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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1967). **22**, 151

Line profiles of neutron powder-diffraction peaks for structure refinement.*

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A structure refinement procedure is described, which obtains a least-squares fit between the calculated and observed intensities measured at equal angular intervals on a neutron powder-diffractometer. It is shown that the structure parameters are significantly more reliable than those determined by a method using the integrated intensities of overlapping peaks.

While the structure determination from a well resolved powder diffraction diagram often proves to be quite feasible, the inherent presence of overlapping reflexions generally prevents the full use of the available information to refine the structural parameters. An obvious solution is to include as observed data in the least-squares refinement the integrated intensities of the composite diffraction peaks (Rietveld, 1966). A major drawback of such a procedure, however, is the fact that any detail in the profiles of these peaks is lost.

In the case of neutron diffraction, a more direct method to solve this problem was found when it appeared that the peak shapes of the single diffraction peaks obtained from the powder-diffractometer at Petten were Gaussian. The profile of a composite peak can then be regarded as the sum total of the constituent Gaussian peaks representing the individual Bragg reflexions. The contributions of each of these constituent peaks to the enveloping peak at position $2\theta_i$ can be written as $a \,.\, \exp\{-4\ln 2(2\theta_i - 2\theta_0)^2/b^2\}$.

The quantities b and $2\theta_0$ in this expression, being respectively the full width at half height (halfwidth) and the position of the peak, can be obtained from an inspection of the diffraction diagram, the unit-cell parameters and the wavelength. The remaining quantity a is then the only unknown. It is proportional to jF^2, where j is the multiplicity of the structure factor F, the precise relation being as follows.

Equating the area of the Gauss curve to the integrated intensity gives

$$\tfrac{1}{2}\sqrt{\pi\ln 2}\; a \,.\, b = cjF^2/(\sin 2\theta_0 \sin\theta_0)\,,$$

from which

$$a = 2cjF^2/(b\sqrt{\pi\ln 2}\sin 2\theta_0 \sin\theta_0)\,.$$

Substituting

$$c' = 2c/\sqrt{\pi\ln 2}$$

gives $a = c'jF^2/(b \sin 2\theta_0 \sin\theta_0)$, where c' represents an overall scale factor.

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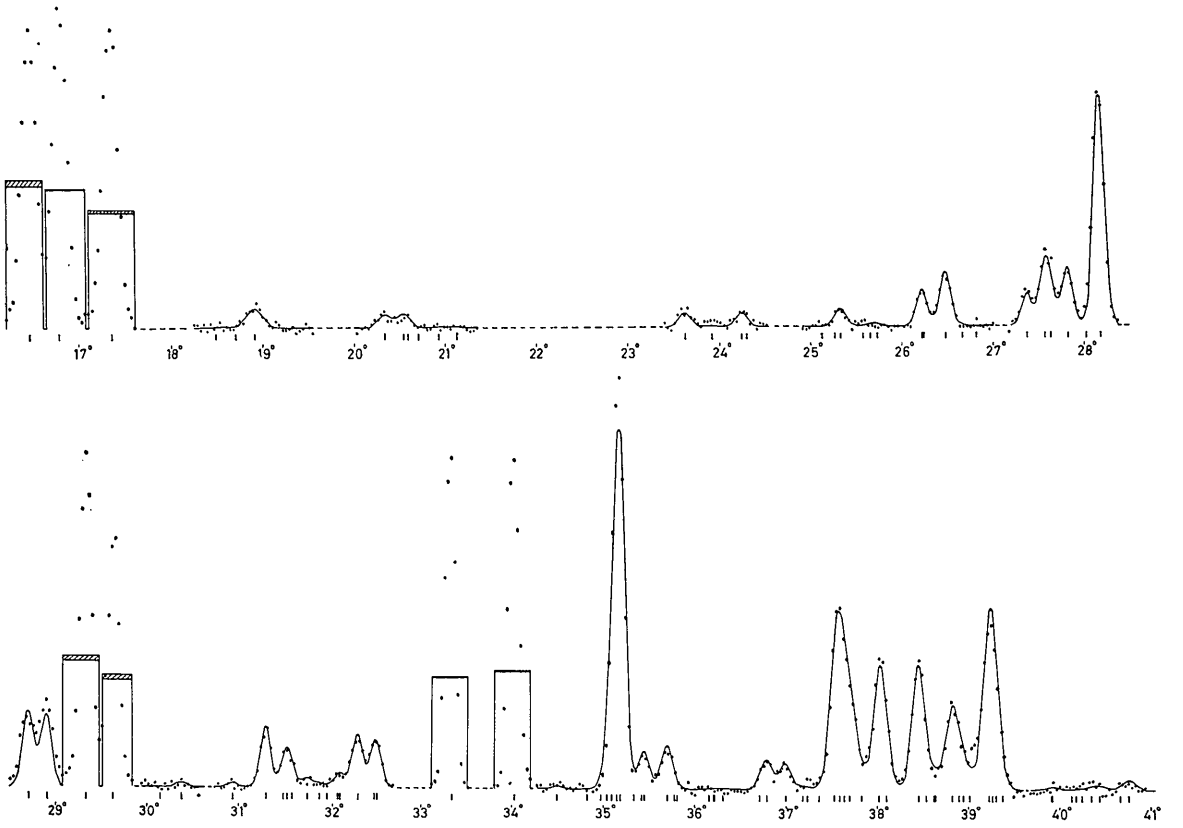

Fig. 1. Neutron powder diffraction diagram of WO_3 (intensity *vs* 2θ). The solid line indicates the calculated profile and the dots the measured intensities. The rectangles represent the integrated single-peak intensities, their different heights the agreement between calculated and observed values.

Finally, putting

$$w_i^k = j_k \exp\{-4\ln 2(2\theta_i - 2\theta_{0k})^2/b_k^2\}/(b_k \sin 2\theta_{0k} \sin \theta_{0k}) ,$$

where w_i^k is a measure of the contribution of structure factor F_k at position $2\theta_{0k}$ to the intensity measured at position $2\theta_i$ and corrected for background, we can say that

$$y^i{}_{\text{obs}} = c' \sum_k w_i^k F_k^2 .$$

The summation is taken over all reflexions F_k which can contribute significantly to $y^i{}_{\text{obs}}$; the effective range of a Gaussian peak for this purpose is set at three times its halfwidth.

In addition, the well resolved peaks are replaced by a δ peak, *i.e.* all $y^i{}_{\text{obs}}$'s in this range are replaced by zero's except for one value which is made equal to the area of the Gaussian peak and

$$w_i^k = \delta_{i,0k} \cdot \{0{\cdot}709667/(\sin 2\theta_{0k} \sin \theta_{0k})\} .$$

This procedure eliminates the (now unnecessary) introduction of an uncertainty due to the supposition of the idealized Gaussian peak shape.

To test the method the structure of WO_3 (Loopstra & Boldrini, 1966) was refined. It was found that the standard deviation of the least-squares parameters improved by an average factor 2·3, compared with those obtained by the method of overlapping reflexions (Rietveld, 1966). Fig. 1 shows the final agreement between calculated and observed values. The dots represent the intensities, measured at each step by the proportional counter and corrected for background, and the full line the calculated profile. The different heights of the rectangles representing the integrated intensities indicate the agreement between those values.

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