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Minimizing "glitches" in XAFS data: A model for glitch formation

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Spikes in X-ray absorption data, which are referred to as "glitches", occur at particular monochromator energies for which multiple diffractions are possible. Measurements of the X-ray beam profile show that large spatial variations of the flux in the vertical direction occur at energies close to a glitch. We develop a simple model of glitch formation in ratioed X-ray absorption data, that shows why glitches remain in the ratioed data for ideal conditions (ideal detectors and no harmonics) if the sample is nonuniform. The model describes experimental observations well, including the occurrence of both negative and positive lobes in a glitch. Some ramifications of the model are presented and some means to minimize the glitches are discussed. The advantages of using pixel array detectors are also briefly presented.

1. Introduction

In measurements of the X-ray absorption fine structure (XAFS), the X-ray absorption is obtained from the ratio, R, of the incident, I_0, to the transmitted intensity, I_T. In such ratioed data, sharp spikes or "glitches" often occur at particular energies. Glitches are observed for all types of samples but are particularly bothersome for low concentration samples when large relative backgrounds must be subtracted. (Similar effects also occur in fluorescence data, but are not considered in this article). The word "glitch" is used to describe the spikes in XAFS data as well as the sharp drops in output intensity from a monochromator at particular X-ray energies. The two are closely related; however, in this article we will focus on the glitches observed in ratioed XAFS spectra.

Previous studies indicate that the origin of most monochromator glitches is the loss of incident X-ray intensity when simultaneous diffractions occur at the same energy [1–3]. For the same angle of incidence relative to the monochromator crystal's physical surface, several different sets of planes can diffract the same energy over a narrow range of angles, In some cases, the extra reflection may leave the monochromator crystal; for many others, the beam can undergo multiple reflections and end up parallel to the main beam [3] through the double monochromator. In either case, the integrated intensity of the beam varies with energy, and is decreased over a small range of energies. (The positions of the dips in intensity can be used to calibrate the energy accurately [2,4].) In some cases there may only be a uniform decrease of intensity across the beam; this will not cause glitches in R. However some multiple diffractions should result in a spatial variation across the output beam that changes with energy. It is this case that we are considering.

Many authors state that for linear X-ray detectors such as gas ionization chambers, intensity variations of I_0 caused by steps in beam current or by glitches, are *expected* to ratio out in the measurement of R [2,3,5]. However, in practice, part of the glitch remains in the ratioed data and can be as large as the XAFS oscillations in low concentration samples. We note that it has long been recognized that harmonics in the beam can aggravate the problem of glitches [6]; in the data discussed here, the monochromator was detuned by 50% and the harmonic content was negligible.

Another cause of glitches in XAFS data, particularly for some solid state detectors, is non-linearity in the detector. When the output signal is not a linear function of the number of incident photons, changes in the intensity will not ratio out. However, gas ionization chambers are very linear. Furthermore, when the feedback is used to keep the incident intensity constant [7], changes as a result of loss of beam current are usually not observed, yet the glitches remain, although reduced somewhat in amplitude. The lack of a significant step (i.e. much less than typical glitch amplitudes) in the ratioed data for a significant step decrease in beam current indicates that detector nonlinearity cannot be the explanation for the presence of glitches in many XAFS spectra.

The problem with the standard statement – "for linear detectors the variation in intensity at a glitch should ratio out" – is the assumption that the spatial distribution of the incident flux does not change. At a glitch, this assumption is not valid. We have examined the vertical spatial intensity profile of I_0 in the glitch region and found that the variation is strongly dependent on energy. This dependence is expected for some multiple diffractions, as the angular Darwin width of the intrinsic multiple scattering peak can be very small, smaller than the angular divergence of the beam.

We propose that for the case of linear detectors and no harmonics, an XAFS glitch results from the combination of a nonuniform sample and a change in the spatial distribution of the incident intensity over the sample as the monochromator moves through the glitch region. In this article we show that when the sample is nonuniform in the vertical direction, variations in I_0 will not ratio out in R if the spatial distribution of the incident flux changes. One way to visualize this effect is in terms of an effective average sample thickness $\bar{t}_{eff}$. We will show in sec. 3 that $\bar{t}_{eff}$ varies over a small energy range near a glitch. The glitch amplitude is directly proportional to the variation in sample thickness and in the vertical spatial distribution of the flux. Dobson et al. [5] have considered reducing glitches in XAFS spectra from the viewpoint of improving the alignment of the double monochromator crystals. They suggest that in transmission XAFS experiments, glitches would not be observed in the ratioed data if the sample and the detectors were perfect; however, they do not consider changes in the spatial distribution of the incident flux.

