X-ray Absorption Spectroscopy in the Dispersive Mode with Synchrotron Radiation: Optical Considerations

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Abstract
Aspects of the optics of the energy-dispersive scheme for X-ray absorption spectroscopy are discussed. The idea of a set of monochromatic focus points related to a set of local Rowland circles is introduced to account for the source-size effect on the energy resolution. It is shown that there exists an optimized location of the position-sensitive detector where the energy resolution is no longer source-size dependent. In addition, the stability of the dispersive optical system has been estimated and a 10 meV energy-scale reliability is currently achieved.

I. Introduction
Great interest exists in extreme energy resolution in X-ray absorption spectroscopy. XANES (X-ray absorption near edge structure) is the more demanding since the exact shapes and positions of the edges are strongly correlated to the effective charge of the absorbing atom and its local environment (symmetry and bond lengths) (Benfatto, Natoli, Bianconi, Garcia, Marcelli, Fanfoni & Davoli, 1986). Furthermore, it has recently been demonstrated that information about spin densities in ferromagnetic metals can be derived and fit exactly theoretical predictions (Schutz, Wagner, Wilhem, Kienle, Zeller, Frahm & Materlik, 1987). Besides the circular polarization of the X-ray beam available with synchrotron radiation, such an experiment requires a very good signal/noise ratio to be sensitive to absorption changes as small as a few times $10^{-3}$ in a signal which is currently of the order of a few units. Since the derivative of an absorption edge is large, the data collection calls for an extremely reproducible energy scale from one spectrum to another. This is in principle easier to achieve with the energy-dispersive scheme than with the scanning mode.

By contrast X-ray absorption spectroscopy can be performed in a single shot as short as 6-7 ms when dispersive optics is combined with a position-sensitive detector able to work at the high flux of the synchrotron radiation. In our experimental station at LURE, a 23 cm long bent crystal is illuminated by the white X-ray beam. The incident angle varies continuously, yielding a continuous change of energy of the Bragg-reflected photons. The energy–direction correlation is transformed into an energy–position correlation on the detector. Since there is no mechanical movement during data collection the origins of possible shifts of the energy scale come from the crystal temperature and horizontal instabilities of the orbit (averaged over a few thousand turns) of the positron bunch stored in the ring. These points will be detailed in the second part of the present paper.

The cylindrical shape of the reflecting crystal yields a focus point which is the image of the source through the optics. This is the optimized position for the sample. Besides this polychromatic imaging, we shall examine in detail the beam paths followed by photons of the same energy coming from different positions in the source. In fact, these photons exhibit a second type of focalization, called herein monochromatic focalization, according to the local Rowland circle. This strongly controls the achievable energy resolution provided by the dispersive scheme and this is the main point of the first part of the paper.

To conclude the comparison of the two schemes one must recall that the energy-dispersive mode is incompatible with detection of the decay channels (electron yield and fluorescence yield), which has proved to be very efficient for surface investigation and extremely dilute samples. On the other hand, it permits in situ time-resolved structural investigations of numerous materials (Tourillon, Dartye, Fontaine & Jucha, 1986).

II. Energy resolution
(a) Geometrical considerations
The geometry of the curved crystal is shown in Fig. 1. The source-to-crystal distance $p$ is large compared with the radius of curvature $R$ of the crystal, which is bent in order to achieve a change of the Bragg angle large enough to open an energy bandpass of a few
hundred electronvolts in the case of EXAFS (extended X-ray absorption fine structure) but limited to about 100 eV for XANES. In both cases the polychromatic focus point is within the so-called Rowland circle whose diameter is equal to the radius of curvature of the crystal. (In fact there is a set of Rowland circles tangent to the crystal and passing through the centre of curvature of the crystal.) With the usual definitions of the parameters $p$, $q$, $R$, $\theta$ as shown on Fig. 1, it is easy to find the well known relationship of cylindrical optics,

$$\frac{1}{p} + \frac{1}{q} = \frac{2}{R \sin \theta},$$

giving the transmitted energy bandpass as

$$\Delta E = E \cot \theta \Delta \theta = E \cot \theta \left(\frac{l}{R} - l \sin \theta / p\right),$$

where $l$ is the illuminated length of the crystal. The last term in the brackets means that the initial curvature is first used to compensate for the horizontal divergence of the beam. When the expression in parentheses is equal to zero the Guinier conditions are fulfilled: the direction normal to the reflecting plane is changing along the crystal at exactly the same rate as the angle of the incident direction. Then the optics is reflecting a monochromatic beam. A curvature greater than this critical value of $R$ opens up the energy bandpass.

