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Quantitative determination of the effect of the harmonic component in monochromatised synchrotron X-ray beam experiments

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ABSTRACT

Harmonic contamination has limited many synchrotron experiments, often without the users realising the magnitude of the problem. We demonstrate a multiple-foil method for the quantitative determination of the fraction of the (333) third-order harmonic in a synchrotron x-ray beam monochromatised by a monolithic silicon (111) channel-cut monochromator. The method is able to produce quantification of the effect of the harmonic component below the 0.01% level for the first time.

1 Introduction

Monochromators select from a given spectrum a series of harmonics whose wavelengths satisfy the Bragg equation for the monochromator diffracting planes. Some harmonics can be minimized using diffracting planes with 'forbidden' second-order reflections as in the case of the (111) planes of silicon and germanium monochromators. However, third-order and higher harmonics may be present, especially when their intensity in the source spectrum is significant. Accurate studies in which the monochromatic nature of the x-rays is important require, therefore, a method for the quantitative determination of the harmonic component in the x-ray beam. The International Union of Crystallography (IUCr) project to resolve discrepancies between experimentally determined attenuation coefficients reported that in earlier experiments 'one quarter had an incident beam which may have had second-harmonic contamination', and so were rejected. [1] Such harmonic components occur in synchrotron and laboratory x-ray beams and are often assumed to be insignificant without quantification of their effect on experimental results.

Most experimental configurations minimise the harmonic component in the beam (e.g. by detuning), but the reduction of the harmonic fraction by two orders of magnitude may still be unacceptable for many studies. The primary problem with many studies relating to attenuation or scattering is alluded to by Creagh and Hubbell [1] when they observe that 'if a plot of $\ln(I/I_0)$ against thickness... does not yield a straight line then no unique x-ray attenuation coefficient exists and an investigation must take place to establish what is the cause of this nonlinearity.' Determination of the harmonic components by absorption of the monochromatised beam by multiple foils is well known in the literature. [2] We have developed this technique for use with synchrotron beams and ion-chamber detectors, and extended it to provide accurate knowledge of the beam spectral composition.

This approach is an essential ingredient in recent form factor measurements. [4] The technique relies on the log-linearity of x-ray absorption by atomic materials. Scattering cross-sections are often non-linear on such a log plot, but this non-linearity makes only a small correction in the X-ray range of energies.

2 The effect of harmonics in attenuation measurement

Figure 1 shows the measured attenuation of eleven sets of aluminium foils with thicknesses between 15 μm and 1 mm, in the path of an x-ray beam monochromated by a detuned, double reflection silicon (111) channel-cut monochromator set to select 5 keV X-rays. The slope at low thicknesses gives the attenuation coefficient for dominant first order harmonic radiation (i.e. 5 keV X-rays) while the slope for large thicknesses gives the attenuation coefficient for third order harmonic radiation (i.e. the more penetrating 15 keV X-rays) The second order reflection is 'forbidden'.

The linearity of the slope is compromised even for $-2 < \ln[I/I_0] < 0$, where I_0 is the incident flux and I the attenuated flux. To account for the slope, it is necessary to fit the proper equation for the harmonic fraction x, and the fundamental and higher harmonic attenuation coefficients μ_f and μ_h using $I = I_O[(1-x)e^{-\mu_f t} + xe^{-\mu_h t}]$ for the given series of thicknesses t. The third order harmonic is seen by the deviation from linearity at low attenuation and by the inflection in the plot as the lower energy flux becomes heavily attenuated. However, the harmonic fraction is only obvious as the slope of the second linear part of the graph above log ratios of 5 or

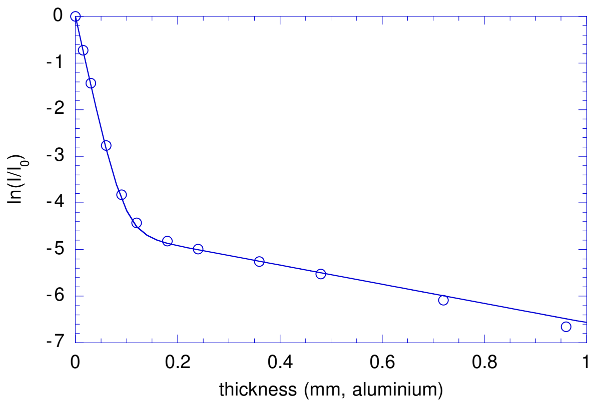

Figure 1: *The attenuation,* $\ln(I/I_0)$*, as a function of the thickness of aluminium absorber in the x-ray beam with a silicon monochromator set to 5 keV.* $\circ$ *- experimental results; solid line - curve of best fit corresponding to an admixture of* $(1.09 \pm 0.02)\%$ *third-order harmonic (15 keV).*