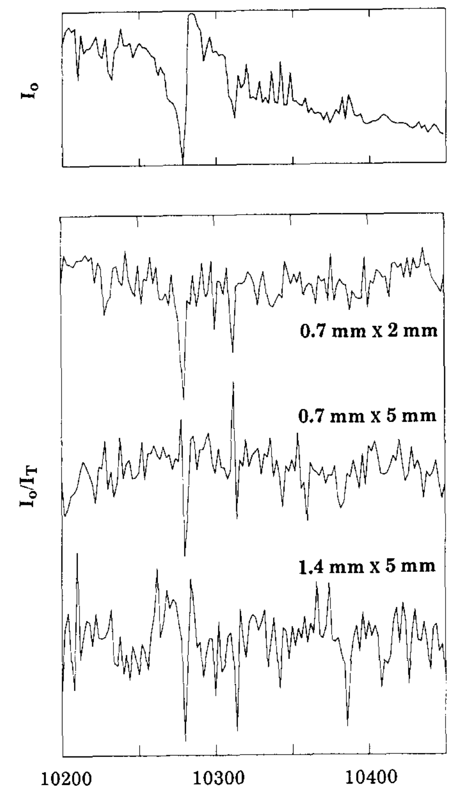

Fig. 1. The ratio I_0/I_T for various slit sizes. The gain is the same for each trace for I_0/I_T, and the large glitch in the lowest trace at 10280 eV has a pp height of 0.004. For comparison, I_0 is plotted in the top trace; the variation in I_0 over this energy range is 5%, a variation roughly a factor of ten larger then the variation in I_0. The sample was moved slightly to crudely minimize the glitch amplitude for the 0.7 mm × 2 mm and 0.7 mm × 5 mm cases. Note the increased "noise" in the lower trace.

2. Energy dependent spatial distribution of flux at a glitch

In this section we present evidence that the spatial distribution of the incident flux varies at energies near a glitch. We consider a model for glitch formation in the following section.

2.1. Vertical nonuniformity

We have found empirically that the size of a glitch and particularly the presence or absence of many small spikes in the spectrum is more dependent on the sample uniformity in the vertical direction than in the horizontal direction. Glitch amplitudes can often be reduced by factors of three or four by selecting a region of the sample such that the transmitted signal does not vary by more than 0.2% for vertical movement of the sample by 0.25 mm when using small slits (0.7 mm(V) × 5 mm(H)). We show that the observation of glitches is more dependent on the vertical slit height than the slit width in fig. 1 for a very low concentration Zn substituted sample of $YBa_2Cu_3O_7$. Here we plot the variations in I_0/I_T (a large background term is subtracted; the magnitude of the maximum variations in I_0/I_T is about ±0.002, whereas the range for I_0 in the top of the fig. is 5%) as a function of energy over the range 10200–10450 eV. At this energy, the XAFS oscillations are very weak.

For the top trace we use a small slit (0.7 mm × 2.0 mm). Two of the main glitches are clearly visible. For this slit size, a 1/2 mm vertical movement of the sample changes I_T by 0.1–0.2%. In the second trace, the slit height remains unchanged and the width is increased to 5.0 mm. The "noise" increases very slightly but the overall change is small. We call the vertical variations in these traces "noise", because they interfere with the desired XAFS oscillations.

We then opened the slits vertically from 0.7 mm to 1.4 mm as shown in the third trace. Some changes in the glitch shape occur, but more importantly, the "noise" increases considerably as additional glitches become visible. The ratioing is now not as complete as for the narrower slits. We found the same situation for many other samples as well. We should point out again that the sample position was roughly optimized to reduce the glitch amplitude in the first two traces. Thus the region of the sample in the beam changed very slightly. Also note that increasing the flux by a factor of 5 by increasing the slit size has *decreased* the S/N. Clearly even at a slit size of 0.7 mm × 2 mm the noise is not determined by photon statistics on a wiggler beamline. Empirically we find that a slit area less than ≈ 1 mm^2 starts to degrade the S/N. This of course depends on the X-ray energy, the beam current and other factors, and is therefore only a rough estimate. This example shows that the fluctuations in the data are more sensitive to the vertical slit height than the horizontal slit width.

2.2. Incident beam profile at a glitch

The model presented in the next section shows that an energy dependent spatial distribution of the flux will couple with sample nonuniformities to produce a glitch. To determine whether this model is relevant to XAFS data, we investigated briefly the spatial dependence of the incident X-ray beam for several energies in the vicinity of the monochromator crystal glitch near 10280 eV (SSRL Si 220 crystals, set 3). First, we looked at the beam profile with wide slits using a pixelized optical CCD detector focused on a fluorescent screen. As the energy was slowly increased through the glitch, a band of reduced intensity moved vertically down the 2 mm high output beam. The width of this band was about 1 mm. (We also scanned several other glitches. At a lower energy, we saw a more complicated structure which may have been two dips in intensity close together in energy.) This observation shows clearly that the spatial distribution of the incident flux is not uniform and changes as the energy is stepped through the glitch region.

