Oscillation Camera Data Processing. 3. General Diffraction Spot Size, Shape and Energy Profile: Formalism for Polychromatic Diffraction Experiments with Monochromatized Synchrotron X-radiation from a Singly Bent Triangular Monochromator

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Abstract

The size and shape of diffraction spots produced by monochromatized synchrotron X-radiation from a singly bent triangular monochromator are derived following a simpler more comparative treatment given in earlier work on reflecting range and prediction of partiality for oscillation camera data [Greenhough & Helliwell (1982). J. Appl. Cryst. 15, 493–508]. In that treatment the possibility of a polychromatic experiment [see Arndt Nucl. Instrum. Methods (1978), 152, 307–311] for an earlier suggestion] was identified and here the energy profile within each diffraction spot is derived along with the spectral resolution \( \delta E / E \) at any point in the profile due to experimental conditions and sample characteristics. A firm theoretical basis is established so that experimental problems and procedures can be discussed with a view to optimizing the method in the light of the presentation of the first reported polychromatic experiment [Arndt, Greenhough, Helliwell, Howard, Rule & Thompson (1982). Nature (London), 298, 835–838].

Introduction

When synchrotron X-radiation is focused by means of a singly bent triangular monochromator [Si or Ge with the (111) planes at an angle of cut \( z \) to the surface], there is one particular curvature of the monochromator for a given Bragg angle \( \theta \), angle of cut and image \( p' \) and object \( p \) distances where all rays at the focus are of the same wavelength. Away from this achromatic condition or Guinier position the monochromator is 'underbent' or 'overbent' and a correlation between the energy and direction of rays at the focus is produced (Helliwell et al., 1982). This can be expressed in terms of the correlated spectral dispersion \( \delta_{\text{corr}} \) signed to distinguish the over- and underbent cases, and the incoming angle of the ray at the focus, \( \gamma' \) (Greenhough & Helliwell, 1982b). In addition to this component of spectral dispersion, rays from different points in a finite source focus at different points producing a finite focus width with an accompanying energy gradient \( (\delta E / E)_{\text{foc}} = 2\delta_{\text{foc}} = (x_p \cot \theta) / p' \) across a distance \( x_p \) of the focus (Greenhough & Helliwell, 1982b). The final contribution to the spectral dispersion is produced by the monochromator rocking width \( \omega \), giving \( (\delta E / E)_{\omega} = 2\delta_{\omega} = \omega_{\text{diff}} \cot \theta \) (Greenhough & Helliwell, 1982b). Both the finite focus and rocking-width contributions to \( \delta E / E \) are present for all curvatures of the monochromator, while the correlated component \( \delta_{\text{corr}} \) is zero at the Guinier position. Indeed, we have shown that at the Guinier position the equations for reflecting range reduce to those for a conventional source with asymmetric beam cross fire in the horizontal (\( \gamma' \)) and vertical (\( \gamma'' \)) directions (Greenhough & Helliwell, 1982b). Detailed descriptions of the diffraction geometry for both conventional and synchrotron X-radiation sources have been given (Greenhough & Helliwell, 1982a, b), leading to the possibility of a polychromatic diffraction experiment (Greenhough & Helliwell, 1982b). Preliminary details of the first experiment, demonstrating the existence of an energy profile across each diffraction spot, and possible methods whereby this approach might be used in structural studies, are given by Arndt, Greenhough, Helliwell, Howard, Rule & Thompson (1982). In order that the structural prospects of the method can be properly evaluated we now derive the formulae necessary for the assessment of the resolution \( \delta E / E \) achievable.

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within each spot, along with a definitive spot-size formalism, allowing each spot to be predicted and sampled in terms of both position and energy.

**Derivation**

With the same notation as in Greenhough & Helliwell (1982b), a particular wavelength \( \lambda \) impinging on the sample may be represented in terms of a Ewald sphere of radius \( 1 + \delta \) where \( \delta = (\lambda - \lambda')/\lambda \) and \( \lambda' \) is the mean wavelength represented by a unit-radius Ewald sphere. The sphere will be centred at a position determined by \( \delta \) and by the horizontal and vertical cross-fire angles for the particular ray being considered. The range of wavelengths in any particular direction is determined by the monochromator characteristics and configuration, with each focused fan of rays having a wavelength/direction correlation away from the Guinier position and each ray having a wavelength spread due to the monochromator rocking width (Greenhough & Helliwell, 1982b). In addition, the mean wavelength within each focused fan of rays changes as we move across the focus due to the finite source size. The mean wavelength for a given ray is thus determined by its incoming direction and its position at the focus.

The range of wavelengths and ray directions which impinge on the sample may be limited by the use of slits, by the crystal size, and by the slit-to-crystal distance. By finding the range which gives rise to diffraction to the same point on the film we may find the energy spread \( \partial E \) and the mean energy \( E \), and hence the resolution \( \partial E/E \) at that point; by finding the film coordinates of each and every diffracted ray the diffraction spots may be mapped in terms of both position and energy. In doing so the effects of crystal size, shape and mosaicity must also be accounted for.

