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GLITCHES COMPENSATION IN EXAFS DATA COLLECTION

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Abstract. In all the Synchrotron X-ray beam lines, one of the major experimental problems is due to the "glitches" that distort the monochromatized radiation. In principle, if the X-ray absorption measuring apparatus were linear, such distortion should be compensated. In practice this is not always so because of many frequent experimental inaccuracies. We analyze the most important of these, and suggest the correct procedure to avoid them.

Introduction

Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy has expanded rapidly in recent years (Lee et al. 1981): its strengths as a structural tool has been fully exploited with the use of Synchrotron Radiation and of double crystal monochromators, which provide an intense and collimated monochromatic X-ray source.

The simplest experimental arrangement to measure an X-ray assorption spectrum consists of two ion chambers, Io and I, monitoring the intensity of the beam before and after the sample. The absorption coefficient, μ, is then obtained from the equation:

$$\mu x = \ln \frac{Io}{I}$$

where x is the sample thickness.

In order to obtain reliable results in EXAFS analysis careful attention has to be devoted to the data collection. The shape of the EXAFS data, indeed, can be affected both by statistical and systematic errors (L. Incoccia and S. Mobilio, 1981), the latters being due to the ion chambers and electronics non linearity, higher harmonics presence in the primary beam, sample inhomogeneities (Stern and Kim, 1981) and monochromator glitches(*). The purpose of this report is to analyze the effect of the glitches on the spectrum and the precautions that must be taken in order to minimize their effects.

1. Glitches origin

Typical shapes of glitches in an EXAFS spectrum are shown in Fig. 1. The sharp decrease in the beam intensity as recorded by the two ion chambers originates when at a given angular position of the crystal monochromator another Bragg reflection is allowed at the same energy beside the primary one. In principle this effect should not influence the data since $\mu x = \ln Io/I$ is insensitive to the absolute value of Io and I: as it is evident from Fig. 1 this is not always true. We want to stress here that in many cases the glitches cannot be removed in data analysis by interpolation techniques, owing to the large energy spread of the glitches themselves, that can affect the spectra in a region as large as 200 eV. This happens when the angle between the "wrong" reflection and the primary one is large and out of the incidence plane.

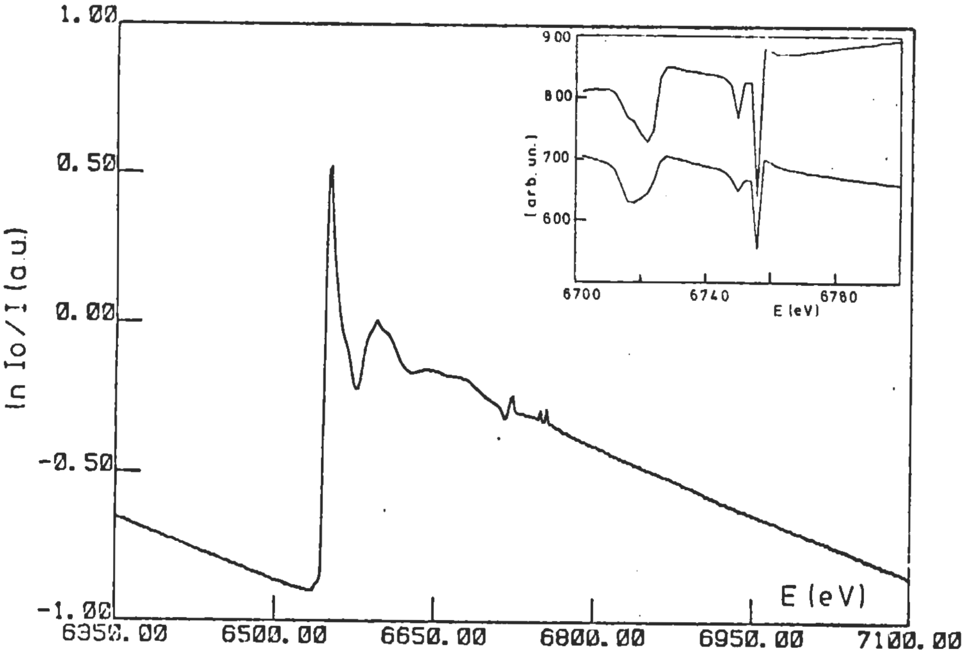

FIG. 1 - K-Absorption spectrum of Mn in Mn-ATP collected at the Frascati X-ray beam line using a channel-cut Si(220) as monochromator. In the inset we show the behaviour of Io and I, in the region of the glitches. It is to be noted that the dip in the intensity occur at different energies, so the glitches are not compensated.

The reason why the glitches on the spectrum of Fig. 1 are not compensated is explained in the inset. As can be observed, the sudden decrease in the beam intensity is located at slightly different energies for Io and I. This is a frequent behaviour that originates either from misalignement of the sample with respect to the entrance slit

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(*) A glitch is an abrupt variation of the intensity of the beam as monitored at the exit of the monochromator that can give rise, in many experimental situations, to a distortion of the absorption spectrum.