A few more detailed measurement of the vertical variation of the incident flux were taken at the end of our run using a small slit height of 0.2 mm (slit size 0.2 mm × 5.0 mm). The intensity was recorded for several vertical positions of the slits at several energies between 10274 and 10284 eV. In fig. 2 the vertical profile of the incident flux is plotted for five energies. (Our coordinate system is as follows: x – horizontal, y – vertical, and z – parallel to incident beam.) Note that for these measurements the slit was not centered on the beam, but is about 1 mm off-center [8]. For the rest of the discussion we assume the usual situation for XAFS experiments for which the slits are centered on the beam.

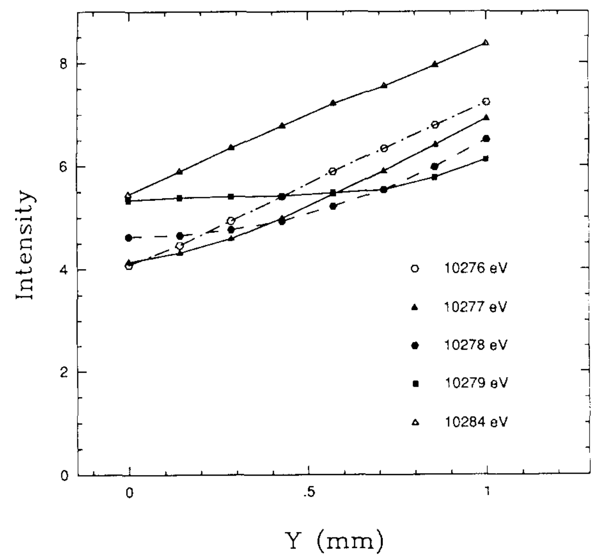

Fig. 2. Measured spatial variations of the beam intensity for several energies near a glitch at 10280 eV. Note that relative changes as large as 30% across 1 mm can occur. (SSRL Si 220 crystals, set 3.)

Well above the glitch, at 10284 eV, the beam intensity varies nearly linearly with y over most of the exit slit height investigated. The same spatial dependence, which we will refer to as the "background variation" is also observed at energies well below the glitch. In the glitch region the net intensity consists of the background variation minus a Gaussian-like dip.

To clarify this picture we show in fig. 3 the idealized profiles for a series of energies near a glitch (typically a 6–10 eV range in energy). Each curve consists of a Gaussian beam profile (half width of 2.2 mm, roughly appropriate for beamline 4-1 at SSRL) with a dip subtracted. The dip profile, which is determined by the Darwin width of the additional diffraction(s) plus multi-scattering effects, is modeled by a Gaussian, with a half width of 1.1 mm. The dip profile for the middle curve is shown at the top of the figure. We have also centered the slits on the beam, as indicated by the vertical lines. As the energy is stepped, the dip moves from left to right across the beam profile.

3. Model of the formation of a glitch in XAFS spectra

To illustrate the effect that a nonuniform spatial distribution intensity has on the ratio I_0/I_T, we consider a simple model. We ignore any horizontal variations of the beam, and take our origin at the center of the slit; the top of the slit is at $y = +a$ and the bottom of the slit at $y = -a$. We define $F(y, E)\,\mathrm{d}y$ to be the incident intensity over a strip of height $\mathrm{d}y$, with the X-ray beam, of energy E, incident along the z direction.

3.1. Equations for the ratio I_0/I_T

The total measured incident intensity at the I_0 detector is:

$$I_0(E) = \int_{-a}^{+a} F(y, E)\,\mathrm{d}y \tag{1}$$

and the transmitted intensity, I_T is given by:

$$I_T(E) = \int_{-a}^{+a} F(y, E)\,\mathrm{e}^{-\mu t(y)}\,\mathrm{d}y \tag{2}$$

where μ is the absorbance and $t(y)$ is the sample thickness. For most of our discussion we keep the product $\mu t(y) \approx 2$ above the absorption edge, corresponding to a typical sample thickness of two absorption lengths. To simulate the XAFS oscillations, we set:

$$\begin{aligned} \mu &= \mu_B, & E &< E_0, \\ \mu &= \mu_B + \mu_0(1 + \chi(E)), & E &\geq E_0, \end{aligned} \tag{3}$$

where μ_B is the background absorbance, μ_0 is the step height, and E_0 is the absorption edge energy. For illustration purposes, we use a simplified form of $\chi(E)$, the XAFS signal, so that the oscillation in the X-ray absorption spectra and the extracted signal appear the same [9]. We use:

$$\chi(E) = A \sin b(E - E_0) \tag{4}$$

where A is the amplitude of the XAFS oscillation. A plot for $\mu t = 2$ near an edge is shown in fig. 4.

