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Texture effect on polarized EXAFS amplitude

Received: 3 February 2000 / Accepted: 26 July 2000

Abstract Application of polarized extended X-ray absorption fine structure (P-EXAFS) spectroscopy to thin films of fine-grained minerals is emerging as a powerful method to investigate the in-plane and out-of-plane local structure of phyllosilicates. Mineral platelets have no preferential orientation in the plane of the film, and their c* axes are oriented essentially along the film normal. The angular dependence of the EXAFS amplitude critically depends on the orientation distribution of c* axes due to mosaic spread. The effect of film texture on EXAFS amplitude has been calculated as a function of the mosaic spread, the orientation of the electric field vector, and the crystallographic orientation of the atomic pair. Calculations show that the reduction in amplitude for partially ordered films is more important when the electric field vector is perpendicular to the film plane. For phyllosilicates, no significant deviation from single crystal dichroism occurs when the mosaic spread is less than ±20°–25° half-width at half-maximum (HWHM) for parallel measurement, and ±15°–20° HWHM for normal measurement. Graphs are given for correcting EXAFS-derived coordination numbers for texture effects.

Key words Polarized EXAFS · P-EXAFS · EXAFS · X-ray absorption spectroscopy · Texture · Orientation distribution

Introduction

In extended X-ray absorption fine structure (EXAFS) spectroscopy angularly resolved structural information can be obtained through analysis of the angular dependence of absorption spectra for anisotropic samples. Originally, polarized EXAFS (P-EXAFS) was applied to single crystals (Brown et al. 1977; Kutzler et al. 1981; Manceau et al. 1988, 1990; Waychunas and Brown 1990), and this technique was recently extended to thin films of fine-grained layered minerals (Manceau et al. 1998). P-EXAFS probes the local structure of layered minerals between two different directional limits, parallel and perpendicular to the (001) plane, by varying the angle between the electric field vector (E) and the layer plane of a single crystal, or the surface of a thin film. In the case of smectites, highly ordered films can be prepared, which allows precise probing of their three-dimensional local structure without loss of spatial resolution as compared to single crystals. However, the dichroism of P-EXAFS spectra can be diminished by an imperfect film texture. Therefore, quantitative determination of the orientation distribution (OD) of individual crystallites in the film is necessary to accurately determine coordination numbers, and to localize scattering atoms relative to the polarization direction. Generally, the OD of a film is quantified by X-ray diffraction (Schulz 1949; Bunge 1981). Texture analyses of smectite films showed that a and b layer axes of crystallites have no preferential orientation in the plane of the film and, consequently, that the complete OD could be obtained by measuring uniquely the misalignment of particles off the film plane. The dispersion of c* axes can be modeled correctly with a Gaussian distribution function centered on the film normal. In previous studies of smectites (Manceau et al. 1998; Schlegel et al. 1999; Manceau et al. 2000a, b), the half-width at half-maximum (HWHM) of the Gaussian distribution ranged from 10° to 22°, and its effect on EXAFS-derived coordination numbers was neglected. Indeed, preliminary calculations (Manceau et al. 1999) suggested that the texture effect was insignificant for HWHM < 15° and limited for 15° < HWHM < 20°. This article aims at evaluating precisely the influence of film texture on the angular dependence of P-EXAFS spectra and at providing simple correlation plots for correcting EXAFS results for texture effects.
Texture effect

Angular dependence for perfectly ordered films

For a single crystal and in the plane-wave approximation, the angular term responsible for the K-edge EXAFS dichroism of a given atomic shell is (Stern and Heald 1983):

\[ \chi(k, \theta) = \sum_{i=1}^{N} 3 \cos^2(\theta_i) \chi_{\text{iso}}(k) = 3 \langle \cos^2 \theta \rangle \chi_{\text{iso}}(k) , \]  

(1)

where \( \theta \) is the angle between \( \mathbf{E} \) and the vector \( \mathbf{R}_i \) that connects the X-ray absorber to the backscattering atom \( i \) in the considered atomic shell, and \( \chi_{\text{iso}}(k) \) is the isotropic contribution of the atomic shell (Fig. 1). The summation runs over all the \( N \) atoms of the shell. In a film, individual mineral platelets display no order with respect to rotation about the film normal and, consequently, \( \theta_i \) varies from one crystallite to another. Thus, Eq. (1) cannot be handled easily, and requires transformation through the introduction of angles that are independent of the orientation of layers in the film plane. Due to the axisymmetrical character of clay films, and assuming an ideal texture, Eq. (1) can be transformed to (Maneau et al. 1998; Schlegel et al. 1999):

\[ 3 \langle \cos^2 \theta \rangle = 3 \cos^2 \beta \sin^2 x + 3/2(\sin^2 \beta \cos^2 x) \]  

