Energy Resolution at LNLS-XAS beam line

Evaluation of the Contributing terms

A.Y. Ramos[1,2], H. Tolentino[1], M.C.M. Alves[1].
[1] Laboratório Nacional de Luz Síncrotron, CP 6192, 13083-970 Campinas SP, Brazil.
[2] Laboratoire de Minéralogie-Cristallographie, CNRS-ParisVI, France.

Abstract

We recall here the main parameters determining the energy resolution in an XAS measurement and the experimental characteristics of the LNLS-XAS beam line necessary to a correct evaluation of this resolution. The XAS beam line has been designed to be used from 2.5 up to 24 keV[1]. At low energy (<6keV) all terms contributing to resolution are of the same order. Above 6keV the resolution is principally limited by the divergence of the beam for K-edge measurements and by the core level width for L-edge ones.

Introduction

The energy resolution determines the FWHM of the thinnest measurable feature in the X-ray absorption experiment and is then a crucial parameter to obtain conclusive electronic and structural information on materials, either in the XANES or in the EXAFS range, when shells beyond the coordination one are involved.

The total energy resolution that can be obtained in an XAS experiment at a chosen absorption edge is limited, intrinsically, by the natural width of the core level Γ and, instrumentally, by the X-ray beam line optics. In a simplified scheme for energy resolution calculation, each contribution can be considered as a gaussian distribution. The resulting overall resolution is simply given by $\Delta E_{total} = \sqrt{\Gamma^2 + \sum_i (\Delta E_i)^2}$, where ΔE_i are the relevant instrumental terms: the energy resolution of the monochromator ΔE_{mono} and the divergence of the beam ΔE_{div}.

In order to support the LNLS XAS users in the choice of the optimal conditions for their experiments, we give in this report an evaluation of these contributions for experiments at the LNLS XAS beam line.

Relevant terms contributing to the energy resolution

a-Natural Core level width

Semi-empirical values for the natural core level widths are tabulated for a large number of elements [2,3]. They are represented in figure 1 for the K and L edges accessible at the LNLS-XAS beam line. For L_3 levels above 10 keV (Z>74) this term is larger than 5eV, giving an intrinsic limitation for the low-k EXAFS information, especially relative to next nearest neigbours.

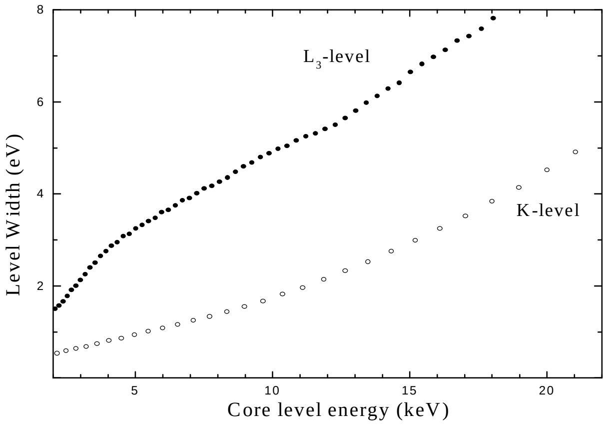

figure 1
Core hole level width as a function of the energy of the level.

b-Resolving power of the monochromator

For the two silicon monochromators in use at the XAS beam line (Si(111) and Si (220)) the resolving power P= $\left(\frac{E}{\Delta E}\right)$ is determined by the intrinsic width -or Darwin width- of the reflection.

According to the dynamical theory of diffraction, $\Delta E / E$ is independent of energy. The values given by Freund [Freund, 1988] are :

$$\left(\frac{\Delta E}{E}\right)_{Si_{111}} = 13.1\ 10^{-5}$$

$$\left(\frac{\Delta E}{E}\right)_{Si_{220}} = 5.37\ 10^{-5}$$

The corresponding resolving powers are 7600 and 18600 for Si(111) and Si(220) reflections, respectively.

