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Accurate Intensity Measurements in Single-Crystal Analysis by Neutron Diffraction*

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Two aspects of the problem concerning accuracy of intensity measurements in single-crystal analysis by neutron diffraction are discussed: (i) the manner in which the experimental value of the intensity of a Bragg reflexion may be affected by the use of the ω- and 2θ-scan techniques; (ii) the manner of controlling, where possible, the effect of simultaneous Bragg reflexions on the intensity. In addition, conceivable experiments of 'elastic' neutron diffraction by means of a triple-axis spectrometer are discussed in connection with an accurate determination of the Debye–Waller factor.

1. Introduction

The purpose of this communication is to review and discuss certain of the factors which should be considered in accurate neutron diffraction work for single crystal analysis.

Discussion will be limited to the following topics:

(i) Effects of the typical collimating elements of a conventional diffractometer on the values of the intensity, as measured by the 2θ- and ω-scans.

(ii) Importance of the simultaneous Bragg reflexions.

(iii) Main features of conceivable experiments of 'elastic' diffraction of neutrons in single crystals.

No detailed consideration will be given to other features of the diffraction experiments, such as crystal extinction, crystal dimensions, second-order wavelength contamination of the neutron beam, *etc.*, which also may strongly affect the accuracy of neutron diffraction work.

2. Effects of the collimating elements of a diffractometer on the intensity, as measured in the 2θ- and ω-scans

In a well-known paper by Alexander & Smith (1962) the problem of the 2θ-scan and ω-scan techniques in X-ray diffraction has been thoroughly investigated.

The analysis of the geometry of the diffraction process of X-rays monochromatized by conventional radiation filters led Alexander & Smith to recommend the use of the 2θ-scan technique rather than the ω-scan technique: in fact, the rays of wavelength λ different from the 'central' λ_0 come into play progressively during the 2θ-scanning and, as a consequence, an accurate subtraction of the intensity due to X-rays of wavelength $\lambda \neq \lambda_0$ at the base of the peak can be performed; the ω-scan technique on the other hand leads to the acceptance of the group of X-rays of wavelengths $\lambda \neq \lambda_0$ in a narrow, well defined symmetrical peak, from which it is practically impossible to unfold the contributions due exclusively to the central wavelength.

The conclusions reached by Alexander & Smith cannot be directly applied to neutron diffraction essentially for two reasons:

(i) As suggested by the authors themselves, the geometry of the X-ray paths is quite different in the cases of *crystal* monochromatized and filtered radiation: this is due in practice to the fact that, in the case of crystal monochromatized radiation, the direction of the X-ray impinging on the sample is intimately coupled with its wavelength.

(ii) The wave vector of the scattered neutron is in general not identical in magnitude with that of the impinging neutron: when neutrons in the thermal energy region (associated for instance with a wavelength $\lambda \sim 1$ Å and an energy $E \sim 0{\cdot}08$ eV) interact with a crystal they, as a rule, are allowed to create or annihilate one (or more) vibrational quantum of the crystal (phonon) associated with the normal modes of vibrations whose superposition conveniently describes the thermal motions within the crystal on a microscopic scale (Seeger & Teller, 1942). Consequently, the condition (valid for the case of X-rays) *magnitude of the impinging wave vector = magnitude of the final wave vector* being relaxed, the 'ridge' of general radiation intensity, which for X-rays piles up around the reciprocal lattice point along the line connecting the reciprocal lattice point to the origin, slides down, showing up again, in principle, in different regions named in neutron spectrometry the 'scattering surface'. This is a further argument against a naive, direct extension to neutron diffraction,

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of the conclusions reached for the geometry of X-ray diffraction by Alexander & Smith.

In view of the above circumstances, in the case of neutron diffraction, the ω-scan procedure deserves close consideration. Some features of the ω-scan technique are presented here with particular reference to the precautions to be taken by experimentalists who may prefer to utilize it rather than the 2θ-scan.

The results to be discussed in this section were derived (Caglioti, Paoletti & Ricci, 1958, 1960; Caglioti & Ricci, 1962; Caglioti, 1962; Caglioti & Farfaletti Casali, 1962) in recent years, during the development of a more general program whose main object was to establish useful criteria for a convenient and eventually inexpensive choice of several important instrumental parameters one must assign in order to perform any neutron diffraction experiment, such as angular divergences of the collimators, Bragg angle and mosaic spread of the monochromator, wavelength of the monochromatic beam. Reference can be made to previous papers for a detailed discussion of the computing techniques utilized in order to establish those criteria. Here it will be sufficient to recall that the procedure systematically followed was that of computing, under reasonably general hypotheses, the instrumental width and the 'instrumental luminosity' (see later) of the diffraction peaks in terms of the angular divergences of the collimators and the mosaic spreads of the monochromating crystal and the sample. In all of the cases considered the approach adopted was:

To follow the path of any individual neutron.
To assign to the neutron the probability of reaching the (BF_3) detector after proceeding through the collimating system of the spectrometer and being Bragg-reflected by monochromator and sample.
To sum such a probability over all of the paths accepted by the geometrical parameters of the spectrometer.

It is not possible here to go through the details of the technique which was adopted to compute the instrumental broadening and luminosity of the Bragg reflexions under the usual experimental conditions (*i.e.* 2θ-scan and ω-scan for single-crystal, and 2θ-scan for powder diffraction). We will therefore only list the most important approximations which underlie the calculations:

(i) The attenuation of the neutrons passing through any of the (Soller) collimators in the spectrometer is a Gaussian (rather than a triangular) function of the angular displacement of any individual ray with respect to the centre line of the collimator itself.

(ii) The linear dimensions of the monochromator and the crystal sample are assumed to be large in comparison with the size of the Soller slits.

(iii) Only the parameters describing the *angular* acceptance of the collimating elements of the diffractometer (such as horizontal angular divergences of the collimators, mosaic spreads of the crystals) have a direct influence on its resolution. The actual geometry of the spectrometer (determined by the distances between typical elements of the experimental set up, such as radiating surface within the reactor, monochromator, sample and counter) is assumed to be less important.

The first of the hypotheses listed above was proved by Shull (1960) to be very reasonable. Hypothesis (ii) is usually not satisfactorily verified in single-crystal neutron diffraction work; nevertheless, when such is the case, it should be possible to introduce a kind of 'effective' angular divergence of the monochromator-sample and sample-counter collimators in order to take into account the additional collimating action due to the (small) size of the (extinction-free) crystal sample. The third point has been very recently studied by Sabine & Browne (1963), who suggest that, in principle, one might improve the resolution of a diffractometer by a suitable choice of the ratio between the source–monochromator distance and the monochromator–specimen distance.

Under the hypotheses listed above, it was established that the actual shape of a Bragg reflexion, as seen by the diffractometer, is indeed a Gaussian function of the angular displacement of the rocking crystal (ω-scan) or the detector (2θ-scan) with respect to the peak value; these Gaussian distributions of intensity are found to have, as expected, identical values at their peak (that is for $\delta\omega=0$, and for $\delta 2\theta=0$). Nevertheless, owing to the different behaviour of their width as a function of the 'dispersion parameter' (see later) in the two cases, the instrumental luminosities are not equal.

In this section we will limit ourselves to discussing some details of the ω- and the 2θ-scan techniques, in view of possible applications in the automatic collection of the data by means of modern neutron diffractometers. To this end, we will start by listing a set of four formulae (Table 1) which express the width and the instrumental luminosity of any Bragg reflexion in terms of the angular parameters of the collimating system and the 'dispersion parameter'.