(2)

or

\[ 3 \langle \cos^2 \theta \rangle = 1 - 1/2(3 \cos^2 \beta - 1)(3 \cos^2 x - 2) , \]  

(3)

where \( x \) is the angle between the film or platelet normals (the two normals are aligned in a perfectly vectorially ordered sample) and the beam direction (or the angle between \( \mathbf{E} \) and the sample plane), and \( \beta \) is the angle between \( \mathbf{R}_i \) and the sample normal (Fig. 1). The polarization term in Eqs. (2) and (3) is now independent of the relative position of crystallites in the film plane, and of the variation of \( \theta_i \) from one atom to another in the atomic shell \( i \). The amplitude of \( \chi_{\text{iso}}(k) \) is obviously proportional to \( N_i \) and in a polarized experiment one detects an apparent number of atomic neighbors \( (N_{\text{app}}) \), which is the effective number of atoms really seen at the \( x \) angle. Then:

\[ N_{\text{app}} = N - 1/2N(3 \cos^2 \beta - 1)(3 \cos^2 x - 2) . \]  

(4)

In the curved-wave EXAFS formalism, however, the angular dependence of EXAFS spectra is not correctly accounted for by this single angle-dependent apparent coordination number because an angular term in \( \sin^2 \theta \) should be added to Eq. (1) (Benfatto et al. 1989; Brouder 1990). The strength of the \( \sin^2 \theta \) term versus the \( \cos^2 \theta \) term depends on the angular momentum \( l \) of the scattering wave, on the wave vector value \( k \) and on the interatomic distance \( R \); for K-edge \( (l = 1) \) it is maximum for \( kR < 5 \) and becomes progressively negligible for \( kR > 10 \) (Benfatto et al. 1989). Therefore, the importance of the deviation from the usual plane-wave limit can be neglected in the analysis of the EXAFS contribution \( (k > 3 \text{ Å}^{-1}) \) of nearest \( (R = 3 \text{ Å}) \) and higher distance cationic shells in phyllosilicates.

Angular dependence for partially ordered films

In practice, the particle packing is always disrupted to some degree, and the distribution of \( c^* \) axes of individual particles around the film normal has to be introduced in Eq. (1). The angular dependence of apparent coordination numbers then becomes (Dittmer and Dau 1998):

\[ N_{\text{app}} = N - 1/2N(3 \cos^2 \beta - 1)(3 \cos^2 x - 2)I_{\text{ord}} \]  

(5)

with

\[ I_{\text{ord}} = \frac{\int_{0}^{\pi/2}(3 \cos^2 x - 1)P(x) \sin x \, dx}{2 \int_{0}^{\pi/2} P(x) \sin x \, dx} . \]  

(6)

The function \( I_{\text{ord}} \) accounts for the particle disorder, and its value is one for perfectly ordered films and zero for an isotropic sample. \( P(x) \) represents the profile shape function used to model the distribution of \( c^* \) axes around the film normal.

\[ P(x) = \exp(-x^2 \ln 2/\Omega^2) \]  

(7)

for a Gaussian distribution, where \( \Omega \) is the HWHM of the mosaic spread.

Numerical application

Equation (6) was solved numerically because the integral in the numerator has no analytical solution. Figure 2a shows that \( I_{\text{ord}}(\Omega) \) does not vary linearly with the mosaic spread. The disorder parameter has little sensitivity to \( \Omega \) when the texture strength is high and low but a high sensitivity in the 15° < \( \Omega < 30° \) interval. Experimental \( \Omega \) values measured on different film preparations of nontronite and hectorite smectites are reported in Fig. 2b. Except for the two most well-oriented samples, which have an HWHM as low as ~10° and ~12.5°, all

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**Fig. 1** Vectors and angles relevant for P-EXAFS measurements on thin films of fine-grained layered minerals. \( E \) is the electric field vector, \( F \) is the film normal, \( P \) is the particle normal, and \( R_i \) is the vector connecting the X-ray absorbing and the backscattering \( i \) atom. \( \alpha \) is the angle between \( E \) and \( F \) (experimental angle), \( \theta \) is the angle between \( E \) and \( R_i \), and \( \beta \) is the angle between \( R_i \) and \( P \). In a perfectly vectorially ordered film, \( P \) and \( F \) are aligned.