ReflXAFS data analysis

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Reflection X-ray absorption fine structure (ReflXAFS) draws local structural information on near-surface layers from the fine structure of the reflectivity spectrum above an absorption edge. As reflectivity depends on both the real and the imaginary part of the refraction index of the sample, analysis of ReflXAFS data is not as straightforward as in the conventional case. Particular data-treatment procedures have been developed for a rigorous analysis, and a review of the proposed methods is presented in this chapter.

1. Principles of reflection XAFS

Reflection X-ray absorption fine structure (XAFS), also called grazing-incidence XAFS (GIXAFS) or ReflXAFS, is based on the total external reflection of X-rays at the interface between two media, the deeper of which possesses the higher electronic density. If the impinging (probe) beam shines upon the material below a given angle (the critical angle \( \theta_c \)) it is completely reflected and only enters an extremely thin layer of the medium. This is an optical phenomenon that is also widely observed in the visible range; the difference here is that in the case of a vacuum–material interface the former plays the role of the ‘high-density’ medium. The phenomenon can be understood by considering the refraction index of an idealized system consisting of electrons (with mass \( m_e \) and charge \( q_e \)) bound to the nuclei via a harmonic potential (spring constant \( \kappa \)). Neglecting dissipation, the equation of motion of electrons \( i \) responding to an external field \( E_0 \) at angular frequency \( \omega \) is

\[
m_e \ddot{x} + \kappa x = q_e E_0 \exp(i \omega t),
\]

and it can be demonstrated (d’Acapito, 2003) that such a system has a refraction index \( n \),

\[
n = \left( 1 + \frac{Na}{\varepsilon_0} \right)^{1/2} \simeq 1 + \frac{Nq_e^2}{2\varepsilon_0 m_e} \sum_i \frac{1}{\omega_{ix}^2 - \omega^2},
\]

in which the sum is over all electrons, \( N \) is the atomic volume density and \( \alpha \) is the polarizability. When the energy of the X-rays is sufficiently high, most electrons are above their resonance frequencies and will respond in antiphase with respect to the field (and similarly for \( \alpha \)); the resulting refraction index will exhibit a real part slightly less than 1. This means that the phase velocity in the medium is higher than the speed of light in the vacuum and the medium acts as if it has a lower electronic density than the vacuum. In a more complete treatment (Parratt, 1954) the refraction index can be written as

\[
n = 1 - \delta - i \beta,
\]

where \( \beta \) and \( \delta \) come from the scattering factors (in particular it holds that \( \beta = \lambda \mu / 4 \pi \), where \( \lambda \) is the X-ray wavelength and \( \mu \)
is the absorption coefficient) and they are linked by the Kramers–Kronig (KK) relation.

Using the Fresnel formulae for the modelling of refraction at an interface, a complete description of the reflectivity can be given in homogeneous as well as stratified media. Defining

\[ X = \frac{\varphi}{\varphi_c}, \quad Y = \frac{\beta}{\delta}, \quad h = X^2 + [(X^2 - 1)^2 + Y^2]^{1/2}, \quad (4) \]

the reflectivity \( R \) expressed as the ratio between the moduli of the impinging and reflected electric fields is

\[ R = \frac{h - X[2(h - 1)]^{1/2}}{h + X[2(h - 1)]^{1/2}}. \quad (5) \]

For the sake of simplicity, we recall here some basic simple formulae such as the expression of the critical angle as

\[ \varphi_c = (2\delta)^{1/2} \quad (6) \]

and of the extinction length \( z_{1/e} \) of the refracted beam in the case of a small incidence angle and negligible absorption as

\[ z_{1/e} = \frac{\lambda}{4\pi \varphi_c}. \quad (7) \]

Since \( \delta \) is of the order of \( 10^{-5} \), \( \varphi_c \) is of the order of a few milliradians and \( z_{1/e} \) is around a few nanometres.