Equations (1) and (2) (after Caglioti & Ricci, 1962) refer to the ω-scan and equations (3) and (4) (after Caglioti, Paoletti & Ricci, 1960) to the 2θ-scan. Equation (1) gives the full width at half maximum $B_{\frac{1}{2}}$ of the rocking curve in terms of the full width at half maximum β_2 of the angular distribution of the blocks of the mosaic crystal sample, the corresponding quantity β_1 of the monochromator, the horizontal angular divergences α_1, α_2, α_3 of the in-pile, monochromator-specimen, and specimen-counter collimators, and of the dispersion parameter $a=\tan\theta_B/\tan\theta_M$ computed at the Bragg angles θ_B and θ_M at which sample and monochromator are supposed to be set. Equation (2) gives the instrumental luminosity of the

Table 1. *Full width at half-maximum and instrumental luminosity of a Bragg reflexion*

Equations (1) and (2) apply to the ω-scan technique, and equations (3) and (4) to the 2θ-scan technique

$$B_{\frac{1}{2}}=\left\{\beta_2^2+\frac{\alpha_2^2\alpha_3^2(\alpha_1^2+4\beta_1^2)-2a\alpha_2^2\alpha_3^2(\alpha_1^2+2\beta_1^2)+a^2\left[\alpha_3^2(\alpha_1^2\alpha_2^2+\alpha_1^2\beta_1^2+\alpha_2^2\beta_1^2)+\alpha_1^2\alpha_2^2\beta_1^2\right]}{\alpha_3^2(\alpha_1^2+\alpha_2^2+4\beta_1^2)+\alpha_2^2(\alpha_1^2+4\beta_1^2)-4a\alpha_2^2(\alpha_1^2+2\beta_1^2)+4a^2(\alpha_1^2\alpha_2^2+\alpha_1^2\beta_1^2+\alpha_2^2\beta_1^2)}\right\}^{\frac{1}{2}} \tag{1}$$

$$R=\frac{\alpha_1\alpha_2\alpha_3\beta_1\beta_2}{\left[\alpha_3^2(\alpha_1^2+\alpha_2^2+4\beta_1^2)+\alpha_2^2(\alpha_1^2+4\beta_1^2)-4a\alpha_2^2(\alpha_1^2+2\beta_1^2)+4a^2(\alpha_1^2\alpha_2^2+\alpha_1^2\beta_1^2+\alpha_2^2\beta_1^2)\right]^{\frac{1}{2}}} \tag{2}$$

$$A_{\frac{1}{2}}=\left\{\frac{\alpha_3^2\beta_2^2(4\beta_1^2+\alpha_1^2+\alpha_2^2)+\alpha_2^2(4\beta_1^2+\alpha_1^2)(\beta_2^2+\alpha_3^2)-2a\alpha_2^2(\alpha_1^2+2\beta_1^2)(\alpha_3^2+2\beta_2^2)+a^2\left[(\alpha_1^2\alpha_2^2+\alpha_1^2\beta_1^2+\alpha_2^2\beta_1^2)\cdot(\alpha_3^2+4\beta_2^2)+\alpha_1^2\alpha_2^2\beta_1^2\right]}{(4\beta_2^2+\alpha_3^2)(\beta_1^2+\frac{1}{4}\alpha_1^2+\frac{1}{4}\alpha_2^2)+\frac{1}{4}\alpha_2^2(4\beta_1^2+\alpha_1^2)}\right\}^{\frac{1}{2}} \tag{3}$$

$$L=\frac{\alpha_1\alpha_2\alpha_3\beta_1\beta_2}{\left[(4\beta_2^2+\alpha_3^2)(\beta_1^2+\frac{1}{4}\alpha_1^2+\frac{1}{4}\alpha_2^2)+\frac{1}{4}\alpha_2^2(4\beta_1^2+\alpha_1^2)\right]^{\frac{1}{2}}} \tag{4}$$

rocking curve. The latter is defined as the scale factor by which the measured value of the luminosity should be divided in order to obtain the integrated reflectivity. Similarly equations (3) and (4) provide the instrumental width and the instrumental luminosity for the case of the 2θ-scan.

Before going into a detailed discussion of the above equations, we should like to make the following remarks.

(i) According to equations (1) and (3), the widths of the diffraction peaks do not depend on the mosaic spread β_1 of the monochromator as strongly as one would anticipate. Actually the quantity more directly connected with the resolution in neutron diffraction is the dispersion parameter (Caglioti, Paoletti & Ricci, 1958):

$$a=\frac{(d\theta/d\lambda)_{\text{sample}}}{(d\theta/d\lambda)_{\text{monochromator}}}=\tan\theta_B/\tan\theta_M\,.$$

The latter is a measure of the relative dispersion undergone by the neutron beam on the sample and on the monochromator. The value of a should be kept (Willis, 1960) within the so-called focusing region ($a\sim 1$), as exemplified by Levy & Peterson, who fixed a value as high as 90° for the take-off angle $2\theta_M$ of their diffractometer at the Oak Ridge high-flux research reactor. A striking, direct experimental proof of the influence of the dispersion parameter on the resolution of a diffraction pattern is given by Caglioti & Ricci (1962).

(ii) Expressions (2) and (4) for the *instrumental* luminosity do not include the crystal reflectivity as determined by the amount of extinction suffered by the ratiation within a single crystal. Work recently performed at the JAERI (Kunitomi, Hamaguchi, Sakamoto, Doi & Komura, 1963) indicates a procedure for taking into account extinction (Bacon & Lowde, 1948) in conjunction with our expressions for the instrumental luminosity, in practical computations of the reflectivity of a single crystal.

2·1. *ω-scan*

Equation (1) gives the full width at half maximum $B_{\frac{1}{2}}$ of the Bragg reflexions as a quadratic combination of the mosaic spread β_2 of the crystal specimen and a sort of 'instrumental contribution to the width'; the latter proves to be extremely small in the focusing region, and adds a sizable contribution to the width $B_{\frac{1}{2}}$, especially at large values of the dispersion parameter, when α_3 is large compared with the other α's and to β_1. Equation (1) may be useful in the automatic collection of the intensity data, since it gives a fairly accurate measure of the angular range of interest at any Bragg reflexion; conversely, equation (1) may be applied (Caglioti & Ricci, 1962) as an operational definition of the mosaic spread of the crystal sample in terms of other known parameters, which in any case are of vanishing importance at the focusing position. The theoretical behaviour of $B_{\frac{1}{2}}$ *versus* $\tan\theta_B/\tan\theta_M$ is shown in Fig. 1(*a*).