Between the intersection of the Rowland circle with the incident ray (B) and the crystal (A) the distance is $b = R \sin \theta$ (Fig. 2). Because of the finite size of the source it is possible to define a span of incident rays passing exactly through B. These rays diffract from the crystal in the Guinier conditions according to Bragg's law: a unique wavelength is reflected. This monochromatic span focuses at $B'$, symmetric to B with respect to the diameter of the local Rowland circle, which is also the local normal to the crystal. Moreover, because of the smallness of the region $\delta l$ that accepts a given energy, the focusing aberration, which is proportional to $(\delta l)^2$ (Ice & Sparks, 1984) is negligible and $B'$ is indeed a focus point. Therefore, if the detector is put at this 'monochromatic focus point' located at the distance $b$ from the very part of the crystal which is reflecting these specified photons, the energy resolution is no longer limited by the source size. All the photons with this energy fall into a single pixel of the detector.

If we consider the current situation on a synchrotron radiation beam line where the distance $p$ is always larger than $q$, one immediately finds that $b$ is almost twice the $q$ value. Therefore, the detector has to be installed at a distance which is almost twice as large as the crystal-to-sample distance.

Of course, this idea can be developed for all the energies included in the bandpass, taking into account the displacement of the Rowland circle along the crystal. The position of the 'monochromatic focus' is Bragg-angle dependent both because $b$ varies with $\theta$ but also because this $b$ value is measured from a point which runs along the crystal (points $A$, $A_1$ and $A_2$ in Fig. 2). Therefore, if the position of the detector is optimized for one photon energy, this will not be the case for the full bandpass. It turns out that the relevant questions deal with the field depth and the interplay of the parameters (pixel size, rocking-curve width, average Bragg angle, penetration depth in the crystal) involved in the energy resolution.

To complete the geometrical parameters needed to calculate the overall energy resolution let us define $\alpha$, the angle of view of the source from point B, as

$$\alpha = S / (p - R \sin \theta) = S / (p - b),$$

where $S$ is the source size.

(b) Energy resolution

The energy resolution of an X-ray reflector comes from the derivative of Bragg's law,

$$\delta E = E \cot \theta \delta \theta,$$

where $E$ is the nominal energy, and $\delta \theta$ is the overall
angular resolution which includes: (i) the spatial resolution of the detector, which is not exactly the pixel size. In a silicon-based photodiode array a bunch of electron–hole pairs can be created deeper than the pixel size even if the photon energy is of a medium value (~8 keV). Consistent with a diffusion length of the electron (mean free path before recombination) limited to about 75 μm (Peckerar, Baker & Nagel, 1977), a spatial resolution ρ = 50 μm has been ascertained by our measurements (Dartyge, Depautex, Dubuisson, Fontaine, Jucha, Leboucher & Tourillon, 1986). (ii) The size of the X-ray source, which contributes only in the conditions mentioned above. (iii) The intrinsic Darwin width of the rocking curve of the perfect crystal which decreases as the Z number (via the structure factor |Fhkl|) and the reciprocal of the classical h^2 + k^2 + l^2 sum (h, k and l being the Miller indices). In addition, one has to stress that reflection in the dispersive scheme occurs in the horizontal plane, which contains also the polarization vector (π polarization). Hence the Darwin width is reduced by the additional polarization factor |cos(2θ)|. (iv) The penetration depth of the incident X-ray into the bent crystal. Since the incident direction is not radial there is a slight change of the Bragg angle along the X-ray path. A dynamical approach must be used to account correctly for this effect. However, an upper limit can be deduced easily with a kinematical approach, which shows that this effect is negligible as long as the curvature of the crystal is not great.

