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A New Rationale of Structure-Factor Measurement in Neutron-Diffraction Analysis

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The Laue method of recording integrated intensities, with certain adjuncts, appears to be in many ways simpler than the rotating-crystal method for single-crystal neutron diffraction analysis, at the same time as offering increased intensities. A proposed technique is discussed, which is particularly suitable for use with pulsed neutron sources such as electron accelerators.

Introduction

Experience of single-crystal neutron diffraction analysis has shown that, with present-day techniques, the collection of structure-factor data is apt to take an inordinately long time. This is a shortcoming which, of course, might be removed at any moment by the adaptation of standard methods such as that of photographic recording. However, suitable neutron sources are sufficiently few and far between that the mere measurement of reflected intensities could become a bottleneck in this branch of crystallography.

Herein is suggested a novel method of measuring integrated intensities with neutrons which offers higher counting rates and a substantially greater speed of operation than the rotating-crystal method. Since the technique is particularly well suited to automation, it would appear to be capable of the high productivity required to break the bottleneck.

The principle is to use a modified form of the *Laue method*. The white spectrum of wavelengths normally provided by a slow-neutron source is treated as a virtue, rather than as a somewhat unsatisfactory object for monochromatization. As will be seen, a broad wavelength band must be selected from the spectrum. With a time-continuous neutron source, such as a reactor, this would normally involve chopping the incident beam, with consequent waste of intensity. On the other hand, a pulsed source of slow neutrons,* in conjunction with time-of-flight apparatus, is ideally suited to such a technique. What is outlined below is, in fact, the natural method of structure-factor measurement with a pulsed source of white neutrons.

Relevance of the Laue method

It is possible to gain a mistaken impression from X-ray technique that there is something inherently desirable about a monochromatic beam for crystal-structure analysis. In the X-ray field, monochromatic radiation has not only been available in sufficient intensity, but also with a wide choice of wavelengths. This happy situation does not exist in neutronics, where one has to be content with a rather weak Maxwell spectrum together with the 'dE/E tail' of epithermal neutrons (Fig. 1).

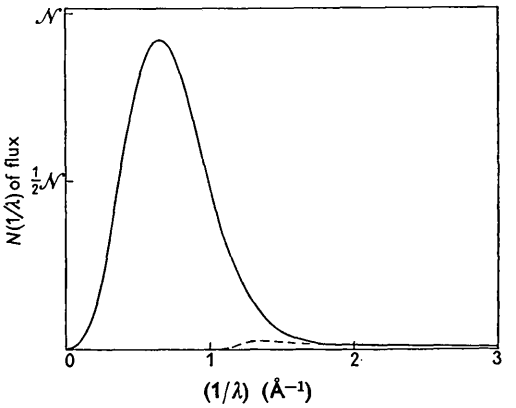

Fig. 1. The inverse wavelength spectrum of neutrons hitting a specimen from a source at 53° C. near the centre of the Harwell pile, multiplied by the efficiency of a 75% (at 1·80 Å) detector. A broken line separates the thermal and epithermal contributions; the former delivers a total of $\mathcal{N}$ thermal neutrons per square centimetre per second at the specimen with an accurately Maxwellian distribution of velocities. (Data taken from Taylor, 1952.)

Most crystallographers have responded by 'monochromatizing' the neutron spectrum. After substantial losses at the monochromator, a wavelength band of about 0·03 Å, sometimes with several per cent second-order contamination, passes on to the specimen with the wavelengths noticeably sorted in angle. The Bragg setting of the reflexion is accurately located and the intensity recorded by the rotating-crystal method; finally the area underneath the curve is derived by integration.

The essential idea now put forward is that many of these operations, and much of the intensity loss, can

* Such as a linear electron accelerator. The neutrons are created in bursts of a few microseconds, and wavelength selection is performed by timing methods. Egelstaff (1953, 1954) has repeatedly emphasized that electron accelerators are capable of providing mean fluxes of thermal neutrons for these purposes equal or superior to the fluxes of modern reactors.

be avoided by performing the integration over wavelength rather than crystal angle. This is done simply by allowing a white beam to fall upon the specimen, and measuring the reflected intensity with the crystal stationary.

