation of the absorption coefficient above the ionization energies of inner shells. It has been attributed to an interference of the ejected photoelectrons at the site of the absorbing atom. For $K$-shell excitation the modulating part of the absorption coefficient called the extended x-ray–absorption fine structure (EXAFS) is described by

$$\chi(k) = -k^{-1}\textstyle\sum_i A_i(k)\sin[2kR_i + \varphi_i(k)] \qquad (1)$$

with

$$A_i(k) = (N_i/R_i^2)\,|f_i(\pi,k)|\exp(-2\sigma_i^2k^2 - 2R_i/\lambda),$$

where $N_i$ is the number of atoms in the $i$th shell at a distance $R_i$ to the absorbing atom, $|f_i(\pi,k)|$ is the amplitude for scattering through angle $\theta=\pi$. $\sigma_i^2$ describes the mean-square displacement of the atoms from their average positions. The mean free path $\lambda$ of the electrons takes into account the observed decreasing contribution of more distant shells. The phase shift $\varphi(k)$ is due to the influence of the potentials of the absorbing atom and the scattering atoms on the electron wave.

Several attempts have been made to extract structural information from EXAFS. The most general methods used are fitting procedures[1,2] and Fourier transform methods.[3-6] A fitting procedure is limited to simple fine structures built up from one or two scattering shells because of the rapidly increasing number of parameters for more shells. The Fourier transform method can be applied to more complicated structures. From $\chi(k)$ a radial structure function $|F(r)|$ can be derived. The maxima of this function are generated by shells of scattering atoms surrounding the absorbing atom. The positions of the peaks in $|F(r)|$ are shifted compared to the true distances due to contributions of the scattering phases that depend on $k$.

Several problems for the determination of atomic distances arise from this Fourier transform method: (i) The scattering phases in general are unknown. Major efforts have been made to calculate the phases[7] or to extract them from experimental data.[6,8] The transferability of phase shifts has been emphasized especially.[8] (ii) The reference energy necessary for the conversion of the energy scale to the $k$ scale is unknown. Usually the inflection point of the $K$ edge is used to fix the $k$ scale. This arbitrary choice leads to distortions, especially in the low-$k$-value region. (iii) Because the range in $k$ space where EXAFS can be observed with sufficient amplitudes is limited, the radial structure function yields broadened features. The widths of these features determine the resolution in $R$ space especially for close-lying shells.

Here an extended Fourier transform method will be presented for pairs of scattering shells. It will be shown that the resolution in $R$ space can be improved compared to the Fourier transform methods used up to now. Further, in contrast to usual Fourier transformations, a knowledge of the phase is not necessary to determine in bond lengths.

We consider an EXAFS spectrum for two contributing shells of identical atoms which are positioned at distance $R_1$ and $R_2$ from the absorbing atom. The scattering amplitudes $|f_i(\pi, k)|$ and the phases $\varphi_i(k)$ are the same for both shells. Then the sum of Eq. (1) over the two shells can be written as

$$\chi(k) = -k^{-1}\tilde{A}(k)\sin[2k\tilde{R} + \tilde{\phi}(k)], \qquad (2)$$

where

$$\tilde{R} = (R_1 + R_2)/2$$

is the average distance of the two shells from the absorbing atom. The envelope function $\tilde{A}(k)$ for the two-shell EXAFS takes the form

$$\tilde{A}(k) = A_1(k)[1 + C^2 + 2C\cos(2k\Delta R)]^{1/2} \qquad (3)$$

with $A_1(k)$ the envelope function of the first shell as defined by Eq. (1) and $C$ the ratio of the envelope functions of the second and the first shell:

$$C = A_2/A_1 = (N_2/N_1)(R_1^2/R_2^2) \times \exp[-2(\sigma_2^2 - \sigma_1^2)k^2 - \Delta R/\lambda]. \qquad (4)$$

The relative distance is given by $\Delta R = R_2 - R_1$. The envelope function $A_1(k)$ is modulated by the presence of a second scattering shell. It shows beats with a wavelength in $k$ space determined only by the relative separation of the two shells. Under the assumption of small differences in the mean-square displacements $\sigma_i^2$ and a $k$-independent mean free path $\lambda$, the modulating term under the square root of $\tilde{A}(k)$ shows minima and maxima for

$$k_E = n\pi/2\Delta R, \quad n = 1, 2, 3, \ldots . \qquad (5)$$

At the same $k$ values the averaged phases $\tilde{\phi}(k)$ show inflection points from which $\Delta R$ can be obtained as well.

