Acta Cryst. (1977). A33, 46–49

Systematic Variations of Bragg Peak Position in Neutron Diffraction Patterns

BY G. E. BACON, N. COWLAM AND A. G. SELF*

Department of Physics, University of Sheffield, Sheffield S3 7RH, England

(*Received* 5 *May* 1976; *accepted* 27 *June* 1976)

Systematic variations in the position of Bragg peaks in neutron diffraction patterns have been studied. The origin of the effects is examined and their influence on peak-fitting techniques is discussed.

Introduction

There are cases in neutron diffraction when it is important to try to measure periodic distances to a higher accuracy than normal, particularly if this is difficult or impossible by X-rays. Examples include the measurement of lattice parameters of highly oxidizing specimens – especially when this is combined with a study of the magnetic structure type, as for certain rare-earth compounds; the measurement of periodicity of non-collinear magnetic structures – when, for magnetic metals, accurate results may give information about the dimensions of the Fermi surface; and also the measurement of lattice parameters of a minority phase in a two-phase specimen (Cowlam, Bacon & Kirkwood, 1975). This latter example has led us to examine the factors influencing accurate measurement of periodic distances by neutron beams, and by implication the measurement of wavelength of the monochromatic neutron beams themselves (Bacon & Cowlam, 1974). The conditions which are necessary for accurate measurements using a neutron diffractometer, and the factors which influence the measurements, are similar to the X-ray case (see Wilson, 1963, for example), except that special tests must be made of such factors as the incident-beam profile, the zero position of the Bragg-angle scale, and the stepping motion of the neutron counter (Self, 1974). Even in the case of ideal experimental conditions, systematic errors or variations remain, and these may be removed by various extrapolation methods (for example, Ketterman, 1929; Nelson & Riley, 1945). It has been established (Bacon & Cowlam, 1974) that systematic variations can indeed be observed in *neutron* diffraction experiments, and this present study concerns a more detailed assessment of these variations.

Systematic variations due to sample misalignment

The rather imprecise methods generally used to align neutron diffraction samples in the beam suggest that sample displacement may be an important source of error. In the case of the two-axis neutron diffractometer, the counter normally travels on *only* the focusing side (Wagner & Kulenkampff, 1922) of the incident beam, so that sample displacement both along *and* perpendicular to the beam must be considered. A displacement of the sample (r,α), in polar coordinates, from the centre of the specimen table, results in Bragg peaks shifted from their true positions, by an amount

$$\Delta\theta = \frac{r}{2R}\sin(\alpha-2\theta)$$

and the fractional change in lattice parameter which results, is

$$\frac{\Delta d}{d} = \frac{r}{2R}\cot\theta\sin(2\theta-\alpha), \qquad (1)$$

where R is the effective sample–counter distance. The curves of $\Delta d/d$ *versus* θ are not simple monotonic functions, as Fig. 1 shows, and there is asymmetry about the beam direction. The cases $\alpha=0°$, 180° give a $\cos^2\theta$ dependence of $\Delta d/d$, as occurs in the corrections used for a Debye–Scherrer camera where only longitudinal sample displacement produces a systematic error.

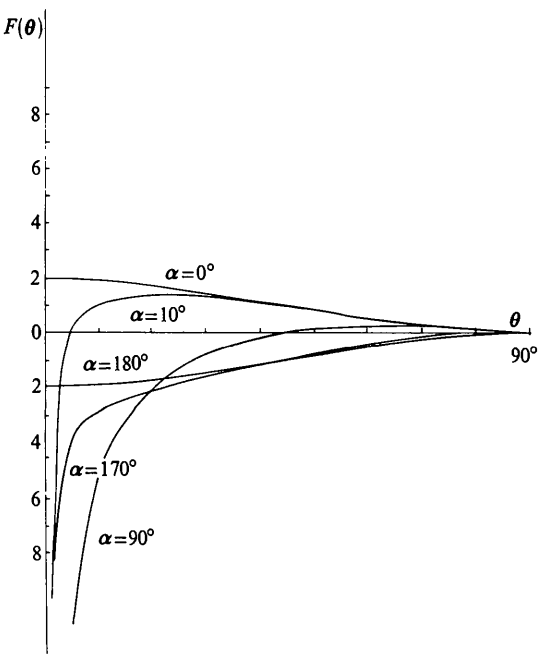

Fig. 1. The variation with θ of the expression $F(\theta)\equiv\cot\theta\sin(2\theta-\alpha)$ for the values of α indicated, for Bragg angles θ between 0° and 90°. Note, from equation (1), that $\Delta d/d=(r/2R)F(\theta)$.

