Abstract

One of the main sources of error when studying weakly absorbing materials using an X-ray diffractometer with Bragg–Brentano focusing geometry is specimen transparency. Its undesired effects (peak displacement and loss of intensity in the medium angular range) can be avoided by using a slab-like specimen in symmetrical transmission, in which case the type of diffractometer is more or less immaterial except that a non-focusing diffractometer offers a series of advantages, e.g. a very simple lining-up procedure and the possibility of using rod-like specimens. Such a diffractometer with a flat monochromator in the primary beam is described and both the equatorial aberration and the axial aberration are discussed.

Introduction

There is no doubt that the Bragg–Brentano focusing arrangement is the most widely spread and the most frequently utilized one in the X-ray diffractometry of polycrystalline and amorphous materials. However, for samples consisting of light elements, the effect of X-rays deeply penetrating into the sample, i.e. the transparency of the specimen, must not be overlooked. It gives rise to a shift of the diffraction peak towards lower scattering angles and to an asymmetrical broadening of the line profile. Although these effects are well known (Wilson, 1963) they seem to be very often ignored or their consequences underestimated in practical X-ray work. Special attention must be called to X-ray diffraction studies on amorphous materials such as common oxide glasses, polymers and liquids such as water, alcohols etc. where a radiation of short wavelength is used for the sake of a high limit in the scattering variable s = (4π/λ) sin θ (where θ is the half scattering angle and λ is the wavelength).

As an example let us consider a sample with a linear absorption coefficient μ = 1.6 cm⁻¹ and a diffractometer with radius r = 25 cm. Specimen thickness should be sufficient to meet the condition for Wilson’s treatment which leads to Tables 4.1–4.3 of his book (Wilson, 1963). The effects of sample transparency are shown in Fig. 1. It can be seen that in spite of relatively small divergence and acceptance angles (both equal to 1°), the angular displacement of a diffraction maximum at 2θ = 90° amounts to 0.26°. Whereas the angular displacement itself monotonically diminishes if the scattering angle decreases from 90 to 0°, the relative error of peak position with regard to the s scale increases. In the vicinity of the strongest diffraction halo the relative error in s is more than 1%, and at 2θ ≈ 45° it is about 0.5%. The exact measurement of atomic distances in amorphous materials (estimated to have an error of about 0.01 Å, see e.g. Gatineau, 1972) assumes, however, that the relative error of s is about 0.5% or smaller in the whole range of measurement. Apart from the fact that the shape of the diffraction peaks is also modified their displacements alone are too great simply to be neglected.

The example given here is not in any way an...
extreme one. Investigating boron oxide by means of Rh $K\alpha$ radiation or Ag $K\alpha$ radiation one has $\mu = 1.2$ or $\mu = 0.97 \text{ cm}^{-1}$, respectively, and the shift of the strongest diffraction halo amounts respectively to 1.4 or 1.6% in the $s$ scale. In the case of water the corresponding values are $\mu = 0.85 \text{ cm}^{-1}$ and 1.6%, and $\mu = 0.7 \text{ cm}^{-1}$ and 1.8%, respectively.

Another disadvantage of a weakly absorbing reflection specimen (Milberg, 1958) consists in considerably reducing the intensity in the medium angular range of measurement (see curve c in Fig. 1), where the intensity is already reduced by polarization. In consequence, the allowance for both absorption and polarization becomes a very critical task. By using a relatively thin slab as a specimen it is, of course, possible to reduce the peak displacements. In this way, however, we have to put up with a considerable loss of overall intensity.

