Multiple scattering approach to DAFS

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In this article we outline a general approach to the anomalous correction to the atomic scattering factor "ab-initio" calculation based on the multiple scattering theory. This approach can be used for structural determination in any system and in particular in the surfaces where symmetry conditions make usual analysis impossible. We show as an application of the formalism calculations related to experimental data of bulk Ge.

Keywords: multiple-scattering theory, DAFS

1. Introduction

The structural characterization of bulk structure and reconstructed surface is of fundamental importance for the determination of the most of their properties. Several techniques employing x-ray beams are normally used for this purpose. Recently, a new approach based on the measurements of the scattered intensity as a function of the energy near and above an absorption edge, usually referred as Diffracted Absorption Fine Structure (DAFS), has been proposed and used to determine bulk structure (Straigier et al. 1992). In principle this technique joins the advantages of the x-ray diffraction (XRD) and the x-ray absorption (XAS) methods and, for this reason, can become one of the most powerful structural technique. Its applications to surfaces can be even more important because it allows a clear separation between surface and bulk signal.

Few examples of such experiments have appeared in the literature so far because of difficulties both in the experimental apparatus and in the data interpretation. The data are usually analyzed by separating the form factor in a smooth part and an oscillating contribution, which is interpreted by following an EXAFS like approach (Pickering et al. 1993). Although this method has been applied to several cases with rather good results, it is not valid in general due to the presence of two different polarizations directions in the anomalous resonant scattering part.

In this paper we derive analytical expressions, using multiple scattering theory, for DAFS cross-section in the general case and we discuss the relation with the standard EXAFS formulation. Applications to the Ge bulk will be shown as test case of the experimental method.

2. Theory and application

The intensity of XRD by crystals depends on both the structure factor and the atomic scattering factor f that is usually calculated in terms of atomic approach and it has a smooth dependence with the energy of the incoming photons. When the energy is close to an absorbing edge, corrections to the atomic scattering factor arise due to the contribution of the second order resonant process. These corrections, usually referred as anomalous corrections, can be described by a complex quantity $\Delta f = f' + if''$ whose real and imaginary part are related by Kramers-Kronig transformations due to the validity of the causality theorem. In the forward scattering limit the imaginary part is proportional to the absorbing cross-section.

In the following a more general derivation of the anomalous corrections is presented using the Multiple Scattering (MS) approach. This method allows us to derive a general expression for the Δf quantity valid for any conditions of scattering and able to account for the presence of an atomic environment around the resonant atom. This derivation is not based on the Kramers-Kroenig (KK) transformations and it is able to calculate the real and imaginary part of Δf directly. Introducing the one-electron Green function G(r,r';E) of the system, the anomalous term becomes (using atomic units):

$$\Delta f = \frac{(\hbar\omega)^2}{2} \left\langle 1s \left| \hat{\varepsilon}_i \cdot \vec{r}\; G(\vec{r},\vec{r}';E) \hat{\varepsilon}_s \cdot \vec{r}' \right| 1s \right\rangle$$

In this theoretical development we have not considered the smooth contribution coming from the integration over the occupied states below the Fermi energy (Vedrinskii et al. 1992) because it does not bare any structural information. Nevertheless it has been included in the numerical applications. Using the MS approach it is possible to introduce the scattering path operator of the theory and to derive the following expression for the anomalous correction (for simplicity we consider only K and L_1 edges):

$$\Delta f = \frac{(\hbar\omega)^2}{2} M_{01}^2 \sum_{\alpha\beta} Y_{1\alpha}(\hat{\varepsilon}_i)\, \tau^{00}_{1\alpha,1\beta}\, Y_{1\beta}(\hat{\varepsilon}_s)$$

all symbols have been introduced elsewhere (Natoli et al. 1986) and here they have the same meaning. M_{01} is the atomic contribution and it has smooth energy dependence. Previous equations have been derived in the dipole approximation limit of the light matter interaction.