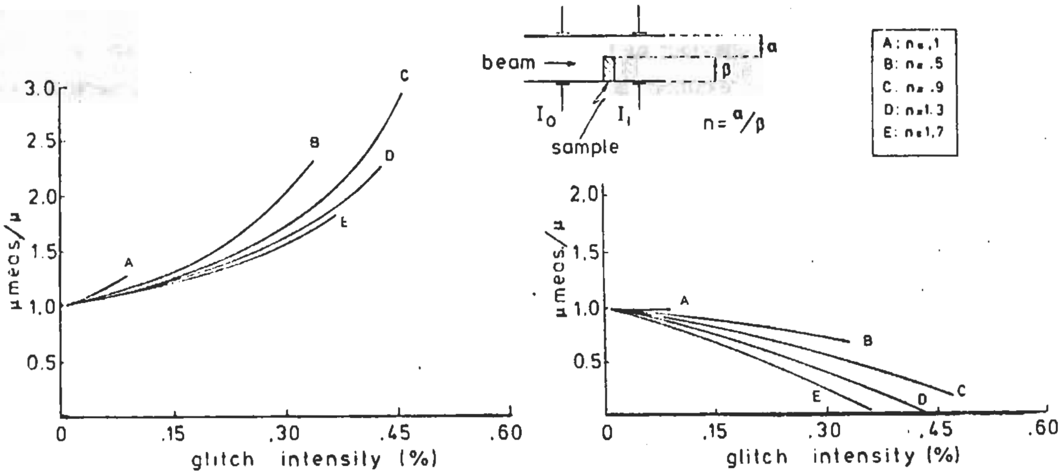

FIG. 3 - Ratio of the measured absorption coefficient μx_{meas} in presence of a glitch to the measured absorption coefficient without glitches as a function of the glitch intensity expressed as a percentage of the incoming beam. The geometry assumed is shown in the inset. a) The glitch does not pass through the sample (region α) b) the glitch passes through the sample (region β). The thickness of the sample is of the order of μx 2.

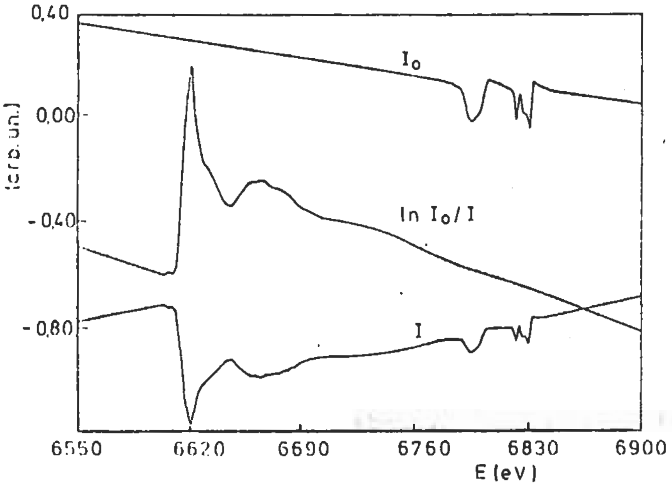

FIG. 4 - Absorption spectrum of MnO_2 powder showing a good compensation of glitches.

2. Higher Harmonics Effect

The effect of the higher harmonics on an absorption spectrum is dual:

1) generally it reduces the value of the measured absorption coefficient, thus enhancing the EXAFS modulation.

2) It prevents the compensation of the glitches. Indeed, although the higher harmonic has glitches at the same energy as the first one, the higher harmonics content in the spurious beam is different from the one in the primary reflection: it is a matter of simple algebra to show that again the glitch cannot be compensated. In Table I we report the higher harmonic content for the X-ray beam line at Frascati. As can be seen the content of 2nd harmonic is completely negligible for E > 6 keV. For lower energy, the second harmonic can be eliminated by lowering the electron beam energy from 1.5 GeV to lower values.

or from inhomogeneities in the sample itself. The detailed shape of the glitch as a function of the energy is strongly dependent on the angular behaviour of the lack of intensity in the incoming beam and on the particular experimental situation. A simplified example is shown in Fig. 2, where the glitch is supposed to be a lack of intensity spanning all the incoming beam in the vertical direction as the energy is increased, and the sample is smaller than the entrance slit while the second ion chamber is shadowed, for ex. by the sample holder. As can be observed, at some energy the glitch is seen only by the first ion chamber, so the system is not linear anymore. Similar considerations can be drawn when part of the incoming beam reaches I without passing through the sample. In this case, there can be an increase and/or a decrease in the absorption coefficient, causing a glitch shape of the kind shown in Fig. 1 around E=6720 eV. This is understood with the aid of Fig. 3. As can be seen, for a value of α/β of 0.5, a typical glitch intensity (~30% of Io) causes an increase in the absorption coefficient of the order of ~ 90% when the glitch is not seen by the sample, and a decrease of ~25% when it is seen only by the sample(*).