Full details of the derivation are given in the Appendix where we begin by finding the film coordinates of a general diffracted ray from Fig. 1. By considering first those rays at the sample which have zero vertical cross fire and which pass through an infinitely small pre-crystal pin hole at the focus, we may map out the diffraction spot produced by the correlated wavelength component alone. This is found to be an inclined line on the film, variable in size and inclination over the film (Greenhough & Helliwell, 1982b), forming the basis of the spot and energy profile about which all else is convoluted. This line contains resolved energies with a linear relationship between position and energy.

Sample mosaic spread may be accounted for by considering the variation in \( \zeta \) over the mosaicity spherical cap, at constant \( d^* \). This is easily shown to be within \( \zeta \pm \eta \zeta/2 \), where \( \eta \) is the full mosaic spread. Introducing this variation in \( \zeta \) into the film-coordinate equations and then smearing out the whole predicted spot vertically according to vertical incident-beam size (or vertical sample size, whichever is the smaller) will give the diffraction spot mapped out in terms of position and energy when all combinations of energy, cross fire, slit position and \( \zeta \) are considered. This vertical convolution is particularly important since, in finding the energy resolution at any point within the spot, we may simply derive the range of energies present at a particular horizontal film coordinate. There is of course an additional horizontal film coordinate. There is of course an additional horizontal film coordinate. There is of course an additional horizontal film coordinate. There is of course an additional horizontal film coordinate.

In building up the energy resolution at a given horizontal coordinate within a diffraction spot, we must derive the horizontal distance over which a given energy is spread by the various factors. This may then be used in conjunction with the correlated energy/position relationship to find the energy resolution. For the spot-size derivation the energy-dependent factors (focus energy gradient, monochromator rocking width) must be considered in terms of the dimensional changes produced in the spot by the effect as a whole, rather than the change produced by each individual energy.

Perfect cylindrical curvature of the monochromator is assumed and for energy-profile experiments it is assumed that the conditions are adjusted such that the crystal can at least accept the whole of the central correlated fan of rays. Thus the crystal horizontal size is not a limiting factor. In the vertical, however, the limiting factor may be the crystal size or vertical slit size if used, but this may be variable over the crystal width dependent on crystal shape as is illustrated below.

From the Appendix we see that the energy resolution at a given horizontal film coordinate \( H \) is given by

\[
\delta E = \frac{2\theta_{\text{corr}}}{|\partial H|_{\text{corr}}} \left\{ |(\partial H)_h| + |(\partial H)_v| + |(\partial H|_{\text{cor}}^e| + |(\partial H|_{\text{cor}}^v|, \right\},
\]

where the various terms are defined in the Glossary of terms. On substituting for the \( \partial H \) parameters and rearranging we get
The diffraction spot itself is then symmetrical about \( V_v = C/L \cos 2\theta \), \( H_v = C_\zeta / \cos 2\theta \) (Wonacott, 1977), being an inclined strip of vertical width \( V_{\text{uncorr}} = V_{\text{tot}} - (\partial V)_\text{corr} \) inclined at \( v = \tan^{-1} [(\partial V)_\text{corr} / (\partial H)_\text{corr}] \) to the horizontal. Since the terms in \((\partial H)_\text{corr}\) and \((\partial V)_\text{corr}\) can be of the same or opposite sign, both spot size and inclination vary over the film with large left/right differences; in particular, for \( +\zeta \) the spots are drawn out into streaks with variable-wavelength information along their length (Greenhough & Helliwell, 1982b; Arndt et al., 1982).

**Discussion**

The possible applications of a polychromatic profile for optimized anomalous-dispersion diffraction experiments in structural studies are discussed elsewhere (Arndt et al., 1982); here we outline the conditions which allow such experiments to be performed. The spot-size calculations are of general use, even at the Guinier position, allowing the calculation of individual integration-box sizes and shapes based on experimental conditions. Their effectiveness is demonstrated by Fig. 2 and Table 1, where three reflections from a single crystal of bis(diisopropylphenyl)phosphineheptahydridorhenium are considered. The energy profile is clearly visible. Experimental conditions are as described by Arndt et al. (1982), and the two reflections considered there, 020 and 120, in terms of \( f' \) variations are included here. The oscillation photographs from which the spots are taken are shown in Fig. 3. Also included is the direct-beam exposure showing the vertical-crystal-size \( l_v \) convolution to be non-symmetrical. The beam passes over the sample due to a slight mis-set of the vertical slit. The non-parallel top and bottom edges of the observed spots are due to this experimental condition, as is the additional dark feature towards the top of the diffraction spots, arising from the rapid falling off of absorption path length at the crystal top edge. The bottom edge of the spots is inclined at \( v \) and the top at \( v' \) where \( \tan v' = \tan v + (l_v) / H_{\text{tot}} \). The success of the spot-size calculations depends on an accurate knowledge of experimental conditions and on a good estimate of mosaic spread. With all machine parameters carefully measured and set, refinement of spot sizes will give a very good estimate of mosaic spread \( \eta \) (and crystal thickness \( t \) if not carefully measured).

Even with the data presented here the spot widths of 120 and 020 are rather more equal in size than is predicted; however, by assuming \( \eta = 0.1^\circ \) and estimating \( t \) as \( 0.2 \) mm \( H_{\text{tot}} \) values are virtually unaffected for 020 and 063 while decreasing 120 by \( 0.017 \) mm. In any case the values of slit-to-crystal distance \( S \) and slit width \( l_s \) would need refinement (not performed here). It is clear then that the first condition for successful application of the polychromatic technique is an accurate knowledge of experimental conditions with subsequent refinement of the various parameters.