The principle

The difference between the two approaches can be understood with the aid of Fig. 2. This shows a surface

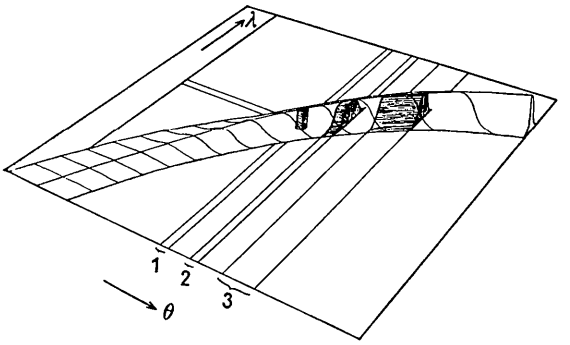

Fig. 2. A surface illustrating the Bragg reflectivity for a given set of planes (*hkl*) in a mosaic crystal, as a function of incident glancing angle θ and diffracted wavelength λ. The volumes of the three shaded solids are proportional to the counting rates obtained in: (1) an idealized 'monochromatic' reflexion; (2) the Laue arrangement; (3) the Laue arrangement with very relaxed collimation.

whose height is proportional to the Bragg-reflected intensity obtainable from a given set of planes (*hkl*) in a mosaic crystal, drawn in such a way as to show the dependence on λ and θ. The incident intensity is to be imagined constant for all λ. For instance, a line through the origin running along the ridge of the surface is proportional to the intensity reflected by a single microcrystal whose plane (*hkl*) is parallel to the nominal plane (*hkl*). The height of this line varies as λ^2. Microcrystals which are slightly misset from the nominal plane (*hkl*) have, in effect, an actual glancing angle slightly different from the nominal angle θ, and therefore give rise to lines similar to that through the origin but somewhat displaced parallel to the θ axis. A surface is thus generated whose intensity falls to zero at a displacement angle beyond which there are no microcrystals.

An idealized 'monochromatic' experiment can be considered as one in which a small band of wavelengths $d\lambda$ falls on the specimen uniformly throughout a spread $d\theta$ of incident angles. In this situation the reflected intensity is the solid volume drawn at (1) of Fig. 2. To measure an 'integrated intensity' in the rotating-crystal method, the solid (1) is tracked along parallel to the θ axis so as to map out the contour of the surface.

Suppose, on the other hand, the incident spectrum is a broad band of wavelengths, wide compared with a section of the surface in Fig. 2. The intensity received in that case is given by the volume at (2), and the received beam is called a Laue reflexion. The essential points to notice are: that this volume is greater than the volume at (1), and that it is already an integrated intensity.

In practice, of course, a crystal-monochromated beam of neutrons has a rather wide $d\lambda$, with some correlation between λ and θ, and the position is more complicated than in Fig. 2(1). Indeed the instantaneous intensity obtained at small d_{hkl} when the 'monochromatic' line is very broad and the specimen crystal rather perfect is probably the full intensity of the Laue arrangement. Nevertheless, it is in general true that by renouncing the narrow monochromatization (i) the counting rate is increased, and (ii) the necessity of tracking through an arc of θ is obviated. To measure an integrated intensity with the Laue arrangement, the crystal and detector are simply turned to calculated positions and a count is taken.

The practical functioning of the technique may be illustrated in an idealized way as follows. An automatic spectrometer supports the specimen in front of the neutron source, which may be represented quite figuratively at this stage by a black box. This box has two dials, labelled λ and $d\lambda/\lambda$; the first is calibrated from about 0·7 Å to 1·6 Å and the second from 0·05 to 0·25. The effective band of wavelengths emerging from the box corresponds to the dial settings. A survey of the background is taken, and then one reading per reflexion, counting rates being proportional to F^2d^2.

What might be inside such a highly convenient accessory is a question discussed on a later page.