Generally speaking, to achieve a good resolution requires decreasing three terms: E, cot θ and δθ. However, there is no real choice for the energy, which is related to the binding energy of the core level of the probed atom. On the other hand, the Miller indices control both the Darwin width and, more importantly, the cot θ value. Thence, real improvements can come only from the third term.

The first contribution δθ_1 proceeds with the angle of view of a pixel from the polychromatic focus point. This angle, ρ/d (d = the detector-to-sample distance), projected onto the crystal, defines a region δl correlated to a Bragg-angle change

\[ \delta \theta_1 = \delta l(1/R - \sin \theta/p) \]
\[ = (\rho/\sin \theta)(q/d)(1/R - \sin \theta/p) \]
\[ = Q(\rho/d) \]

where

\[ Q = [(1 - b/p)/(1 - b/2p)]/2. \]

As mentioned, the size of the source is not the main limitation of the energy resolution in the dispersive scheme, even if this source is large. There exists an optimized detector position for a given energy. But, for the other energies of the bandpass, the detector is misplaced. That offset contributes in the same way as the pixel size since at the detector position the mono-

chromatic span keeps a finite size. This mismatch can be put in terms of an angle δθ_2,

\[ \delta \theta_2 = Q\delta(b/d) \]
\[ = Q(1 - (b - q)/d), \]

where δb = d - (b - q) is the deviation from the best position of the detector for that particular photon energy.

Fortunately, owing to both the limited source size (~6 mm) given by the magnetic dipole of the DCI (LURE) storage ring and the long source-to-crystal distance (~15 m), the field depth, i.e. the acceptable misplacement, is large enough to keep a good resolution within a wide energy range. At the canonical copper K edge (E = 8979.8 eV), with the Si 111 reflection and q = 50 cm, the field depth is approximately 12 cm. In this range this factor is smaller than all other limiting factors.

The third contribution to the overall value of δθ is the angular width of the rocking curve (Darwin width) which is an intrinsic contribution of the crystal. Besides the three parameters already mentioned (Z number, Miller indices and polarization factor) one can change the angular width using asymmetrical cut crystals. If the angle of reflection is larger by 2δ than the incident angle measured from the surface, the rocking-curve width is reduced by [sin (θ + ψ)/sin (θ - ψ)]^1/2.

The last contribution to be considered is due to the finite crystal penetration depth which produces the reflected beam. The geometrical aspects of this effect are sketched in Fig. 3. For a given photon energy, due to the penetration depth 2δ there is a spread δl_d on the detector between the ray reflected from the top surface and the one coming out from the bottom of the typical depth which participates in the Bragg reflection. These two rays originate from two incident rays diverging by γ. After reflection their directions differ by σ. If there were no divergence of the incident beam δl_d should be limited to (δ cos θ sin θ). An additional factor must be included to take into account the divergence effect:

\[ \delta l_d = \delta \cos \theta \sin \theta [(1 - (b - \delta b/p)]/(1 - b/p). \]

A complete calculation is given in the Appendix. In terms of angle spread this gives rise to

\[ \delta \theta_3 = Q(\delta \cos \theta \sin \theta/d)[1 - (1 - b/2p)/1 - b/p]. \]

Since the crystals used in the dispersive scheme are not strongly bent, one must decide what determines the penetration depth. Is it the absorption length or the extinction length? The answer to such a question comes from estimation of δθ_3, in both cases and comparison with the Darwin width Ω. For 2δ to be absorption limited, which is the worst case, the δ cos θ/R factor has to be greater than Ω. For such a case, as at the copper K edge with an Si 111 monochromator, it turns out that R must be smaller than
Therefore, for the current curvature used (always > 5 m), it is nonsense to consider the absorption as the limiting factor which, on the contrary, is related to the extinction length. This gives $\delta \theta_3$ smaller by a factor of the order of ten than $\Omega$ (Freund, 1986). $\delta \theta_3$ should be considered only if one goes to higher-order and/or asymmetric reflections, where the Darwin width happens to be smaller or of the order of $3 \times 10^{-6}$ rad.