In terms of the energy profile it can be seen that

\[
\begin{align*}
\hat{\delta} &\simeq \frac{2\delta_{\text{corr}}}{(\partial H)_{\text{corr}}} \left[ \frac{\eta C + [\zeta]}{\cos 2\theta} + l_H + \frac{\gamma \nu C_\zeta}{L \cos^2 2\theta} \right] \\
&\quad + \left( \frac{(\partial H)_{\text{corr}}}{\delta_{\text{corr}}} - \frac{(\partial \delta_{\text{corr}})}{\delta_{\text{corr}}} \right)
\end{align*}
\]

and this is the resolution at a point after the vertical convolution due to crystal or slit size \( l_v \). The dimensions of the diffraction spot are given by

\[
H_{\text{tot}} \simeq (\partial H)_{\text{corr}} \left[ \frac{\eta C + [\zeta]}{\cos 2\theta} + l_H + \frac{\gamma \nu C_\zeta}{L \cos^2 2\theta} \right] \\
+ \frac{C(2 + d^2)}{\cos^2 2\theta} \left\{ \zeta \delta_{\text{corr}} + \zeta \delta_{\text{foc}} + \delta_{\text{slit}} \right\}
\]

and, for a symmetric \( l_v \),

\[
V_{\text{tot}} \simeq (\partial V)_{\text{corr}} \left[ \frac{\eta C L^2 \zeta^2}{L} + t \right] + l_v \\
+ \frac{\gamma \nu C L_\zeta (d^2 - 2z^2)}{2 \cos^2 2\theta} \\
+ \frac{C L(z^2 - d^2 z^2)}{\cos^2 2\theta} \left( \delta_{\text{corr}} + \delta_{\text{slit}} \right)
\]

\[\text{Fig. 2. The 120, 020 and 063 reflections and the direct-beam exposure from a single crystal of bis(diisopropylphenyl)phosphineheptahydridorhenium (sample courtesy J.A.K. Howard and J. Spencer) indexed as described by Arndt et al. (1982) and having the experimental conditions described in Table 1. The superimposed predicted shapes and sizes of the diffraction spots are to the same scale. The photographs, taken at the Re L_m edge (\( 2 = 1.1772 \) Å) clearly display the energy profiles as illustrated by the 'white line' absorption effect.}\]
Table 1. Spot shapes and sizes and energy resolutions for reflections from a single crystal of bis(diisopropylphenyl)phosphineheptahydridorhenium at the rhenium L\textsubscript{m} edge, $\lambda = 1.1772$ Å, taken at the Daresbury SRS

Parameters used are $C = 54.5$ mm, $S = 100$ mm, $t = 0.1$ mm, $\eta = 0.2^\prime$, $\rho = 2.4$ m, monochromator Si(111) with $\alpha = 6.73^\prime$ and length in use 156 mm (based on direct-beam exposure), $\delta_{\text{corr}} = 0.00316$ (total 67 eV), $\delta_{\omega} = 0.0001027$, $\delta_{\text{rec}} = 0.0001525/2$, $\gamma_{\mu} = 4.66$ mrad. Distances are in mm. The energy resolution is given by $dE = (6\delta/E)$ which is $6\delta$ with $E = 10.535$ keV. The value of $6$ is given by $\delta_{\text{corr}}$ as indicated in the Appendix and hence $6E$ may be obtained from $6E = \delta_{\text{corr}}$. This may also be applied to $6E_1$, $6E_2$ and $6E_3$ to find the individual contributions to $6E$. The quantity $V_{\text{norm}}$ is the vertical size of the spot at a given $H$ value, i.e. $V_{\text{norm}} = V_{\text{corr}} + (\delta H)_{\text{corr}}$, where $V_{\text{corr}}$ is the vertical size of the spot at a given $H$ value, $V_{\text{corr}} = V_{\text{lim}} + (\delta H)_{\text{lim}}$, and $V_{\text{lim}}$ is the vertical size of the spot at the limit of the mosaic spread.