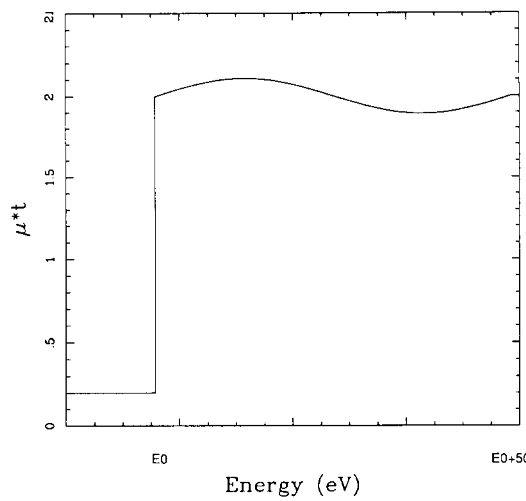

Fig. 4. A typical plot of μt used in our simulations. The background below the step is 10% of the absorption above the step. The oscillation to simulate the XAFS oscillation is 6% ($A = 0.06$) of the step height. For many of our calculations the XAFS amplitude is reduced to 2% of the step height.

For a given spatial variation in intensity and sample homogeneity, I_0 and I_T are calculated from the integrals given by eqs. (1) and (2) and $\ln(I_0/I_T)$ determined. The usual assumption in XAFS studies is that $\mu t = \ln(I_0/I_T)$; however, when $F(y, E)$ (in the integrals for I_0 and I_T) and $t(y)$ are functions of position, this yields an effective value μt_{eff}. Next, a standard XAFS reduction is applied: the background is subtracted, the value of the step height, μ_0, determined, the background under the oscillation removed and the amplitude of the oscillation normalized by the step height. The reduced signal, $\chi_{\mathrm{eff}}(E)$, is then compared with the input signal, $\chi(E)$, to determine the extent and amplitude of the glitch. (We can also determine an amplitude reduction [10–12] of the XAFS that results from sample nonuniformity.)

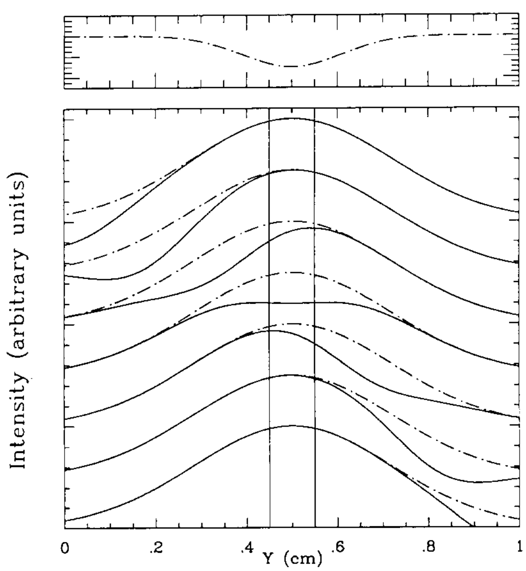

Fig. 3. Schematic presentation of the beam profile over a large vertical distance (y) when a second diffraction is present. The Gaussian half width of the main beam is 2.2 mm while the half-width of the resulting dip, caused by the multiple diffraction, is set at 1.1 mm. The dip for the middle trace is shown at the top of the figure. We assume the slits are centered on the beam, indicated by the vertical lines, as is usually the case. As energy is scanned, the position of the dip moves across the beam profile as shown. Thus, the spatial variation observed through fairly narrow slits will change slope as the energy is changed (see middle three traces). In the lower part of the figure, the solid line shows the total flux for a particular energy with a dip present, while the dot-dash line shows the profile if no dip were present. The data of fig. 2 corresponds roughly to a slit centered between 0.35 and 0.4 cm on this figure.

An analytic solution is easily obtained with the following simplifying assumptions. We assume linear functions for $F(y, E)$ and $t(y)$ defined by:

$$F(y, E) = \bar{F} + \beta(E) y \tag{5}$$

and

$$t(y) = \bar{t} + \alpha y, \tag{6}$$

where $\bar{F}$ is the average value of $F(y, E)$ and $\bar{t}$ is the average sample thickness. $\beta(E)$ is the linearized value of the slope of the intensity variation across the slit. It is this quantity that changes for energies near a glitch. It is important to again emphasize that the E dependence in $F(y, E)$ does not factor out of the integral. If it did, glitches would ratio out well for linear detectors such as the gas ionization chambers.