When considering the \( \beta \) function in a condensed system, it is clear that it contains (due to the dependence on \( \mu \)) an atomic background \( \beta_0 \) plus features coming from the photoelectron interference in the expression of the absorption coefficient (fine-structure effect) \( \Delta \beta \). Similarly, the interference appears in \( \delta \) by virtue of the KK relation with \( \beta \) and the oscillations are called \( \delta \)-XAFS. Thus, the reflectivity \( R \) as a function of the photon energy \( E \) will contain the XAFS features, making an investigation of surfaces within a range of a few nanometres under the surface possible. On the other hand, analysis of the data appears to be extremely complex due to the nontrivial relationship between \( R(E) \) and the quantities \( \beta \) and \( \delta \) (also known as anomalous dispersion effects).

2. Data-analysis methods

The first observation of XAFS features in a reflectivity spectrum was carried out by Barchewitz et al. (1978), and soon afterwards Martens and Rabe pointed out the presence of both \( \beta \) and \( \delta \) contributions to \( R \) and that for data collection below the critical angle \( \beta \)-XAFS dominated in \( R \), whereas well above \( \varphi_c \) \( \delta \)-XAFS dominates (Martens & Rabe, 1980a,b, 1981). They also defined a method for extracting the pure \( \beta \) contribution from a spectrum collected at any angle by considering the atomic and oscillating parts \( \beta = \beta_0 + \Delta \beta \) and \( \delta = \delta_0 + \Delta \delta \) and a relationship \( f = \Delta \beta/\Delta \delta \) linking the two. Considering, however, that the more interesting applications of ReflXAFS are performed well below the critical angle (\( \delta \ll \varphi_c \)), Bosio et al. (1984) and Pumelllec et al. (1989) proposed an approximate method for the treatment of data collected under these conditions, although limited to the case of a semi-infinite solid. In the case of a small incidence angle the following relation between \( \beta \) and the experimental \( R \) holds,

\[ \beta = \delta \left[ (1 - X^2)^{1/2} \right] \frac{1 - R}{X(1 + R)}, \quad (8) \]

where \( X \) has the same definition as above. Starting with an initial value for \( \delta \) a first approximation of \( \beta \) is derived. Using a Kramers–Kronig transformation \( \text{KK}\{\beta_0\} \) a second function \( \delta_{\text{approx}} \) is found that generates \( \beta_{\text{approx}} \). Repeating this procedure several times, a self-consistent solution is rapidly found.

Following the method outlined by Martens and Rabe, Borthen and Strehblow defined a further method based on the expression of the oscillating part of the reflectivity \( \chi_R(E) \) as a linear combination with \( a \) and \( b \) coefficients of \( \Delta \beta \) and \( \Delta \delta \) calculated on a model system (Borthen & Strehblow, 1995a,b; Fig. 1). This method was also valid for semi-infinite solids, but the necessity to also treat the more general case of layered systems was soon recognized.

The first formulation of a method permitting the analysis of this class of samples was presented by Heald and coworkers (Heald et al., 1988; Chen, 1989; Heald, 1992) and was based on the expression of the total \( R(E) \) [or even the fluorescence, \( F(E) \)] as a sum of two contributions, one \( \beta \)-dependent and the

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**Figure 1**

A description of the Borthen and Strehblow method. Left: the ratio between the \( b \) and \( a \) coefficients for the linear combination as a function of the incident angle in the case of a nickel layer. Right: comparison between the exact and linear combination solution for the reconstructed \( \Delta \beta \) signal. This figure is reprinted with permission from Borthen & Strehblow (1995a). Copyright 1995 by the American Physical Society.
other $\delta$-dependent (Fig. 2). This latter part was estimated from a partial derivative $\Delta R/\Delta \beta \ast \Delta \beta/\Delta \delta$, where this last factor was identified as bearing a phase factor of about 75–80$^\circ$ (compared with the value of 90$^\circ$ previously estimated by Martens and Rabe).

The method proposed by Tani et al. (2004) is based on similar principles, with the function $\Delta \beta/\Delta \delta$ being determined via an iterative cycle, and a similar method has been proposed by Abe et al. (2014) for analysis of time-resolved ReflXAFS data collected in energy-dispersive geometry. An extension of this method applied to layered systems has been proposed by López-Flores et al. (2009), in which the quantity $R(E)$ is obtained in a matrix form involving the partial derivatives of $R$ with respect to $\beta$ and $\delta$ relative to each layer of the sample.