* Now at Royal Radar Establishment, Malvern, Worcs.

Experiments were undertaken on the Curran diffractometer at AERE Harwell using an NaCl standard sample, mounted on a special support which allowed very accurate movement of the sample in the beam. Counter scans were made over the full angular range available, and lattice parameter values calculated from the position of each peak in the diffraction pattern. These peak positions were obtained both by manual plotting of the peak and measurement of chords, and by computer fitting to individual peak profiles. In the two cases similar results were obtained. Fig. 2 shows the variations of lattice parameter with Bragg angle, together with the curves given by substituting the sample displacement, as measured from the sample support, and specimen-to-counter distance into equation (1). A value of neutron wavelength obtained in the same series of tests was used throughout. The fit is quite reasonable and suggests that sample displacement was an important source of systematic variation. Therefore equation (1) represents a second, if less convenient, function for extrapolation, than the cot θ term obtained from the earlier study.

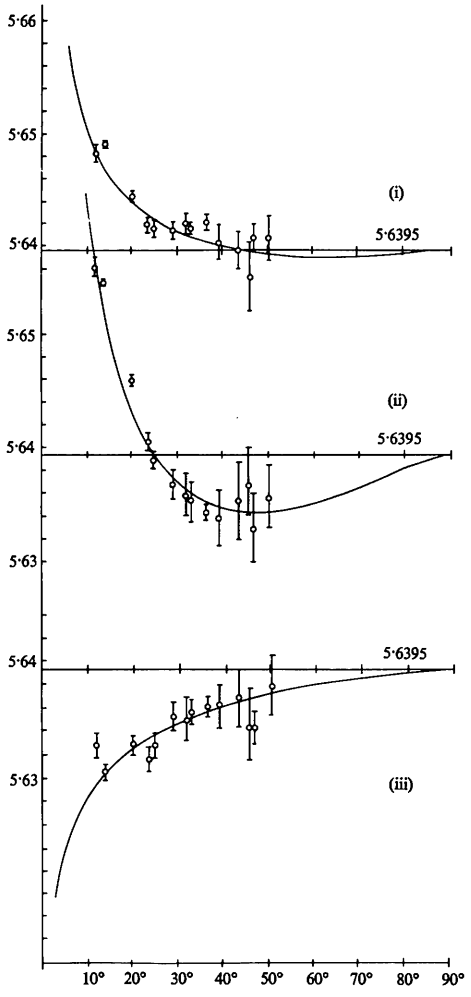

Fig. 2. The apparent variation of lattice parameter of an NaCl sample, with Bragg angle, for various displacements of the sample from the true centre of the specimen table. For curves (i), (ii) and (iii) the values of displacements r and α are (i) $r=0{\cdot}7$ mm, $\alpha=270°$; (ii) $r=3{\cdot}5$ mm, $\alpha=230°$; (iii) $r=1{\cdot}3$ mm, $\alpha=160°$. Effective instrument radius $r=1{\cdot}26$ m, $\lambda=1{\cdot}373$ Å.