**Bragg–Brentano reflection and symmetrical transmission**

In order to find an expedient solution to the problem it is sufficient to point out one fact of the well-known Bragg–Brentano geometry. If the points of the sample surface $E_1$ meet the condition for focusing (see Fig. 2) then the same holds true for the points of a plane $E_2$, which is parallel to $E_1$ but lying deeper within the sample. For these points, however, the effective scattering angle is larger than the scattering angle for the surface points. If there existed another parallel plane, which is nearer to $F$ and $R$ in Fig. 2, then the effective scattering angle would be smaller. Hence it follows that the peak shift is due to the fact that the whole volume of the reflection specimen is normally on one side of the goniometer axis. One might suppose that the shift could be eliminated by displacing the specimen parallel to itself so that the scattering volume should properly be distributed around the goniometer axis. As shown by Wilson (1963) the shift is given by

$$\langle 2\alpha \rangle = \frac{2 \cos \theta}{r} \langle x \rangle,$$

where $x$ is the distance of a scattering volume element from a plane containing the goniometer axis and parallel to the face of the specimen and $r$ is the diffractometer radius. In the simplest case of a large plane-parallel specimen of thickness $t$ we have

$$\langle x \rangle = \int_{x_1}^{x_2} x e^{-kx} dx / \int_{x_1}^{x_2} e^{-kx} dx,$$

where $x_2 - x_1 = t$ and $k = 2\mu / \sin \theta$. Obviously, it is possible to achieve $\langle x \rangle = 0$ by an appropriate choice of the limits of the integrals. However, since the exponential functions depend on $\theta$ each scattering angle would require a new adjustment of the sample which could only be realized by considerable technical expenditure.

The question arises whether the peak shift caused by the transparency could not be avoided by another type of focusing geometry. We refer to the paper by Lang (1956) who discussed four different arrangements with single-bent-crystal monochromators in the diffracted beam and select the combination reflection monochromator and transmission specimen.

Let $E_1$ in Fig. 3 be a plane parallel to the face of our slab-like specimen and situated so that it contains the axis $O$ of the goniometer. Each point of this plane between $A$ and $B$ scatters X-rays in all directions, but the bent monochromator crystal $M$ reflects only those rays to the receiving slit $R$ which apparently come from the virtual focal spot $F^*$. The crucial point is that the upper part of Fig. 3 is essentially the same as Fig. 2, i.e. the points $F, A, O, B, F^*$ correspond with the points $F, A, O, B, R$, respectively. Therefore, we can transfer the above-mentioned results to the transmission specimen too. The scattering of a plane $E_2$ parallel to $E_1$ corresponds to a larger or smaller scattering angle. For a given distance between $E_1$ and $E_2$ the absolute value of the aberration angle $2\alpha$ is the same as in the case depicted in Fig. 2 (provided we have the same diffractometer radius). From this point of view there is no difference between reflection and transmission specimens. There will be a difference, however, if the absorption is taken into consideration. In symmetrical transmission all beam paths within the sample are of equal length, thus all volume elements of

Fig. 2. Focusing of rays scattered by deeper layers of the specimen.

Fig. 3. Focusing diffractometer with transmission specimen.
the same size, independently of their position, contribute equally to the intensity recorded by the detector. By analogy with formula (1) we now have

$$\langle 2\sigma \rangle = \frac{2 \sin \theta}{r} \langle x \rangle.$$  

(2)

Since the contributions of the layers at different depths do not have to be weighted by an x-dependent function, now \(\langle x \rangle\) is simply the x coordinate of the centre of gravity of the irradiated parallelogram-like cross section. If the specimen is adjusted so that its symmetry plane contains the goniometer axis \(O\), the displacements of the diffraction peaks are zero for all scattering angles.

As can be seen, the effects due to specimen transparency only depend on the specimen itself and are independent of the special kind of focusing geometry. Provided that a transmission specimen in the symmetrical position and with its centre of gravity in the goniometer axis is used, any arrangement precludes peak displacements owing to transparency. This also holds true, for example, for diffractometers which have the monochromator in the primary beam. To show this one has simply to exchange the detector for the X-ray source in Lang's schemes.

The great advantages of symmetrical transmission were first utilized by North & Wagner (1969) in their studies on liquid metals and by Ergun, Braun & Fitzer (1970). Both groups made use of a bent monochromator crystal in the primary beam. Such a scheme is better than those given by Lang (1956) because very small scattering angles are attainable. Lang's diffractometers have the disadvantage that the monochromator enters the divergent primary beam at the back of the transmission specimen. On the other hand, some difficulties arise from the fact that Lang and Ergun et al. use an asymmetrically ground and bent crystal. Not only the preparation of the crystal but also the adjustment is more intricate.