The overall angular resolution $\delta \theta$ is given by the convolution of all contributions:

$$\delta \theta^2 = \delta \theta_1^2 + \delta \theta_2^2 + \delta \theta_3^2 + \Omega^2$$

or

$$\delta \theta = \sqrt{\{\rho^2 + (a \delta b)^2 + (\delta \sin \theta \cos \theta)^2 \	imes [1 - (b - \delta b)/p]^2/(1 - b/p)^2\} (Q/d)^2 + \Omega^2}.$$

It is easy to show that this function reaches a minimum, for a given energy, at

$$\langle \delta b \rangle_{\text{min}} = \rho^2/[(a^2(b - q)]$$

or

$$\langle q + d \rangle_{\text{min}} = b + \rho^2/[(a^2(b - q)],$$

which is always almost equal to $2q$.

(c) Experimental approach

In order to check the dependence of the energy resolution on the detector-to-sample distance, we carried out three sets of measurements, two on the copper K edge using an Si 111 Bragg reflector with two different curvatures, the last one on the arsenic K edge of a chalcogenide sample, As$_2$S$_3$, which exhibits a well defined white line, using an Si 311 monochromator to achieve a good resolution.

Tests on the copper K edge ($E = 8979.8$ eV). Fig. 4 shows a series of XANES spectra of copper K edges for which the evolution of the energy resolution is quite clear, when focusing the attention on the pre-edge feature. Since each of them is the result of the addition of 1920 shots, which means 13 s in total for the acquisition time, the statistics are excellent. The energy resolution of each spectrum has been measured just at the edge and then compared with theoretical predictions. To perform such an estimation, one needs to know the hypothetical perfect spectrum. This role can be given to the one measured with an Si 311 crystal asymmetrically cut by $\psi = -12^\circ$ which reduces the Darwin width to $9 \times 10^{-6}$ rad and limits $\cot \theta$ to 2.15, instead of $3.3 \times 10^{-5}$ rad and 4.43 for Si 111 (Freund, 1986), respectively. By taking this last spectrum as a standard and by convoluting it with a window shaped as a binomial distribution, we fit the Si 111 measured XANES spectra. Such a window provides a width which is said to be the energy resolution. An asymmetrically cut Si 311 crystal has a theoretical energy resolution very much smaller than the width of the core hole ($\sim 1.5$ eV). Figs. 5(a) and (b) show the results for two bending radii of the crystal, 697 and 422 cm. These two values are directly derived from the location of the polychromatic focus point. The theoretical behaviour is clearly reproduced by our measurement. There exists a minimum of the resolution function which is smaller as expected when the crystal is less bent. Hence it is possible to collect data with an Si 111 crystal set at the copper edge with an energy resolution better than 2 eV, which is mostly controlled by the intrinsic angular Darwin width.

Test on the arsenic K edge ($E = 11855$ eV). Evidence for an optimized position of the detector is clearly shown in Fig. 6 which compares the white line of As$_2$S$_3$ according to the detector position. Essentially this set exhibits the same behaviour. By taking an approach similar to the previous one, we plot the variation of the measured energy resolution (Fig. 7). In this case the ideal reference was not available. So we chose to take the best one as the standard. Only the variation of the energy resolution is meaningful. However, to maintain consistency with the other curves, we plot the data points on the theoretical curve; the experimental minimum of the energy reso-

![Fig. 3. Geometrical aspects of the penetration-depth effect in the crystal. Two rays with the same energy are reflected at different positions owing to the penetration $\delta$ into the crystal. After reflection they diverge by an angle $\sigma$.](image)

![Fig. 4. Series of absorption spectra at the copper K edge with an Si 111 crystal monochromator for different detector positions. One can observe the evolution of the energy resolution as a function of the distance from the crystal by looking at the fine structure at the edge.](image)
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Fig. 5. Resolution as a function of the detector distance from the crystal monochromator at the copper K edge for two different curvature radii: (a) 697 and (b) 422 cm. Si 111 crystal monochromator was used. The source size used for the theoretical curve is 6 mm. The experimental points (+) are in good agreement with the theoretical curve (——).