Formulae

In the rotating-crystal method the integrated intensity is customarily expressed as

$$\mathscr{I}_H = I_0(\theta).Q^\theta dV \text{ neutrons min.}^{-1}, \qquad (1)$$

I_0 being the incident intensity, dV the volume of the specimen and Q^θ the quantity usually called Q. It is useful to have a corresponding notation in the Laue method:

$$\mathscr{I}_{\text{Laue}} = I_0(\lambda).Q^\lambda dV \text{ neutrons min.}^{-1}, \qquad (2)$$

where I_0 is on the wavelength scale (Zachariasen, 1945, equations (3·79) and (3·72)). Again

$$\mathscr{I}_{\text{Laue}} = I_0\left(\frac{1}{\lambda}\right).Q^{\frac{1}{\lambda}}dV \text{ neutrons min.}^{-1}, \qquad (3)$$

where I_0 is on the $(1/\lambda)$ scale of Fig. 1, familiar in neutronics as the velocity scale. Then

$$Q^\lambda = 2N^2F^2d^2\lambda^2 \qquad (4)$$

and

$$Q^{\frac{1}{\lambda}} = 2N^2F^2d^2, \qquad (5)$$

N being the number of unit cells per cm.^{3}. Equations (2)–(5) are the equations which show that, if readings

are taken at constant wavelength, the counting rates are proportional simply to F^2d^2.

In equation (3), the only λ dependence on the right-hand side is through $I_0(1/\lambda)$. It follows that the maximum $\mathscr{I}_{\text{Laue}}$, and therefore the maximum counting rate, is obtained when the experiment is designed to use the peak wavelength of the Maxwell spectrum *expressed on the* $(1/\lambda)$ *scale*. Calling this, apart from a factor h/m_0, the velocity scale, one has a spectrum given by $n(v) \sim v^2 \exp[-\alpha v^2]$, with $\alpha = m_0/2k_0T$. The spectrum of neutrons *hitting* the crystal is this multiplied by v, or $n_h(v) \sim v^3 \exp[-\alpha v^2]$; the wavelength for the maximum of this function is

$$\lambda_{\text{max.}} = h/\sqrt{(3m_0k_0T)} . \qquad (6)$$

With $T = 45°$ C., $\lambda_{\text{max.}}$ is 1·41 Å from (6), and this is the practical value for that temperature if the counter is 100% efficient. If the counter is less than 100% efficient the figure is shifted to longer wavelengths; with a 75% counter it works out at $\lambda_{\text{max.}} = 1{\cdot}55$ Å. All reflexions studied with the wavelength $\lambda_{\text{max.}}$ are observed at their maximum counting rate.

Evidently equations (3) and (5), in conjunction with Fig. 1, give a very simple account of the Laue intensities.

Incidental advantages

Certain other features of the arrangement may be considered:

(*a*) On the score of intensity: (iii) the instrumental loss caused by a monochromating crystal, due to incomplete reflexion and angle limitation, is avoided (it is replaced, of course, by the loss at the black box, if any); (iv) the incident collimation can be relaxed by a substantial factor, as in Fig. 3.

The loss (iii), due to a monochromating crystal, is probably a factor of about 2 or 3. The effect of (iv) is illustrated at (3) of Fig. 2; it introduces a large gain directly. At very low Bragg angles the variation of true incidence angle from one side of the collimator to the other tends to falsify the apparent structure factor; however, in the author's Laue spectrometer, with an open cone of apex angle $\Delta\theta = 2\frac{3}{4}°$ as collimator, the error introduced above $\theta = 5°$ is less than 1%.

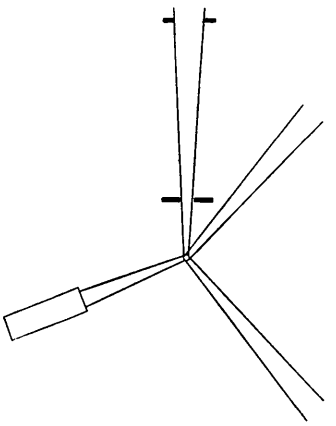

Fig. 3. A Laue arrangement for crystal analysis, showing a small specimen used with very relaxed collimation. All reflexions have the same width and shape. If necessary, the collimation angle can be effectively cut down at the counter.

