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BRIEF REPORTS

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X-ray-reflectivity fine structure and EXAFS

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A simple and fast method is given for the extraction of extended x-ray-absorption fine structure from x-ray-reflectivity spectra. The method is based on the description of the x-ray-reflectivity fine structure as a linear superposition of the fine structures in the real and in the imaginary part of the refractive index. It is applicable at all glancing angles, i.e., above as well as below the critical angle. Besides the smooth part of the refractive index, no other additional information is necessary. As an example, results obtained with calculated nickel data are presented.

I. INTRODUCTION

Whereas the extended x-ray-absorption fine structure (EXAFS) can be easily obtained from an absorption or a fluorescence measurement, an analogous spectrum obtained in the reflection mode cannot be straightforwardly evaluated. The reason for that is that, in contrast to the absorption, the x-ray reflectivity depends on both the real and the imaginary part of the refractive index. As a consequence, x-ray-reflectivity fine structure (XRFS) spectra cannot directly be compared with the EXAFS theory. In this paper, we present a fast and straightforward method for the extraction of EXAFS from XRFS spectra obtained with homogeneous materials in the hard energy range.

II. LINEAR APPROXIMATION FOR XRFS

The optical properties of condensed matter in the x-ray energy range are described by the complex, energy-dependent index of refraction $n=1-\delta-i\beta$. Above an absorption edge, both $\delta(E)$ and $\beta(E)$ exhibit EXAFS-like oscillatory structures.[1] However, the name EXAFS is usually connected with the fine structure in the absorption $\mu(E)$ or, equivalently, in the $\beta(E)$: $\beta=\mu\lambda/4\pi$ (λ is the wavelength). If we denote the oscillatory parts in $\beta(E)$ and $\delta(E)$ by $\Delta\beta$ and $\Delta\delta$, respectively, then we have $\beta(E)=\beta_0+\Delta\beta$ and $\delta(E)=\delta_0+\Delta\delta$, where β_0 and δ_0 are the smooth, atomiclike backgrounds. $\beta(E)$ and $\delta(E)$ are not independent; they form a Kramers-Kronig transform pair. The same is also valid for $\Delta\beta(E)$ and $\Delta\delta(E)$. As a consequence, $\Delta\delta(E)$ contains no new information compared to $\Delta\beta(E)$.

Above an absorption edge, the x-ray reflectivity R can be split into a smooth part R_0 and an oscillatory part ΔR with $R=R_0+\Delta R$. In our considerations, R denotes the Fresnel reflectivity from an interface between vacuum and a homogeneous, half-infinite, and isotropic medium. While R_0 is a function of β_0 and δ_0 only (with the glancing angle Θ as a parameter), the fine structure in R is a function of the smooth part as well as of the oscillatory part of the refractive index:

$$\Delta R(E;\Theta)=R(\delta(E),\beta(E);\Theta)-R_0(\delta_0(E),\beta_0(E);\Theta)\ . \quad (1)$$

Despite this complicated form, $\Delta R(E)$ was found to be, to a good approximation, a linear superposition of $\Delta\beta(E)$ and $\Delta\delta(E)$: $\Delta R(E)\approx a\Delta\delta(E)+b\Delta\beta(E)$, where the parameters a and b depend, for a given system, only on Θ.[2,3] An improved approximation is obtained if the reflectivity fine structure normalized with respect to R_0 (χ_R) is considered,[4]

$$\chi_R(E)=\frac{R(E)-R_0(E)}{R_0(E)}=\frac{\Delta R(E)}{R_0(E)}\ , \quad (2)$$

with

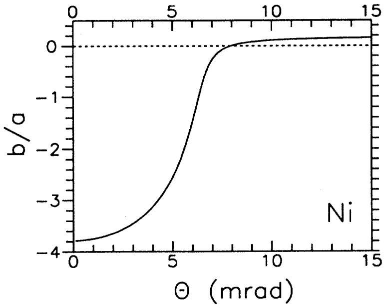

FIG. 1. The ratio of the parameters b and a according to Eq. (3) for the calculated nickel data as a function of the glancing angle Θ. The x-ray-reflectivity fine structure was calculated in the vicinity of the Ni K edge (8333 eV).

$$\chi_R(E) \approx a\Delta\delta(E) + b\Delta\beta(E) \ . \tag{3}$$

The decomposition of χ_R according to Eq. (3) is unique for given functions $\Delta\beta(E)$ and $\Delta\delta(E)$ (Appendix).