Equation (2) expresses the dependence of the instrumental luminosity R of the spectrometer as

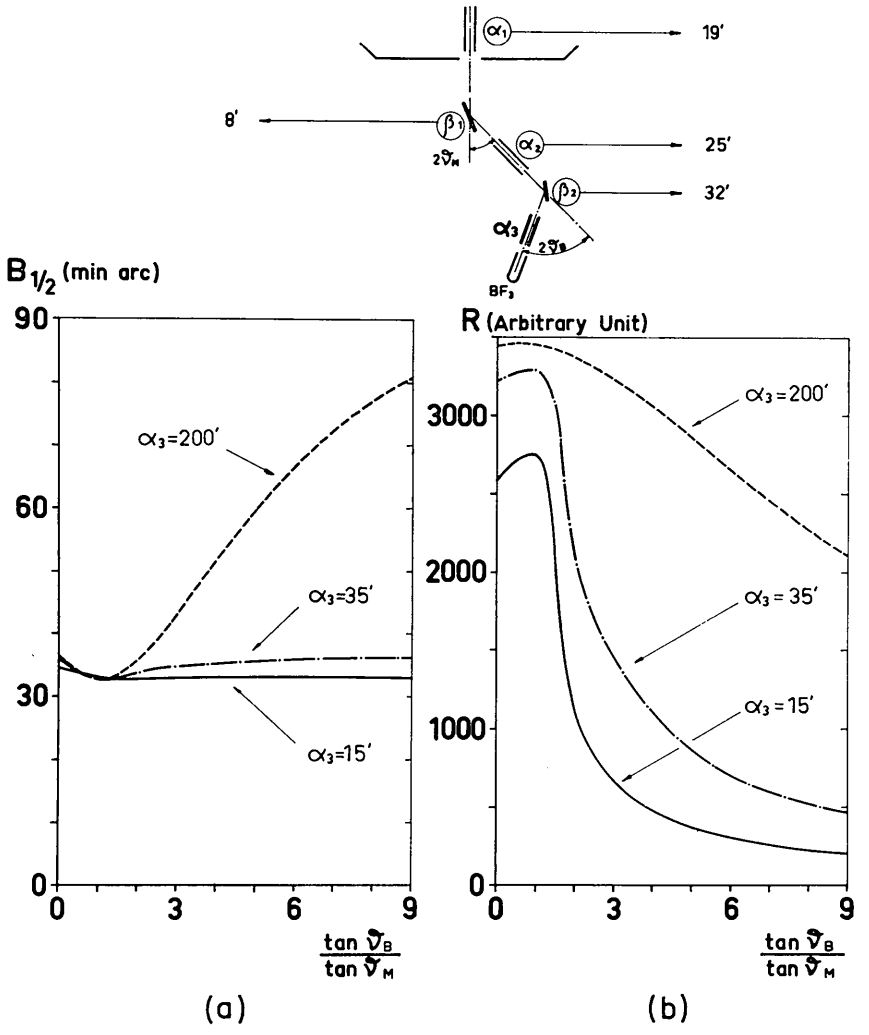


Fig. 1. (*a*) Full width at half maximum $B_{\frac{1}{2}}$ of a rocking curve as a function of the dispersion parameter $a=\tan\theta_B/\tan\theta_M$ in typical cases. Notice the minimum at the focusing position. This minimum is pronounced when the angular divergence α_3 of the sample-counter collimator is large. (*b*) Instrumental luminosity R of a rocking curve as a function of the dispersion parameter, for various typical cases. Notice the presence of a maximum at the focusing position.

a function of its collimating parameters *and* the dispersion parameter. It has long been known by X-ray crystallographers that, in order to perform a reliable intensity measurement with the ω-scan technique, it is necessary to operate with a 'broad' window in front of the counter. Equation (2), which applies to crystal-monochromatized radiation, allows us finally to control in a predictable way the amount of reduction of the integrated intensity produced by the diffractometer at any Bragg angle as a consequence of the limited angular acceptance of the collimator in front of the counter. In Fig. 1(*b*) we show how strongly the instrumental luminosity may depend on the dispersion parameter and, through it, on the Bragg angle, when the diffractometer is set for ω-scan. The variation of the instrumental luminosity with a, which is negligible in the focusing region since the instrumental luminosity reaches a maximum there, may become dramatic at higher values of the dispersion parameter, especially when the specimen-counter collimator has a narrow angular divergence.

In Fig. 2 the theoretical dependence of the instrumental luminosity R *versus* $\tan\theta_B/\tan\theta_M$ (full line) is compared with experimental results (open circles) we recently obtained in Ispra with a value of α_3 intentionally selected as unusually small. This comparison was performed by considering, at several values of the dispersion parameter a, the experimental and theoretical ratios of the a-dependent instrumental luminosity obtained in ω-scan to the constant (see equation (4)) instrumental luminosity obtained for the same Bragg reflexion in 2θ-scan. The intensities of the 200, 400, 600 and 800 ω-scan reflexions

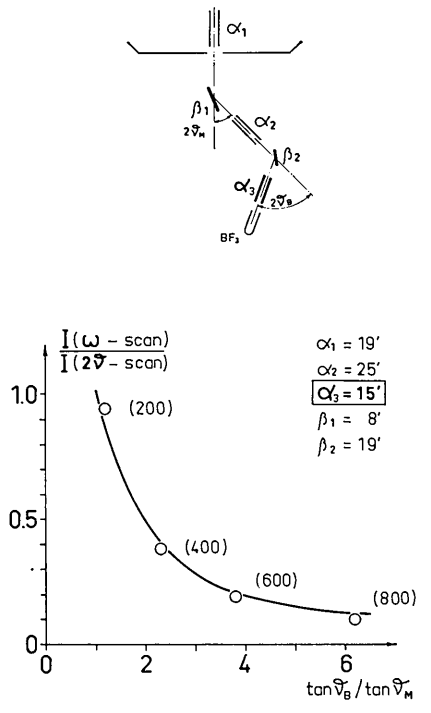


Fig. 2. Instrumental luminosity R *versus* $a = \tan\theta_B/\tan\theta_M$ for several rocking curves of an aluminum single crystal. The ratio $I(\omega\text{-scan})/I(2\theta\text{-scan})$ of the experimentally determined intensity of the 200, 400, 600 and 800 reflexions in the ω- and 2θ-scan procedures is compared with the corresponding ratio for the instrumental luminosities obtained through equations (2) and (4). The angular divergence of the sample-counter collimator ($\alpha_3 = 15'$) was intentionally selected as unusually small. Throughout these measurements a neutron wavelength $\lambda = 0{\cdot}75$ Å was utilized.

of an aluminum single crystal mounted in reflexion were normalized to the corresponding ones obtained by 2θ-scan, so as to avoid corrections for extinction.

2·2. 2θ-*scan*

Equation (3) gives the full width at half maximum $A_{\frac{1}{2}}$ of the Bragg reflexions as a function of the collimating parameters of the diffractometer and the dispersion parameter a. In this equation the mosaic spread of the crystal sample does not play a major role as in equation (1), but a remarkable minimum is still found at the focusing position. It has been proved that equation (3) satisfactorily explains experimental results (Caglioti & Ricci, 1962). Equation (3) is useful whenever one wishes to control the resolution of a diffractometer or to have an *a priori* knowledge of the range of the widths of the Bragg reflexions to be covered by the instrument.

Finally, equation (4) gives the instrumental luminosity L of the diffractometer in terms of its collimating parameters. In contrast with the corresponding equation (2) valid for the ω-scan, equation (4) shows that L is *independent* of the dispersion parameter. This fact will in any case simplify the treatment of the experimental 2θ-scan data, since no additional unusual instrumental corrections are needed. Nevertheless the widths of the peaks as determined by equation (3) are, *ceteris paribus*, generally larger in the 2θ-scan than in the ω-scan, so that the use of the ω-scan may ultimately result in an overall shorteni ng of the counting time, especially when the take-off angle of the monochromator is not large.

3. Importance of simultaneous Bragg reflexions

Many neutron experiments have been recently performed on the Renninger effect (Renninger, 1937), since it became clear (Moon & Shull, 1961) that the intervention of multiple Bragg reflexions may strongly affect the accuracy of intensity measurements in single-crystal analysis by neutron diffraction.

The discussion of this topic will be confined here to a broad outline of 'the effects of simultaneous reflexions on single-crystal neutron diffraction intensities': reference can be made to some very comprehensive work on this subject, recently performed at the Massachusetts Institute of Technology by Moon & Shull (1964). These authors discuss this problem both theoretically and experimentally, and indicate practical criteria to evaluate its importance and to overcome experimental difficulties connected with it.