Fig. 6. The energy resolution as a function of the detector distance from the Si 311 crystal monochromator is clearly seen by the attenuation of the strong white line at the arsenic K edge of a chalcogenide sample As₂S₃.

resolution is fitted a priori to the theoretical one, which is 1.2 eV.

(d) Discussion

The results given above clearly confirm the idea of a 'monochromatic focus point' according to each specific energy of the diffracted beam. This approach, related to the idea of a set of Rowland circles, was not included in earlier treatments (Greenhough & Helliwell, 1982; Matsushita & Phizackerley, 1981), which discussed the energy resolution in terms of energy bandpass. In our approach we trace all paths of photons of the same energy coming from the extended source and reflected by the crystal, and finally we analyse them at the detector position. These geometrical aspects are important to evaluate the source-size and penetration-depth contributions. The overall energy resolution is then obtained by convoluting them with the Darwin width and the pixel size.

It should be emphasized that the energy resolution is not dependent on the source size (for a quite large range in energy owing to the large field depth) and, in first order, it is not controlled by the optical aberrations of the curved monochromator. The aberrations just work to enlarge the polychromatic image of the source. Therefore, the limiting factors turn out to be the Darwin width and the spatial resolution of the position-sensitive detector. The last can be reduced by setting the detector far from the crystal and the first by going to higher-order and/or asymmetric reflections. However, if the detector is pushed away from the polychromatic focus point or if higher-order reflections are used the total energy bandpass is reduced according to the overall $\Delta \theta$ and/or to the cot $\theta$ terms.

III. Measurement accuracy and signal reliability

In order to demonstrate that the quality of the signal is photon limited we performed successive measure-
ments, decreasing for each spectrum the number of added frames. The six spectra shown in Fig. 8 are the results of the addition of 1920 single frames for (a), 320 for (b), 32 for (c), 8 for (d), 3 for (e) and one for (f). Each individual frame needs only 6.76 ms of acquisition time, with an Si 111 crystal bent to a radius of 676 cm. We decided to take the spectrum with the longest exposure time as a reference and calculated the root mean square (r.m.s.) of the difference from the other spectra. The saturation of the pixel, which is an individual detector itself, is given by 7.3 \times 10^4 photons at 9 keV, converted into 1024 ADU (analogue–digital units) for the ten-bit ADC used. So 1 ADU is equivalent to 72 photons. Each pixel collected, on average, 100 ADU per single frame above the absorption edge, i.e. 7200 photons. This value was used to calculate the r.m.s. As far as the statistics are concerned, one expects a r.m.s. value which varies according to the number of frames N as 

\[ \sigma_{\text{N}} = \sigma_{1920} \left( \frac{N}{1920} \right)^{1/2} \]

where \( \sigma_{1920} \) is the r.m.s. for the 1920-frame reference spectrum. This law was verified except for the spectrum comprised of 320 frames, as shown in Table 1.

**Table 1. Theoretical and measured root mean square (r.m.s.) for the absorption spectra shown in Fig. 8, with the first one (Fig. 8a) as reference**

<table>
<thead>
<tr>
<th>N</th>
<th>r.m.s. theor</th>
<th>r.m.s. meas</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0130</td>
<td>0.0110</td>
</tr>
<tr>
<td>3</td>
<td>0.0074</td>
<td>0.0075</td>
</tr>
<tr>
<td>8</td>
<td>0.0046</td>
<td>0.0046</td>
</tr>
<tr>
<td>32</td>
<td>0.0023</td>
<td>0.0021</td>
</tr>
<tr>
<td>320</td>
<td>0.0007</td>
<td>0.0018</td>
</tr>
</tbody>
</table>

verified for the measured r.m.s. of the 320-frame spectrum is due to that shift and, in fact, what we measured was not a real statistical noise, but a signal due to the difference between two shifted spectra, which is proportional to the local derivative. In addition, because each pixel is an individual detector with slightly different response, we were not able to compensate for this effect by shifting one of the spectra by the same fraction of a pixel.