The non-focusing diffractometer

In this paper an alternative diffractometer scheme will be presented which excels in a simple lining-up procedure and versatility. The diffractometer is a non-focusing instrument and has proved a success in many cases, above all in studies of weakly absorbing amorphous materials, such as water (Hajdu, Lengyel & Pálinkás, 1976), carbon (Cervinka, Dousek, Jansta, Neumann & Steil, 1981), vitreous silica (Steil & Herm, 1980), but also in studies of amorphous materials with higher densities, e.g. metallic glasses (Vajsz et al., 1980; Hajdu, 1980; Svab, Fergacs, Hajdu, Krod & Tokacs, 1981) and chalcogenide glasses (Pohle, Feltz, Steil & Herm, 1984).

The geometry of the non-focusing diffractometer, outlined earlier by Hajdu & Pálinkás (1972), is shown in Fig. 4. A flat-crystal monochromator directly attached to the X-ray tube reflects the K\(\alpha\) doublet so that its 'centre of gravity' lies on the axis of the goniometer. Normally the specimen is a thin slab in symmetrical transmission. Only those scattered rays which can pass the receiving slit \(S_4\) are recorded by the detector. The diaphragms \(S_1, S_3\) and \(S_4\) eliminate undesired scattered radiation. The slit of \(S_3\) is so wide that the detector can 'see' the whole irradiated volume of the specimen, except possibly for very large scattering angles. Such a design has the following advantages:

1. Although the merits of the transmission method can be fully utilized (Hajdu & Pálinkás, 1972) the lining-up procedure is much simpler than in the case of a focusing diffractometer.

2. The almost inevitable minor changes of the adjusted device do not seriously affect the measured intensity. So the device is exceptionally suitable for long-time measurements and data accumulation in the sense of Peters & Milberg (1966), provided that the monochromator mounting is well constructed and the temperature of the cooling water is controlled (Herm, Derno & Steil, 1980; Herm, 1980).

3. Because the cross section of the primary beam is a relatively narrow rectangle with its longer side parallel to the goniometer axis the specimen can also have the form of a cylindrical rod. This enables the investigation of very small quantities of powders or liquids enclosed in a capillary tube or free running jets of liquids (Herm, 1980). It has been shown that the radial distribution curve derived from powdered material in a capillary tube is in best accordance with the radial distribution curve derived from a slab-like specimen (Herm, Derno & Steil, 1983).

4. Even reflection specimens can be used without changing the adjustment. This allows the investigation of materials with higher absorption coefficients or measurement up to very high scattering angles where the transmission method becomes susceptible to certain systematic errors (Klug & Alexander, 1974; Wright, 1974). In both cases the transparency effect is negligible.

5. The scatter of a transmission specimen or of a rod-like specimen can be measured down to very small
angles (2θ = 2°). In this respect the non-focusing instrument is superior to the Bragg–Brentano device, but also to focusing transmission devices with diffracted-beam monochromators. Hence an additional measurement with a longer wavelength (e.g. Cu Kα) is unnecessary and so the fitting procedure of two data sets, a well known source of error (Grjotheim, 1958; Wright, 1974), is unnecessary.

6. The use of an incident-beam monochromator is the best way to handle the Compton scattering if no extreme resolution of the radial distribution function is required (Ruland, 1964; Black & Cundall, 1965; Wright, 1974).

7. If high resolution needs to be attained the diffractometer can easily be supplemented by a fluorescence excitation device (Warren & Mavel, 1965) without altering the alignment.

On the other hand, the described non-focusing arrangement exhibits some disadvantages too:

1. Fluorescence radiation possibly originated by the sample is fully recorded by the detector. This is, however, of no importance if the sample consists exclusively of light elements (about Z < 29, depending on the wavelength used; see e.g. Bol, 1967).

2. The intensity across the irradiated area of the specimen is not constant. The intensity profile is bell shaped and slightly asymmetric. This renders the allowance for absorption of rod-like specimens more difficult, but the problems are not insurmountable (Zickert & Vandrey, 1980).