Assuming a perfect black box, the net gain from (iii) and (iv) will be roughly about, say, $2\frac{1}{2} \times 8 = 20$. A practical illustration may be taken from two simultaneous experiments at the Harwell pile. The 13,0,9 reflexion of KH_2PO_4, which has an interplanar spacing of 0·459 Å and a structure factor of $1{\cdot}09 \times 10^{-12}$ cm., was recorded at $\lambda = 0{\cdot}81$ Å by Bacon & Pease (1953) in their structure analysis, using a copper-monochromated incident beam. The peak intensity was 0·054 neutrons min.$^{-1}$ per cubic millimetre of specimen irradiated. In the Laue diffraction pattern of iron, using the direct pile beam with no black box at all (Lowde, 1954), the $11\bar{6}$ reflexion with $d = 0{\cdot}464$ Å, structure factor $0{\cdot}92 \times 10^{-12}$ cm., $\lambda = 0{\cdot}78$ Å, gave 282 neutrons min.$^{-1}$ per cubic millimetre. Correcting for the different unit-cell volume, the advantage in the Laue experiment is a factor of 30. This is clearly of such magnitude that the black box can introduce a loss factor of 5 and still leave a worth-while overall improvement.

(*b*) Concerning ease of operation: (v) the shapes of all reflected peaks are identical; (vi) the angles θ and 2θ to which the spectrometer is set need not be more accurate than, say, 10′.

Both these points are manifestly suited to the requirements of automatic registration.

Conditions

The method of increasing intensity by enlarging $\Delta\theta$ has a basic limitation. If the wavelength band called into use is too wide, other crystal planes of similar d to the one examined will also begin to reflect into the counter. As an example, consider the observation of an nth order line. It is easy to show that if $\Delta\theta$ is enough to allow reflexion of a wavelength band wider than $\lambda/(n+\frac{1}{2})$, then the line of order $(n+1)$ will also be registering. More exactly

$$\frac{d\lambda}{\lambda} < \frac{2}{n+1} - \frac{n \cot\theta . \Delta\theta}{n+1} \qquad (7)$$

is a necessary condition; and since the absolute intensity is proportional to $d\lambda$, (7) favours the employment of long wavelengths. Again, because $d\lambda/\lambda = \cot\theta . d\theta$, one must have

$$\cot\theta . \Delta\theta < d\lambda/\lambda , \qquad (8)$$

so that the collimation does not allow incidence angles for which wavelengths are not supplied. Equation (8) leads to an upper limit on $\Delta\theta$ or a lower limit on θ.

The situation is illustrated in Fig. 4, which shows the reciprocal lattice of a crystal set up for inspection of the $\{hk0\}$ zone. Strictly speaking, each lattice point

should be drawn out into a small arc by virtue of the mosaic spread of the specimen. Because of the relaxed collimation, the band $d\lambda$ of wavelengths is incident

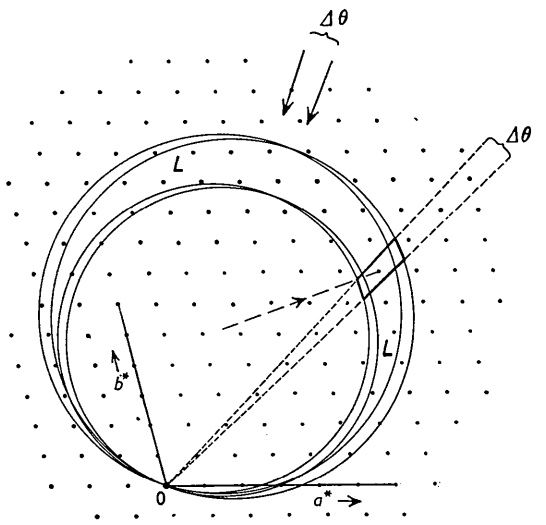

Fig. 4. The reciprocal lattice of a crystal set up to record a 770 integrated intensity by the Laue method. Radiation comprising a wide band $d\lambda$ of wavelengths is incident over the angular range $\Delta\theta$ marked with arrows, and limiting spheres of reflexion show the 'coverage' of reciprocal space thereby provided. Lattice points within the crescent-shaped area L are giving Laue reflexions; in particular, the diffracted beam 770 emerges about a central direction parallel to that of the radius vector indicated by a broken line. The framed region around the point 770 is the area which must be clear of other points if confusion between different reflexions is to be avoided.

effectively over a range $\Delta\theta$ of angle, and spheres of reflexion are drawn at the limits of this variation. The planes (770) are clearly reflecting; equation (7) expresses the fact that (660), (880) and other orders are not.