From Fig. 3 it is easily seen (Renninger, 1937) that when a single crystal happens to be oriented in a monochromatic beam with *two* sets of crystal planes simultaneously in Bragg reflecting positions, there is always a *third* set of crystal planes oriented so as to enhance the intensity of the primary reflexion at the expense of the secondary one or *vice versa*. As a consequence, when the diffractometer is set for detecting a primary Bragg reflexion ($\mathbf{k}_0 \rightarrow \mathbf{k}_1$) one may excite the intervention of another simultaneous secondary Bragg reflexion ($\mathbf{k}_0 \rightarrow \mathbf{k}_2$) reorienting the crystal through an azimuthal rotation around the axis normal to the (primary) reflecting plane, the latter being preserved in reflecting position during this rotation. When the reciprocal lattice vector of another reflexion plane touches the sphere of reflexion, some of the radiation $\mathbf{k}_0 \rightarrow \mathbf{k}_1$ originally taking part in the primary reflexion will take part in the secondary reflexion $\mathbf{k}_0 \rightarrow \mathbf{k}_2$. In turn, since the reflexions $\mathbf{k}_1 \rightarrow \mathbf{k}_2$ and $\mathbf{k}_2 \rightarrow \mathbf{k}_1$ may occur on the third set of reflecting planes one has to face

(i) Reduction of intensity of the primary reflexion due to both of the processes $\mathbf{k}_0 \rightarrow \mathbf{k}_1 \rightarrow \mathbf{k}_2$ and $\mathbf{k}_0 \rightarrow \mathbf{k}_2$, and

(ii) Increase of intensity of the primary reflexion due to the process $\mathbf{k}_0 \rightarrow \mathbf{k}_2 \rightarrow \mathbf{k}_1$.

The identification of the azimuthal angles of occurrence of secondary reflexions (Cole, Chambers & Dunn, 1962) is straightforward for simple lattices and, even for complicated crystals (Santoro & Zocchi,

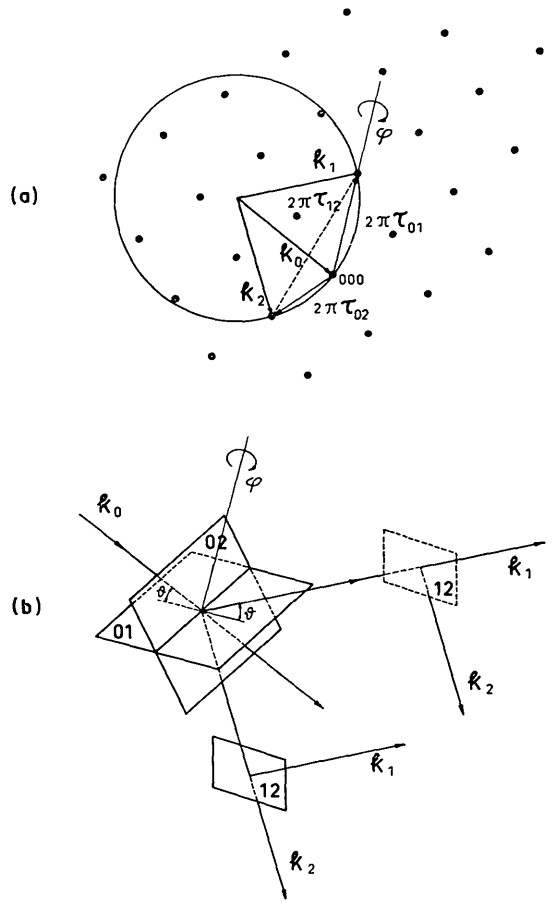


Fig. 3. Scheme of a multiple Bragg reflexion in (*a*) reciprocal space and (*b*) crystal space. The set of primary reflecting planes 01 may have any azimuth φ around the corresponding reciprocal lattice vector $2\pi\tau_{01}$, when the end point of $2\pi\tau_{01}$ lies on the sphere of reflexion. The existence of a competitive reflexion is determined by the value of the azimuth φ, which affects the mutual orientation of the wavevector $\mathbf{k}_0$ of the impinging neutron and the reciprocal lattice vector $2\pi\tau_{02}$ perpendicular to the set of (secondary) reflecting planes 02. When the planes 02 are also in reflecting position, there is always a *third* set of crystal planes 12 in conditions of enhancing the intensity of the primary reflexion ($\mathbf{k}_0 \rightarrow \mathbf{k}_1$) at the expense of the secondary one (process $\mathbf{k}_0 \rightarrow \mathbf{k}_2 \rightarrow \mathbf{k}_1$) or *vice versa* (process $\mathbf{k}_1 \rightarrow \mathbf{k}_1 \rightarrow \mathbf{k}_2$), all along the path of the radiation within the specimen, as indicated.

1964) does not present major difficulties. By contrast, the calculation of the intensity changes of the primary reflexion due to simultaneous reflexions may constitute a very intricate problem, especially when more than one secondary reflexion at a time arises in the Renninger pattern. This problem has been discussed so far only for mosaic crystals. The hypothesis is made that the neutron, in choosing among the competitive crystal planes, in a way, weights its decision over the structure factors rather than the scattering amplitudes. On this basis an approximate solution of this problem, suitable for a detailed comparison with the experimental data, was obtained by Moon & Shull for a crystal of iron, as an extension of the theory of secondary extinction for mosaic crystals (Renninger, 1937; Bacon & Lowde, 1948); an exact solution of the same problem was worked out by Borgonovi (1961), but extensive and detailed comparisons with the experimental data available at that time were not made.

In their paper Moon & Shull stress the criteria for minimizing the intensity of the competitive reflexions. These criteria may be listed as follows:

(i) To operate with crystals free from secondary extinction, that is 'small crystals with broad mosaic character'; the role played by competitive reflexions is in fact expected to have an importance increasing with the size of the corrections necessary to take account of secondary extinction.

(ii) To reduce as much as possible, especially for primary reflexions of low intensity, the length of the path responsible for the reflexions $\mathbf{k}_0 \rightarrow \mathbf{k}_2 \rightarrow \mathbf{k}_1$ and $\mathbf{k}_0 \rightarrow \mathbf{k}_1 \rightarrow \mathbf{k}_2$, by a convenient choice of the crystal shape and dimensions.

Another approach directed to by-pass the difficulties originated by the simultaneous Bragg reflexions in accurate intensity measurements has been proposed by Santoro & Zocchi (1964); they suggest the use of a 4-circle goniometer operating under instructions from an electronic computer, capable of measuring the intensity of the Bragg reflexions at controlled values of the azimuths of the reflecting planes. This instrument should be very useful when the linear dimensions of the unit cell are not too large with respect to the neutron wavelength, and, in general, for systematic studies of the Renninger effect in neutron crystallography.

It should be interesting at this point to indicate the actual amounts of the intensity changes due to simultaneous reflexions in the cases of extreme and moderate secondary extinction. In the former case, which is generally encountered in the process of selecting a monochromatic beam by Bragg reflexion from a crystal, the intensity variations are extremely serious — a factor of 5 for the peak values — (see for instance Fig. 2 of Borgonovi & Caglioti, 1962). In the second case, of more direct interest in crystal analysis, the intensity variations are of the order of 15%, as shown, for instance, in Fig. 4 (after Borgonovi, 1961), and found in iron by Moon & Shull.