Non-focusing diffractometers have a bad reputation for their weak intensity. Is that really so? To give a passably true idea we will compare the described non-focusing arrangement with the Bragg–Brentano arrangement because this is much better known than the focusing devices with a transmission specimen. For this we will refer to an (otherwise equivalent) instrument with a Johansson crystal monochromator (LiF) in the diffracted beam and a divergence angle of 2°, and we will consider the study of vitreous silica. The transmission specimen was given as a thin slab of about 1 mm thickness and the reflection specimen as a slab of 5 mm thickness. Provided the other conditions are equal then the non-focusing diffractometer yields about the threefold intensity if a flat graphite crystal (Union Carbide Corp.) and a receiving slit 4 mm wide is used. Of course this superiority is partly purchased with a greater divergence. By careful inspection of the two scattering curves, however, differences with respect to the breadths of the diffraction haloes are not detectable. This is not astonishing if one takes into consideration that the aberrations we will discuss in the next chapter are still small compared with the breadths of the diffraction haloes. Comparing the intensities we, of course, confined ourselves to such an angular range in which the Compton component is still small and its experimental elimination by the diffracted beam monochromator is not yet effective (2θ < 20°, Mo Kα, 35 kV).

Equatorial aberrations of the non-focusing diffractometer

Using an unconventional diffractometer design one must be sure that the geometrical aberrations produced by the instrument remain within proper limits. Among others the most important questions are how the aberrations depend on scattering angle and specimen thickness, and whether there are limitations of the applicability of the instrument. Firstly, let us consider the equatorial aberrations due to (1) the divergence of the primary beam and (2) the finite width of the receiving slit and the extent of the irradiated part of the specimen.

1. Though the monochromator crystal is chosen with a view to providing as intense reflection as possible, and often special techniques are employed to increase the mosaic character, the angular divergence of the primary beam is small compared with that of usual diffractometers and also with the aberrations described in (2). Both lines of the Kα doublet are reflected. Using, for example, an LiF crystal and Mo Kα radiation the centroids of the two superimposing lines have a distance of about 0.27 mm in the centre of the goniometer (r = 250 mm). So the intensity profile is asymmetric with a shoulder at one side. The basis width is about 0.8 mm if a line focus is used.

2. The factors in this case give rise to much greater aberrations. To clarify the conditions it is sufficient to calculate the limiting values of the aberration angles 2e. Fig. 5 illustrates the situation in the equatorial plane. We see the specimen with thickness t; the primary beam which can be regarded as a parallel beam of width s; and the detector slit of width b. The

Fig. 5 Calculation of the limiting aberration angle for a transmission specimen.
centre of gravity of the irradiated cross section should lie in the goniometer axis \( O \). In the symmetric transmission arrangement the angle \( \psi \) subtended by the primary beam and the front face of the specimen is equal to that subtended by the back face and the connecting line from the goniometer axis to the middle of the receiving slit and is \( 90^\circ - \theta \). For the sake of clarity, in Fig. 5 the distance \( r \) between the goniometer axis and the receiving slit is drawn on a smaller scale.

The greatest aberration angles obviously correspond to the ray scattered from the left corner point \( M \) of the irradiated area to the right edge of the detector slit, and to that from the right corner point \( N \) to the left edge, respectively. For the angle mentioned first we can see from Fig. 5 that

\[
\tan 2\epsilon = \frac{MQ + b/2}{r - OQ}
\]

where

\[
\begin{align*}
MQ &= MR + s/2 \\
&= t \cos \psi + s/2
\end{align*}
\]

and

\[
\begin{align*}
OQ &= OP + PQ \\
&= OT \cos \psi + MT \cos 2\psi \\
&= \frac{s}{2 \tan \psi} + t \cos 2\psi
\end{align*}
\]

Therefore,

\[
\tan 2\epsilon = \frac{b + s + 2t \cos \psi}{2r - (s/tan \psi + t \cos 2\psi/\sin \psi)}
\]

or

\[
\tan 2\epsilon = \frac{b + s + 2t \sin \theta}{2r - (s \tan \theta - t \cos 2\theta/\cos \theta)}. \tag{3}
\]

