The theoretical expressions of Cooper & Sayer [J. Appl. Cryst. (1975), 8, 615] for the peak shift from the true Bragg angle and for the peak broadening in powder neutron-diffraction patterns are confirmed experimentally for detectors with finite aperture. It is shown that these factors can be important even at relatively large scattering angles.

Introduction

Recently, theoretical expressions have been derived by Cooper & Sayer (1975)(C & S) in which the shape functions of powder neutron-diffraction peaks have been derived as functions of the finite vertical and horizontal divergence angles of the instrument. This topic has become increasingly important for two reasons. The first is that the advent of profile-analysis techniques for analysing neutron-diffraction data (Rietveld 1967, 1969) has meant that more attention must be paid to detailed peak shapes and the second is that one can collect more neutrons with counters with large vertical apertures. Because of the finite aperture of the detector C & S predict that the observed peaks will be shifted from the true Bragg angle and will be broadened. The purpose of this note is to test the mathematical expressions obtained by C & S with some experimental measurements.

Experimental

Experiments were carried out on the PANDA two-circle diffractometer at AERE Harwell using four Bragg peaks from a nickel powder sample. The wavelength was chosen as 1.382 Å. At this wavelength the first nickel peak occurs at 2θ = 39.71°. This rather high 2θ position was chosen to ensure that the distortion of the observed peak from a Gaussian shape would be negligible. The resolution of the instrument was degraded by choosing a low take-off angle of 47.5° to increase the horizontal half widths of the nickel peaks. In order to determine the shape accurately the instrument was stepped in units of 0.02° in 2θ. A least-squares program was then used to fit the observed peaks to a Gaussian plus a linear background. For all peaks the fits were very good. The differences in integrated intensities and the Gaussian fit were always less than 0.5%.

The PANDA diffractometer has detector Soller slits which are seen by three BF3 counters end on. Also, one can consider the three counters together as forming one counter with an effective vertical divergence of 5.9° (defined here as half the full width at half maximum) or alternatively the central counter alone with a vertical divergence of 2.5°. Finally one can consider the two off-centre counters together, to form a single counter with a still larger effective aperture.

Results

If the central counter is taken as measuring the 'true' 2θB position and also the 'effective' horizontal half width determined by the sample and instrument then one can examine the shift, δ1, in 2θB and the increase in half width, δ2, due to the finite aperture for the three counters and for the two off-centre counters. It should be pointed out that this will underestimate δ1 and δ2 as the central counter has a vertical divergence of...
of 2.5°. However, the expressions of C & S suggest this latter correction will be small. The results obtained for the shift $\delta_1$ in $2\theta_B$ for the three counters and for the two off-centre counters are shown in Fig. 1. Also shown is a least-squares fit of the observations to a function suggested by C & S which is of the form

$$\delta_i = F_i (\cot 2\theta_B)^{g_i}$$

(1)

where $F_i$ and $g_i$ are functions of the horizontal and vertical divergence angles. The increase in half width, $\delta_2$, is shown in Fig. 2 for both cases. Again these shifts will be minimal values. The results of a least-squares fit to equation (1) is also shown and the results for both $\delta_1$ and $\delta_2$ are summarized in Table 1 together with their associated estimated standard deviations.

### Discussion

As one can see from Fig. 1 the fit of the observations to the formula given by C & S for $\delta$ is remarkably good. Using the horizontal and vertical divergence angles of 0.2 and 6° and the empirical formula of C & S one obtains, for $F$ and $g$, 0.048 and 0.4 respectively. Although their value of $F$ agrees with that of Table 1, the value of $g$ is lower. However, these are not completely comparable. The formulae of C & S were fitted for values of $2\theta_B$ below 32°. The values reported here were fitted above 32° where the effect is less but still measurable. Unfortunately at very low angles the peak shape becomes non-Gaussian and so one cannot fit the observed data accurately to a Gaussian distribution. Moreover, the coefficients, $M_{ki}$, of the resolution function (Cooper & Nathans, 1968) depend on additional parameters such as the mosaic spread of the monochromator, the monochromator angle, and the Soller slits before and after the monochromator.

Hence one should not expect the correction terms $F_i$ and $g_i$ to agree completely quantitatively with the expressions of C & S. However, the formulae of C & S do show the same angular dependence. It is therefore tempting to suggest that $F_i$ and $g_i$ could be treated as least-squares parameters in the profile refinement. In this way one should be able to utilize off-equatorial counters and still obtain a good fit between calculated and observed profiles. Moreover, as these are instrumental parameters rather than structural parameters, they should show little variation from sample to sample.

In conclusion then, the formulae of C & S seem to predict the correct form of angular dependence for finite aperture counters. However, these measurements indicate that the effect due to finite apertures can be easily observed above 32° and can in fact be measured up to 80°.

### Table 1. Least-squares fit to $\delta_i = F_i (\cot 2\theta_B)^{g_i}$

<table>
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<th>$F_i$</th>
<th>$g_i$</th>
<th>Weighted residual</th>
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<td>Three counters</td>
<td>0.046 (2)</td>
<td>1.03 (4)</td>
<td>0.0026</td>
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<tr>
<td>Two counters</td>
<td>0.0756 (1)</td>
<td>1.00 (1)</td>
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<table>
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<th>$g_2$</th>
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<tr>
<td>Two counters</td>
<td>0.035 (21)</td>
<td>2.03 (33)</td>
<td>0.028</td>
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### References