more. In this example, this corresponds to thicknesses of 0.6 mm and to a first order attenuation log ratio of $\ln[I/I_0] \simeq -25$. We have probed the attenuation over a range far exceeding the 'recommended' [1] Nordfors [3] range of $(-4 < \ln[I/I_0] < -2)$; corresponding to $(-30 < \ln[I/I_0] < 0)$ for the fundamental energy. Sampling the linearity of the attenuation over a much wider range than in previous investigations enables a more extensive diagnosis of systematic effects including detector linearity, harmonic content, dark current offsets and saturation.

Experimental results based on a small part of this curve will be in significant potential error, especially where the absorption coefficients are not known (and they are rarely known to better than 1%). In this example, the thicknesses of the aluminium foils were not well known. The requirement of precise knowledge of foil thickness was avoided by using multiples of a single foil for each of these thicknesses. In this way the ratio of thicknesses of each of the absorbers was well defined. The determined harmonic percentage is 1.09% with an uncertainty of 0.02% as the one standard deviation uncertainty to a function fitting for both orders of radiation (without any assumption as to the attenuation coefficients for either).

The measurements were carried out by using a metal 'daisy wheel' on whose perimeter were mounted eleven different thicknesses of foils. These foils were placed in the beam by suitable rotation of the daisy wheel. This technique is accurate, reproducible and rapid. The monitor and detector used throughout this work were matched nitrogen gas-flow ion-chambers. The work was performed at the bending magnet beamline 20B of the Photon Factory synchrotron at Tsukuba.

Use of relatively calibrated sample thicknesses prevents us from determin-

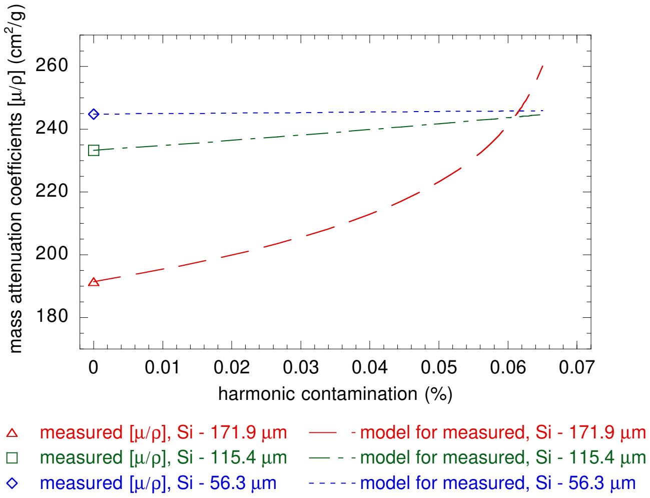

Figure 2: *Effect of third-order harmonic contamination in attenuation measurements using Si(111) monochromator and three silicon sample thicknesses at 5 keV. All three measurements are consistent with a unique percentage of third-order harmonic contamination of about 0.06%.*

ing the attenuations μ_f and μ_h from this measurement, but the harmonic component remains very well defined. Any good attenuation measurement should probe the harmonic component of the beam if it aims to be accurate at the sub-percent level. Surprisingly, the harmonic contamination in numerous experiments may exceed 10% without the major problem being obvious to the experimenters.

3 A three-foil experiment showing the effect of the harmonic fraction and its energy dependence

To perform an actual attenuation measurement, it is efficient to use a smaller number of carefully calibrated thicknesses. A minimum of three samples of accurately known thickness is required to simultaneously determine the harmonic percentage, and the fundamental and higher harmonic attenuation coefficients.