Such accuracy in measuring the energy scale shift is only possible because of the strong derivative of the absorption edge. Subtraction of two successive spectra (Fig. 9a) partly reproduces the derivative of the single spectra in which one pixel covers 600 m eV (Fig. 9b). Hence, it is possible from the ratio of the peaks in Figs. 9(a) and (b) to measure the magnitude of the displacement of the energy scale, since the effective energy shift is small enough to keep a true linearity.

Furthermore, considering the r.m.s. of the quasi-flat differential signal before the absorption edge one can estimate the detectability of the energy shift to be 10 m eV, i.e. 0.015 of a pixel.

This extreme sensitivity qualifies X-ray absorption spectroscopy in dispersive mode as a probe to measure very minute changes in XANES related to the structural evolution of the sample. Once again we insist that such accuracy is achievable only because we are looking at an absorption edge whose large derivative gives rise to extreme sensitivity to any energy drift. In the general case, this shift has a physical basis and

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**Fig. 8.** Set of spectra with different acquisition time. Each spectrum represents the addition of (a) 1920, (b) 320, (c) 32, (d) 8, (e) 3 and (f) 1 frames. Each individual frame lasted 6.76 ms of acquisition time. Si 111 crystal monochromator curved to 697 cm was used.

**Fig. 9.** Comparison of the difference between the 1920-frame and 320-frame spectra (a) from Fig. 8 and the derivative of the 1920-frame spectrum (b). The ratio between amplitudes gives the shift of the energy scale in terms of a fraction of pixel.
arises from structural or chemical changes of the probed atom or ion. It is always possible to wait before data collection to ensure temperature stabilization of the optics. A more convenient way to cure this problem will be to put helium inside the vacuum chamber of the bent crystal, which allows more efficient heat transfer than radiation itself.

To close this section we remark that it is easy to convert the drift of the energy scale into a change in lattice parameter and then into a temperature increase since the expansion coefficient of silicon is well known:

$$\Delta E / E = - \Delta d / d = 0.1 / 9000 \approx 10^{-5},$$

which leads to an overall heating after the 1920-frame spectrum of ~4 K. Fig. 10 shows the temperature gradient as a function of time, measured from the drift of the energy scale. The crystal reaches equilibrium after about 5 min.

This study addresses indirectly the question of the beam instability which is a relevant question for synchrotron radiation sources. Within the present study, the fluctuations of the X-ray source are not larger than the lower limit of edge-shift detectability, i.e. 10 m eV. In the dispersive scheme we are only sensitive to the horizontal instabilities. In the present study the upper limit of the possible angular fluctuations is $\delta \theta = 2 \times 10^{-7}$ rad which, in terms of horizontal displacement of the source, yields an upper magnitude of 3 μm, with a source-to-crystal distance of 15 m. This figure is given at the copper K edge using Si (111) as the reflecting plane. It is obvious that this value is very dependent on the probed element and the average Bragg angle, via $E$ and $\cot \theta$, which amplifies any change in $\delta \theta$. The LURE-DCI storage ring has the recognized quality to give a very stable source since it is injected with positrons. The vertical stability of this storage ring has also been measured previously and compares favourably with other European sources.

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**APPENDIX**

When a ray penetrates a length $\delta$ into a curved monochromator, its angle with the lattice planes changes by $\delta \cos \theta / R$, where $\theta$ is the Bragg angle with those planes and $R$ the curvature radius (Fig. 3). Owing to the beam divergence, another ray diffracted at the surface with the same angle $\theta$ will not be parallel to the first one. These two extreme rays with the same energy come from different positions in the crystal and have a divergence $\sigma$. They will reach the detector at different positions, giving rise to a spatial broadening of the resolution.