For the other limiting angle we find an analogous formula but with opposite sign of the bracketed expression in the denominator. The two values differ only very little because the term in brackets is small as against \( 2r \); this is true except for extremely large \( 2\theta \) angles, which are in any case not attainable. The results are represented in Fig. 6 by the curves \( a, b, c \) assuming \( r = 250 \) mm, \( b = 3 \) mm, \( s = 0.8 \) mm and \( t = 1, 2 \) and \( 3 \) mm, respectively. The function \( \tan 2\epsilon \) has its smallest value \((b + s)/(2r + 2t)\) at \( 2\theta = 0^\circ \) and increases monotonically with growing scattering angle. Excluding the highest scattering angles the function is approximately of the type \( m + n \sin \theta \) (\( m \) and \( n \) constants) since the denominator hardly deviates from the constant \( 2r \). The behaviour of the functions in the closest neighbourhood of \( \theta = 90^\circ \) is of no practical interest.

Bearing in mind that \( 2\epsilon \) given by (3) is a limiting value, we can say that the aberration remains within tolerable limits compared with the width of the diffraction halos of amorphous materials. If necessary the aberration could easily be diminished by choosing a smaller width \( b \) of the receiving slit. The corresponding change of the curves can approximately be described as a parallel shift towards the abscissa axis. The thickness \( t \) should not exceed 1–2 mm even if \( \mu \) is very small.

In the case of a reflexion specimen with usual adjustment (goniometer axis touching the front face of the specimen) the formulae

\[
\tan 2\epsilon' = \frac{b + s}{2r + s \cot \theta} \tag{4}
\]

\[
\tan 2\epsilon'' = \frac{b + s + 4t \cos \theta}{2r - (s \cot \theta + 2t \cos 2\theta/\sin \theta)} \tag{5}
\]

for the limiting values of the aberration angles can be derived. Through the receiving slit one can see the scattering volume limited on one side by an edge lying in the front face of the specimen and on the other side by an edge lying in the back face. The aberration angle \( 2\epsilon' \) in (4) corresponds to the first edge and \( 2\epsilon'' \) in (5) to the second. Except for close vicinity to \( \theta = 90^\circ \) we always find \( 2\epsilon'' > 2\epsilon' \) indicating the one-sidedness of the broadening effect. Under realistic conditions \( 2\epsilon' \) is almost independent of the scattering angle \( 2\theta \) apart from \( 2\theta \rightarrow 0 \) where for an extremely long specimen \( 2\epsilon' \) drops abruptly (Fig. 6). The function \( 2\epsilon'' \), on the other hand, has its minimum value \((b + s)/(2r + 2t)\) [a little smaller than the upper limit \((b + s)/2r\) of \( \tan 2\epsilon \)] at \( \theta = 90^\circ \) and increases monotonically if the scattering angle decreases. In a wide range the func-

![Fig. 6. Maximum aberration angles as a function of Bragg angle \( \theta \).](image)
tion can be approximated by \( m + n \cos \theta \) (where \( m \) and \( n \) are constants) but for \( \theta \to 0 \) the values exceed all limits. This emphasizes the incapacity of the Bragg-Brentano reflexion method for precise measurements in the small-angle range, especially if \( \mu \) is low.

