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Diffractometer measurement of low-order powder reflexions.

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1. Introduction

A precise determination of low-order lines is necessary when the high-angle region is too crowded, or too weak, to be of any use for:

(i) indexing of patterns when the unit cell is unknown;
(ii) measuring lattice parameters;
(iii) measuring differences in line position between various specimens, caused e.g. by solid solution or by structure defects.

A vast number of research problems falls into the above categories if the angular region is specified as $2\theta = 0°$–$45°$, with special emphasis on the region 5°–30°, though of course no fixed limits can be given.

As to precision, present diffractometer as well as focusing-camera techniques allow measurements of 2θ to within $\pm 0{\cdot}01°$ in routine determination. Such an accuracy is usually sufficient to make indexing possible (de Wolff, 1957). There can be no doubt, however, that improved accuracy greatly simplifies the indexing problem (Pike, 1959) and that it would be very useful for applications (ii) and (iii) as well. Accordingly, the present paper deals with attempts to reduce the error to a few thousandths of a degree.

2. Existing methods

One way of dealing with the problem is to use an internal standard with known cell constants. This solution is, in principle, capable of yielding a precision limited by the instrumental accuracy and the precision of the lattice parameter of the standard. However, its application is often tiresome, because the necessary sequence of standard lines in the low-angle region is likely to cause frequent overlappings with lines of the unknown. Also the proportion of the mixture is not easily matched to give satisfactory conditions of intensity, and the background is higher than it is for the pure sample. Finally, a suitable standard is sometimes difficult to find because of physical or chemical requirements.

The internal-standard method therefore cannot be regarded as universal. In looking for other methods, one cannot escape an investigation of line profiles, shifts and breadth as caused by various instrumental effects. It then turns out that photographic methods are ruled out because the strongly asymmetric profiles caused by vertical divergence cannot be measured with the required precision; essentially these methods have too many non-linear properties. To reduce the asymmetry very long exposure times are needed. Moreover, photographic methods suffer essentially from the same difficulty in eliminating the 'specimen-displacement error' as other existing methods, as described below.

The normal 'reflexion-type' diffractometer has been investigated thoroughly. A diffraction line can be measured by determining its centre of gravity and applying a few simple corrections (see for example, Parrish & Wilson, 1959). The basic difficulty appears to be the uncertainty of the spectral line profile. This is not very important for our problem, since the ensuing angular error does not exceed $0{\cdot}001°\ \theta$ in the low-angle region.

One correction, however, the 'specimen-displacement error' cannot be made in the usual way by extrapolation, since it is assumed no high-angle lines are available. Once the low-angle lines have been indexed, this correction could of course be found as an extra parameter. For low-symmetry compounds this is by no means easy, and it is of no help in the cases (i) and (iii) mentioned above. The error is likely to be important; it is equal to $114{\cdot}6\ (t/R)\cos\theta$ (in degrees 2θ) where t = displacement and R = goniometer radius (Wilson, 1951).

3. Advantages of 'transmission-type' diffractometer

A much more favourable situation exists for the diffractometer combined with a focusing monochromator as shown in Fig. 1. This instrument is closely related to

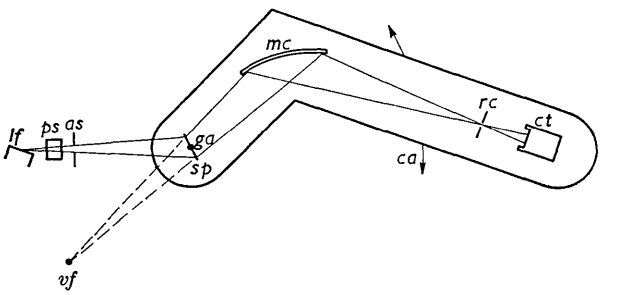

Fig. 1. Geometry of the transmission-type diffractometer.

lf: tube line focus.
ps: parallel (Soller) slits.
as: aperture slit.
sp: specimen, rotating at half the speed of the counter arm.
vf: virtual focal line of monochromator.
ga: goniometer axis.
mc: bent monochromator crystal, mounted on counter arm.
ca: counter arm.
rs: receiving slit.
ct: counter tube.

the conventional 'reflexion type', since one can regard the virtual focal line of the monochromator as a slit, scanning the virtual focused pattern of diffracted rays. For a given angle 2θ, the geometry of this device is therefore almost identical to that of a conventional diffractometer for the angle $180° - 2\theta$. Apart from that, the only geometrical difference lies in the fact that the virtual slit is not sharply defined in the axial direction and may have 'tails' in the azimuthal direction.