The condition for the two rays to have the same energy is

$$(\delta \cos \theta + \varepsilon) (1 - b/p)/R = \delta \cos \theta / R.$$

The divergence after diffraction is given by

$$\sigma = \gamma p/q - 2 \delta \cos \theta / R = \delta \cos \theta \sin \theta / [p(1 - b/p)]$$

Hence, the spatial resolution is

$$\delta r = \sigma [d + q + (\delta \cos \theta - \varepsilon) \sin \theta / \sigma] = \delta \cos \theta \sin \theta / [p(1 - b/p)][d + q + p(1 - 2b/p)]$$

which converted into an angular resolution gives

$$\delta \theta = Q \delta r / d = \delta \cos \theta \sin \theta / (1 - (b - 2b)/p)Q/d.$$

**References**


Simultaneous Structure Refinement of Neutron, Synchrotron and X-ray Powder Diffraction Patterns

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Abstract
A technique has been developed for the simultaneous analysis of several powder diffraction data on the basis of the Rietveld method. Counting rates from one specimen at a given temperature taken at neutron, synchrotron or X-ray powder diffractometers are joined to one single data set with weights given by the counting statistics. The structure is refined from this data set with a parameter field containing one structural model and individual zero points, scale factors and FWHM parameters for each of the methods and data sets. A new definition of the residuals is given. The residuals and goodness-of-fit values are calculated for all as well as for the individual data sets.

1. Introduction
The structure refinement by profile fitting introduced by Rietveld (1967, 1969) for fixed-wavelength neutron powder diffraction data and modified by Hewat (1974) for anisotropic thermal vibration opened the way for the revival of powder methods in crystallography. Numerous authors used Rietveld’s fundamental idea as the basis for several modifications dedicated to special experimental techniques, in particular for the structure refinement of X-ray data (Young, Mackie & Von Dreelle, 1977; Wiles & Young, 1981; Young & Wiles, 1982). A comprehensive review of developments up to 1982 is given by Albinati & Willis (1982).

Since 1982 quite a few authors have focused on improving the profile function, because the Gaussian approximation turned out to be insufficient for the description of high-resolution X-ray or synchrotron data. Lorentzian, Voigt and pseudo-Voigt functions were very valuable improvements of the X-ray refinement procedures (Young & Wiles, 1982). With the program of Wiles & Young (1981) two different structures may be refined from one diffraction pattern collected from a mixture of two different compounds. A further extension to multistructure refinement from one data set was done by Bendall, Fitch & Fender (1983).

The different diffraction methods available allow the collection of several, in many respects complementary, data sets from one kind of specimen. Structure refinements with these data in general yield different results, so it is difficult to extract a single model from the data of various methods. Neutron diffraction data, for example, are in many cases more sensitive to oxygen positions. They may at the same time be very insensitive to weak lattice distortions. Just the opposite situation may occur, for instance, with synchrotron data taken from heavy-metal oxides.

In this paper we present a program for the structure refinement of several diffraction data sets collected with different methods from one kind of material at a given temperature. All data may be combined, so the user is able to fit X-ray, neutron and synchrotron diffraction profiles simultaneously to find a single structural result. Furthermore this method can be applied to several data sets collected with the same apparatus if, for example, a diffraction pattern is measured in several parts, with different fixed wavelengths or with multiple counters. In the latter case, each counter contributes one data set to the collective refinement.

A matrix formalism of Rietveld’s method for one data set is outlined in § 2. In § 3 the theory is given for several data sets. Fit criteria are discussed in § 4. The realization of the program is described in § 5. In § 6 a summary of the options of the program is given.

2. Theory of the Rietveld method for one data set
The structural model is refined by minimizing the residual $R$ with respect to parameters $\alpha$ in the least-squares sense

$$R(\alpha) = \sum_i w_i [Y_{i}^{\text{obs}} - Y_{i}^{\text{back}} - Y_{i}^{\text{calc}}(\alpha)]^2.$$  

The summation is over all points which participate in the refinement. $Y_{i}^{\text{obs}}$ and $Y_{i}^{\text{calc}}(\alpha)$ are the observed and calculated intensities at the $i$th step (i.e. at the angle $\theta_i$) with background $Y_{i}^{\text{back}}$. The vector $\alpha$