Systematic variations due to axial divergence

A further source of error was suggested by experiments performed on the D2 diffractometer at the Institut Laue–Langevin, Grenoble. The results of our earlier experiments undertaken there were extrapolated against cot θ. In more recent work the scanning range was extended, and peaks on both sides of the incident beam were examined. Normally, it is not considered worthwhile to examine peaks on the antifocusing side of the incident beam (see Bacon, 1975, Fig. 49) but for the ILL experiment it was hoped that the higher flux available would allow reliable measurements to be made. A standard NaCl sample, and two Fe–C–Si alloys were examined. Analysis of the result followed the method described in the previous section, except that the variations were not consistent with either of the functions given previously, and were first analysed in an empirical way (Cowlam, Bacon & Kirkwood, 1975). In looking for the source of these new variations it was recalled that axial divergence, that is beam divergence along the axis of the specimen, produces an apparent shift in peak position, through distortion of of the peak profile, especially at those smaller Bragg angles where neutron peaks are often recorded. The influence of axial divergence on neutron peak *profiles* has already been described by an empirical correction (Rietveld, 1969), but estimates of the effective peak *shifts* based on this correction were not entirely successful, since amongst other things singularities developed at low and high Bragg angles. The problem of axial divergence in X-ray diffractometers on the other hand has been considered in detail (see Wilson, 1963, for a comprehensive review). The geometrical results may be applied to the two-axis *neutron* diffractometer if it is assumed that the monochromator crystal is the effective neutron source, subject to further qualifications given below.

The expression for the shift in the centre of gravity ($\Delta 2\theta$) of a Bragg peak is given by

$$\Delta 2\theta = \left(\frac{Z_s - Z_f}{S}\right)\left(\frac{Z_r - Z_s}{R}\right)\operatorname{cosec} 2\theta - \tfrac{1}{2}\left[\left(\frac{Z_s - Z_f}{S}\right)^2 + \left(\frac{Z_r - Z_s}{R}\right)^2\right]\cot 2\theta \quad (2)$$

where Z_f = (axial) height of source (monochromator), Z_s = height of sample, Z_r = height of counter, S = source-to-specimen distance (along flight tube), R = specimen-to-counter distance (effective radius). The apparent change in lattice parameter $\Delta d/d$ can be found as before. Substitution of the dimensions of the D2 diffractometer into equation (2) gives the curve of

Δd/d versus θ (Fig. 3) which shows that the effect of vertical divergence on peak position is small except at small values of 2θ. The effect is symmetrical about the incident beam, as the diffraction haloes themselves are. The curve will have the same shape but different magnitudes for different diffractometers. In fact for the Harwell instrument the effect was calculated to be more than an order of magnitude smaller, and this is consistent with the fact that the results of the previous section could be analysed in terms of sample displacement alone. Thus it appeared that the experimental points obtained (Fig. 4) might be described in terms of a combination of sample-displacement and axial-divergence effects.

The first attempts to fit the points with the sum of terms derived from equations (1) and (2) were only partly successful. The fit was worst at low angles suggesting that the axial term was overestimating the effect; this term was therefore arbitrarily reduced to two-thirds. Such a reduction would be consistent with both a non-uniformity in the intensity of the source and of the efficiency of the detector, over their axial heights. Fig. 4 shows the results obtained in which the observed lattice-parameter values are fitted by a curve expected to result from axial-divergence and sample-displacement effects. The coordinates (r,α) of the displacements are given in the figure caption. The fitting has been by trial and error and the displacement coordinates (r,α) and the amount of 'axial' term as explained above, have all been changed to produce the agreement. Nevertheless, the curves shown in Fig. 4 are quite sensitive to small changes in the parameters, perhaps because, in this case, the two terms add on the antifocusing side and subtract on the other. Substantially worse fits are produced by altering the parameters from the values given, even by quite small amounts.

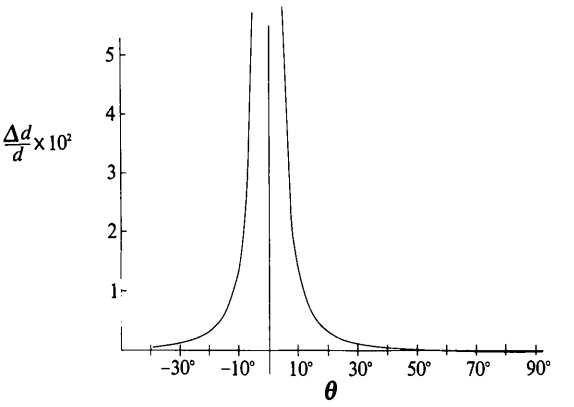

Fig. 3. The apparent variation of interplanar spacing with Bragg angle predicted to occur for the D2 diffractometer at the ILL, Grenoble, as a result of axial divergence. The curve is derived by substitution of the diffractometer parameters into equation (2) in the text. (The instrument has since been modified substantially, in a way which would increase this effect.)