4. Main features of conceivable experiments of 'elastic' diffraction of neutrons in single crystals

As indicated in § 2, the energy/momentum relationship for neutrons is fundamentally different from the corresponding one valid for X-rays. When an X-ray of about 12 keV (wavelength $\lambda \sim 1$ Å) is scattered by a solid and allowed to create or annihilate one or more phonons, it does not suffer any perceptible

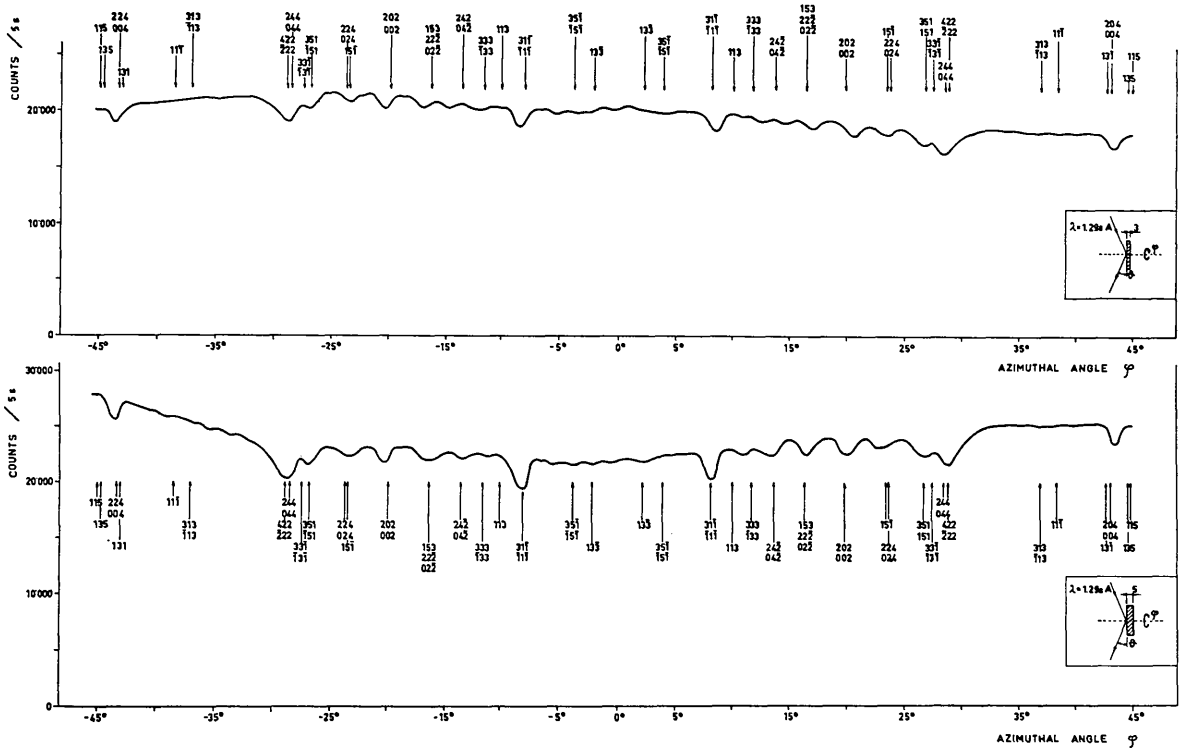


Fig. 4. Renninger patterns of the 200 reflexion by Al single crystals (discs 1·25 cm dia., 0·3 and 0·5 cm thick) cut with their base parallel to the reflecting planes, as indicated in the insets (Borgonovi, 1961).

change of energy, wavelength or wavevector magnitude, since the energy of a phonon cannot exceed, in practice, 0·1 eV; on the contrary, when a neutron of the same wavelength (energy 0·08 eV) is scattered by a solid interacting with the phonons, it generally undergoes radical changes of energy, which are naturally coupled with important changes of wavelength and wavevector magnitude.

One is then ready to accept that the basic phenomena regulating the intensity of the diffuse scattering of X-rays — as comprehensively discussed by James (1954) and, more recently, by Wooster (1962) — should be reconsidered for a sound treatment of the case of neutron scattering. The thermal diffuse scattering of neutrons, in fine detail, has indeed been the object of both theoretical (Weinstock, 1944; Waller & Fröman, 1952; Fröman, 1952; Placzek & Van Hove, 1953; Van Hove, 1954; Sjölander, 1958; Maradunin, Montroll & Weiss, 1963) and experimental (see, for instance, the IAEA Proceedings of the Vienna (1960) *and* Chalk River (1963) Symposia on Inelastic Scattering of Neutrons in Solids and Liquids) investigations during the last two decades. These investigations, devoted to a detailed analysis of the individual contributions to the overall thermal diffuse intensity, induced by single- or multi-phonon processes in slow neutron scattering, have led, during the last ten years, to the development of a kind of generalized crystallography: *any* point within a Brillouin zone in reciprocal *space* is now worthy of special consideration, since it has the physical meaning of wave vector of a 'measurable' phonon, that is of a phonon to which, as a consequence of the possibility of perceiving energy transfers as small as 1 meV, one may also attach the appropriate frequency (or, so to say, reciprocal *time*).

A delicate problem (Nilsson, 1957) in the intensity measurements of the Bragg reflexions from a crystal is to extract, from the diffraction pattern, the 'zero-phonon' term: this is the term representing scattering processes which leave the crystal in its initial state; these processes, unaccompanied by energy transfers from the neutron to the crystal or *vice versa*, constitute the prominent part of the scattering and should enable the experimentalist to draw a picture of the crystal structure which realistically includes the effects of the thermal motions, but is unaffected, in the limiting case, by the very act of observation.

The possibility of measuring the energy of the outgoing (as well as the impinging) neutrons by means of a triple-axis spectrometer (Brockhouse, 1961) stimulates some speculations about the usefulness of experiments of 'elastic' neutron diffraction by a solid, which nowadays could be easily performed by methods common in neutron spectrometry.

Apparently, as explicitly suggested by Arndt & Willis (1962), the most promising experimental set-up plainly derives from that utilized in 'elastic' diffraction

by liquids (Brockhouse, 1958; Caglioti & Ascarelli, 1963). Actually, in one instance, (Calder, Cochran, Griffiths & Lowde, 1962) an experiment of 'elastic' neutron diffraction by (solid) lithium hydride has been performed with a triple-axis spectrometer, for a precision determination of the size of the Debye–Waller clouds in that compound. The experimental procedure (Fig. 5) consists in the measurement of the intensity of those among the diffracted neutrons, which have an energy ideally equal to that of the impinging neutrons. This energy selection is accomplished in practice by substituting, for the usual BF_3 counter arm of a diffractometer, an analysing crystal spectrometer set for Bragg reflexion ('only') of the neutrons having the same energy as those impinging on the specimen.

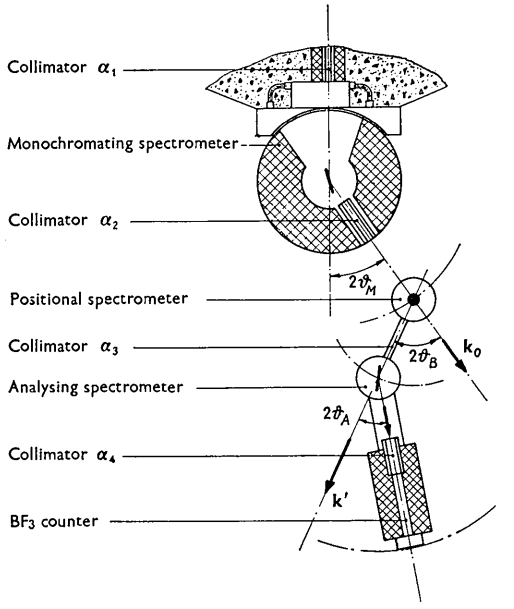


Fig. 5. A triple-axis spectrometer prepared for 'elastic' diffraction. As in a conventional diffractometer, the monochromating spectrometer provides a monochromatic beam of neutrons impinging on the specimen.