Roughly, however, the geometrical causes of line broadening and shift are the same and their effects are equal to those in the conventional diffractometer, though valid for supplement of the angle:

(*a*) Shift due to specimen displacement is equal to $114{\cdot}6\ (t/R) \sin\theta$. Thus it is very small for low angles. The same applies to the 'flat-specimen error', and to the breadth caused by specimen thickness.

(*b*) Axial divergence causes asymmetrical broadening and shift (Pike, 1957), which in the normal diffractometer are much larger for a given angle 2θ in the front-reflexion region than for its supplement in the back-reflexion. For the transmission type the reverse holds. Hence the low-angle lines, though still markedly asymmetric, are fairly sharp even if only one set of parallel (Soller) slits is used (close to the aperture slit). A second set near the detector has not much effect.

Special advantages of the transmission-type instrument are the following.

(*c*) The chromatic line width caused by the $K\alpha$ doublet can be made to vanish for, say, $2\theta = 30°$, and is very small in the entire low-angle region.

(*d*) The primary beam is accessible for direct measurement through a filter of suitable thickness.

(*e*) The peak-to-background ratio is usually large, owing to monochromatization and to the reduced line width ((*a*), (*b*) and (*c*)).

4. Complete elimination of specimen-displacement error

The advantage mentioned under (*a*) still does not quite eliminate the difficulty of accounting for specimen displacement. The latter has to be less than 0·006 mm. for $2\theta = 30°$ in order to cause an error less than 0·001°. In the conventional diffractometer the corresponding permissible displacement is only 0·002 mm. This is quite impracticable. The limit for the transmission type, however, also appears to lie far beyond what is possible. For instance, Tournarie (1958) with great care did achieve 'less than 0·025 mm.' uncertainty in the position of the specimen.

Thus, special stress should be given to the possibility, offered by the transmission arrangement, of eliminating the specimen displacement completely. This is done simply by repeating the measurement of a given line after rotating the specimen 180° around the goniometer axis. The resulting profile is shifted with respect to the first by twice the displacement error. Hence the profile of a perfectly positioned specimen is situated midway between the two curves. The angular separation of the two profiles is a direct measure of the displacement and is proportional to $\sin\theta$. This allows correction of all lines once the 180° rotation shift has been measured for one of them, preferably at a not-too-small angle.

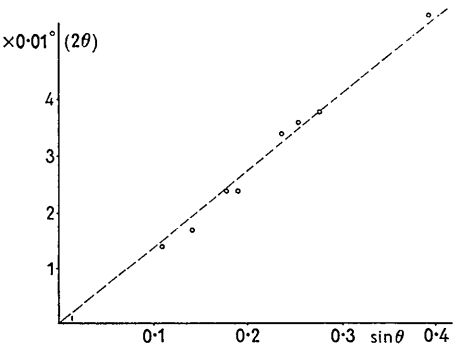

Fig. 2. Measured values of the 180° rotation shift as a function of $\sin\theta$. The specimen is ammonium alum (Cu K). The straight line corresponds to a displacement of 0·105 mm.

We used the following procedure to measure the 180° rotation-shift. The steepest edge of the profile is scanned in steps of 0·01° and the shift is measured from the 2θ values of equivalent points. In Fig. 2, the results obtained for an ammonium alum specimen (Cu $K\alpha$) have been plotted against $\sin\theta$. It is seen that the linear relation is corroborated to within a few thousands of a degree. The correction, being half the shift, is accurate to about 0·001° (2θ).

It has also been verified that the corrected 2θ value of a given point of the profile (say at half maximum height) is constant for varying displacements (up to 0·5 mm.) of the same specimen.

5. Use of an external standard

The remaining problem of determining d values is essentially the same as in the case of the conventional diffractometer. The arguments in favour of using the centre of gravity are equally valid, though the necessary corrections take a slightly different form because of differences in geometry; hence these would have to be established first.

For the low-angle region, however, an empirical approach is conceivable. In fact, if the lattice parameter of, say, a cubic compound has been determined by back-reflexion methods, we know its d values to an accuracy of better than 0·01%. This means that the angular uncertainty for $2\theta = 30°$ is less than 0·003°. Considering that the error of 0·01% is a very pessimistic estimate, one may conclude that low-angle lines of this compound may very well serve as standards for precision measurements.