<table>
<thead>
<tr>
<th>$d^*$</th>
<th>0.21</th>
<th>0.63</th>
<th>0.20</th>
</tr>
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<tr>
<td>$\zeta$</td>
<td>-0.03</td>
<td>0.35</td>
<td>-0.10</td>
</tr>
<tr>
<td>$H_{\parallel}$</td>
<td>-1.6719</td>
<td>22.6222</td>
<td>-6.0893</td>
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<td>$V_{\perp}$</td>
<td>-11.5177</td>
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<td>-7.5571</td>
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<tr>
<td>$(\delta H)_{\text{corr}}$</td>
<td>0.0040 (3.79 eV)</td>
<td>0.0045 (2.76 eV)</td>
<td>0.0045 (2.85 eV)</td>
</tr>
<tr>
<td>$(\delta V)_{\text{corr}}$</td>
<td>0.0059</td>
<td>0.0048</td>
<td>0.00139</td>
</tr>
<tr>
<td>$(\delta H)_0$</td>
<td>0.0004</td>
<td>0.0064</td>
<td>0.00013</td>
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<tr>
<td>$(\delta V)_0$</td>
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<td>0.0066</td>
<td>0.00016</td>
</tr>
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<td>$(\delta H)_0$</td>
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<td>0.0047</td>
<td>0.00016</td>
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<tr>
<td>$(\delta V)_0$</td>
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<td>0.0049</td>
<td>0.00012</td>
</tr>
<tr>
<td>$l_{\perp}$</td>
<td>0.63-0.72</td>
<td>0.63-0.72</td>
<td>0.63-0.72</td>
</tr>
<tr>
<td>$(\delta H)_{\text{foc}}$</td>
<td>0.0236 (2.21 eV)</td>
<td>0.0236 (3.67 eV)</td>
<td>0.0236 (3.79 eV)</td>
</tr>
<tr>
<td>$(\delta V)_{\text{foc}}$</td>
<td>0.0525 (4.92 eV)</td>
<td>0.0525 (5.12 eV)</td>
<td>0.0525 (5.12 eV)</td>
</tr>
<tr>
<td>$H_{\text{foc}}$</td>
<td>0.8285</td>
<td>12283</td>
<td>0.7954</td>
</tr>
<tr>
<td>$\delta E_{\text{foc}}$</td>
<td>0.1196</td>
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<tr>
<td>$\delta_{\omega}$</td>
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<td>0.00136</td>
<td>0.00105</td>
</tr>
<tr>
<td>$\delta E_{\text{foc}}$</td>
<td>0.06613-0.7513</td>
<td>0.7745-0.8645</td>
<td>0.6681-0.7581</td>
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<tr>
<td>$(\delta H)_{\text{corr}}$</td>
<td>0.7149 (67 eV)</td>
<td>1.0071 (67 eV)</td>
<td>0.6874 (67 eV)</td>
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<td>$(\delta V)_{\text{corr}}$</td>
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<td>0.00479</td>
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<tr>
<td>$\nu$ (')</td>
<td>-5.9</td>
<td>+12.0</td>
<td>-4.0</td>
</tr>
<tr>
<td>$\nu$ (')</td>
<td>+0.3</td>
<td>+16.0</td>
<td>+2.5</td>
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Resolutions of $10^{-3}$ $\delta E/E$ are obtained in this case. with a 67 eV energy spread over the correlated contribution to spot length. The energy resolution will clearly benefit from a reduction in slit size $l_{\parallel}$ and crystal thickness $t$, but is very dependent on mosaic spread. Although in the mosaic cap there are many points at $\zeta$ but only one at the extremes $\zeta \pm \delta_{\omega}$, the number of points at $+0.9\delta_{\omega}$ is 44% of that at $\zeta$ itself, so to all intents and purposes the whole of the mosaic spread is effective in the degradation of resolution. An increase in the slit-to-crystal distance will increase the resolution but this must depend on the crystal size being capable of accepting the whole of the correlated energy spread. It should be noted that consideration of the energy/direction correlation and mosaic spread alone produces perfectly resolved energies. Thus with a very fine vertical slit $l_{\perp}$ only the central vertical distance $l_{\perp}$ will be resolved according to $\delta_{\omega}$ with the remainder much better resolved. However, as may be seen in Table 1 the $l_{\perp}$ term produces the great majority of the vertical strip size of the spot. Such a narrow slit would demand vertical focusing which introduces a slight degradation of resolution. For a vertical-beam cross-fire angle $\gamma_{\nu}$ of the order of 0.25 mrad (Greenhough & Helliwell, 1982b), this additional contribution is around 0.2 eV for the 063 reflection considered here.

The scanning of the diffraction spots introduces a further resolution degradation. A scan along the streaks with raster sizes $R_{\parallel}$ (along the streak axis) and $R_{\perp}$ covers a horizontal distance $R_{\parallel} \cos \nu + R_{\perp} \sin \nu$ which should be accounted for in $\delta E$. For the 063 reflection with $R_{\parallel} = 10 \mu m$, $R_{\perp} = 100 \mu m$, this gives an additional 1.9 eV in $\delta E$, only 0.7 eV for 10 x 10 \mu m. Even though $\nu$ is small for the 120 and 020 the additional degradation is around 1.8 eV for 10 x 100 \mu m and 1 eV for 10 x 10 \mu m.

In order to illustrate the resolution the 063 reflection is considered. From the basic equations (1) to (4) (Appendix), the central reference ray with $\delta_{\text{corr}} = 0$, for $\delta_{\omega} = 0$, arises on the film at $V_c = 26.375$, $H_c = 22.622$ mm. For this case we get $\delta_{\omega} = 0.00136$, so rays of energies given by $\delta_{\omega} = 0$ should impinge on the film at the same horizontal coordinate $H$. These rays will be at the extremes of the slit and $\delta_{\omega}$. Taking $\delta_{\omega} = 0.00068$ at $(l)^2/2 = +1_{\parallel}/2$, and setting this at the
OSCILLATION CAMERA DATA PROCESSING. 3

\[ \delta_c + \delta_o \rightarrow \text{extreme, we get } \delta_c = 0.00068 - \delta_o \text{ in the extreme fan, then } \delta_c = 0.00068 - \delta_o + \delta_{toc} \text{ at the same horizontal divergence } (\gamma)^H \text{ in the central fan, giving } (\gamma)^H/2 \text{ from } K_m \text{ as } 0.000482. \]

