

Harmonic contamination for Si(111) monochromator at the XAS beam line – up to August 1999

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Abstract

An experimental measurement of the harmonic contamination for low energy transmission measurements with Si(111) channel-cut monochromator on the XAS beam line is reported. The ratio of flux due to the third order harmonic, measured with air-filled ion chamber is less than 0.1%, for energies above 4300eV and less than 1% for energies above 3900eV. Below 3900eV the harmonic contamination increases strongly and reaches values greater than 10% below 3500eV.

Introduction

The XAS beam line [1] was operating from June 1996 to August 1999 with a 425 μ m thick beryllium window (125 μ m before the monochromator and 300 μ m at the end of the line). In these conditions the two channel cut monochromators (Si(111) and Si(220)) available for x-ray absorption measurements provide high photon flux (above 10^8 photons s^{-1}) in the energy range 3.5keV to 15keV, the Si(111) monochromator being the only one used for the low energy range (below 10KeV).

One of the commonly concerned problem in conventional absorption measurements is the harmonic contamination from the monochromator, i.e., the contamination of output beam with higher order reflections [2]. The consequence of the harmonic contamination is an alteration of the amplitude of the EXAFS oscillations leading to systematic errors in the number of neighbours and the Debye-Waller terms. This problem, enhanced for thick samples, is difficult to appreciate *a posteriori* and not easily corrected [3-5].

Due to the low critical energy of the LNLS storage ring (2 keV), third order harmonic contamination of the Si(111) monochromatic beam is expected to be very low above 6 keV range. However it might not be negligible at the lowest accessible energies of the measurements (below 5keV). We report here an experimental measurement of the harmonic contamination for three energies (3.5, 4 and 5keV), allowing a quantitative evaluation of this contamination over the whole accessible energy range.

Principle of the measurement

The output beam delivered by the Si (111) monochromator is : $I_0 = I_{0f} + I_{0h}$, with I_{0f} being the fundamental beam and I_{0h} the third order reflection beam. A measure of the harmonic contamination is made by evaluating the ratio $\alpha = I_{0h} / I_{0f}$ of the intensity of the output third-order reflection beam to the intensity of the fundamental one. After the sample the intensity of the beam can be written in the same way: $I = I_f + I_h$, with $I_f = I_{0f} e^{-\mu_f x}$ and $I_h = I_{0h} e^{-\mu_h x} = \alpha \cdot I_{0f} e^{-\mu_h x}$; x is the sample thickness; μ_f and μ_h are the linear absorption coefficients of the sample respectively for the energy of the fundamental beam (E) and the energy of the third order harmonic beam (3E).

The measured absorption of the sample within an energy range ΔE around E is given by:

$$\frac{I}{I_0} = \frac{I_{0f} e^{-\mu_f x} + \alpha \cdot I_{0f} e^{-\mu_h x}}{I_{0f} (1 + \alpha)}$$

If the sample does not present any absorption edge in the range ΔE of the fundamental energy, the variations of μ_f are weak and smooth and μ_f can be considered as constant in this range. On the other hand, if this sample is also chosen in order to present an absorption edge around the energy 3E, the coefficient μ_h will vary strongly within a short energy range. The presence of the third order harmonic is revealed by the presence of a jump by scanning the monochromator within the range of the fundamental energy.

An illustration is given on the figure 1. The sample is a 12 μ m thick foil of Ga (K-edge energy at 10368eV). Figure 1a is the absorption spectrum measured at one third the energy of the K-edge (10368/3 ~3458eV), hence due to the third order harmonic contamination. Figure 1b is the “true” absorption spectrum measured with Si(111) at the energy of the K edge.

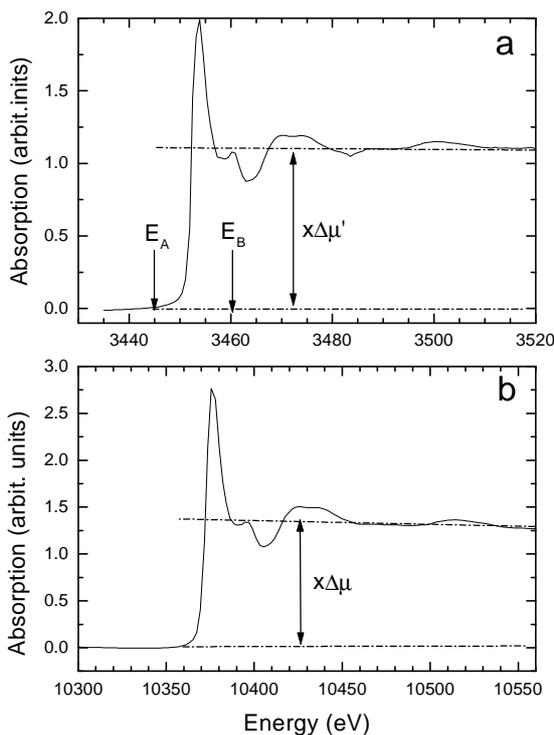


Figure 1a. Absorption spectrum obtained with the Si(111) monochromator set within one third the energy region of Ga K-edge. The jump is due to the harmonic contamination coming from the Si(333) reflection.

figure 1b. “True” absorption jump using Si(111) monochromator set within Ga K-edge region

As a matter of fact, the “true” absorption jump $x\Delta\mu$ equals about 1.4 (fig. 1b), while the value measured with the third order harmonic (333) is smaller ($x\Delta\mu' \sim 1.1$, fig. 1a). This reduction comes from the “contamination” by the fundamental reflection (111).

