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Treatment of Secondary Extinction and Multiple Scattering in Polarized Neutron Scattering: An Improved Method. I. Method

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Abstract

A new method for the treatment of secondary extinction in polarized neutron diffraction data has been developed. As in previous models, the Zachariasen solutions to the Darwin intensity transfer equations are used, but in this case the extinction corrections are made on a point-by-point basis across the rocking curve and the corrections are determined by the absolute reflectivity at each point. There are no adjustable parameters (other than background). Measurement of the reflectivity also provides a simple test for multiple scattering, since the sum of diffracted and transmitted intensities should equal the direct-beam intensity, corrected for absorption, if no multiple scattering is present. The present method should give more reliable results than parametrized models where the correlation between the extinction and other parameters, such as the scale factor and temperature factors, are important.

1. Introduction

Scattering of polarized neutrons has provided nearly all of the information presently available about the

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distribution of magnetization (spin) density in solids. In these experiments, the flipping ratio, which is the ratio of neutron intensities scattered by a magnetized sample in a spin-up (+) and a spin-down (−) state, is measured for those reflections which have an observable magnetic contribution. From the flipping ratio the magnetic contribution to the intensity is calculated, and those data are then Fourier transformed to give the magnetization density. This density, which is associated with the unpaired electrons, is generally diffuse (especially for the first transition series) and hence the transform is localized close to the origin and diminishes quite rapidly with increasing $\sin\theta/\lambda$. This leads to the principal limitation in the technique. Relatively few reflections contain significant magnetic intensities and thus all of the available information about the spin density is contained in a small number of observations. It is necessary to measure these reflections as accurately as possible. With a good polarized beam spectrometer (incident flux 10^5–10^6 n cm^{-2} s^{-1}) high statistical accuracy is generally easy to achieve, especially for low-order reflections which are most intense, but systematic errors are much more difficult to account for and are more likely to influence these low-order reflections than higher-order reflections for which the intensity is lower, and flipping ratios are approaching 1. These errors include extinction, both primary and secondary, and multiple scattering, *i.e.* parasitic reflections.

A variety of techniques has been developed to correct for or to eliminate these phenomena. For example, measurements on successively thinner samples should, in principle, eliminate secondary extinction and multiple scattering, since both processes depend upon the reflectivity of the sample (see, for example, Mook, 1966). However, the signal-to-noise ratio gets worse as the reflectivity is decreased, and statistical accuracy suffers even when long counting times are used. Furthermore, the process of extrapolation is time consuming both in measuring time and in sample preparation. A further drawback is the problem of preparation of samples of different thickness which have equal bulk properties. The method may break down if primary extinction is present, since extinction lengths are generally less for strong reflections than the thinnest samples which can be prepared. A similar technique is to make measurements on a single sample as a function of wavelength (Bonnet, Delapalme, Becker & Fuess, 1976). An extrapolation (*vs* λ^2) to zero wavelength should be linear if only secondary extinction is present, and will have different behavior if primary extinction is also present. The $\lambda = 0$ value is taken as the extinction-free flipping ratio. However, only a limited wavelength range is available to the experimenter, and small systematic errors (such as multiple scattering) may significantly alter the final result. A further drawback of the method is the need for a variable-wavelength polarized-beam spectrometer.

Recently, two techniques have been introduced into the study of ferromagnetic alloys to eliminate the errors due to extinction. Firstly, samples are mechanically treated to remove primary extinction and the mosaic distribution is broadened so that the narrowest feature in the mosaic distribution is broader than the instrumental resolution, (Kwiatkowska, Maniawski, van Laar & Kaprzyk, 1982). Secondly, the flipping ratio R_{obs} is measured across the rocking curve and not merely at the peak (R-on-rocking) and the curve is fitted on a point-by-point basis to a function in which the secondary extinction appears as a parameter (van Laar, Maniawski & Kaprzyk, 1979). The fitting function is derived from Zachariasen's (1967) solution to the Darwin (1922) intensity transfer equations and should be excellent for weakly absorbing specimens. Unfortunately, the mechanical treatment of the sample increases the likelihood of multiple scattering and this, in turn, changes the measured flipping ratio at some or all points on the rocking curve, so that the fitting function no longer accurately describes the intensity distribution and unrealistic values for the extinction parameters and R may result.

In this paper we present a new method for determining secondary-extinction-free values of the flipping ratio. The method also provides a convenient test for the presence of multiple scattering which can be used to eliminate affected data. In the subsequent paper we present the results of application of this method to the polarized neutron scattering data on Ni.