More recently, due to the interest in layered systems, the problem of correctly including the surface roughness became the subject of investigations (Lützenkirchen-Hecht & Frähm, 2000). Martens and Rabe first underlined the importance of this parameter in ReflXAFS data analysis (Martens & Rabe, 1980a,b, 1981) and a series of papers (Keil et al., 2005a,b; Keil & Lützenkirchen-Hecht, 2009) have addressed this aspect in detail, also considering the distorted-wave Born approximation (DWBA; Sinha et al., 1988) as a possible alternative theory to that of Fresnel (Fig. 3).

In these papers, the importance of considering the surface roughness mainly for possible artefacts affecting the signal amplitude was recognized and treatment using Parratt’s (Fresnel) formulae corrected by a Névot–Croce roughness parameter (Névot & Croce, 1980) gave the same results as the more complex DWBA model in the case of specular reflection. However, use of the DWBA model permitted the elaboration of a variant of the ReflXAFS technique based on the off-specular reflected beam, i.e. collecting the data at the so-called Yoneda peak (Yoneda, 1963). Nonspecular effects are not included in Parratt’s formalism, but can be obtained from the DWBA model, and this opens the opportunity for a new experimental technique with increased sensitivity to the interfaces in the sample presenting a higher degree of lateral heterogeneity (Lützenkirchen-Hecht et al., 2007). In these papers, the quantitative XAFS analysis was carried out using the Borthen and Strehblow method.

As also suggested by Lützenkirchen-Hecht & Frähm (2006), Benzi et al. (2008) have proposed a code, Code for the Analysis of ReflXAFS Data (CARD; https://www.esrf.fr/computing/scientific/CARD/CARD.html), that works in a completely different way with respect to the previously mentioned methods (Fig. 4). Instead of converting $R(E)$ to a $\beta(E)$ for successive analysis with conventional tools, they proposed the use of modified XAFS theoretical paths for modelling the oscillating part of $R(E)$. In practice, the relevant reflectivity parameters (layer thickness, roughness and composition) of the sample are determined by fitting one or more reflectivity spectra at a fixed energy (and variable angle $\varphi$) of the sample. Using these parameters, the reflectivity $R(E)$ of the sample is simulated including the individual theoretical EXAFS paths generated by a suitable code (FEFF in the present version of the code).

From this reflectivity function a new theoretical EXAFS signal is extracted and can be used for data analysis. In this case the full Fresnel formulae (with Névot–Croce corrections for roughness) are used with no additional approximations in the case of layered systems (Costanzo et al., 2014).

Thus far, the case has been considered in which the optical constants of the absorbing species contribute significantly to the refraction index of the probed layer (the concentrated sample case). In the case of a very thin film this is no longer the case: the refraction index of the probed layer is dominated by the matrix and does not exhibit edge jump or XAFS oscillations in the region investigated (the diluted sample case). In this case the reflectivity signal does not possess any XAFS modulation and fluorescence detection must be used. In

![Figure 2](image_url)

**Figure 2**
Illustration of the method proposed in Heald et al. (1988). The continuous lines are the uncorrected (lower amplitude) and corrected EXAFS spectra (fluorescence mode) of a gold film measured at the Au $L_{III}$ edge at an incidence angle of 6.2 mrad (0.35$^\circ$) and the dashed line is the EXAFS spectrum of a gold film measured in transmission mode. This figure is reprinted from Heald et al. (1988). Copyright 1988 by the American Physical Society.

![Figure 3](image_url)

**Figure 3**
Comparison between the off-specular experimental data (squares) of a gold layer (Au $L_{III}$ edge) measured at an incidence angle of 12.7 mrad (0.73$^\circ$) and the calculated $\chi_R$ function using the DWBA method. This figure is reprinted with permission from Keil et al. (2005a).
reality, fluorescence could also be used in the analysis of thick samples, but it was pointed out many years ago (Affrossman et al., 1986) that reflectivity has a greater surface sensitivity in the case of rough samples. The great advantage in this case is that it can be demonstrated that no corrections are necessary and the collected data can be treated in the conventional way, as discussed by Jiang et al. (1991) and Jiang & Crozier (1997).

3. Conclusion
Since the discovery of the ReflexAFS effect, many groups have worked to make this technique reliable via rigorous data-analysis procedures. At present, several data-analysis methods are available to users for analysis of the data collected with this particular method.

References