Then

$$I_0 = \int_{-a}^{+a} (\bar{F} + \beta(E) y)\, \mathrm{d}y; \quad I_0 = 2a\bar{F} \tag{7}$$

and

$$I_T = \int_{-a}^{+a} (\bar{F} + \beta(E) y)\, \mathrm{e}^{-\mu(\bar{t} + \alpha y)}\, \mathrm{d}y. \tag{8}$$

Eq. (8) can be integrated to give

$$I_T = \frac{2\mathrm{e}^{-\mu\bar{t}}}{\alpha\mu} \left[(\bar{F} + (\beta(E)/\alpha\mu)) \sinh(\alpha\mu a) - \beta(E) a \cosh(\alpha\mu a) \right] \tag{9}$$

and the ratio R is

$$R = \bar{F} e^{\mu\bar{t}} (\alpha\mu a) / \left[(\bar{F} + (\beta(E)/\alpha\mu)) \sinh(\alpha\mu a) - \beta(E) a \cosh(\alpha\mu a) \right]. \tag{10}$$

For XAFS we normally take the natural log of eq. (10) to extract μ; it is not easy, however, to visualize the spatial dependence of R in this form. If the spatial variations in X-ray intensity and sample thickness are small, we can expand the functions in the above expression to obtain

$$\ln(R) = \mu\bar{t} \left[1 + 1/3 \left(\frac{\beta(E) a}{\bar{F}} \right) \left(\frac{a\alpha}{\bar{t}} \right) \right] = \mu\bar{t}_{\mathrm{eff}}. \tag{11}$$

Thus the measured ratio is $\mu\bar{t}_{\mathrm{eff}}$ where $\bar{t}_{\mathrm{eff}}$ is the effective average value of the sample thickness. If the incident flux is higher at the thick side of the sample, $\bar{t}_{\mathrm{eff}}$ is larger than $\bar{t}$. Conversely, if more of the incident flux passes through the thinner side of the sample, the effective sample thickness is decreased. When $\beta(E)$ changes with energy, it is equivalent to changing the effective sample thickness. Note that if the incident flux is uniform across the slit ($\beta(E) = 0$), or the sample thickness is completely uniform ($\alpha = 0$), then the correction term is zero.

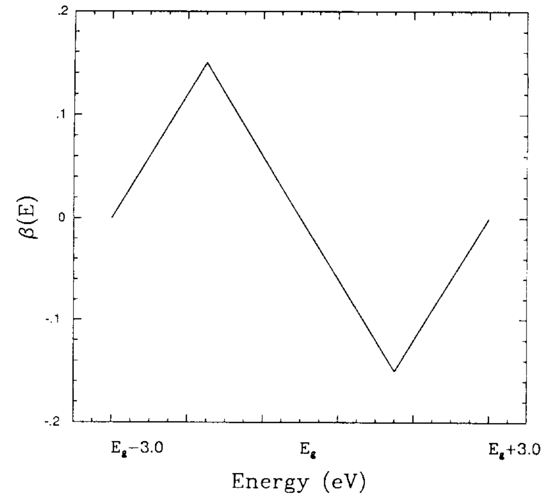

Fig. 5. The simple linearized form of $\beta(E)$ used in our simulations. $\beta(E)$ is the slope of the spatial intensity variation of the flux in eq. (5). The glitch is assumed to occur at an energy E_g, and the energy range is from $E_g - 3.0$ to $E_g + 3.0$ eV.

μ is the quantity we are trying to measure. For a given absorption edge one normally subtracts the background component $\mu_B\bar{t}$, and normalizes the data by dividing by the step height $\mu_0\bar{t}$, or dividing by a smooth function that passes through the XAFS oscillations. The second term in eq. (11), which involves $(\beta(E))$, gives the first order estimate of the glitch amplitude when spatial variations are present. If $\mu\bar{t}_{\mathrm{eff}}$ were constant, the same analysis would hold with $\bar{t}$ replaced by $\mu\bar{t}_{\mathrm{eff}}$. However, when $\mu\bar{t}_{\mathrm{eff}}$ is not constant as a result of the energy dependence of $\beta(E)$, variations in the incident flux do not ratio out. Moreover the correction term added to $\mu\bar{t}$ is proportional to the *total* absorbance μ and can be a very large contribution in the XAFS spectra of a dilute atom. Note that the correction term is proportional to the fractional variation of the sample thickness and the fractional variation of the intensity across the slit.

At a monochromator glitch, $\beta(E)$ changes rapidly with energy over a small range in energy, of the order of 6 eV, and in general will change sign. A simple form for $\beta(E)$ near a glitch that has the features of the data presented in fig. 2 is shown in fig. 5. In this figure we have linearized the slope, assumed that the dip, that is removed from the main beam (figs. 2 and 3) as a result of multiple scattering, is symmetric, and assumed that the slits are centered at the top of the beam profile.