If μ_h is provided by a separate experiment (or theory) then use of three samples overdetermines the problem and allows for error analysis or the possible observation of an additional harmonic or other non-linearity. Figure 2 shows the variation of the attenuation of these three thicknesses at 5 keV when an admixture of 15 keV x-rays (due to diffraction by the (333) plane of the silicon monochromator) is present in the incident x-ray beam. The three points are experimental curves, where the measurements only become consistent for the correct admixture of 15 keV X-rays. This (least-squares) fit can be performed using theoretical values for the absorption of silicon for 15-keV x-rays. [5, 6] The uncertainty of 1% in the tabulated value has negligible effect on the uncertainty. The three lines converge for a fraction 0.06% of 15-keV x-rays. The fitted one standard deviation uncertainty is

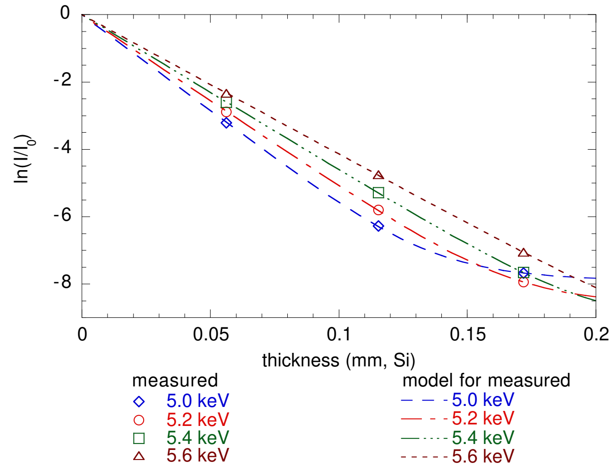

Figure 3: *A harmonic component measurement with three well calibrated thicknesses provides a constant and reliable indicator of accuracy in attenuation measurements. Error bars are given by the thickness of the line.*

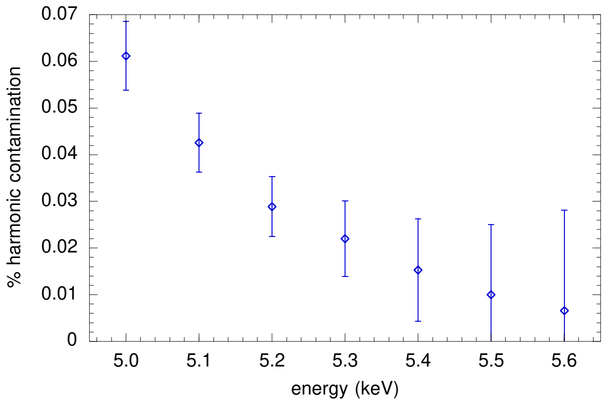

Figure 4: *Energy variation of the fraction of harmonic contamination in the example chosen (at maximum detuning).*

0.007%. For this analysis, a quite thick sample is crucial.

Figure 3 shows the fitted $\ln(I/I_0)$ curves of the three-foil measurements as functions of thickness, with decreasing harmonic contamination as the energy is raised. [4] The final uncertainty depends on the accuracy of the sample thicknesses and the counting statistics. Larger attenuation ranges also yield higher accuracy.

Figure 4 shows the percentage of third-order harmonic as a function of the energy of the fundamental x-rays. The energy dependence of the percentage of harmonic contamination detected in our experiment is due to the fundamental output spectrum of the synchrotron, the intensity of the monochromator diffraction of x-rays of the various energies (with the given detuning current and its effect on the suppression of the harmonic), and the relative detection efficiency of the detector for the fundamental and harmonic x-rays. Using this technique it is possible to correct for very small fraction of harmonic contamination eg. 0.01% at 5.6 keV.

In other work, [7] we show that the likelihood of residual harmonic contamination significantly affecting synchrotron experiments is much higher than often assumed, especially on an ID line where the third harmonic can often have high intrinsic flux and be transmitted with minimal loss of intensity by any monochromator crystals and through any windows or other attenuation path.

The multiple-foil method can be used as a sensitive diagnostic method for the quantitative determination of the fraction of harmonic radiation in a monochromatised x-ray beam. The method can simultaneously also provide quantitative information about nonlinear detector response such as may occur at high counting rates. The determination of the harmonic fraction is the result of a number of measurements and thus is insensitive to errors in the thickness determination of the individual foils. The simplicity of the method and the ease with which it can be automated renders it suitable as a diagnostic test in a large variety of experiments.

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