

# Non-normalization behavior of crystal glitches in an EXAFS spectrum: Is it possible to remove crystal glitches?

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The existence of crystal glitches in EXAFS data is widely recognized and is usually dealt with during data analysis. However, in many cases, especially as samples become more dilute, the disruption of the data can become irretrievable. The advent of new, high output, double-crystal x-ray monochromators has made it necessary to investigate the cause of such glitches with a view to reducing them in the original data. The occurrence of multiple reflections within the crystal gives rise to the glitches seen in EXAFS data when the two crystals in a double-crystal monochromator are not accurately aligned. The results of a simple alignment of such a double-crystal monochromator are presented and show a reduction of the glitches in the recorded data. A purpose-built monochromator for further investigation of this problem is described and some results towards the further reduction of glitches are presented. It is shown that the removal of crystal glitches from EXAFS data is possible

Many EXAFS spectra contain spurious features not attributable to the primary absorption process.<sup>1-4</sup> They may often be explained as artifacts introduced by the monochromators. Some features are due to Laue spots from the crystals; extra reflections at wavelengths different to the primary Bragg reflection.<sup>6,7</sup> However, when the ion chambers and samples are situated far from the monochromator the Laue spots are spatially separated from the primary beam and may be removed by appropriate slits. In addition, many spectra show narrow features ( $< 10$  mdeg, typically) commonly called "glitches" which appear as spikes, dips, or more complicated structures.<sup>1</sup> In simple transmission experiments they are often unimportant, often spanning only a few data points and so are easily edited out. In general however, as samples become more dilute and wider aperture monochromators become available, the glitches often disrupt the data past the point of easy correction, so elimination of the features in the original data is crucial. They appear in the final spectra due to their dis-similar behavior in the incident ( $I_0$ ) and transmitted ( $I_t$ ) or fluorescence ( $I_f$ ) channels.

These glitches arise from multiple reflections<sup>5,8,9</sup> in the monochromator crystals, which give rise to outgoing beams of the same energy and direction as the primary Bragg reflection. Figure 1(a) shows a simplified example of such a situation. A fuller understanding of the mechanisms underlying multiple reflection can be gained by considering Fig. 1(b) [Ref. 1], which shows the reflections plotted in the  $k$  space. The primary reflection from the reciprocal lattice vector,  $H$ , is represented by the vectors,  $K_1$  and  $K_2$ , centered on the Ewald sphere,  $E$ . This does not represent a multiple reflection condition, but if the wavelength were changed so that

the Ewald sphere lies on  $C_1$ , then the reciprocal lattice point,  $P_1$ , lies on the Ewald sphere and multiple reflection may take place. The reflection is described by the noncolinear reciprocal lattice vectors  $H_1$  and  $H_2$ . Note also that a rotation about the  $H$  vector also brings the lattice point,  $P_2$ , onto the Ewald sphere so multiple reflection can again take place. As glitches arise from planes tilted away from the primary plane, a diverging beam incident at a specific incident angle on the crystals, will not satisfy the glitch condition at all points over the crystal, resulting in a rapidly changing spatial variation in intensity with the Bragg angle. Note also that the resolution of the extra reflections will differ, causing a slight change in energy content, especially of any higher harmonics.

In transmission EXAFS experiments these variations would still not be detected if the sample and detectors were perfect. If the incident and transmitted beam ion chamber response are not spatially identical or the count-rate responses is not linear, they will couple with any nonuniformity in the sample so that normalization of the absorption will be incorrect.

## I. DISTRIBUTION OF MULTIPLE REFLECTIONS

Multiple reflections giving rise to glitches occur abundantly, especially at smaller Bragg angles. The geometrical arguments outlined in the section above can be used to calculate at what Bragg angle and (azimuth) rotation about the  $H$  vector multiple reflections will occur. Figure 2 shows such a plot for the  $\langle 220 \rangle$  reflection in silicon. Alongside the calcu-