Using the notations of the figure 1, and assuming that E_A and E_B are taken close enough that I_{of}, α and μ_f can be considered as constant, the apparent absorption coefficients μ_A and μ_B for the energies E_A and E_B of the fundamental beam can be given by:

$$e^{-\mu_A x} = \frac{I_{of} e^{-\mu_f x} + \alpha \cdot I_{of} e^{-\mu_{hA} x}}{I_{of} (1 + \alpha)} \quad (1a)$$

$$e^{-\mu_B x} = \frac{I_{of} e^{-\mu_f x} + \alpha \cdot I_{of} e^{-\mu_{hB} x}}{I_{of} (1 + \alpha)} \quad (1b)$$

The measured jump $x\Delta\mu' = \mu_B x - \mu_A x$ is expressed through the ratio r of (1a) over (1b)

$$r = e^{-x\Delta\mu'} = \frac{e^{-\mu_f x} + \alpha \cdot e^{-\mu_{hA} x}}{e^{-\mu_f x} + \alpha \cdot e^{-\mu_{hB} x}}$$

Hence α is given by:

$$\alpha = \frac{(1 - r) \exp(-\mu_f x)}{r \exp(-\mu_{hB} x) - \exp(-\mu_{hA} x)}$$

$x\mu_{hA}, x\mu_{hB}$ and $x\Delta\mu'$ are obtained experimentally. Due to the presence of harmonic contamination $x\mu_f$ cannot be measured experimentally and is obtained from the sample thickness and tabulated values of the absorption coefficient [6]

Measurements and Results

Measurements of the absorption at the energy of the edge and at one-third the energy of the edge were performed using two ion chambers filled with air at ambient pressure.

We measured the value of the harmonic contamination for three energy points:

3450eV using a 12 μ m-Ga foil (Ga K-edge at 10368eV)

3970 eV using a 5 μ m-Au foil (Au L_{III}-edge at 11920eV)

4780eV using a 5 μ m-Au foil (AuL_I-edge at 14353eV).

On the basis of the precedent calculations we found:

E (eV)	α (%)
3450	14 \pm 2
3970	0.6 \pm 0.3
4870	<0.1

For the samples considered the total absorption at low energy is high ($\mu x > 3$ for Ga at 3500eV, >7 for Au at 4000eV and 4800eV). The main source of error in the determination of α is the accuracy on the measurement of the apparent absorption jump $\Delta\mu'$ at low energy. As a first approximation, the accuracy given for α has been evaluated taking into account only this factor.

From these data points and assuming an exponential decrease of the harmonic beam, we obtained the curve on figure 2, for the harmonic contamination at low energy for Si(111) on the XAS beam line.

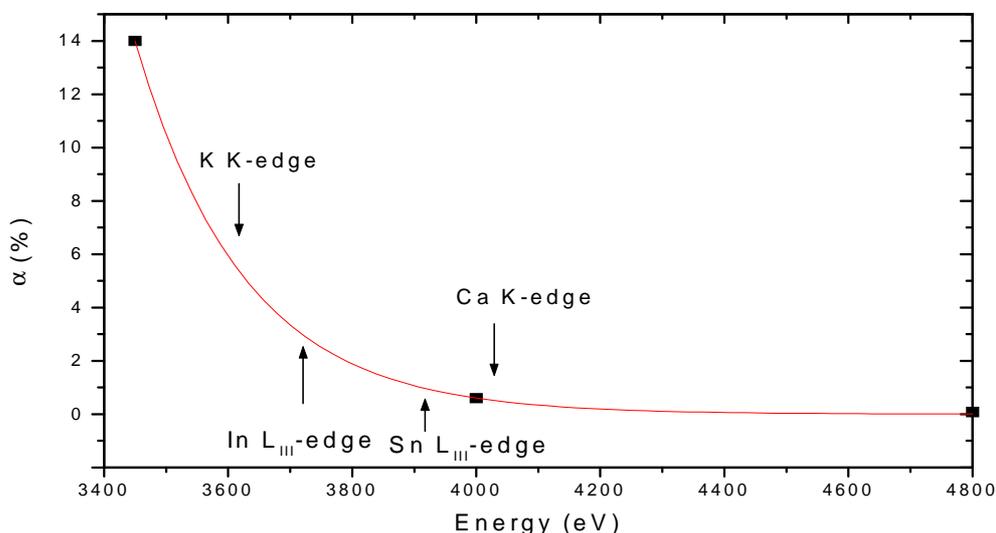


figure 2: Harmonic contamination for Si(111) monochromator as a function of the energy

It is noteworthy that in the usual conditions of the low energy measurements the ion chambers are filled with He instead of air. The contamination measured here is then reduced due to the variations with the energy of the ionization cross section of He and air.

Conclusions

For a sample with a typical total absorption $\mu \cdot x \leq 2$, the effect of 10% of harmonic contamination is a decrease of about 10% of the amplitude of EXAFS oscillations [7]. The harmonic contamination at the XAS beam line is less than 1% for all experiments performed at energies higher than 3900eV. The resulting alteration of the EXAFS signal is negligible for typical samples. Below 3900eV, the harmonic contamination increases strongly and its effect on the EXAFS signal could be significant.

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