The contribution of these intrinsic terms to the resolution as a function of the energy of the photons is shown in the figure 2

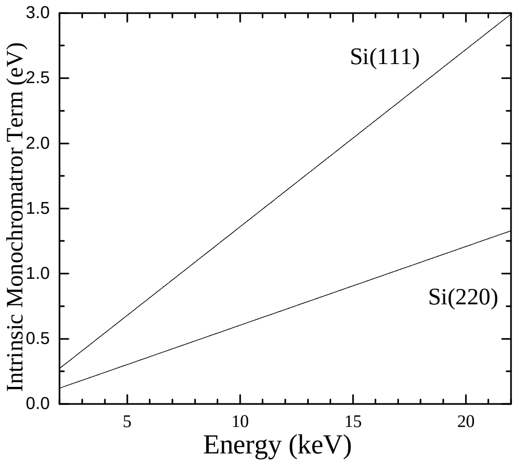

figure 2 Intrinsic energy resolution limited by the reflection width of the monochromator crystal.

c-Divergence of the photon beam

The resolution term related to the divergence of the beam is derived from the Bragg's law:

$$\frac{\Delta E_{div}}{E} = \cot(\theta_B)\Delta\theta$$

where Δθ is the divergence of the beam and θ_B is the Bragg angle of the monochromator:

$$\theta_B = \arcsin\left(\frac{\lambda}{2d_{hkl}}\right)$$

with λ[Å]= 12.4/ E [keV] and $2d_{111}$=6.271Å, d_{220}=3.8402Å [4].

Δθ is controlled by the vertical slits aperture - the user controllable term - and the vertical size of the source $fwhm_y$, which depends on the electron beam optics of the storage ring. The electron beam divergence does not contribute to the photon beam divergence because, in usual XAS experimental conditions (vertical slits aperture smaller than 4.5mm), the total divergence of the beam is actually limited, over the whole accessible energy range, by the vertical slits aperture (figure 3). $\Delta\theta$ is then simply related to source size and vertical slits aperture:

$$\Delta\theta = \frac{s + fwhm_y}{D}$$

where *s* is the vertical slits aperture and *D* the distance source-to-vertical slits (figure 4).

In the usual conditions of experiment, the vertical slits limiting the beam are the pre-monochromator slits at a distance D= 10.4m.

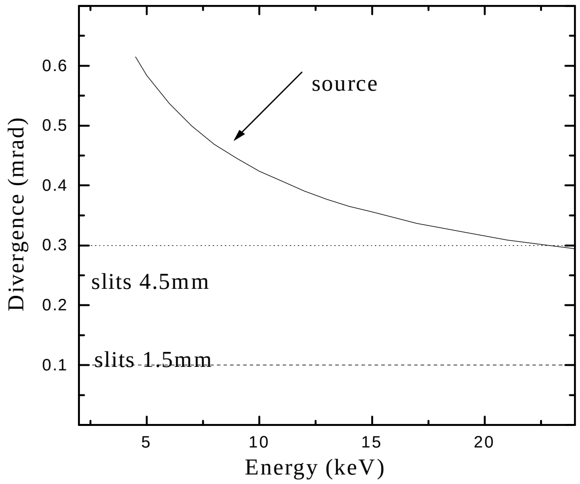

figure 3: Comparison between the divergence due to the source (including the cone emission of the photons and the divergence of the electron beam)[5] and the divergence limited by the vertical post monochromator slits. Over the whole energy range, the divergence of beam is limited by the slits .

At the LNLS-XAS beam line, the vertical beam size is measured at the sample holder position (at a distance D_{sh}=14.5m from the source). Hence another convenient way of expressing $\Delta\theta$ is in terms of this measured value:

$$\Delta\theta = \frac{bpsh + fwhm_y}{D_{sh}}$$

where D_{sh} is the source-to-sample holder distance and *bpsh* the FWHM of the beam profile at the sample holder position, usually measured by placing a 200µm-slit at the sample lodging.