Using these values in (1) to (4) with the maximum \( \zeta \) of \( \zeta + \eta \zeta/2 \) we get \( V = 26.310, H = 22.602 \),
then, adding in half the crystal-thickness \( \delta H \) term, we get \( H = 22.623 \text{ mm. Similarly, taking } \delta = 0.00068 \) at
\( -l_H/2, \) at \( \delta_c - \delta_o \) in that fan, the minimum \( \zeta \) and
subtracting half the crystal-thickness term, we get \( V = 26.439, H = 22.622 \text{ mm. There are of course other}
rays of these energies but they do not give the same \( H \)
values. The vertical separation of the two points is
0.13 mm, much less than the \( l_v \) convolution which
thus smears them together.

The left-of-film reflections are clearly those to be
used in extracting anomalous-dispersion-based
information from the energy profile since the drawing
out of the spots enables scanning without too much
loss of resolution. The successful unravelling of the
information stored in the streaks demands careful
optimization of all parameters and, as far as can be
seen at the moment, crystals which are not only
suitable chemically but also in terms of size and
mosaicity. It is worth pointing out that Friedel reflec-
tions recorded with the same sign of \( H \) will, for a well-
set crystal, have identical shape and size diffraction
spots mirrored across the mounting axis. The use of
Bijvoet ratios (Unangst, Muller, Muller & Keinert,
1967; Bartunik, 1978) rather than differences would
then directly cancel out absorption effects and avoid
all problems due to different spot-profile widths
(Arndt et al., 1982).

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APPENDIX

The relationship between the direction and energy and
energy spread of each incoming ray to the sample are
given by Greenhough & Helliwell (1982b). All terms
including their sense are as described therein; a brief
description is given in the Glossary of terms. Perfect
cylindrical curvature of the monochromator is as-
sumed. From Fig. 1, the film coordinates of a diffrac-
ted ray for a given point at \( d^*, \zeta \) in reciprocal space for
a general incoming ray are given by

\[ V = \pm \left\{ C \tan \left[ v_V - \left( \frac{\gamma}{2} \right)^V \right] + \left( \frac{1}{2} \right)^V - S \left( \frac{\gamma}{2} \right)^V \right\} \]

\[ H = \frac{C \tan v_H}{\cos \left[ v_V - \left( \frac{\gamma}{2} \right)^V \right]} + \left( \frac{1}{2} \right)^H - S \left( \frac{\gamma}{2} \right)^H, \]

where

\[ \sin v_H = \frac{\zeta - \left( \frac{\gamma}{2} \right)^H}{1 + \delta} \]

and

\[ \cos v_V \frac{(1 + \delta)^2(1 + \cos^2 v_H) - \zeta^2}{2(1 + \delta)^2 \cos v_H}, \]

where \pm in (1) refers to the bottom and top of film.
respectively, and $\delta$ and $\gamma/2$ give the energy and direction of an incoming ray relative to the origin ray with $\delta = 0$, $\gamma/2 = 0$. For the definition and explanation of terms see the Glossary of terms.

In order to understand the way in which the various factors contribute to the spot size, shape and energy resolution, we begin by considering only those rays which have zero vertical divergence and which pass through the vertical centre of the slit as a horizontal sheet. Thus with $(\gamma/2)^H$ and $(\gamma/2)^V = 0$ we may substitute for $\cos \gamma v$ from (4) into (2), leaving a $\sin \gamma v$ term in the result, which may be substituted for from (3). Rearrangement of the resulting expression then gives

$$H \approx \frac{2C\zeta(1 + \delta) + \delta p(d*2S - 2C - 2S)}{4\delta + 2 - d*2 + 2\delta p} + \left(\frac{l}{2}\right)^H$$

where the variable $p$, relating the energy and direction of an incoming ray, has been introduced as

$$p = \frac{(\gamma/2)^H}{\delta}.$$  

By considering only the central fan of rays passing through the slit origin, i.e. $(\gamma/2)^H = 0$, and by leaving out the monochromator rocking-width contribution to begin with, the effect of the energy/direction correlation on the diffraction spot size, shape and energy resolution can be established. For this particular fan of rays the energy/direction relationship for each ray is given by a special condition of (7), namely

$$(\gamma/2)^H = p = \frac{\gamma v}{\delta} = K_m,$$

where $K_m$ is a constant and $\delta_v$ represents a particular ray in the correlated fan (Greenhough & Helliwell, 1982b). The extreme values of $H$ from (5) occur as a result of the extremes of $\delta_v$; i.e. where $\delta_v = \pm \delta_{cor}$, occurring at the angular extremes of the fan. Using these values for $\delta_v$ along with $p$ from (8), alternately in (5), or by differentiating (5) with respect to $\delta_v$, we derive the change $\left(\partial H\right)_{cor}$ in horizontal film coordinate due to the correlated component of energy.