The ratio b/a describes the relative contributions of $\Delta\beta$ and $\Delta\delta$ to χ_R. Whereas a is always positive as a function of Θ, b vanish at a certain angle $\Theta=\Theta^*$, i.e., $b/a=0$ at that angle. As a consequence, for all angles except Θ^*, χ_R is a linear superposition of both $\Delta\beta$ and $\Delta\delta$. However, measurements performed at $\Theta=\Theta^*$ yield an x-ray-reflectivity fine structure that is proportional only to $\Delta\delta(E)$. Figure 1 shows the ratio b/a as a function of Θ obtained for nickel. In the limit of $\Theta=0$, the b/a value for nickel is about -3.8. Therefore, the influence of $\Delta\delta$ on the fine structure in the reflectivity cannot be neglected even at very small angles. For fixed angles, b/a depends on the edge energy and the density but only weakly on the structure of the investigated material.[4]

The error of the approximation given by Eq. (3), defined as the normalized sum of the squared residuals of the exact and the approximate values, is a characteristic function of the glancing angle Θ (Fig. 2). It has a maximum at a glancing angle $\Theta=\Theta_\epsilon$, at which $|a| \approx |b|$, but is very small for other angles. However, as shown in Fig. 3 for nickel data at 6.3 mrad, the approximation is also very good for the worst case $\Theta=\Theta_\epsilon$. The linear approximation given by Eq. (3) for XRFS is excellent for angles different from Θ_ϵ.

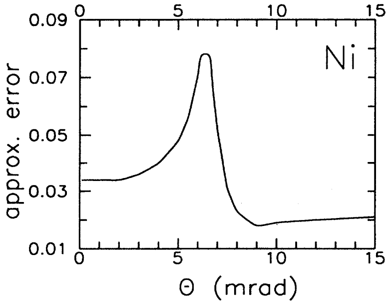

FIG. 2. The error of the linear approximation according to Eq. (3) for the normalized x-ray-reflectivity fine structure $\chi_R=\Delta R/R_0$ obtained with calculated nickel data as a function of the glancing angle.

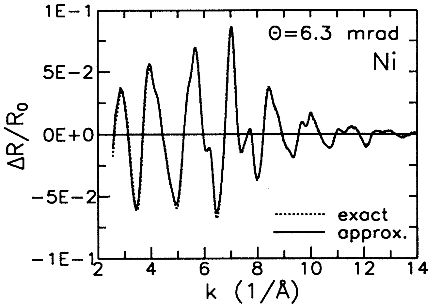

FIG. 3. Exact (dotted) and approximated (solid) normalized nickel x-ray-reflectivity fine structure χ_R obtained for the glancing angle $\Theta=6.3$ mrad. This is the angle with the greatest approximation error (Fig. 2).

III. EXTRACTION OF EXAFS

The application of the Kramers-Kronig transform on both sides of Eq. (3) and some algebra yield immediately for the fine structure in the absorption the following equation:

$$\Delta\beta(E) \approx B\chi_R(E) - AKK(\chi_R(E)) \ , \tag{4}$$

and for $\Delta\delta(E)$,

$$\Delta\delta(E) \approx BKK(\chi_R(E)) + A\chi_R(E) \ , \tag{5}$$

where $B=b/(a^2+b^2)$, $A=a/(a^2+b^2)$, and KK denotes the Kramers-Kronig transform: $KK(\Delta\beta)=\Delta\delta$. In Eq. (4) we have also used the identity $KK(\Delta\delta)=-\Delta\beta$. Equation (5) is the Kramers-Kronig transform of Eq. (4). According to Eq. (4), the fine structure in the absorption is simply a linear superposition of the fine structure in the reflectivity and its Kramers-Kronig transform. Due to the uniqueness of a and b, the numbers A and B in Eqs. (4) and (5) are also unique. Therefore, they can be unequivocally determined with a parameter-fitting procedure. The only information needed in addition to the measured XRFS spectrum are the functions $\beta_0(E)$ and $\delta_0(E)$. $\beta_0(E)$ and $\delta_0(E)$ can be determined from reflectivity curves taken at a few fixed energy values in the vicinity of the absorption edge,[5] using transmission EXAFS spectra with appropriate standards or, alternatively, calculated theoretically. After a single Kramers-Kronig transform of the normalized reflectivity fine structure, the determination of EXAFS from an XRFS is reduced to only a search of two numbers. With a first guess for A and B, the fine structures $\Delta\beta$ and $\Delta\delta$ calculated according to Eqs. (4) and (5), and the previously determined smooth functions $\beta_0(E)$ and $\delta_0(E)$, a test $\chi_R(E)$ function can be easily obtained and compared with the measured one. With the use of the fast Fourier transform for the Kramers-Kronig transform of $\chi_R(E)$,[6] the whole fitting procedure takes only a few seconds on a typical personal computer. The accuracy of the determination of

$\Delta\beta(E)$ from the measured x-ray-reflectivity fine structure is similar to that of the linear approximation of Eq. (3) (Fig. 2) and is very good for all glancing angles.

IV. EXAMPLE

Figure 4 shows fit results according to Eqs. (4) and (5) with calculated nickel data. The absorption data $\beta(E)$ were obtained with a metal foil from a transmission EXAFS spectrum and the smooth part $\beta_0(E)$ was determined using a standard EXAFS procedure.[7] In order to obtain $\delta(E)$ and $\delta_0(E)$, the $\beta(E)$ and $\beta_0(E)$ functions were first extrapolated to 1 and 50 keV below and above the measured spectrum, respectively, using the Victoreen functions[8] and subsequently Kramers-Kronig transformed. With these data, the $\chi_R(E)$ function was then calculated according to Eq. (2) for the glancing angle of 6.3 mrad. The $\chi_R(E)$ function and its Kramers-Kronig transform, as well as $\delta_0(E)$ and $\beta_0(E)$, were the inputs for a parameter-searching procedure.[9]

V. CONCLUSIONS

We have shown a fast and straightforward method for the extraction of EXAFS from the x-ray-reflectivity data. No additional data, except the measured spectrum and the smooth parts of the refractive index, are required. The method is based on a description of the normalized x-ray-reflectivity fine structure as a linear superposition of the fine structures in the real and imaginary parts of the refractive index. It is well suited for reflectivity data obtained at all glancing angles.

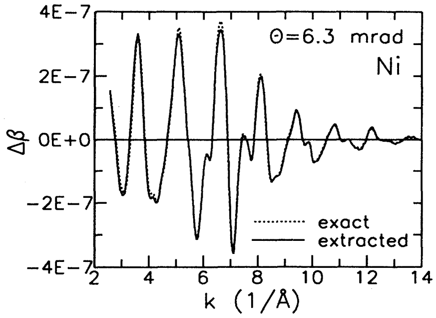

FIG. 4. Fine structure in the absorption for nickel: original data (dotted) and extracted according to Eqs. (4) and (5) from the χ_R function calculated for $\Theta = 6.3$ mrad (solid).

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APPENDIX

Consider two oscillatory functions α and β that form a Kramers-Kronig transform pair, i.e., $\alpha = KK(\beta)$, and a linear superposition of them with nonzero coefficients a and b: $F = a\alpha + b\beta$. Suppose there were two other nonzero numbers c and d with $F = c\alpha + d\beta$. Then we had $\alpha = \beta(d-b)/(a-c)$, in contradiction to the above definition of α as the Kramers-Kronig transform of β.

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