As well as avoiding the orders $(n-1)$ and $(n+1)$ it is, of course, equally important to prevent reflexion from neighbouring reciprocal-lattice points of any index, for instance 760 in the above example. This is not simply a question of order. The 1,10,0, which is also reflecting in Fig. 4, is a first-order line, but must obviously be treated like tenth order to avoid confusion with the 190. Now, crystal planes reflect like mirrors, and by reference to Fig. 3 it is clear that another plane in the same zone must be within $\pm\frac{1}{2}\Delta\theta$ of the chosen plane to reflect into the counter simultaneously. An appropriate angular range $\Delta\theta$ has therefore been drawn about 770 in Fig. 4, to define the region of reciprocal space in which such a plane must be represented. It will be seen that a small area can be marked out around the chosen reciprocal-lattice point, which must be clear of other points if the desired reflexion is to be received without adulteration.

No doubt a set of analytical rules governing θ, λ and $d\lambda$ could be found, ensuring that every desired reflexion is obtained pure. For the present purpose it suffices to remark that this problem is soluble, and that surprisingly few λ, $d\lambda$ combinations are required to cope with a complete analysis. For instance, only about half a dozen would have been needed for KH_2PO_4. This is essentially because $\Delta\theta$ is instrumentally limited to about three or four degrees, an amount which is intrinsically 'small'; in a tetragonal substance the 10,10,0 beam overlaps neither the 9,10,0 nor the 10,11,0 with this collimation.

Cases of particular difficulty can occur which must be met with very small $d\lambda/\lambda$, or by reducing $\Delta\theta$ with a slit at the counter. The most important provision in the black box is evidently a sufficient choice of wavelengths λ, in order to be able to take any reflexion at will to high θ. For, according to (8), a large θ permits the collimation to remain wide although $d\lambda/\lambda$ has been reduced.

A procedure

The first operation is to select an economical number of λ, $d\lambda$ combinations to deal with the problem. To do this, either the construction of Fig. 4 may be employed, or analytical methods developed. The procedure would then be to take the main bulk of the readings in batches at fixed wavelength, each reflexion being allotted to the longest appropriate wavelength below about 1·6 Å.

There remain the lines of large d. If the maximum $d\lambda/\lambda$ is about 0·25 and the maximum λ about 1·6 Å, then, by equation (8), lines of spacing greater than $2\frac{1}{2}$ Å cannot be dealt with. However, these will have such favourable intensity, on account of the d^2 term, that they can easily be taken by the rotating-crystal method on the same apparatus. The incident beam having insufficient $d\lambda/\lambda$ for the Laue method, it becomes 'monochromatic radiation', and is to be employed accordingly.

Exceedingly weak lines

If the black box is of a type that involves intensity losses, there is still one last resort which may be employed with exceedingly weak reflexions, and that is to abandon the box and allow the whole neutron spectrum to fall unhindered on to the specimen. As the author pointed out some years ago (Lowde, 1951), even in this situation it can often be arranged that the peak of the Maxwell spectrum discriminates in favour of the order of reflexion required. In particular, if the line to be examined is first order, the amount of intensity available for higher-order contamination is very small. Supposing all orders to have the same structure factor, Fig. 1 shows that at $\lambda = 1$ Å the second and third orders together contribute only 1% of the counting rate. With increasing order of reflexion these contamination difficulties eventually become insuperable; nevertheless, most of the lines in a typical structure analysis are, in fact, first order.

When this expedient is tried, there are two complications. The entire incident spectrum contributes to the background, thermal neutrons scattering on the disordered cross-sections s and epithermals on the free scattering cross-sections σ of the atoms; and very strong lines of different (hkl) may also appear, superposing their diffuse scattering on the reflexion examined. As an example, iron at $11\bar{6}$ gave approximately 806 counts min.$^{-1}$ above an isotropic background of 123, plus another 128 due to inelastic scattering at $11\bar{4}$. It must be remembered that the disordered scattering from iron is small but the inelastic scattering unusually large.