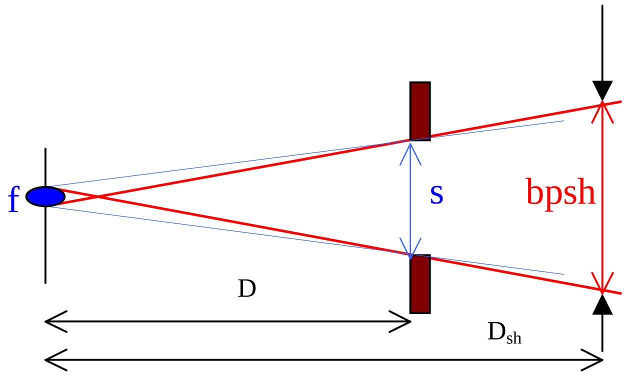

figure 4: Schematic geometry for the beam divergence at the XAS beam line. s size of the vertical slits, D distance source–slits. bpsh full width at half maximum of the vertical beam measured at the position of the sample holder (distance D_{sh} from the source), $fwhm_y$ vertical size of the source.

The size of the slits and the beam profile are easily related from geometrical considerations by:

$$bpsh = s\left(\frac{D_{sh}}{D}\right) + fwhm_y\left(\frac{D_{sh}}{D} - 1\right) \quad \text{or either} \quad s = bpsh\left(\frac{D}{D_{sh}}\right) + fwhm_y\left(\frac{D}{D_{sh}} - 1\right)$$

The XAS beam line is installed on the D04B bending source (dipole at 15°). The size of the electron beam source depends on the working mode of the synchrotron ring: large beam mode (vertical coupling of 3.5%) or small beam mode (vertical coupling of 0.35%). The normal operation mode from July 97 until November 99 had been the large beam mode, with $fwhm_y$ =0.522mm. From November 9th, 1999, the normal operation mode has been the small beam mode, with $fwhm_y$ =0.168mm [5].

Hence in the large beam mode bpsh=1.394s+0.205

in the small beam mode bpsh=1.394s+0.066 (s and bpsh in mm) [*]

The ΔE_{div} dependence as function of the energy of the photons is given in the both cases (figure 5) for different slits sizes s for the two monochromators, in their domain of use (2.5-14keV for Si(111), 10-24 keV for Si(220)).