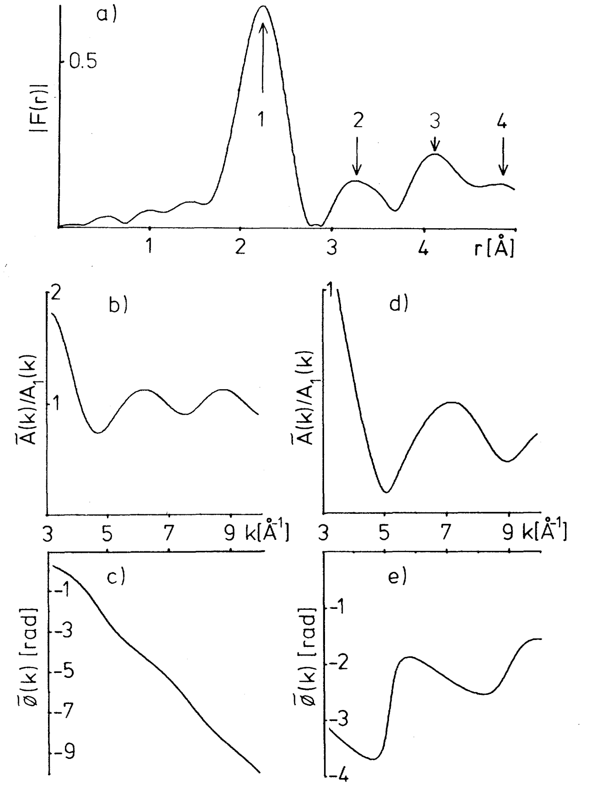

FIG. 1. Test of the beat method with an experimental EXAFS spectrum of Cu. (a) Fourier transform $|F(r)|$, (b) modulating part of the envelope function [Eq. (3), $\tilde{A}(k)/A(k)$] derived from the first and second shells, (c) average phase $\tilde{\phi}(k)$ derived from the first and second shells, (d) same as (b) for the second and third shells, (e) same as (c) for the second and third shells.

We have tested the EXAFS beat method on the spectra of Cu and CuO [Fig. 2(a)]. The spectra have been taken with statistics better than 0.1%, a resolution of 5 eV, and a step width of 2 eV using a 12-kW rotating-anode x-ray generator as light source and a LiF single crystal for nonchromatization. Complete experimental details, which are unimportant in the present discussion, are given in Ref. 6. First we show a test on the EXAFS spectrum of Cu. The radial structure function $|F(r)|$ [Fig. 1(a)] has been calculated by the Fourier transform method as described by Stern and co-workers.[4,5] The influence of the limited range in $k$ space has been minimized by using a window function consisting of a convolution of a Gaussian and a square window. The optimal resolution in $R$ space, i.e., the separation $\Delta R$ for which two scattering shells are clearly separated in $|F(r)|$, is 0.3–0.4 Å when only the available $k$ space ($\approx$10 Å$^{-1}$) is taken into account. This $k$ range is typical for EXAFS spectra and cannot be increased significantly (i.e., > 20 Å$^{-1}$) experimentally because the decrease in the EXAFS amplitudes is due to the energy dependence of the envelope function $A_i(k)$ [Eq. (1)]. The features in the structure function are broadened additionally by the window function. Window functions which yield sharper features cause more pronounced side lobes which also disturb the structure function. The contributions of four different scattering shells can clearly be seen [Fig. 1(a)] and the resolution is equal to the best obtained elsewhere.[4] From this radial structure function, the contributions of the first and second and of the second and third shells, respectively, have been transformed back to $k$ space

TABLE I. Comparison of differences in bond lengths of Cu and CuO determined with the EXAFS beat method ($\Delta R_{\text{beat}}$) and with x-ray diffraction ($\Delta R_{\text{diff}}$).