The wavelength selector

Little will be said on this topic except to remark that it is a technical possibility. A specified wavelength band $d\lambda$, as nearly as possible 'square' and centred on a given λ, is to be provided uniformly over a rather wide angle $\Delta\theta$ with the maximum efficiency. There are various ways of doing it:

(1) With a time-continuous source, such as a reactor. (*a*) Mechanically, with some adaptation of the rotating-disc monochromator discussed by Hughes (1953), perhaps with the last rotor 'gating' the counter directly. (*b*) Electronically, using chopper techniques but with electronic 'gating'. Both (*a*) and (*b*) can only provide a 'square' wavelength band by sacrifice of intensity, and an efficiency of 5% must be expected. They are also 'in-line' methods, so that it is essential to make the choppers opaque to epithermal neutrons. (The 123 background from 25 mm.^{3} of iron, quoted above, contained 72 counts min.$^{-1}$ due to epithermals.) (*c*) A third possibility is that the conventional monochromating crystal be simply oscillated so as to draw a wider spectrum of wavelengths from the pile. This would, of course, give counting rates similar to those of the rotating-crystal method, the difference being that integrated intensities were measured by the Laue method, rotation of the monochromator replacing that of the specimen.

(2) With a pulsed source of thermal neutrons. Egelstaff has pointed out that this type of source is ideally suited to the Laue technique, since the operation of standard time-of-flight methods allows any appropriate wavelength band to be selected without loss of efficiency. At the same time the 'gating' of the scalers ensures complete freedom from background troubles due to epithermals. This is evidently the field in which the new technique can be applied most profitably.

Notes on extinction

When extinction effects are estimated for the Laue method, using the discussion of Bacon & Lowde (1948), the integrated reflexion $\mathscr{R}^\theta$ in their paper is to be replaced by $\mathscr{R}^\lambda/2d\cos\theta$. However, the Q in their formulae is, and remains, Q^θ.

The criterion of whether extinction is serious with the Laue method reduces to a simple numerical condition on the counting rate. According to Bacon & Lowde's Fig. 6, the condition for a reading to be accurate to 5% is

$$\mathscr{R}^\theta/\eta < \tfrac{1}{4}\,. \tag{9}$$

Thus the maximum allowable $\mathscr{R}^\lambda$ for 'no extinction' is

$$\mathscr{R}^\lambda_{\max.} = \tfrac{1}{2}\eta d\cos\theta\,, \tag{10}$$

and, since $\mathscr{R} = \mathscr{I}/I_0$, the corresponding maximum rate of neutrons min.$^{-1}$ is

$$\mathscr{I}_{\max.} = \tfrac{1}{2}I_0(\lambda)\eta d\cos\theta\,. \tag{11}$$

With an η value of 2′ for the iron crystal this came to 7,400 neutrons min.$^{-1}$ at $11\bar{6}$.

It will also be noticed that the provision of many incident wavelengths is extremely convenient for the use of Bacon & Pease's method (1953) for measuring extinction corrections.

Conclusions

A Laue method of integrated intensity measurement is possible which is both simpler and quicker to operate than the rotating-crystal method. The apparatus required, however, has more to go wrong, and it will require some effort to establish the technique in the first place. This effort may be worth while if intensity difficulties continue to hamper the production of structure analyses.

References

Bacon, G. E. & Lowde, R. D. (1948). *Acta Cryst.* **1**, 303.

Bacon, G. E. & Pease, R. S. (1953). *Proc. Roy. Soc.* A, **220**, 397.

Egelstaff, P. A. (1953). A.E.R.E. N/M 60.

Egelstaff, P. A. (1954). Third Congress of the International Union of Crystallography, Paris.

Hughes, D. J. (1953). *Pile Neutron Research.* Addison: Wesley Press.

Lowde, R. D. (1951). *Nature, Lond.* **167**, 243.

Lowde, R. D. (1954). *Proc. Roy. Soc.* A, **221**, 206.

Taylor, B. T. (1952). A.E.R.E. N/R 1005.

Zachariasen, W. H. (1945). *Theory of X-ray Diffraction in Crystals.* New York: Wiley.