To illustrate how an intensity variation, corresponding to the change in $\beta(E)$ shown in fig. 5, results in a glitch in the ratioed XAFS data, we carry out the usual data reduction process using eq. (10). We choose a sample thickness variation (see eq. (6)) of $\pm 10\%$ ($\alpha =$

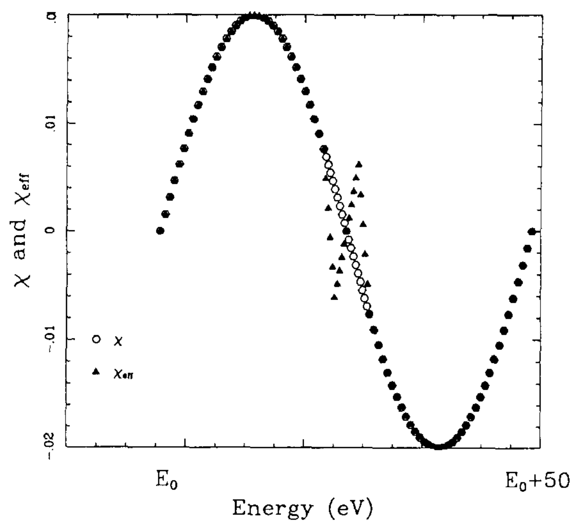

Fig. 6. The extracted XAFS signals normalized to the observed step height for $\mu_0 = \mu_B = 1$. χ(hexagons) corresponds to a homogeneous sample. while χ_{eff}(triangles) corresponds to a 20% vertical variation in sample thickness ($\alpha = 0.1$), and a 30% vertical spatial variation ($\beta(E)$ varies from -0.15 to 0.15) For this calculation $A = 0.02$. (Note that for this case, the amplitude reduction is negligible (0.2%).)

0.1), a reasonable value (very good samples are probably uniform to $\pm 1\%$, poor samples usually do not exceed $\pm 25\%$). We also choose the maximum spatial variation (see eq. (5)) in the incident flux, over a 6 eV range, to be $\pm 15\%$, comparable to the measurements of fig. 2. A large glitch similar to the glitches observed experimentally, is clearly present in the simulation presented in fig. 6. For the simple assumed model, for which the profile of the dip in intensity is symmetric, $\beta(E)$ will have both negative and positive values; consequently, the glitch should have both negative and positive lobes. In XAFS experiments for which the steps in energy may be 2–4 eV, only one of the lobes may be observed if the lobes are narrow in energy. For real spectra, the height of each lobe will, of course, depend on the shape of the actual intensity depression profile; if the profile is very asymmetric, only one of the lobes will be large.

3.2. Glitches from "pinholes" and "antipinholes"

Any nonuniformity in sample thickness should in general result in the formation of a glitch. This includes small pinholes in the sample as well as small regions in the sample where the thickness is larger; for example, as a result of a large crystallite in a fine powder sample. The latter case causes a reduction in intensity over a small region which we refer to as an "antipinhole".

The variation of R in the glitch region for a sample that is spatially uniform except for a small pinhole (we assume a 2% area pinhole), depends on the relative intensity variation at the pinhole, relative to the average intensity. We can again obtain an analytic expression for I_T and R. Now we assume that the sample is uniform except for the pinhole. The position of the pinhole is at y_1 and extends from $(y_1 - pa)$ to $(y_1 + pa)$, where p determines the extent of the hole and gives the fractional area. Then

$$I_T = e^{-\mu t}\int_{-a}^{+a}(\bar{F} + \beta(E)y)\,dy + (1 - e^{-\mu t})\int_{y_1 - pa}^{y_1 + pa}(\bar{F} + \beta(E)y)\,dy,$$

$$I_T = 2a\bar{F}\left[e^{-\mu t} + p(1 - e^{-\mu t})\left(1 + \frac{\beta(E)y_1}{\bar{F}}\right)\right] \qquad (12)$$

and

$$R = \frac{e^{\mu t}}{1 + p(e^{\mu t} - 1)\left(1 + \dfrac{\beta(E)y_1}{\bar{F}}\right)}. \qquad (13)$$

The correction term is more complicated as it includes $e^{\mu t}$. However, the general features can be seen. The local intensity varies from below $\bar{F}$ to above $\bar{F}$ as the energy is changed through the glitch region corresponding to negative and positive values for $\beta(E)$; consequently for this model, the observed glitch will again have positive and negative lobes. Further, the phase (or sign) of the glitch will depend on whether the intensity at the pinhole first increases or first decreases. Therefore, glitches from pinholes at the top of the sample ($y_1 > 0$) will be out of phase with pinholes at the bottom of the sample ($y_1 < 0$). For our model, with its assumed symmetric dip profile, a pinhole at the center ($y = 0$) produces no glitch, and two identical pinholes symmetrically located about the slit center (in the vertical direction) will exactly cancel. In general, the size of the glitch increases as the pinhole is moved to the top or bottom of the sample. As an illustration, we show the calculated glitches that result from a 2% pinhole ($p = 0.02$) at various vertical positions in the sample in fig. 7.

Antipinholes form similar but generally smaller glitches, of the *opposite* sign. Thus, a pinhole and an antipinhole at the same vertical position in the sample (but different horizontal positions) could result in a small or unobservable glitch if the amplitudes of the pinhole glitch and the antipinhole glitch were the same.