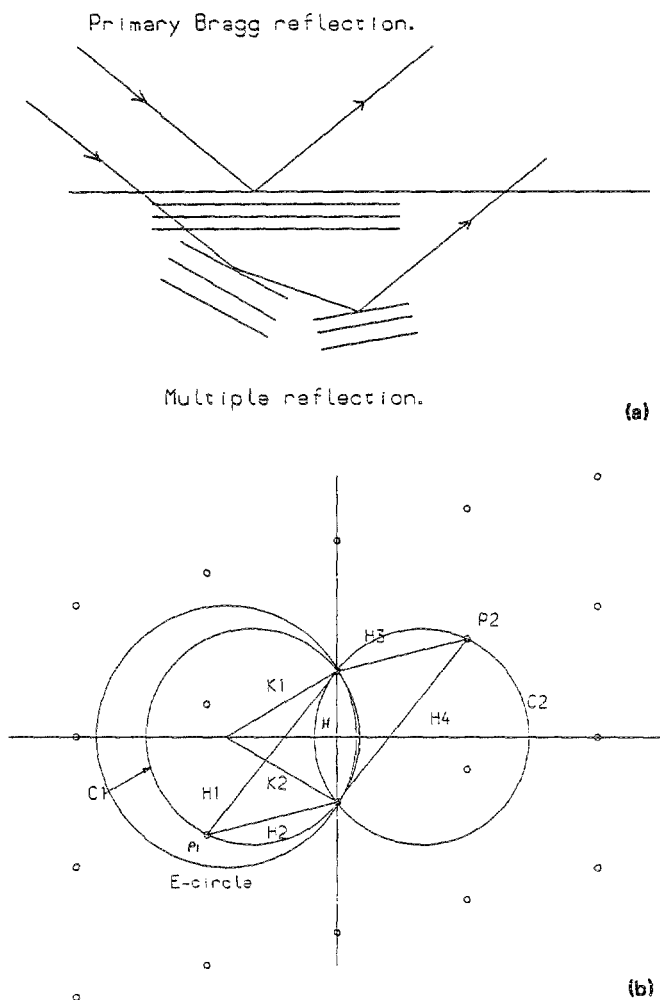


FIG. 1. (a) 2-D schematic representation of a multiple reflection condition. (b) Reflections shown in reciprocal space. The figure does not show a multiple reflection condition, but if the Bragg angle is changed so that the *E* circle lies on *C*1, then the lattice point, *P*1, lies on the circle and double reflection can take place.

lations are measured positions for comparison. The crystals were  $0.2^\circ$  in azimuth from the nominal  $\langle 100 \rangle$  direction.

To investigate these effects in detail a special double-crystal monochromator has been built. In general, it is similar to our bent-crystal monochromators described before,<sup>4</sup> except that both crystals are flat. The crystals are cut with the Si  $\langle 111 \rangle$  plane parallel to the physical surface. The first crystal is water cooled and maintained at the same temperature as the second crystal (to better than 0.5 K). The second crystal is also circular and mounted such that it can be rotated about the normal to the crystal surface. The second crystal can be tilted across the width of the beam by a piezoelectric actuator and tilted along the direction of the beam to effect harmonic rejection. The first crystal is water cooled to avoid any heating effects. The whole assembly can be rotated by a rotary table, to select the required Bragg angle. The rotary table is mounted with sufficient adjustment so that the axis of rotation can be made horizontal and perpendicular to the incident beam.

## II. SUPPRESSION OF GLITCHES IN EXAFS DATA

One common suggestion to remove glitches is to rotate the second crystal away from azimuth setting of the first crystal.<sup>10,11</sup> We have tried this, but as might be expected from inspection of Fig. 2, this merely increases the number of glitches. We have begun a systematic investigation of the problem and now have a few means of improving the normalization of the monochromator output to prevent glitches appearing in EXAFS spectra.

(i) Align the Bragg angle rotation axis so that it lies horizontal and so that it is perpendicular to the incident beam direction. This can be done by survey and by checking that some reference absorption edge occurs at the same measured Bragg angle at the extremes of the horizontal aperture.

(ii) Align the Bragg planes of the two crystals. There is generally a cutting error such that the physical surface and the crystal planes are not parallel, so an optical method is needed. We rotate the second crystal azimuth so that the glitch patterns from the first and second crystals superimpose. Fine adjustment of the cross tilt with the piezoelectric actuator to achieve maximum output intensity then ensures the crystal planes are parallel across the width of the beam. This also ensures that any setting of the harmonic rejection tilt does not couple in any unwanted cross tilt.

(iii) Ensure the  $I_0$  and  $I_t$  ion chamber responses are uniform over the beam area. This is of crucial importance. The requirement of a linear response to input intensity is well understood, but the spatial dependence of the glitch condition (described above) requires an accurate *spatial* uniformity of response of the ion chambers. Figure 3 shows the effect on the absorption measurement of a  $5 \mu\text{m}$  aluminum foil of a small movement of an overfilled  $I_0$  (40 mbar argon,