| Compound | Shell | $\Delta R_{\text{beat}}$ (Å) | $\Delta R_{\text{diff}}$ (Å) |
|---|---|---|---|
| Cu | 1+2 | 1.05 | 1.06 |
| Cu | 2+3 | 0.87 | 0.82 |
| CuO | 2+3 | 0.17 | 0.19 |

simultaneously and the envelope functions $\tilde{A}(k)$ and the phases $\tilde{\varphi}(k)$ have been calculated. To reduce the influence of the slope of the envelope of a single shell on the determination of $\Delta R$, $\tilde{A}(k)$ has been divided by the envelope function of a single shell of Cu. The results for $\tilde{A}(k)/A(k)$ and $\tilde{\varphi}(k)$ are shown in Figs. 1(b)–1(e). From the $k$ values of the minima and maxima of $\tilde{A}(k)/A(k)$ and the inflection points of $\tilde{\varphi}(k)$ the relative separation $\Delta R$ has been calculated using Eq. (5). The values of $\Delta R$ determined by the beat method are compared with values determined by x-ray diffraction[9] in Table I. For the first two shells we find excellent agreement. The larger difference of 0.05 Å results from the fact that the third and the fourth shells overlap strongly in the radial structure function. Therefore the region in $R$ space to be transformed back is difficult to determine the large error shows in influence of the contribution of the fourth shell.

In a second test we will demonstrate the application of the EXAFS beat method for the determination of distances of close-lying shells. For this test we use an experimental EXAFS spectrum[6] of CuO [Fig. 2(a)]. In this compound, the central Cu atom is surrounded by a planar arrangement of four oxygen atoms with a distance of 1.95 Å from the absorbing atom. The next two shells are built up from four Cu atoms each with distances 2.88 and 3.07 Å. The Fourier transform of the EXAFS is shown in Fig. 2(b). A shoulder in the second peak of the structure function points to the contribution of the two Cu shells but a determination of the relative separation is impossible. To determine $\Delta R$ a limited range in $R$ space as indicated by bars in Fig. 2(b) has been transformed back to $k$ space. The resulting envelope [Fig. 2(c)] shows a pronounced minimum at 9.1 $\text{Å}^{-1}$. At the same point $\tilde{\varphi}(k)$ [Fig. 2(d)] shows the expected inflection point. With this $k$ value, a distance between the two shells of 0.17 Å is obtained. This distance is in good agreement with that obtained from x-ray diffraction data[10] (Table I).

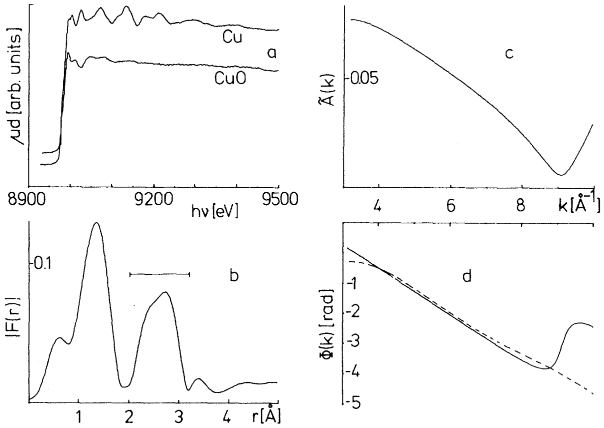

FIG. 2. (a) Absorption spectra of Cu and CuO, (b)–(d) application of the beat method to an experimental EXAFS spectrum of CuO. (b) Fourier transform $|F(r)|$, (c) envelope function $\tilde{A}(k)$ derived from the second and third shells, (d) averaged phase $\tilde{\varphi}(k)$ derived from the second and third shells (dashed line, phase of a single Cu shell).

Finally we would like to point out two further applications of the method described above:

(1) In the envelope function of EXAFS, the magnitude of the scattering amplitude is always combined with the $k$-dependent Debye-Waller factor. The $k$ dependence of the scattering amplitude is characteristic for the scattering atoms. Thus with the aid of the Debye-Waller factor it should be possible to identify the contributing atomic species. It is sufficient to know only the differences of the mean-square displacements of the atoms. On the other hand, the variation of the amplitudes $\tilde{A}(k)/A(k)$ allows one to study these differences.