3.3. Implications of the glitch model

The above model provides a means of understanding the formation of glitches in absorption spectra for linear detectors with no higher harmonics present. Based on this analysis, we outline some steps that should help minimize the size of glitches. (The pixel array detectors

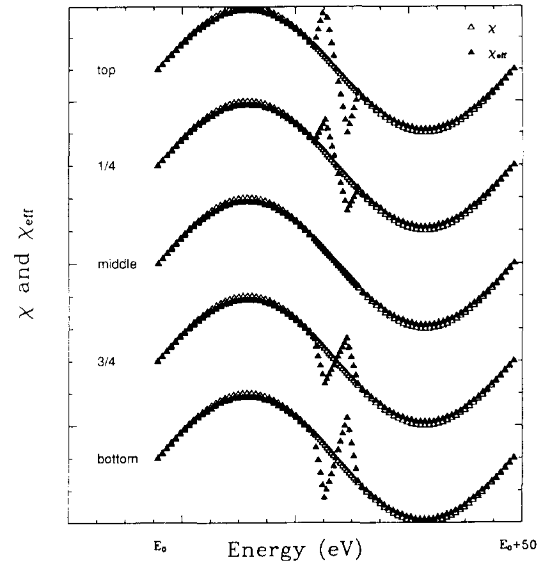

Fig. 7. Plots of $\chi_{eff}(E)$ vs. E for 2% area pinholes at various vertical positions in the slit ($A = 0.02$). Open triangles, no pinhole; filled triangles, pinhole. From top to bottom, top of slit, 1/4 slit down, middle of slit, 3/4 slit down, and bottom of slit. Note, the amplitude reduction is about 6% for each case.

discussed in the next section have important advantages in this regard.) We also discuss some aspects of beamlines that may play a role in estimating glitch amplitudes.

1) First and foremost, as has been pointed out several times in the past, the sample should be as uniform as possible. For a completely uniform sample, the above glitch model yields no glitches in the data.

2) Since a totally uniform sample is difficult to achieve, a narrow slit in the vertical direction is helpful in two ways. First, the correction term in eq. (11) is proportional to a^2. Thus reducing a by 2, reduces the glitch amplitude by 4. Second, the narrow slit provides more flexibility for moving the sample to find the region that is most uniform. This is accomplished by monitoring I_T and finding the region of the sample with the smallest variation in I_T as the sample is moved vertically. An amusing result of these calculations is that on a low-emittance storage ring such as the PEP ring at SSRL, the problems of glitches may be much reduced. For beamlines with a very small vertical divergence, the vertical slit height can be small and still pass most of the flux. The important ratio is the slit height to the effective Darwin width of the unwanted diffractions.

3) The amplitude of the glitch depends on the total absorption between the I_0 and I_T counters. μ_B includes windows in cryostats, as well as material used for sample containment or support (i.e., tape, vacuum grease, plastic holders, etc.). It is very important that these additional absorbers be as uniform in thickness across the beam as possible. At high X-ray energies, the background absorption of these components is small, and the contribution to glitches is likely negligible. However, at low energies for which 20–30% of the beam may be absorbed by windows etc., nonuniformity in other components will contribute to glitches. It is therefore important at lower energies that the windows of the cryostat have no condensation. If water (or even worse, ice) condenses on the window and a droplet of water forms in part of the slit region, it can contribute to the glitch problem.

4) Glitches formed by nonuniformities at different positions in the sample can have different signs and amplitudes. Thus, if the observed glitch is a combination of a tapered sample plus pinholes, it should be possible to move the sample such that the net glitch observed is greatly reduced. (For samples at room temperature it may be possible to rotate the sample to obtain a similar reduction of glitch intensity; for example a rotation about a horizontal axis through the center of the slit inverts the sample, and therefore inverts the glitch [13].) For the simplified model presented here, a minimization of one glitch minimizes all glitches. It is not clear at this point whether this is a good approximation for real spectra. It will depend on the shape of the dip profile and how well the intensity variation of the flux across the slit can be modeled by a linear slope. Measurements to check this result of the simple model are planned.

5) For samples made of fine powders, it is important to make the samples very uniform. Then one ends up with a homogeneous array of very fine pinholes. For such a sample, the effects of glitches can be very small; glitches produced by pinholes at the top of the sample cancel pinholes at the bottom of the sample. Note that such samples may still have a significant amplitude problem. The absence of large glitches does not mean that no pinholes are present.