2. Extinction treatment

Treatment of extinction in the new method, which we refer to as R-on-reflectivity is based on the same theoretical model as the R-on-rocking method of van Laar, Maniawski & Kaprzyk (1979), which will be referred to as LMK. This treatment uses the Zachariasen (1967) solution to the Darwin (1922) intensity transfer equations and is valid only for secondary extinction and small absorption. In addition, it is assumed that the crystal has a uniform cross section $\sigma(\omega)$ over the irradiated volume and that the mosaic structure is sufficiently broad that the geometrical conditions for diffraction are satisfied for all neutrons in the incident beam. This last requirement is easily met for γ-rays for which $\Delta\lambda/\lambda \simeq 10^{-6}$ (Schneider, 1974; Alkire & Yelon, 1981) if the angular divergence of the beam is controlled. It is not often met for X-rays or neutrons but with highly deformed specimens and good monochromators the conditions can be satisfied. Data which satisfy this requirement are then corrected on a point-by-point basis rather than on the basis of the integrated intensity as is most commonly done.

The important feature of the new method is the recognition that the extinction parameter G which appears in LMK is always multiplied by the diffracted current I and that the product GI is the reflectivity. In LMK the solutions to the Darwin equations are examined for the case of a plane parallel plate in both Bragg and Laue geometry. These solutions were first given by Bacon & Lowde (1948) for the case of zero absorption. The solutions are combined for the two neutron spin states to give extinction-corrected flipping ratios. Using the definitions and symbols from LMK (which are those used in Becker & Coppens, 1974) the extinction parameter φ is defined by the relationship

$$I_B^{\pm} = \mathcal{J}_0 v \sigma^{\pm}(\varepsilon)\varphi^{\pm}(\varepsilon), \tag{1}$$

where $\sigma^{\pm}(\varepsilon)$ is the cross section (reflectivity per unit thickness) at position ε, $\mathcal{J}_0$ is the incident flux and v is the (irradiated) sample volume. $I_B^{\pm}$ is the diffracted-beam current. The superscripts + and − refer throughout to spin-up (+) and spin-down (−) neutrons. The extinction parameter φ is found by Zachariasen in symmetric Bragg geometry as

$$\varphi^{\pm}(\varepsilon) = 1/[1+\sigma^{\pm}(\varepsilon)\bar{T}], \tag{2}$$

where $\bar{T}$ is the effective plate thickness $T/\cos\theta$. In many treatments of extinction the expression for φ is expanded in a power series in $\sigma\bar{T}$ and then the series is truncated, usually after the first-order term in $\sigma\bar{T}$. For Bragg geometry the full series expansion of (2) is

$$\varphi = 1-\sigma^{\pm}(\varepsilon)\bar{T}+[\sigma^{\pm}(\varepsilon)\bar{T}]^2-[\sigma^{\pm}(\varepsilon)\bar{T}]^3+\ldots. \tag{3}$$

The reflectivity $r^{\pm}$ is the ratio of diffracted power to incident-beam power, corrected for absorption (assuming that the geometrical conditions for diffraction are satisfied) and is equal to

$$r^{\pm}(\varepsilon) = \frac{I_B^{\pm}(\varepsilon)\bar{T}}{\mathcal{J}_0 v} = \sigma^{\pm}(\varepsilon)\bar{T}\varphi^{\pm}(\varepsilon), \tag{4}$$

where the expression on the right is derived from (1). Substituting $\sigma^{\pm}(\varepsilon)\bar{T} = r^{\pm}(\varepsilon)/\varphi^{\pm}(\varepsilon)$ from (4) into (2) leads directly to the simplified expression

$$\varphi^{\pm}(\varepsilon) = 1-r^{\pm}(\varepsilon). \tag{5a}$$

The cross section $\sigma\bar{T}$ is calculated from (5a) and (2) and is given by

$$\sigma(\varepsilon)\bar{T} = \frac{r(\varepsilon)}{1-r(\varepsilon)}. \tag{5b}$$

While this appears to be a trivial manipulation, it is quite useful, in that $\sigma\bar{T}$ can be directly extracted from a reflectivity measurement without passing through a series expansion. Since in scattering experiments reflectivities (or integrated reflectivities) are ultimately determined, this is an important consideration. Even in non-absolute measurements, the integrated reflectivity is fixed by the scale factor, although it may be strongly correlated with the extinction parameters fitted with a given model [which depends on the form of $\sigma(\varepsilon)$]. Comparison of (3) and (5a) provides direct physical insight. The odd powers of $\sigma\bar{T}$ correspond to processes where the beam is scattered an odd number of times and is directed along the diffraction direction. The even powers correspond to processes in which the scattered beam is directed along the incident-beam direction. The sum of all powers except zero is the total removed from the primary beam and is equal to the reflectivity. In symmetrical Laue geometry the extinction parameter for a plane parallel plate is given by Zachariasen (1967) as

$$\varphi^{\pm}(\varepsilon) = \frac{1-\exp[-2\sigma^{\pm}(\varepsilon)\bar{T}]}{2\sigma^{\pm}(\varepsilon)\bar{T}}. \tag{6}$$

Similar manipulations lead to

$$\varphi^{\pm}(\varepsilon) = \frac{-2r^{\pm}(\varepsilon)}{\ln[1-2r^{\pm}(\varepsilon)]} \tag{7a}$$

and to

$$\sigma^{\pm}(\varepsilon)\bar{T} = \frac{-\ln[1-2r^{\pm}(\varepsilon)]}{2}. \tag{7b}$$

This expression (7b) has been used by Schneider (1976) to correct for secondary extinction in γ-ray data.