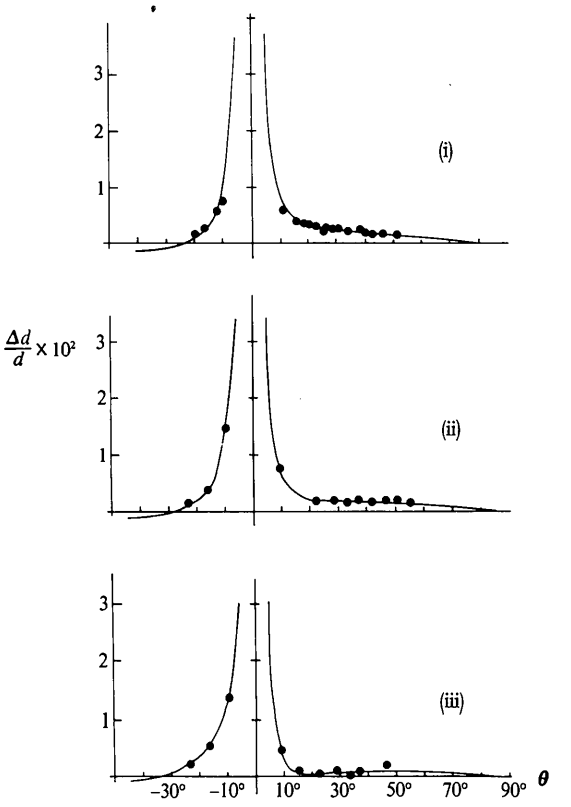

Fig. 4. Graphs of the apparent variation of interplanar spacing as a function of Bragg angle, observed for NaCl and C–Fe–Si samples. The curves show the calculated variations, based on the assumption that sample displacement and axial divergence both contribute to the variations. Curve (i). NaCl sample: $\frac{2}{3}$ axial divergence term + displacement term (0·3 mm, 25°). Curve (ii). Fe–C–Si sample: $\frac{2}{3}$ axial divergence term + displacement term (0·3 mm, 40°). Curve (iii). Fe-C–Si sample: $\frac{2}{3}$ axial divergence term + displacement term (0·3 mm, 60°). Effective instrument radius $R = 0{\cdot}85$ m; $\lambda = 1{\cdot}12011$ Å.

Accurate measurement of lattice parameters

In previous sections two of the error factors in diffraction measurements have been identified, and the systematic variations of lattice parameter which they cause have been investigated. These systematic variations observed in neutron diffraction experiments are not described by the same simple functions as the variations seen in X-ray experiments. This makes the adoption of the extrapolation technique, and hence the measurement of lattice parameter, most difficult in neutron diffraction. For example, the experiments on the Fe–C–Si alloys, performed to determine the lattice spacing of the graphite, were originally analysed (Cowlam, Bacon & Kirkwood, 1975) in an empirical way, starting from the fact that the data on the focusing side showed only a small variation of lattice parameter with Bragg angle. The data have now been re-analysed (Fig. 4) in accordance with the description of the systematic variations given above, and this results in a remarkably similar set of values of lattice parameter, as shown in Table 1. One explanation

for this similarity, is that the values obtained are based on a series of experiments, rather than on a single isolated measurement. In the case of the present measurements the lattice parameter values of the 'calibrating' (NaCl) sample and of the majority phase of the Fe–C–Si alloys – the 'standard' sample – were known at all sample temperatures used. Experience has also shown that the apparent variations of lattice parameters with Bragg angle tend to follow similar curves for series of uninterrupted measurements. Finally, an additional check on the values obtained was provided by the lattice parameter value measured by X-rays of graphite extracted from a sample. This extra information acts as a framework within which the derived values of lattice parameter must fit. In fact there was enough information to provide strict constraints on the values obtained, and the problem was effectively overdetermined, so that the values obtained did not depend on the particular method of analysis, providing it was sensible. As a corollary to this, a deduction of a lattice parameter value from a single neutron-diffraction pattern must be regarded as impractical, including, as it does, the unknown spacing, the unknown neutron wavelength, and an unspecified variation of lattice parameter with Bragg angle. In this case the problem is underdetermined and this suggests that it may not be generally possible to measure lattice parameters accurately by neutron beams, in this simple way.