In principle, only those diffracted neutrons of energy equal to the energy of the impinging neutrons are allowed to be Bragg-reflected in the analysing spectrometer and to reach the BF_3 detector. In practice, the energy resolution of the spectrometer turns out to affect strongly, in several cases, the efficiency of the method of the 'elastic' diffraction.

A theory to establish the nature of the information obtainable by experiments of this sort can be easily worked out for the case of a monatomic incoherent scatterer. The calculations are, however, much more complex in the case of a coherent scatterer.

In practice one has generally to deal with substances which exhibit both coherent and incoherent contributions to the total scattering cross section, so that the preliminary conclusions we will attempt to draw for the limiting cases of purely incoherent and purely coherent scatterers should be considered only as a guide in evaluating more realistic cases.

The discussion which follows takes as a starting point the papers of Sjölander (1958) and Waller & Fröman (1952).

(a) 'Elastic' diffraction of neutrons by a monoatomic incoherent scatterer

The partial differential cross section of a nucleus in the crystal for the scattering of a neutron of initial energy ω_0 into the unit solid angle around $d\Omega$ and the unit final energy range around $(\omega, \omega+d\omega)$, is

$$\frac{d^2\sigma_{\text{inc}}}{d\Omega d\omega} = a_{\text{inc}}^2 \frac{k}{k_0} e^{-2W} \exp\left\{-\frac{(\omega-\omega_0)}{2K_BT}\right\} \times\left[\delta(\omega-\omega_0)+\frac{W}{\hbar\omega_D}+\ldots\right]. \quad (5)$$

The above expression can be easily derived from equation II.28 of Sjölander, if one neglects terms of order higher than one in the phonon expansion, and utilizes the Debye model for describing the frequency distribution of the normal modes inside the crystal. In equation (5) a_{inc} is the scattering amplitude of the supposedly incoherent scatterer, e^{-2W} is the Debye–Waller factor, K_B the Boltzmann constant, T the absolute temperature, ω_D the Debye frequency and $\hbar$ is Planck's constant divided by 2π.

As indicated in the Appendix, the angular distribution $(d\sigma/d\Omega)_{\text{elastic}}$ of the 'elastically' scattered neutrons may be conceived as the integral of equation (5) over the final energy $d\omega$, weighted by the energy resolution function of the spectrometer:

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{elastic}} = a_{\text{inc}}^2 e^{-2W}\left[1+\frac{\sqrt{\pi}}{2\sqrt{(\ln 2)}}\frac{\Delta}{\hbar\omega_D} \times W\exp\left\{\frac{\Delta^2}{64\ln 2(K_BT)^2}\right\}\right]. \quad (6)$$

In equation (6) Δ is a measure of the energy resolution of the spectrometer, as obtained by a suitable extension of the formulae of Sailor, Foote, Landon & Wood (1956), and its value is generally of the order of 10^{-3} eV. Correspondingly, since in practice $\Delta \ll 8K_BT\sqrt{(\ln 2)}$, one gets:

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{elastic}} \simeq a_{\text{inc}}^2 e^{-2W}\left\{1+1{\cdot}03\frac{\Delta}{\hbar\omega_D}W\right\}. \quad (7)$$

Equation (7) should allow one to extract rather easily the Debye–Waller factor, once the energy resolution of the instrument is satisfactorily known.*

It should be remarked that, on the contrary, the conventional neutron diffraction pattern of an incoherent scatterer (*e.g.* vanadium) is flat (that is

* In principle equation (7) is valid only for small values of the wave vector transfer $Q \equiv |\mathbf{k}_0-\mathbf{k}'|$, since at large values of Q higher order terms in the phonon expansion may become important.

$d\sigma/d\Omega \simeq a_{\text{inc}}^2$, since the scattering by a nucleus can be considered isotropic if one neglects the difference between the center of mass and laboratory system (as was done also in the derivation of equation (6)).

(*b*) *'Elastic' diffraction of neutrons by a monatomic coherent scatterer*

In their fundamental paper on the diffuse scattering of slow neutrons Waller & Fröman (1952) considered, for order-of-magnitude computations, the idealized case of a simple monatomic lattice exhibiting a sound velocity c independent of direction and polarization, and normal modes of vibration unaffected by dispersion. In a subsequent paper Sjölander (1954) treated in detail more realistic cases of isotropic and anisotropic crystals.

The differential scattering cross section $\sigma_1(\mathbf{k}_0, \mathbf{K})$ of the crystal for a process in which a neutron of wavevector $\mathbf{k}_0$ is scattered in the direction of a vector $\mathbf{K}$ (defined in terms of the wavevector $\mathbf{k}'$ of the outgoing neutron by the relationships $\mathbf{k}'/k' = \mathbf{K}/K$ and $K = k_0$) as a consequence of a one-phonon interaction, is found to be (Waller & Fröman, 1952):

$$\sigma_1(\mathbf{k}_0, \mathbf{K}) = N a_{\text{coh}}^2 e^{-2W} \cdot \frac{K_B T}{Mc^2} \cdot (2\pi\tau)^2 \cdot \frac{1}{\eta^2} \qquad (8)$$

for faster-than-sound neutrons, and

$$\sigma_1(\mathbf{k}_0, \mathbf{K}) = N a_{\text{coh}}^2 \cdot e^{-2W} \times \frac{K_B T}{Mc^2} \cdot \frac{(2\pi\tau)^2}{\eta^2} \cdot \frac{\beta}{1-(\beta^2-1)\cdot(\eta_\perp/\eta_{\parallel})^2} \qquad (9)$$

for slower-than-sound neutrons.

In the formulae above, N is the number of nuclei in the crystal, a_{coh} is the scattering amplitude of the supposedly coherent nucleus, M its mass, and $2\pi\tau$ is the reciprocal lattice vector under consideration, around which the thermal diffuse intensity assembles. $\boldsymbol{\eta}$ is defined as the vector distance $\mathbf{K} - \mathbf{k}_0 - 2\pi\tau$ expressing the deviation from the exact Bragg condition, and the symbols $\perp$ and $\parallel$ refer to the direction of $\mathbf{K}$ (Fig. 6). $\beta = c/v$ is the ratio of the velocity of sound to the neutron velocity v. While the cross section for faster-than-sound neutrons (equation (8)) is independent of their velocity, that for slower-than-sound neutrons (equation (9)) is strongly dependent on the ratio $\beta = c/v$.