$$\left(\frac{\partial H}{\partial \delta}\right)_{cor} = \frac{C\zeta[2 + d*2]}{2\cos^22\theta} + \frac{K_m[S + C(\cos 2\theta + \zeta^2)]}{\cos^22\theta},$$

and with $\partial \delta = 2\delta_{cor}$ we may write

$$\left(\partial H\right)_{cor} = \left(\partial H\right)_{2\delta} + \left(\partial H\right)_{cor},$$

where

$$\left(\partial H\right)_{2\delta} = \gamma_{2\delta}\left\{S + \frac{C(\cos 2\theta + \zeta^2)}{\cos^22\theta}\right\}$$

and

$$\left(\partial H\right)_{cor} = \frac{\delta_{cor}C\zeta(2 + d*2)}{\cos^22\theta}.$$  

Since $\left(\partial H\right)_{cor} \propto (\partial \delta)_{cor}$, the energies are resolved linearly in $H$ for a given point in reciprocal space.

The change $\left(\partial V\right)_{cor}$ in the vertical film coordinate due to the correlated component may be obtained by differentiating (1) with respect to $v$ and (4) with respect to $\delta$. Thus we get

$$\left(\frac{\partial V}{\partial v}\right)_{cor} = \left(\frac{C}{\sin \gamma v \cos^22\theta}\right)\left(\frac{\partial \delta}{\partial \gamma v}\right)$$

and

$$\left(\frac{\partial V}{\partial \delta}\right)_{cor} = \left(\frac{C}{\sin \gamma v \cos^22\theta}\right)\left(\frac{\partial \gamma v}{\partial \delta}\right),$$

giving

$$\left(\partial V\right)_{cor} = \left(\partial \delta\right)_{cor} \frac{C}{\sin \gamma v \cos^22\theta} \left(\frac{\partial \gamma v}{\partial \delta}\right).$$

By substituting for $\gamma v$ in (4) and then neglecting terms in $\delta^2$ we get

$$\cos \gamma v \approx \frac{(2 - d*2) + \delta(4 + 2K_m\zeta)}{2\sqrt{1 + \delta^2 + \delta(4 + 2K_m\zeta - 2\zeta^2)}},$$

and using expression (16) in (15) then gives

$$\left(\partial V\right)_{cor} = \left(\partial \delta\right)_{cor} \left\{\frac{C}{4\cos^22\theta} \left[2K_m\zeta(2 - d*2) + 2(2d*2 - 2\zeta^2 - d*2\zeta^2)\right]\right\},$$

when terms in $\delta^2$ are neglected and the $\delta$ terms which do not directly cancel are recognized as insignificant. Since $\left(\partial V\right)_{cor} \propto (\partial \delta)_{cor}$ the energies are resolved linearly for a given point in reciprocal space. Substituting for $K_m$ from (8) and with $(\partial \delta)_{cor} = 2\delta_{cor}$ we may write

$$\left(\partial V\right)_{cor} = \left(\partial V\right)_{\gamma v} + \left(\partial V\right)_{\gamma \delta}_{cor},$$

where

$$\left(\partial V\right)_{\gamma v} = \gamma_{\gamma v} \left\{\frac{C\zeta(2 - d*2 - 2\zeta^2)}{2\cos^22\theta}\right\}$$

and

$$\left(\partial V\right)_{\gamma \delta}_{cor} = \frac{\gamma_{\gamma v}}{\gamma_{\gamma \delta}_{cor}} \left(\partial V\right)_{\gamma \delta}_{cor}$$

By reference to (10) and (17), with substitution from (11), (12) and (18), (19), we see that $\left(\partial V/\partial H\right)_{cor}$ is constant for a particular point in reciprocal space and we have an inclined line on the film, variable in size and inclination over the film, due to the energy/direction correlated component of the incident beam (Greenhough & Helliwell, 1982b).

The effect of sample mosaicity $\eta$ for the central fan of rays under consideration may be found by introducing the variation in $\zeta$ which occurs as a result. This variation is easily shown to be

$$\left(\partial \zeta\right) = \eta \zeta$$
over the mosaicity spherical cap (Wonacott, 1977). By differentiating (5) with respect to \( \zeta \) we get

\[
\frac{\partial H}{\partial \zeta} = \frac{2C(1 + \delta_c)(4\delta_c - d^2* + 2)}{(4\delta_c - d^2* + 2 + 2\delta_c K_m)^2}.
\]

This expression is constant, to an excellent approximation, with respect to \( \delta_c \), and substitution from (20) gives

\[
(\partial H)_{\|} \approx \eta \zeta C / \cos 2\theta
\]

as the horizontal film-coordinate spread due to mosaicity for each and every ray. The vertical spread \((\partial V)_{\|}\) may be found by differentiating (16) with respect to \( \zeta \) and combining the result with (13). The resulting expression is again approximately constant with respect to energy and we get

\[
(\partial V)_{\|} \approx \eta \zeta C L_\nu / \cos 2\theta.
\]

A crystal of finite thickness \( t \) may be accounted for by replacing the crystal-to-film distance \( C \) by \( C + t \) and the slit-to-crystal distance \( S \) by \( S - t \) in (1) and (5) and differentiating with respect to \( t \). Thus for the fan of rays under consideration we get

\[
\frac{\partial V}{\partial t} = \tan \nu_p
\]

and

\[
\frac{\partial H}{\partial t} = \frac{2\zeta(1 + \delta_c) - \delta_c K_m d^2*}{4\delta_c + 2 - d^2* + 2\delta_c K_m^2}.
\]