(2) In the past, the correct choice of the reference energy either has been regarded as of minor importance[4] or it has been used as fitting parameter.[6] Because of its great influence on a reliable determination of bond lengths especially in the low-$k$-value region, an independent method to evaluate this parameter is of great importance for the practical application of EXAFS. From the extreme values of the EXAFS beats determined experimentally together with Eq. (5) the reference energy can be calculated. For shells with a larger relative distance a great number of beats show up in the observed $k$ region. From these beats the $k$ dependence of the reference energy can be studied.[11]

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# Tricritical Transitions, Interface Roughening, and the Classical $XY$ Model

V. J. Emery and R. H. Swendsen
*Brookhaven National Laboratory, Upton, New York 11973*

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Space renormalization group calculations are performed for a class of spin-$S$ Ising systems, using a modification of Migdal's recursion relation. Interface-roughening models are obtained when $S\to\infty$ and tricritical points and critical lines become the roughening temperature and rough phase. The latter corresponds to the low-temperature phases of the classical Coulomb gas and two-dimensional $XY$ model and implications for the $XY$-model exponent $\eta$ are discussed.

We have used a generalization of Migdal's approximation to study a particular class of Ising models with Hamiltonian

$$H = J\sum_{(i,j)} |S_i - S_j|^p + m_0 \sum_i S_i^2, \qquad (1)$$

where the exchange interaction acts between nearest neighbors and the spins $S_i$ have values $-S$, $-S+1, \ldots, S-1, S$. Although $H$ is far from the most general Hamiltonian which could be written down for arbitrary $S$, it encompasses a remarkable variety of systems of considerable theoretical and practical interest. When $S=1$ and $p=2$, $H$ is a well-studied model[2,3] of critical-tricritical phenomena, whereas for $S\to\infty$ and $m_0=0$ it describes interface roughening[4] in the theory of crystal growth. For the latter application, $S_i$ is the height of the crystal surface above some arbitrary level, and to describe a three-dimensional solid, the model lattice has $d=2$. The solid-on-solid model[4] $p=1$ is of most direct physical interest and the basic problem is to demonstrate the existence of a roughening transition at which there is a change in growth rate and crystal perfection. However, other values of $p$ also are of importance. For $d=2$, $H$ is related by a duality transformation[5-7] to various forms of the classical $XY$ model and, in particular, the limit $p=\infty$ (which produces a restriction $|S_i - S_j| = 0, 1$) corresponds to the approximation used by Luther and Scalapino[8] for this problem. The discrete Gaussian model, $p=2$, is equivalent to the Coulomb gas[4,9] and also plays a special role as a fixed-point Hamiltonian in renormalization-group calculations.

Kadanoff[10] has discussed the virtues of Migdal's recursion relation and has given a rather simple derivation by bond moving. For application to the present problem, it is necessary to divide the Hamiltonian into bonds $\mathcal{K}(S_i, S_j)$ which are to be moved and site-diagonal terms $G(S_i)$ which give weights in the one-dimensional decimations. Our prescription is to arrange that $\mathcal{K}(S,S') = \mathcal{K}(S',S)$ and $\mathcal{K}(S,S)=0$ for all $S,S'$ after each renormalization.[11] Results will be quoted for scale factor $\lambda=2$.

Figure 1 shows the $d=2$ phase diagrams in the $(m_0, T)$ plane for $S=1$, 2, and 3, all of which have a critical line and coexistence curve meeting at a tricritical point. For $S=1$, this is well known[2,3] and the tricritical values $m_{0t} = -0.135$ and $T_t/T_c(m_0=-2) = 0.475$ are in good agreement with Monte Carlo[3] results. When $S$ increases, the critical line becomes more vertical as a result of two effects. For $m_0$ large and negative, the states $\pm S$ dominate and $T_c$ is that of a spin-$\frac{1}{2}$ Ising model with exchange integral $4S^2J$. At the same time the tricritical point moves very rapidly towards $m_0=0$ with $T_t$ increasing slowly. This indicates that as $S\to\infty$ the critical line and coex-