Once it is recognized that a variation in the spatial distribution of the flux (i.e. the parameter $\beta(E)$ in eq. (11)) will couple with sample inhomogeneities, we can consider other types of noise in XAFS spectra. One noise source is caused by beam motion. The above model predicts that vertical shifts of the beam position will produce steps in the data that do not ratio out. First assume that the slits are narrow, and are centered on the beam profile. Then the spatial variation of the flux across the slit is small, and $\beta(E) = 0$. If the beam now moves such that the slits are on the side of the beam profile, the spatial variation of the flux across the slit will increase, $\beta(E) \neq 0$. For a nonuniform sample this will produce a step in the value of R. Continuous small variations in beam position will generate many small fluctuations in the ratioed data. Note that in contrast to the glitch problem, the steps in R as a result of beam motion, will be increased on low-emittance beamlines compared to other beamlines.

Another possible XAFS noise source is related to fluctuations in the emittance of the beam when the slits are somewhat off-center. The fluctuation of the emittance gives a changing width to the beam profile, and therefore a change [14] in $\beta(E)$. This will again couple to the sample inhomogeneities. To minimize these effects, it is important to ensure that the slits are always well centered on the beam. It is clear experimentally, that beam instabilities do contribute to the glitches and steps found in XAFS data. Our model shows why these effects do not ratio out even for linear detectors and no harmonics.

Finally we note that, although we have focused here on the vertical spatial variations, in general both horizontal and vertical spatial distributions of the flux may be important. For example, the flux at the side-station of a wiggler beam line clearly has a strong horizontal variation. If the beam motion is such that the photon beam moves horizontally, this will couple to horizontal sample inhomogeneities.

4. Pixel array detectors

Significant advances have been made in recent years on Si pixel or strip detectors for high energy physics, astronomy and X-ray detectors. Astronomers have Si detectors as thin as 10 μm [15], and other materials have been considered as well. It is therefore feasible to consider the advantages of pixel array detectors for transmission XAFS. One major improvement is an increase in the detector current by an order of magnitude for a given incident flux.

Pixel array detectors for both I_0 and I_T would greatly minimize the effects of sample inhomogeneity. The two detectors must have good registry and the I_0 detector must, of course, be nearly transparent to the incident radiation. Then one has n independent channels, each of which measures I_0/I_T and yields a value for χ_n. Such detectors should improve the quality of the data for all types of samples, but for the case of a low concentration sample such as considered in fig. 1, they are particularly important. First, each pixel area corresponds to a small slit size; this significantly reduces the glitch height as discussed above. Second, when some pinholes are present, the amplitude in these channels will be low. This part of the sample could be excluded in data analysis, again reducing the glitch size (as well as minimizing amplitude reduction problems). Third, because the sign of a glitch in a given channel depends on the sample variations over that small part of the sample, the sign of the glitch may vary from channel to channel. A judicious choice of weighting when adding χ_n together may allow nearly complete cancellation of a glitch. Fourth, after χ_n is extracted for each of the n channels, they can be added together and improve the S/N of statistical fluctuations. If other types of noise are sufficiently reduced, one may be able to approach the S/N expected from counting statistics. For example, if the incident flux through the slits from a wiggler beamline has 10^{10} photons, the S/N should be 10^5. Because of several noise sources, including the presence of many small glitches in XAFS spectra, the S/N is usually less than 10^4. If the main limitation to the noise is the presence of tiny glitches, an improvement in the achieved S/N by a factor of 3–10 may be possible with an array detector. We emphasize that it is crucial to minimize the effect of glitches as much as possible before averaging. Therefore the more uniform the sample thickness is, the better the data. This has been noted previously by several investigators [10–12] for single channel studies and remains true with a pixel array detector.

5. Conclusions

We have presented data that suggests that some glitches in an absorption spectrum are determined by sample and incident beam inhomogeneities in the vertical direction. We have investigated the beam profile at several energies close to a glitch and shown that the intensity profile across the slit (vertically) varies considerably. The formation of a glitch (again assuming linear detectors and no harmonics) is attributed to the combined effect of a nonuniform sample plus a changing intensity profile over a small range of energy near a glitch.

We have developed a model for glitch formation based on our experimental observations that the intensity profile is energy dependent at a glitch. We have shown that large glitches are expected for spatially nonuniform samples because variations in intensity do not ratio out when the intensity also varies spatially. This model also predicts both positive and negative lobes to a glitch and thus can explain either upward or downward glitches in real XAFS data for coarse steps in energy. Some ways to minimize glitches are given and some advantages of using pixel array detectors for I_0 and I_T are presented.

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[8] Normally the position of the slits is recentered on the beam each time we change the X-ray energy. This maximizes the flux and makes the detected signal less sensitive to small beam fluctuations. Because of the limited time available at the end of our run, the slits were not re-centered when we returned to energies near 10.3 keV for these intensity measurements. Glitches in ratioed data, caused by multiple diffractions, are relatively insensitive to the slits being exactly centered on the beam for the linearized model presented here.

[9] The XAFS signal is expected to be the sum of sine functions in k-space, e.g. $\chi(E) = A \sin(2kr + \delta)$, where k is proportional to $(E - E_0)^{1/2}$. This detail is not needed to show a glitch.

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