The anomalous scattering polarization dependence is generally different from the corresponding absorption polarization dependence due to the presence of the two different polarization directions of the incident and scattered beams. In the dipole approximation limit, for the σ to σ scattering process, it is possible to establish a direct link between absorption and anomalous scattering because the polarization directions of the incident and scattered photons are parallel. In this case f'' is still proportional to μ. To emphasize the structural information contained in the Δf, it is convenient to introduce a spherical tensor develop of the scattering path operator already used in the theoretical analysis of the geometrical properties of the absorption cross section. Following this approach the scattering path operator can be written as:

$$\tau^{00}_{a\alpha,b\beta} = \sum_{c\gamma} \tau(a,b;c\gamma)(-1)^{a-\alpha} C^{c\gamma}_{a-\alpha,b\beta}$$

where $\tau(a,b;c\gamma)$ is a $(c\gamma)$-spherical tensor which contains the structural information presented in the experimental data. Using this expansion the anomalous term finally becomes:

$$\Delta f(\hat{\varepsilon}_i,\hat{\varepsilon}_s;E) = A(E)\frac{\sqrt{3}}{4\pi}\tau(11;00)\hat{\varepsilon}_i\cdot\hat{\varepsilon}_s + A(E)\sum_{c\gamma\neq 0,} \tau(11;c\gamma) B_{11}^{c\gamma}(\hat{\varepsilon}_i,\hat{\varepsilon}_s)$$

In this equation the spherical part has been separated from the anisotropy contribution in analogy with the general structure of the polarization dependent absorption cross section. In the atomic limit only the spherical $\tau(1,1;00)$ term survives and the usual expression for the anomalous term can be recovered. The anisotropic contribution is proportional to the bipolar spherical harmonics:

$$B_{11}^{c\gamma}(\hat{\varepsilon}_i,\hat{\varepsilon}_s)=\sum_{\mu,\mu'}(-1)^{1-\mu}C^{c\gamma}_{1-\mu,1\mu'}\,Y_{1\mu}(\hat{\varepsilon}_i)Y^{*}_{1\mu'}(\hat{\varepsilon}_s)$$

which depends both on the polarization vector directions of in-coming and out-coming light. The Thompson scattering amplitude f_0 has the same polarization vector dependence of the spherical term and it can be added to it to calculate the total elastic cross section. We refer, for brevity, to reference (Benfatto et al. 1999) for details on the meaning of all symbols. Previous equations are valid for any scattering conditions and they allow a direct calculation of the Δf term also in the cases where a direct link between f" and μ can not be done. The $(c\gamma)$-spherical tensor can be expanded in terms of n-scattering contributions. The n=2 term is the EXAFS like contribution and the higher order terms are proportional to MS events, following exactly the considerations done for the absorption spectroscopy. The no-polarized n=2 term is the usual curved wave EXAFS signal.

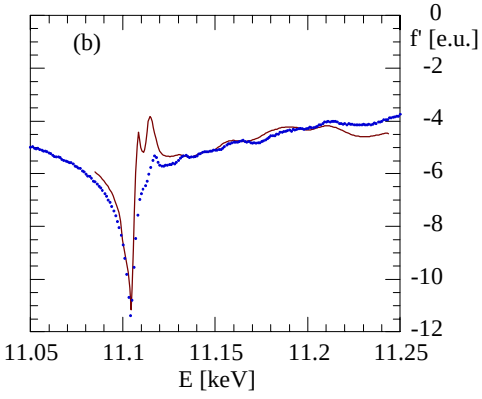

Figure 1
Comparison between experimental f' data and theoretical "ab-initio" calculation (solid line).

As an application of this formalism we show in Fig. 1 the comparison between the experimentally determined f', measured using several bulk Ge Bragg peaks, and the calculation carried out employing the described formalism. The experiment has been carried out at ESRF, using the ID32 beam line, in the so-called "top mode" DAFS. Because of the symmetry of Ge bulk, the f' term does not depend on the Bragg peaks. It can be extracted directly from the experimental intensity data by normalization to the isolated atomic f' signal given in the Sasaki tables. We have used the CONTINUUM program (Natoli et al. 1986) to obtain the theoretical curve; this program, already widely used for absorption analysis, has been modified to calculate Δf as previously defined. A cluster of 45 atoms has been considered and the complex Hedin-Ludqvist potential has been used for the exchange part. Neither the finite experimental resolution nor thermal effects in the atom positions have been considered in the calculations. Their effects would result in a smearing out of the sharp features of the theoretical curve. The agreement between experimental data and theoretical calculation is more than satisfactory considering the absence of any corrections and fitting procedure.

As a summary we have presented a general formalism for the "ab-initio" calculation of the DAFS signal valid for any possible scattering conditions. Applications to low symmetry cases, like the surfaces, will be the subject of a forthcoming paper.

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