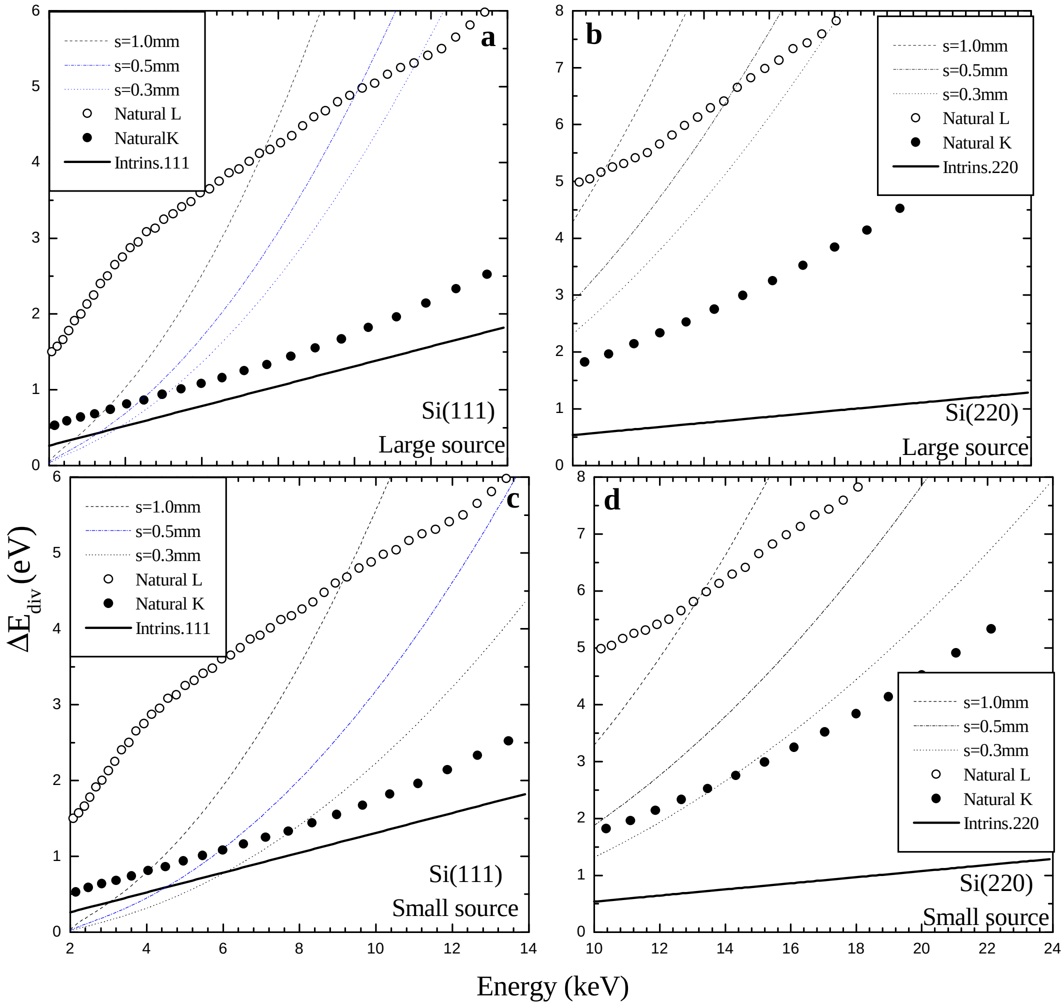

figure 5 : variation of ΔE_{div} as a function of the energy of the photons for different slits sizes s for the two monochromator in their domain of use For large source (a) Si(111) (b) Si(220) For small source:(c) Si(111) ,(d) Si(220

---

[*] It should be noted that a collective beam instability effect has recently been observed with the increase in the stored beam current. This effect increases the coupling factor above a threshold current (about 100mA) in the small beam mode. The instability effect is being studied and the $fwhm_y$ above the threshold has not been measured yet

The expected instrumental resolution ΔE_{inst} accounts for the contributions of the two instrumental terms $\Delta E_{inst} = \sqrt{\Delta E_{mono}^2 + \Delta E_{div}^2}$. It is given (figure 6) for the two monochromators for the small source and some typical slits sizes:

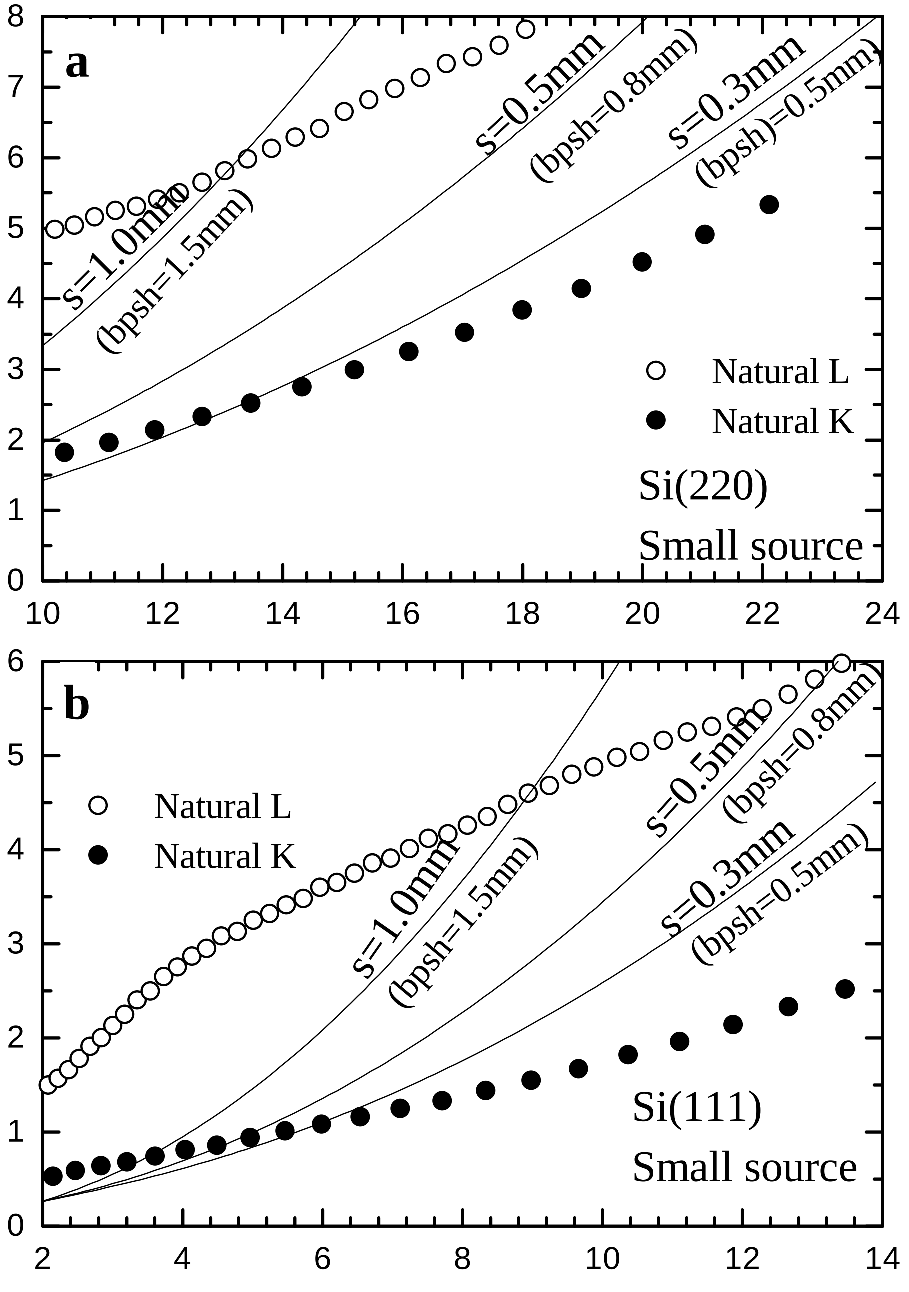

figure 6 : Expected instrumental resolution for a small source experiment, compared to the natural width of the core levels: (a) monochromator Si(220) with s=1mm, 0.5mm and 0.3mm (b) monochromator Si(111) with s=1mm, 0.5mm and 0.3mm.

Energy step of the monochromator

A key point concerning energy resolution and optimization of the acquisition parameters is the energy step of the monochromator. It has to be small enough compared to the overall energy resolution – to not spoil it - but not too small to be time consuming or to reach the accuracy of the monochromator mechanics. Concerning the last point, the smallest angular step of our goniometer is 5 μrad, related to a single step of the motor. This value is rather close to the accuracy of the goniometer mechanics and a safe procedure is to limit the minimum angular step to two motor steps, i.e., to assume $\delta\theta=10$ μrad as the minimum angular step. The minimum energy step δE is given by $\delta E/E = \cot\theta_B\ \delta\theta$ and depends on energy of the measurements and on the reflection of the monochromator (figure 7).