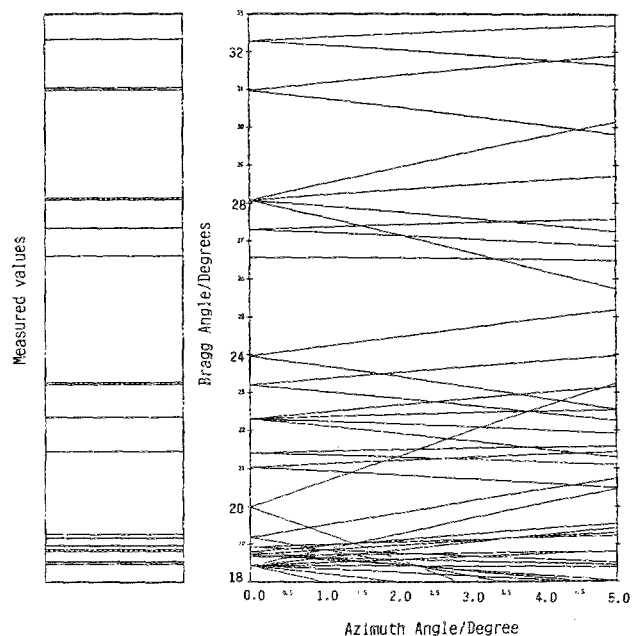


FIG. 2. Calculated multiple reflections in silicon. The primary plane is the  $\langle 200 \rangle$ , a range of incident angles from  $18^\circ$  to  $33^\circ$  are presented for a range of  $5^\circ$  of azimuth from the  $\langle 001 \rangle$  direction. The measured values are shown for comparison on the left.

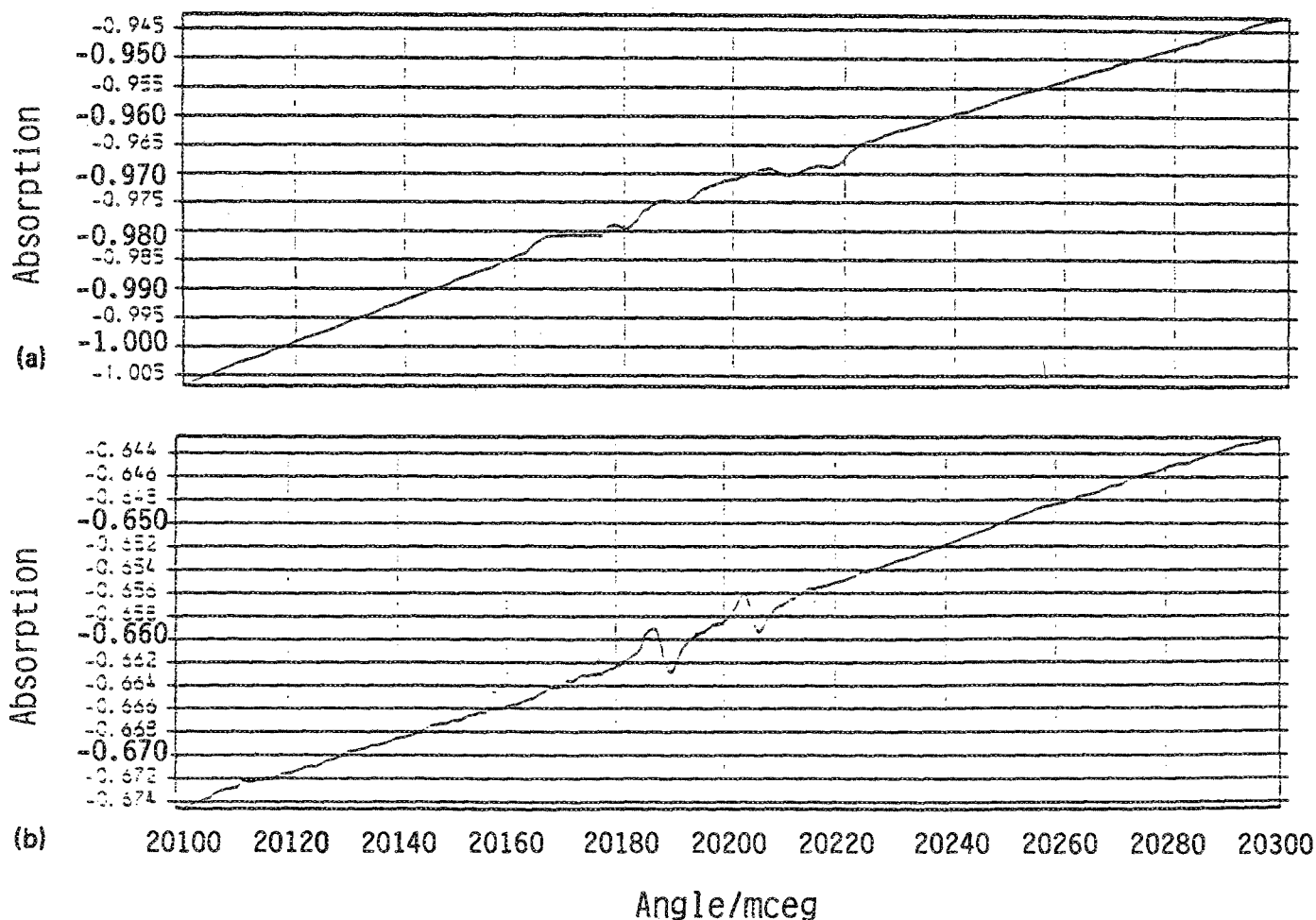


FIG. 3. Comparison of the glitches in the absorption spectrum of an aluminum foil. The spectrum should be smooth in this range. (a) shows the spectrum recorded with narrow ion chambers lined up accurately; (b) shows the effect of a small horizontal displacement of the  $I_0$  chamber.