**Axial aberration of the non-focusing diffractometer**

The use of a plane monochromator in the primary beam necessitates a special consideration of the effects of focal, specimen and receiver height. In Fig. 7 let \( F \) be a point-like X-ray source, \( E \) the surface plane of the monochromator crystal and \( A \) a point of \( E \) fulfilling the conditions for Bragg reflexion of the \( K_\alpha \) wavelength. If \( P \) is the foot of the perpendicular from \( F \) to plane \( E \) we can say that all points lying on the circle \( PA \) (dotted in Fig. 7) are able to reflect the \( K_\alpha \) wavelength. Since the pencil of rays coming from \( F \) is limited by the casing of the X-ray tube or the entrance aperture of the monochromator housing, only a part of this circle (e.g. the arc \( AB \) in Fig. 7) really reflects. All reflected rays seem to come from \( F^* \), the reflected image of \( F \). Restricting ourselves to the merely geometrical description of the reflected beam, we can replace the reflecting plane \( E \) by an opaque screen with an arc-like slit \( AB \) if, additionally, the point focus is displaced from \( F \) to \( F^* \). Further, we can neglect the bend of the slit \( AB \) because in reality the height of the crown is very small against the distance \( AB \). Thus, concerning the primary beam alone, we have reduced the problem to the case first treated by Wilson (1941). If we now replace the point focus by a focal line parallel to the line \( AB \) we have the case described by Pike (1957). Contrary to common treatment, however, in our non-focusing arrangement the distance \( s \) between the virtual focal spot \( F^* \) and the goniometer axis \( O \) is usually greater than the goniometer radius \( r \). The choice of \( s > r \) is the simplest way (1) to make room for the monochromator; and (2) to reduce the axial aberration. In doing this we profit from the fact that the intensity approximately decreases with the first and not the second power of the distance from the virtual focal spot \( F^* \).

We start from equation (12) of Eastabrook (1952) because this comprises the case \( s \neq r \). Introducing a parameter \( v \) defined by \( r = vs \) (\( 0 < v \leq 1 \)), we obtain for non-focusing diffractometer

\[
\langle 2\epsilon \rangle = \frac{1}{3} \left( \frac{h}{r} \right)^2 \left[ \left( \frac{v^2}{2} + 1 \right) \cot 2\theta + v \cosec 2\theta \right]
\]

if a point source is used and

\[
\langle 2\epsilon \rangle = \frac{1}{3} \left( \frac{h}{r} \right)^2 \left[ (v^2 + 1) \cot 2\theta + v \cosec 2\theta \right]
\]

if a focal line (as high as sample and receiving slit) is used. Here the multiplying factors of the trigonometric functions (denoted by \( Q_1 \) and \( Q_2 \) in the literature) depend on \( v \) and are generally not integers. For the special value \( v = 1 \) we find \( Q_1 = 2 \) and \( Q_2 = 1 \) in (7), but \( Q_1 = 1.5 \) and \( Q_2 = 1 \) in (6).

Making use of these formulae, we will now compare the axial aberration of the non-focusing diffractometers used by us with that of customary diffractometers of the following designs:

(1) source, specimen and receiver of equal height (2h) without Soller slits (this design denoted by \( W \));
(2) the same but with one set of Soller slits (\( O \))
(3) the same with two sets of Soller slits (\( T \)).

From the Soller slits we assume that the ratio 'spacing of foils to length of foils' is 1:33 times greater than \( h/r \).

The one non-focusing diffractometer is characterized by \( v = 0.69 \) and a point focus \( 0.5 \times 1 \) mm (\( R \)), the other by \( v = 0.83 \) and a line focus (\( B \)). For all five diffractometers the ratio \( h/r \) is assumed to be equal to 0.025.

As examples we will consider the scattering angles \( 2\theta = 5, 10 \text{ and } 20^\circ \). The values of \( \langle 2\epsilon \rangle \) are given in Table 1.

<table>
<thead>
<tr>
<th>( \theta (^\circ) )</th>
<th>( W )</th>
<th>( B )</th>
<th>( R )</th>
<th>( O )</th>
<th>( T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.14</td>
<td>0.26</td>
<td>0.22</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
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<td>0.17</td>
<td>0.13</td>
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<td>0.053</td>
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<td>0.10</td>
<td>0.084</td>
<td>0.065</td>
<td>0.054</td>
<td>0.026</td>
</tr>
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</table>

It can be seen that the asymmetric lay-out (\( s > r \)) and especially the use of a point source are suitable as a means of reducing the axial aberration. So, with the design 'R' the characteristics of the design 'O' (with one set of Soller slits) can nearly be achieved. For scattering angles greater than 10–20° the peak displacements are small compared with those which can occur due to specimen transparency (see e.g. Fig. 1). Deriving advantage from the non-focusing arrangement down to very small angles requires, however, additional measures, e.g. the insertion of Soller slits into the diffracted beam. Whether such measures are necessary or not depends somewhat on the angular position of the innermost diffraction halo.
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