Now 'standard' should not be taken as 'internal standard' here, for the reasons given before. However, these lines can be used, independent from any particular investigation, to *measure* the instrumental corrections as a function of 2θ. This approach requires, of course, that the conditions of measurement be the same for the standard and for the sample to be investigated. Two possibilities arise:

(i) In both cases the centres of gravity are determined, using the 180°-rotation shift to correct for displacement of either specimen. Then the correction function found for the standard sample is rigourously valid for any other sample.

(ii) A more convenient fiducial point than the centroid

is chosen, for instance the point situated on the steep outer edge of the line profile at half maximum height. Even if specimen displacement is corrected for as in (i), the standard correction function will generally depend on the thickness and on the non-planarity (if any) of the standard specimen. Therefore this correction function will not in general be valid for other samples having different thicknesses and non-planarities.

Some preliminary measurements which we made on alum samples have shown that this irreproducibility is by no means to be neglected. Specimens varying from 0·2–0·4 mm. in thickness gave results differing by 0·005° (2θ) in the position of the fiducial point just mentioned. It was also found, however, that the shift of this point towards higher angles is closely correlated with an increase in the width at half height, which ranged from 0·0095° to 0·012° (2θ).

6. Suggestions for rapid precision measurements

From the above we conclude that it may be possible to derive reliable results from measurements as under (ii), provided the influence of specimen thickness is taken into account. That again we propose to do empirically, in one of two ways:

(ii*a*) The thickness effect can be measured directly on a thin specimen by measuring the positions of the half-height points for various mis-settings of the specimen inclination. Indeed, if the specimen plane makes an angle with the focusing circle instead of being tangent to it, the effect is almost identical with that of a thickness equal to the projected specimen length (Fig. 3). In this way the function giving the correction (to be applied to the fiducial point on the outer flange) as a function of 2θ and of the width at half height can be established.

(ii*b*) Using the same inclination procedure, it will not be difficult to give any specimen an 'artificial' thickness yielding a line width equal to that of the standard specimen, or *vice versa*, if the latter is smaller. It should be sufficient to adjust this inclination for only one line.

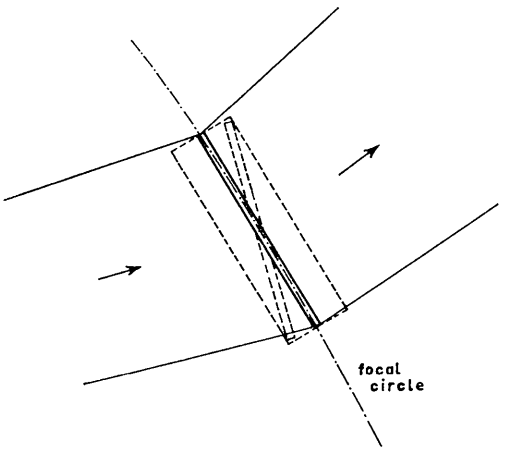

Fig. 3. The specimen with mis-setting of inclination (cutting the focal circle) and the thick specimen (both in dashed lines) cause the same amount of line broadening.

Obviously, much experimental work is needed in order to confirm the usefulness of these methods. We think it is worthwhile to do this work, because it may yield a precision method based on an utterly simple procedure. As compared to the centroid method, the measurement of only one fiducial point is vastly more economic in time. Moreover, the particular fiducial point suggested above (at half maximum height on the outer flange) is probably less sensitive to background errors (tails of neighbouring lines, hidden weak lines) than the centroid. It should be kept in mind that the monochromator makes the outer flange very steep even for lines far beyond $2\theta = 30°$, because the α_2 component just about coincides with α_1 at that angle, instead of beginning to be resolved as in the case of the conventional diffractometer.

Summary

It is shown that the transmission-type diffractometer with focusing monochromator, as compared with the conventional diffractometer, has a geometry more suitable for measuring low-order reflexions as far as the magnitude of line shift and broadening from various causes is concerned. Moreover, it allows of complete elimination of the specimen-displacement error by measuring line profiles for two positions of the specimen 180° apart. Experimental results show that the correction for this effect can thus be made accurate to 0·001° using commercially available equipment. It is suggested that rapid precision measurements of low angles be made using a fiducial point on the line profile (e.g., the point on the steep outer flange at half maximum height) instead of the centroid. This should give reliable results if combined with a substitution standard specimen, special attention being given to the elimination of the effect of any differences in specimen thickness.

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