Substituting for \( \tan \nu_p \) from (13), we find that both expressions are approximately constant for all energies, and with \( \partial t \) set to \( t \) we get

\[
(\partial V)_{\|} \approx t / L \cos 2\theta
\]

and

\[
(\partial H)_{\|} \approx t \zeta / \cos 2\theta.
\]

Mosaic spread and crystal thickness thus amend the spot shape by smearing each energy out over a line defined by (21) and (22), with each point in that line also drawn out over a line defined by (23) and (24). The energy resolution within the diffraction spot is thus degraded.

For each incoming ray in the fan under consideration the value of \( \delta_c \) is amended by the monochromator rocking width to assume values in the range \( \delta_0 = \delta_c \pm \delta_o \) (Greenhough & Helliwell, 1982b). The scale factor \( p \) in (7) thus assumes extreme values for each ray of \( p = (\gamma/2)H / \delta_c \pm \delta_o \) and with substitution for \( (\gamma/2)H \) from (8) rearrangement gives

\[
p = K_m(1 \pm \delta_o / \delta_0).
\]

In terms of the energy resolution, the distances over which a given energy, represented by \( \delta_0 \), is spread on the film must be found. Within a given fan there are many rays of a given energy because of the monochromator rocking width, and this may be represented by a variation in \( p \) as \( \delta_o \) varies in the range \( \pm \delta_o \) to give a constant \( \delta_0 \). By differentiating (5) with respect to \( p \) we get

\[
\frac{\partial H}{\partial p} = \frac{\delta_o(2 - d^2*)(d^2* - 2C - 2S) - 4C^2 \delta_o}{(4\delta_o + 2 - d^2* + 2\delta_o p \zeta)^2},
\]

when terms in \( \delta_o^2 \) are neglected, giving by rearrangement and approximation of the denominator,

\[
\frac{\partial H}{\partial p} \approx \delta_o \left\{ S + \frac{C(\cos 2\theta + \zeta^2)}{\cos^2 2\theta} \right\}.
\]

By differentiating (25) with respect to \( \delta_o \) and substituting for \( \delta_o(\text{max}) = 2\delta_o \) we get

\[
\frac{\partial H}{\partial p} = 2\delta_o K_m / \delta_0,
\]

which on substitution into (26) gives the horizontal coordinate spread on the film for a particular energy. Substituting (27) into (26) and comparing with (11), we get

\[
(\partial H)_{\|} \approx \delta_o C (2 + d^2*) / \cos^2 2\theta.
\]

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\[
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\]

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\[
p = K_m(1 \pm \delta_o / \delta_0).
\]

In terms of the energy resolution, the distances over which a given energy, represented by \( \delta_0 \), is spread on the film must be found. Within a given fan there are many rays of a given energy because of the monochromator rocking width, and this may be represented by a variation in \( p \) as \( \delta_o \) varies in the range \( \pm \delta_o \) to gives a constant \( \delta_0 \). By differentiating (5) with respect to \( p \) we get

\[
\frac{\partial H}{\partial p} = \frac{\delta_o(2 - d^2*)(d^2* - 2C - 2S) - 4C^2 \delta_o}{(4\delta_o + 2 - d^2* + 2\delta_o p \zeta)^2},
\]

when terms in \( \delta_o^2 \) are neglected, giving by rearrangement and approximation of the denominator,

\[
\frac{\partial H}{\partial p} \approx \delta_o \left\{ S + \frac{C(\cos 2\theta + \zeta^2)}{\cos^2 2\theta} \right\}.
\]

By differentiating (25) with respect to \( \delta_o \) and substituting for \( \delta_o(\text{max}) = 2\delta_o \) we get

\[
\frac{\partial H}{\partial p} = 2\delta_o K_m / \delta_0,
\]

which on substitution into (26) gives the horizontal coordinate spread on the film for a particular energy. Substituting (27) into (26) and comparing with (11), we get

\[
(\partial H)_{\|} \approx \delta_o C (2 + d^2*) / \cos^2 2\theta.
\]
The horizontal distance over which a given energy is spread by the focus width and energy gradient may be obtained by differentiating (5) with respect to \( p \) as for the monochromator rocking width. In this case, however, the slit parameter \((l/2)u\) in (5) must be replaced by substitution from (31) before differentiation which gives

\[
\frac{\partial H}{\partial p} \simeq -\delta \left\{ S + \frac{C(\cos 2\theta + \zeta^2)}{\cos^2 2\theta} \right\} + \frac{l_H \delta}{2K \delta_{\text{foc}}}.
\]

From (31) we get

\[
\frac{\partial p}{\partial (l_H)^H} = \frac{K \delta_{\text{foc}}}{l_H \delta},
\]

which, since \([\partial (l_H)^H]_{\text{foc}} = 2l_H\) over the slit width, may be substituted into (32) to give

\[
(\partial H)_{\text{foc}} = l_H - \frac{\delta_{\text{foc}}}{\delta_{\text{corr}}}(\partial H)_{\gamma_H}
\]

after comparison with (11). Equation (34) shows that with a zero focus energy gradient, i.e. \( \delta_{\text{foc}} = 0 \) with all rays in a given direction then having the same energy, the slit width gives each energy smeared out over a distance equal to the slit size, as expected. In addition, it is noted that with the monochromator overbent, i.e. \( \delta_{\text{corr}} \) positive (Greenhough & Helliwell, 1982b), the energy smearing is reduced.