Table 1. *Lattice parameter and wavelength values for* Fe–C–Si *experiments* (Å)

	Empirical analysis	Analysis with axial and displacement variations
Wavelength value	1·11988	1·12011
Lattice parameters	$a = 2{\cdot}8873$	2·8873
Stressed sample	$c = 6{\cdot}801$	6·784
Lattice parameters	$a = 2{\cdot}8875$	2·8875
Relieved sample	$c = 6{\cdot}829$	6·824
% difference in c	0·4%	0·6%
Relieved graphite extrapolated to 20°C	$c = 6{\cdot}722$	6·717

The effect of systematic variations on peak fitting

The conclusion reached above, that any neutron diffraction pattern, if examined in sufficient detail, will consist of peaks at low angle which are shifted and distorted and peaks at higher angle which are shifted, but undistorted, may affect the analysis of diffraction experiments in which details of peak position or shape are important. One example is a peak-fitting procedure, either the simple technique of fitting individual experimental peaks or the profile-refinement method (Rietveld, 1969) in which all the peaks in a diffraction pattern are fitted simultaneously. It is possible to consider the first of these cases quantitatively if the equations describing a 'data' peak and also a 'fitting' peak are written down and the integral equations, which describe a least-squares fitting procedure, obtained from them. These equations being based on Gaussians can generally be solved, to give the parameters describing a 'fitting' peak, in cases when the 'data' peak is shifted and distorted in various ways. This has been done in some detail, and qualitative conclusions about the use of the profile refinement for diffraction patterns with systematic variations have been drawn from these results. These calculations will not be discussed in detail, as they indicate that the effects are small. One reason is that in using the profile-refinement method it is usual to make the first refinements by changing only the instrument parameters – peak half-width, asymmetry-parameter, zero of the angular scale and overall scale factor – and it is possible that by suitably adjusting these parameters from their true values the effects of the systematic variations may be adequately imitated, within a framework which does not specifically take them into account. The systematic variations may therefore be minimized both by the artificial variations in instrument parameters and by the natural loss of instrument resolution at high angles, particularly when the Bragg peaks merge into a continuum. This being so it is probably only worthwhile investigating these systematic effects when successive refinements fail to produce satisfactory results. An estimate of the size of the systematic variations would then be used to find the level of accuracy to which the refinement process could be taken.

Help of many kinds from colleagues at Sheffield, AERE, Harwell and ILL, Grenoble – particularly Drs L. Gillott, T. M. Searle and D. Hohlwein – is gratefully acknowledged. Financial support was received from the Science Research Council.

References

BACON, G. E. (1975). *Neutron Diffraction*. Oxford: Clarendon Press.

BACON, G. E. & COWLAM, N. (1974). *Acta Cryst.* A **30**, 467–469.

COWLAM, N., BACON, G. E. & KIRKWOOD, D. H. (1975). *Scripta Met.* **9**, 1363–1366.

KETTERMAN, G. (1929). *Z. Phys.* **53**, 198–209.

NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc.* **57**, 160–177.

RIETVELD, H. M. (1969). *Acta Cryst.* **2**, 65–71.

SELF, A. G. (1974). Ph. D. Thesis No. 3667, Sheffield Univ.

WAGNER, E. & KULENKAMPFF, H. (1922). *Ann. Phys.* **68**, 396–413.

WILSON, A. J. C. (1963). *Mathematical Theory of X-ray Powder Diffractometry*. Eindhoven: Philips Technical Library.