960 mbar helium) chamber across the beam. The actual beam size was less than half the width of the electrodes, and the horizontal adjustment less than a quarter of the plate width. The plate width is the same as the plate separation and such an arrangement is obviously very sensitive to exact alignment. To reduce this problem ion chambers with a larger width/separation ratio help, but more sophisticated designs than a parallel plate arrangement may be required.

(iv) Good, uniform thickness samples are essential EXAFS spectra of pure metal foils often do not show glitches due mainly to their excellent uniformity. Powdered samples are more difficult to prepare.

Figure 4 shows a spectrum of  $\text{VOSO}_4 \cdot 5 \text{H}_2\text{O}$  after ensuring that all the precautions mentioned above had been taken. The glitches are obvious in both channels, but they normalize out extremely well in the absorption spectrum. The obvious feature in the  $I_0$  channel at 21 200 mdeg is due to a beam movement.

The above considerations are for transmission geometry. The same is true for fluorescence EXAFS geometry but there are further difficulties in this mode. In a typical fluorescence geometry using scintillators and photomultipliers the detectors have little energy resolution, so they detect both scattered and fluorescence radiation. In general, the

scattering is nonhomogenous and does not vary with the absorption cross section, in contrast to the fluorescent signal which is spatially homogenous. Thus, normalization is severely compromised especially where a number of detectors

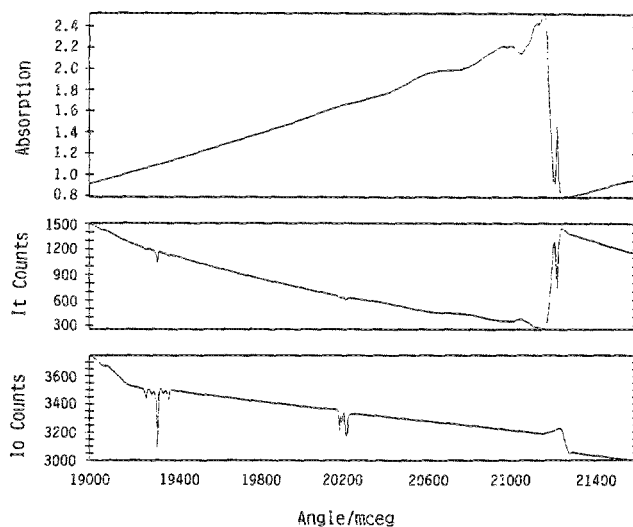


FIG. 4. Transmission EXAFS spectrum of powdered  $\text{VOSO}_4 \cdot 5 \text{H}_2\text{O}$ , after all precautions had been taken to ensure normalization of the glitches.

at different angles are in use. The problem is further aggravated in dilute systems where the scattered component may be much larger than the fluorescence signal. Some early experience with a 13-element solid-state detector capable of discriminating out the scattered signal is very encouraging, showing much improved normalization of the glitches.

### III. CONCLUSION AND FURTHER WORK

Unwanted artifacts in EXAFS spectra arising from multiple reflections in the monochromator crystals can be reduced. Careful alignment, detector design, and sample preparation to minimize spatial variations, allow better normalization in the resultant spectra.

Further work will incorporate all the improvements in order to achieve still better spectra, especially for fluorescence studies of very dilute systems.

<sup>1</sup>Z. U. Rek, G. S. Brown, and T. Troxel, *EXAFS and Near Edge Structure*, 1983, Vol. III, pp. 208 and 335.

<sup>2</sup>K. R. Bauchspiess and E. D. Crozier, *EXAFS and Near Edge Structure*, 1983, Vol. III, pp. 208 and 514.

<sup>3</sup>G. van der Laan and B. T. Thole, *Nucl. Instrum. Methods A* **263**, 515 (1988).

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<sup>7</sup>V. O. Kostroun and G. Materlik, *Rev. Sci. Instrum.* **51**, 81 (1980).

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<sup>11</sup>M. Hart and A. R. D. Rodrigues, *J. Appl. Cryst.* **11**, 248 (1978).