The change in spot size due to the slit width and focus energy gradient is found by a process similar to that for the monochromator rocking width. The effect as a whole is considered by use of a particular incoming direction over the whole slit width. Thus with \((l_H)^H\) constant in (7) substituted into (5) we get \((\partial H)_{\text{foc}} = H - H'\) where \( H \) is (5) with \( \delta = \delta_0 - \delta_{\text{foc}} \) [from (30) with \((l_H)^H = l_H\)] at the left of the slit and \( H' \) has \( \delta = \delta_0 + \delta_{\text{foc}} \) and \((l_H)^H = l_H\). This gives

\[
(\partial H)_{\text{foc}} \simeq \delta_{\text{foc}} \frac{C(2 + \cos^2 \theta)}{\cos^2 2\theta} + l_H,
\]

and we again note that the spot-size change is equal to the slit width when no focus energy gradient is present.

The final effects to be considered are vertical beam cross fire and vertical slit or sample size, although in most cases the cross-fire contribution will be negligible since this quantity is extremely small.

Differentiating (1) and (2) with respect to \((v/2)^V\), we get

\[
\frac{\partial V}{\partial (v/2)^V} = -\frac{C}{\cos^2 [v_H - (v/2)^V]} - S
\]

and

\[
\frac{\partial H}{\partial (v/2)^V} = \frac{C \tan v_H \sin [v_H - (v/2)^V]}{\cos^2 [v_H - (v/2)^V]}.
\]

By replacing \( \partial(v/2)^V \) by \( \gamma_V \) and substituting for \( v_H \) from (4) with \( v_H \) from (13), the approximate energy-independent results

\[
(\partial V)_{\gamma_V} \simeq \gamma_V \left\{ S + \frac{C(1 - \zeta^2)}{\cos^2 2\theta} \right\}
\]

\[
(\partial H)_{\gamma_V} \simeq \frac{\gamma_V}{L} \frac{C \zeta}{\cos^2 2\theta}
\]

are obtained.

The vertical size of the slit or crystal simply gives

\[
(\partial V)_{\gamma_V} = l_V,
\]

where \( l_V \) is the smaller of the two sizes. This may of course be variable over the crystal width as is illustrated in the main text. This contribution is particularly important since it will provide the majority of the vertical size of the spot, virtually all where the vertical beam cross fire is small, allowing the energy resolution at a given point in the diffraction spot to be calculated solely from the horizontal coordinate. A given energy in the correlated component is spread out over a horizontal distance \( \partial H^E \) on the film, given by the sum of the energy smearing factors, and the resolution of the correlated component is thus degraded to give

\[
\partial \delta = \frac{(\partial H^E)(\partial \delta_{\text{corr}})}{(\partial H)_{\text{corr}}} 2\delta_{\text{corr}}
\]

as the energy resolution at each point within the diffraction spot. Since \( 2\delta_{\text{corr}} = (\partial \delta/\partial \zeta)_{\text{corr}} \) (Greenhough & Helliwell, 1982b) we may write

\[
\partial E = \frac{(\partial H^E)}{(\partial H)_{\text{corr}}} (\partial E)_{\text{corr}}.
\]

**Glossary of terms**

- \( C \) crystal-to-film distance
- \( S \) crystal-to-slit distance
- \( H \) horizontal film coordinate
- \( V \) vertical film coordinate
- \( l_H \) slit size, horizontal width
- \( l_V \) vertical slit or crystal size, whichever is smaller
- \((l_H)^H\) slit-width coordinate, horizontal
- \((l_V)^V\) slit-height coordinate, vertical
- \( \delta_{\text{corr}} \) correlated spectral dispersion component
- \( \delta_{\text{c}} \) general value of \( \delta_{\text{corr}} \)
- \( \omega \) monochromator rocking width
- \( \omega_{\text{a}} \) monochromator rocking-width spectral-dispersion component
- \( \delta_0 \) general value of \( \delta_{\text{a}} \)
- \( \delta_{\text{foc}} \) focus-width spectral-dispersion component
- \( \gamma_H \) beam cross fire, horizontal
- \( \gamma_V \) beam cross fire, vertical
(γ)_H \quad \text{general value of } \gamma_H

(γ)_V \quad \text{general value of } \gamma_V

p \quad \text{variable scale factor relating } \delta \text{ and } (γ)_H, \text{ i.e. energy and direction}

K_m \quad \text{special value of } p, \text{ constant when only correlated spectral dispersion is considered}

δ \quad \text{general relative spectral dispersion } (\delta \lambda/\lambda) = (\lambda_{\text{mean}} - \lambda)/\lambda_{\text{mean}}

H_{\text{tot}} \quad \text{diffraction spot horizontal size}

V_{\text{tot}} \quad \text{diffraction spot vertical size}

References