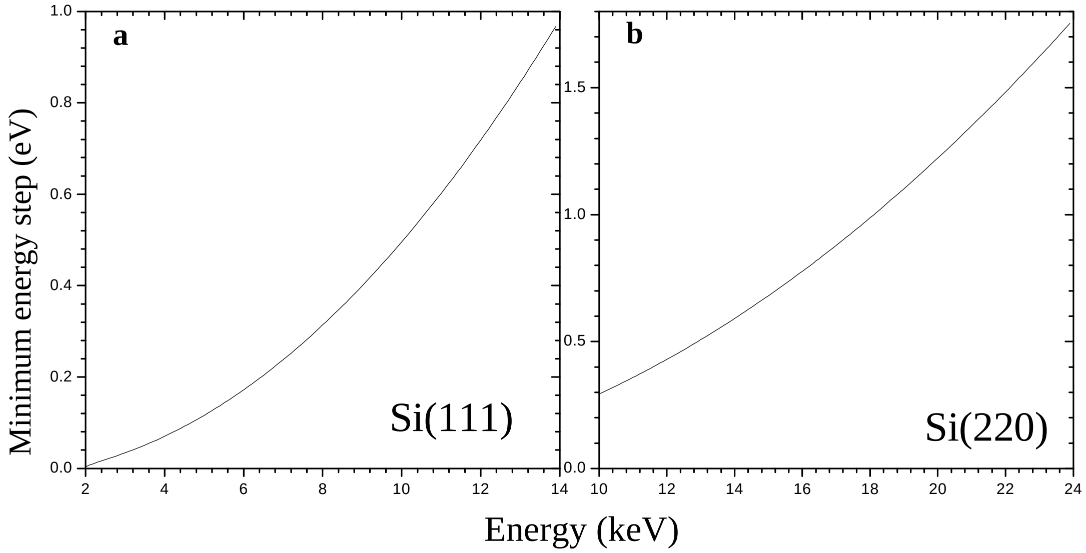

figure 7: Minimum energy step as a function of the energy of the measurement for the Si(111) and Si(220) monochromators.

To preserve the overall energy resolution a rule of thumb is to have at least five points inside the resolution. For instance, if the total energy resolution (including core hole, monochromator and divergence) is 2 eV, the energy step is usually chosen close to 0.4 eV.

In the figure 8, we compare the minimum energy step of our monochromator with the core level width (K and L_3), which are end-limits of the energy resolution. Over the whole range of the measurements the minimum energy step is lower than 1/5 of this limit.

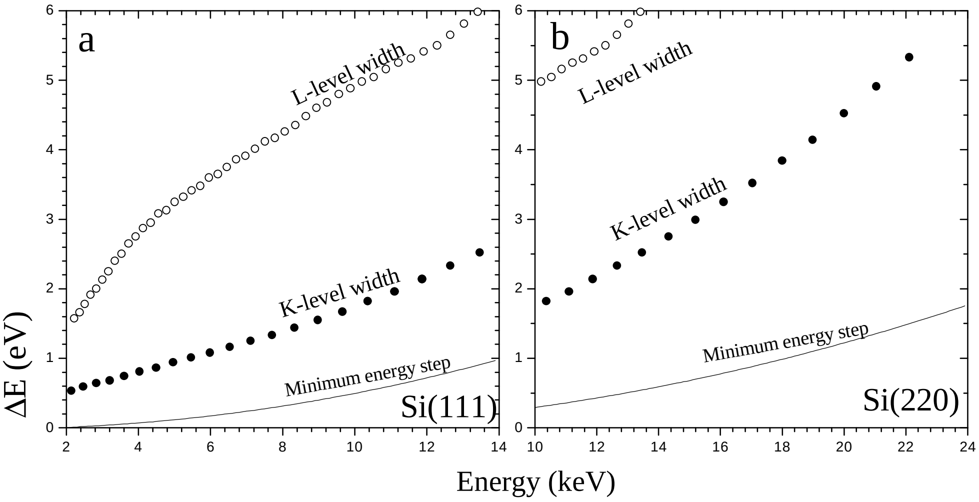

Figure 8: Comparison between the core level width (K and L_3) and minimum energy step of the monochromator (a) Si(111) (b) Si(220). Over the whole range of the measurements the minimum energy step is lower than equal 1/5 of the resolution.

Conclusions

We give in this report the expression of the relevant terms limiting the energy resolution at the LNLS XAS beam line and the parameters necessary to evaluate this resolution. The XAS beam line has been used from 2.5keV up to 24 keV. At low energy (<6keV) all terms contributing to the resolution are of the same order. Above 6keV the resolution is principally limited by the divergence of the beam for K-edge measurements and by the core level width for L-edge ones. The minimum step of the monochromator matches all the needs in terms of preserving the energy resolution over the whole range of the measurements.

Acknowledgements

The XAS beam line staff thanks a lot the help of the LNLS accelerator group.

References

[1] H. Tolentino, J. C. Cezar, D. Z. Cruz, V. Compagnon-Cailhol, E. Tamura and M. C. M. Alves, J. Synchrotron Rad**. 5**,521 (1998).
[2] M.O. Krause and J. H. Oliver, J. Phys. Chem. Ref. Data, **8**, 329 (1979).
[3] J.C. Fuggle Appendix B in Unoccupied Electronic States, Topics in Applied Physics, Volume 69 Springer Verlag Berlin (1992).
[4] A.K. Freund, Nucl. Inst. Meth. A266 (1988) 461.
[5] LNLS home page http:://www.lnls.br/