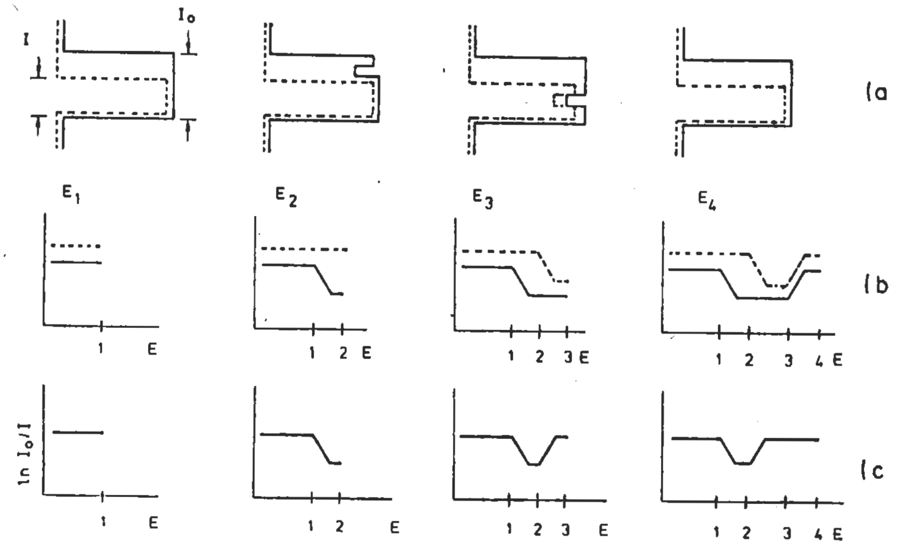

FIG. 2 - Schematic diagram explaining the origin of a not-compensated glitch when the entrance slit of I is shadowed by the sample holder. a) Spatial distribution of Io(–) and I(...) beam intensity in the vertical plane at different energies: E_1 before the glitch, E_2 the glitch is seen only by Io, E_3 the glitch is seen by both Io and I, E_4 after the glitch. The part of the beam seen by the two chambers is indicated by the arrows. b) Intensity as measured by the two ion-chambers. c) Resulting absorption coefficient.

Obviously similar effects occur if the sample itself is inhomogeneous, since in this case the distribution of thick and thin areas (or pinholes) mimics the experimental cases discussed. The only way to overcome the problem is to prepare samples finely grinded (Stern 1981) and/or with even thickness. Fig. 4 shows how a glitch can be well compensated when the sample is of good quality and properly aligned.

(*) In general, when the sample is misaligned, even without glitches one measures a wrong μx, but one can still extract reliable informations from the EXAFS spectrum. For example, in the geometry of Fig. 2, the error made is an additive constant factor over the whole spectrum, so it can be treated as a pre-edge background. In the case of Fig. 3, on the other hand, the error made reduces the edge strength but leaves the EXAFS frequencies unchanged.

TABLE I - Characteristics of the channel-cut Si(220) crystal used as monochromator at Frascati. The higher harmonic content has been measured by a Si(Li) detector.

Type: Si(220) Channel-cut crystal
Vacuum: 10^{-7} torr
Scan: Stepping motor ($\nabla\theta$: 7")
Angular readings: Contact Encoder ($\Delta\theta$: 3.523)
Control: PDP 11/03
Beam size: 13 x 6 mm^2
Automatic exclusion of the crystal from the beam
Range: 3.5÷12 keV
Resolution: $<$ 1.0 eV at 5 keV
Photon/sec: $\sim 10^9$ ph/sec (av.)

2nd harmonic:	E (keV)	%
	5.0	1.4
	6.0	0.6
	7.0	0.3
	8.0	0.1
	11.0	0.04

3. Other Detection Systems

For experiments that need either fluorescence or electron detection, further precautions must be taken. In these cases to preserve the linearity of the system it is important that the whole monitored incoming beam hits the sample. Furthermore the whole illuminated sample area has to be seen by the detector with the same efficiency. When using scintillation counters this means that each point of the sample has to be seen by the counters under the same solid angle and this can be easily accomplished. When using CMA detection the constraint is that the monitored incoming beam hits the sample only in the focussing region of the CMA itself.

Conclusions

Although the physical origin of the glitches has long been understood, the glitches are still a great problem in all the synchrotron radiation laboratories. In this report we have clarified why in many cases the glitches are not compensated. We have also shown that if careful attention is paid to the geometry of the detection system, to the alignement of the whole apparatus and to the quality of the sample, the glitch problem can be overcome.

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