In order to get some feeling about the main features of an experiment of 'elastic' neutron diffraction, we will try to establish, through a semiquantitative treatment, a comparison between the cases of conventional and 'elastic' diffraction for faster-than-sound neutrons. (The case of slower-than-sound neutrons is in general more complex but we feel that a solution could eventually be worked out.) We take equation (8) as a starting point of our computation, and we make the further simplifying assumption that in the cases of 'elastic' and conventional

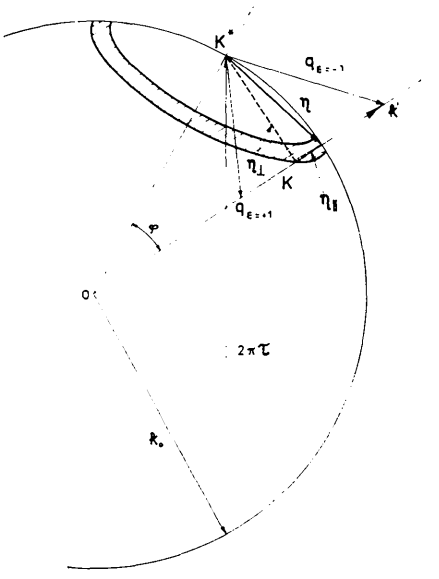


Fig. 6. Geometry of coherent scattering processes in a single crystal. The positional spectrometer and the crystal specimen are supposed to be set in the central position (dashed line) for a Bragg reflexion characterized by $2\pi\tau$. Nevertheless, the finite divergences of the collimating elements of the spectrometer permit the neutrons to undergo inelastic scattering processes characterized by phonon creation ($\varepsilon = +1$) or annihilation ($\varepsilon = -1$), as indicated. As a consequence, if k' is very different from k_0 (or K) the analysing spectrometer (not represented in this figure) will not allow it to reach the BF_3 detector. The individual contributions to the peak value of the diffuse intensity may be represented as a surface integral over the portion of the sphere of reflexion determined by the collimating elements of the spectrometer, as indicated in the text.

diffraction the monochromating spectrometer produces a strictly parallel and monochromatic beam of neutrons impinging on the crystal specimen. The problem of integration of equation (8) for the two types of diffraction has a simple solution for the particular case of the computation of the *peak* value of the diffuse intensity; this is practically obtained when the tip of the central value $\mathbf{K}^*$ of the vectors $\mathbf{K}$ accepted by the angular resolution of the positional spectrometer (collimator α_3) is exactly located at the tip of the reciprocal lattice vector $2\pi\tau$. It will become apparent that in this configuration of the positional spectrometer the effectiveness of the filtering action exerted on the neutron energies by the analysing spectrometer reaches a minimum. Nevertheless such effectiveness is generally larger in all of the other orientations of the positional spectrometer contributing to the integrated intensity, so that the conclusions to be reached here, concerning the region of peak intensity, should be of help in evaluating a *lower* limit of the power of the technique of 'elastic' diffraction.

With reference to Fig. 6, in the case of conventional diffraction, the peak intensity I^* is represented by

the integral of the cross section (9) over the solid angle $d\Omega$ centered around $\mathbf{K}^*/K^*$ representing the angular acceptance of the positional spectrometer. If the collimator α_3 has equal vertical and horizontal angular divergences, we may write

$$I^* = \int_{\Delta\Omega} \sigma_1(\mathbf{k}_0, \mathbf{K}) d\Omega \,. \tag{10}$$

Since (Fig. 6) $\eta = 2k_0 \sin \frac{1}{2}\varphi$ and $d\Omega = 2\pi\eta d\eta / k_0^2$, we may also write

$$I^* = N a_{\mathrm{coh}}^2 e^{-2W} \frac{K_B T}{Mc^2} \tau^2 \lambda^2 2\pi \int \frac{d\eta}{\eta}. \tag{11}$$

The limits of integration in (11) are of the order of $k_0\alpha_3$ and $N^{1/3}/a_0$, where a_0 is here the lattice parameter. Rather than in the actual value of this integral, we are interested here in a point by point comparison between the individual contributions to the diffuse intensity in the cases of conventional and 'elastic' diffraction.

The specific importance of these individual contributions has now been seen to be of the type η^{-1} in conventional diffraction. Let us then proceed to evaluate the behaviour of these contributions in the case of the 'elastic' diffraction.

When a neutron is scattered in a direction $\mathbf{K}/K$, and $\mathbf{K} \mp \mathbf{K}^*$, a phonon is created ($\varepsilon = +1$) or annihilated ($\varepsilon = -1$) within the crystal, as sketched in Fig. 6. The wave vectors $\mathbf{q}_{\varepsilon=+1}$ and $\mathbf{q}_{\varepsilon=-1}$ of these phonons are such as to close the polygonal $\mathbf{k}_0$, $\mathbf{k}'$ and $2\pi\boldsymbol{\tau}$, in accordance with the conservation of momentum. Furthermore the conservation of energy fixes in a compatible way the energy $(\hbar^2/2m)(\mathbf{k}_0^2 - \mathbf{k}'^2)$ lost ($\varepsilon = +1$) or gained ($\varepsilon = -1$) by the neutron and the energy $\hbar\omega(\mathbf{q})$ associated with the phonon taking part in the interaction.

The procedure to obtain an expression analogous to (11) for the peak intensity I^*_{elastic} of 'elastic' diffraction is similar to that outlined above. Nevertheless, in principle, one should start from equation (6′) of Waller & Fröman, instead of equation (8) reported above, and consider separately the interactions leading to energy gained ($\varepsilon = -1$) or lost ($\varepsilon = +1$) by the neutron. For any given value of η, the contributions to the total diffuse intensity should then be weighted by the appropriate value of the energy resolution function of the analysing spectrometer, while summing as before over the effective solid angle. Under the above assumption of a strictly monochromatic and parallel neutron beam impinging on the specimen, the energy resolution function of the spectrometer is

$$\exp\left\{-4 \ln 2 \frac{[\hbar\omega(\mathbf{q}_\varepsilon, \boldsymbol{\eta})]^2}{\Delta_A^2}\right\}$$

where Δ_A is the energy resolution (full width at half maximum) of the analysing spectrometer — as determined by a convenient generalization* of the treatment by Sailor, Foote, Landon & Wood (1956) — and $\hbar\omega(\mathbf{q}_\varepsilon, \boldsymbol{\eta})$ is the energy associated with each of the two phonons ($\varepsilon = \pm 1$) which can take part in the scattering process at any given value of $\mathbf{K}$. In order to simplify the arguments, we will make the numerical approximation — which is not strictly necessary — that, for a given value of $\mathbf{K}$, the squares of the energy of the annihilated ($\varepsilon = -1$) and created ($\varepsilon = +1$) phonons can both be assumed to be equal to their mean value

$$\hbar^2 c^2 q^2 = \frac{\hbar^2 c^2}{(1-\beta^2)^2} [(1-\beta^2)\eta^2 + 2\beta^2 \eta_{\parallel}^2] \,. \tag{12}$$

This conveniently allows us to start again with equation (8), which now will be weighted over the energy resolution function of the analysing spectrometer $\exp\{-(4 \ln 2 . \hbar^2 c^2 q^2)\}$ before considering the integration over η.

We can write:

$$I^*_{\mathrm{elastic}} = N a_{\mathrm{coh}}^2 e^{-2W} \frac{K_B T}{Mc^2} \tau^2 \lambda^2$$

$$\times 2\pi \int \frac{d\eta}{\eta} \exp\left[-\frac{4 \ln 2 . \hbar^2 c^2}{(1-\beta^2)^2 \Delta_A^2} \{(1-\beta^2)\eta^2 + 2\beta^2 \eta_{\parallel}^2\}\right]. \tag{11′}$$

We observe that, for β^2 not too close to unity, the term $2\beta^2\eta_{\parallel}^2$, which is of the order $2\beta^2 . 10^{-3}\eta^2$ at most, can be safely neglected with respect to $(1-\beta^2)\eta^2$. Furthermore, from equations (11) and (11′) it is seen that the specific importance of the individual contributions to the peak values of the diffuse intensity in the conventional and 'elastic' diffraction for a coherent scatterer is roughly given by the functions

$$1/\eta \quad \text{and} \quad \frac{1}{\eta} \exp -\left(\frac{4 \ln 2}{\Delta_A^2} . \frac{\hbar^2 c^2 \eta^2}{1-\beta^2}\right)$$

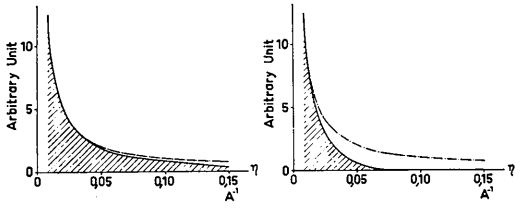
respectively. The areas subtended by these functions will be proportional to I^* and I^*_{elastic} respectively.

In Fig. 7 we plot the diagrams of the above functions in cases which can eventually be assimilated (*a*) to lead ($c = 1{\cdot}2 . 10^5$ cm.sec^{-1}) and (*b*) to copper ($c = 3{\cdot}8 . 10^5$ cm.sec^{-1}), as investigated by 1·01 Å ($v = 4{\cdot}91 . 10^5$ cm.sec^{-1}) neutrons. The three-axis spectrometer, set for 'elastic' diffraction as indicated in Fig. 5, is supposed to be prepared with very small values of α_1 and α_2, while $\alpha_3 = \alpha_4 = 30'$. The corresponding energy resolution Δ_A of the analysing spectrometer, which depends also on the choice of the analysing crystal, is found to be 2·6 meV if the Al(220) reflexion is utilized. Since $\eta \simeq 2\pi\alpha/\lambda_0$, the interesting range of η extends to about 0·1 Å^{-1}.*

From Fig. 7 it is seen that in both cases the energy selection operated on the diffracted neutrons by the analysing spectrometer is poor, as expected, when the deviation η from the exact Bragg condition is

* See also the Appendix.

* It should be remarked that a sizable amount of diffuse intensity may be due to the customary utilization of coarse vertical collimators. In this instance the vertical and horizontal angular divergences are supposed to be about equal.



(*a*) (*b*)

Fig. 7. The functions

$$1/\eta \quad \text{and} \quad (1/\eta).\exp\{-(4\ln 2/\Delta_A^2).\hbar^2c^2\eta^2/(1-\beta^2)\}$$

versus η (see Fig. 6). The area defined by these functions and the η axis may be assumed to be proportional to the peak value of the diffuse intensity for conventional (chain-dotted line) and 'elastic' diffraction (full line) respectively. (*a*) Pb, (*b*) Cu.

extremely small. For other values of η it seems that the analysing spectrometer could really operate an energy selection on the diffracted neutrons, especially for substances characterized by a comparatively high value of the Debye temperature or sound velocity. Nevertheless it should be remarked that, unfortunately, for substances which could most efficiently be studied by the method of 'elastic' diffraction, the intensity of the thermal diffuse scattering is intrinsically low; and *vice versa*, for 'soft' substances, where the diffuse intensity is high, the method of 'elastic' diffraction turns out to be less effective that one would wish, at least for faster-than-sound neutrons.

The above discussion refers to the case of *peak* intensity, where only small values of η are allowed, and correspondingly the effectiveness of the filtering action exerted on the neutron energies by the analysing spectrometer reaches a minimum. Furthermore only substances whose sound velocity is smaller than neutron velocity have been considered above. It seems then that in practice one might often deal with more favorable situations, so that experimental tests of the effectiveness of the method of 'elastic' diffraction could be worthy in view of the difficulties one would have to face in order to make a more satisfactory theoretical analysis. The loss of intensity one would suffer in performing experiments of 'elastic' — as compared with 'conventional' — diffraction is expected to be of the order of ten. Nevertheless, it should be pointed out that the arrangement proposed for experiments of 'elastic' diffraction necessarily leads to an improvement in resolution, and should be of assistance for reducing the effects of second order wavelength contamination in the monochromatic beam.

Work is in progress in our laboratory to establish some criteria for optimizing resolution and luminosity of a three-axis spectrometer prepared for 'elastic' diffraction, and a report on our results will be published in the near future.

5. Conclusions

A comparative study is presented of the 2θ- and ω-scan techniques and additional, satisfactory experimental tests of general and useful formulae previously established are reported; in particular, a method is discussed in some detail to evaluate the integrated intensity of a Bragg reflexion from the value of the intensity as measured with the ω-scan technique. The influence of the simultaneous Bragg reflexions on the values of the measured intensities is also discussed. Finally, the main features of 'elastic' diffraction experiments which now may be performed by means of a triple-axis spectrometer are discussed, for the first time, for the limiting cases of incoherent and coherent scatterers. In this preliminary treatment it is found that the method of 'elastic' diffraction should be useful for an accurate measurement of the Debye–Waller factor, and that the loss of intensity, associated with the energy selection, should be at least in part counterbalanced by the improvement in resolution and by the reduction of the effects due to the second order contamination in the monochromatic beam.

APPENDIX

We show here the procedure followed to perform the integrations indicated in § 4(*a*).

In Fig. 5, suppose both the monochromating and analysing spectrometers to be set so as to accept a central value E_* of the energy of the neutrons passing through them. If there is no specimen on the crystal table, amongst X neutrons impinging on the monochromating spectrometer per unit energy interval around E_*, *one* will reach the detector if X is given by the equation:

$$1 = X\int \exp\left[-4\ln 2\,\frac{(\omega_0-E_*)^2}{\Delta_A^2}\right] \times \exp\left[-\frac{(\omega_0-E_*)^2}{\Delta_M^2}4\ln 2\right]d\omega_0 \qquad \text{(A1)}$$

where Δ_M and Δ_A (Sailor, Foote, Landon & Wood, 1956) are the full widths at half maximum of the energy distributions of the neutrons Bragg-reflected by the monochromating and analysing crystal respectively and can be immediately computed for any given geometry of the spectrometers.*

* By a suitable generalization of equation (14) of Sailor, Foote, Landon & Wood (1956) it is found that the energy resolution Δ_M (full width at half maximum expressed in eV) is given by the equation

$$\Delta_M = 4d_M\cos\theta_M(0{\cdot}286)^{-1}E_*^{3/2}.\Delta\theta_M \qquad \text{(A3)}$$

where d_M is the spacing of the Bragg-reflecting crystal planes in units of 10^{-8} cm, E_* is the central value of the energy of the monochromatic beam expressed in eV, and

Solving (A1) we get:

$$X = \frac{2\sqrt{(\ln 2)}}{\sqrt{\pi}} \cdot \frac{\Delta}{\Delta_A \Delta_M}, \tag{A2}$$

where

$$\Delta = \sqrt{(\Delta_A^2 + \Delta_M^2)}\,. \tag{A5}$$

The number of neutrons capable of reaching the detector when the specimen is mounted on the crystal table if X neutrons imping on the monochromator is:

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{elastic}} = X \int d\omega_0 \exp\left[-4 \ln 2 \frac{(\omega_0 - E_*)^2}{\Delta_M^2}\right] \times \int \frac{d^2\sigma_{\text{inc}}}{d\Omega\, d\omega} \exp\left[-4 \ln 2 \frac{(\omega - E_*)^2}{\Delta_A^2}\right] d\omega\,. \tag{A6}$$

Substitution of (5) in (A6) leads eventually to expression (6) of the text.

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$$\Delta\theta_M = \left[\frac{\beta_1^2(\alpha_1^2 + \alpha_2^2) + \alpha_1^2 \cdot \alpha_2^2}{\alpha_1^2 + \alpha_2^2 + 4\beta_1^2}\right]^{\frac{1}{2}}. \tag{A4}$$

A similar expression holds for Δ_A when α_1, α_2 and β_1 are replaced by α_3, α_4 and the mosaic spread β_3 of the analysing crystal respectively.

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