It is interesting to examine in detail (5a) and (7a). In the limit of large r both expressions behave properly. For the Bragg case as r approaches 1, $\varphi \to 0$ corresponding to infinite $\sigma\bar{T}$. In this case no intensity emerges from the rear of the crystal (in the transmitted beam). However, the intensity approaches this limit only very slowly as $\sigma\bar{T}$ increases. For example, at $r = 0{\cdot}8$, $\sigma\bar{T} = 40$, and at $r = 0{\cdot}9$, $\sigma\bar{T} = 90$. In the Laue case $\varphi \to 0$ at $r = 0{\cdot}5$, the well known result, and the intensity transfers between diffracted and transmitted beams which leave the crystal with equal strengths. In the Laue case the reflectivity limit is approached for much smaller values of $\sigma\bar{T}$. For example, for $r = 0{\cdot}4$ (80% of maximum), $\sigma\bar{T} = 0{\cdot}8$ and, at $r = 0{\cdot}495$, $\sigma\bar{T} = 2{\cdot}3$. Adding thickness beyond this point has no observable effect.

In the limit of $r \ll 1$ it is immediately found by expansion of (7a) that the two cases are equivalent. For intermediate values of r it is somewhat surprising how slowly the two cases diverge. Table 1 gives the extinction parameter φ for the symmetrical Laue and Bragg cases for $0{\cdot}00 \le r \le 0{\cdot}495$. At $r = 0{\cdot}2$ (7a) and (5a) disagree by only about 2%. For $r \le 0.1$ the two expressions are likely to be indistinguishable within the statistical accuracy of an experiment. This is an important result since simple closed-form solutions to the Zachariasen model are not known for asymmetric geometries, although a series solution has been

Table 1. *Values for the extinction parameter φ as a function of the reflectivity r, calculated for the symmetrical Bragg case (with equation 5a) and the symmetrical Laue case (with equation 7a)*

In the last column the ratio of the values for the two cases is given.

Reflectivity (r)	φ(Bragg)	φ(Laue)	φ(Bragg)/φ(Laue)
0·000	1·0	1·0	1·00000
0·005	0·9950	0·9950	1·00001
0·010	0·9900	0·9900	1·00003
0·015	0·9850	0·9849	1·00008
0·020	0·9800	0·9799	1·00014
0·030	0·9700	0·9697	1·00032
0·040	0·9600	0·9594	1·00058
0·050	0·9500	0·9491	1·00092
0·060	0·9400	0·9387	1·00136
0·070	0·9300	0·9282	1·00189
0·080	0·9200	0·9177	1·00253
0·090	0·9100	0·9070	1·00328
0·100	0·9000	0·8963	1·00415
0·120	0·8800	0·8745	1·00627
0·140	0·8600	0·8523	1·00898
0·160	0·8400	0·8297	1·01236
0·180	0·8200	0·8067	1·01654
0·200	0·8000	0·7830	1·02165
0·250	0·7500	0·7213	1·03972
0·300	0·7000	0·6548	1·06901
0·350	0·6500	0·5814	1·11797
0·400	0·6000	0·4971	1·20708
0·450	0·5500	0·3909	1·40714
0·495	0·5050	0·2150	2·34910

given by Sears (1977). There is no reason to suppose, however, that the geometrically intermediate cases are not also intermediate mathematically. It is likely that for r small (<0.1) the linear model of (5a) is good enough to describe secondary extinction in all geometries. Series-expansion solutions to the Zachariasen equations in these geometries, truncated after the first-order term $1-\sigma T$, will presumably also be valid if $r \leq 0.1$ since σT is of order 0·11 at this point.

The major advantage of the exact reflectivity formula compared to series expansions of (2) or (6) is seen in the plot of r as a function of $\sigma\bar{T}$ for both geometries (Fig. 1). It is clear that the series expansions, truncated after the first-order term will be seriously in error ($\Delta\varphi/\varphi \geq 0{\cdot}5$) for $r \geq 0{\cdot}3$, while (5a) or (7a) can be used for all values of r.

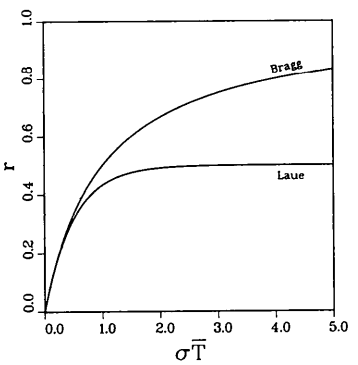


Fig. 1. Reflectivity *versus* the effective cross section $\sigma\bar{T}$ for Bragg and Laue geometries.

Both DeMarco (1967) and Suortti (1982*a*, *b*) have used absolute reflectivity measurements in symmetric Laue geometry to correct for extinction. By this means they attempt to calculate absolute structure factors from individual rocking curves, measured with high statistical accuracy. Both workers, however, used series expansion solutions rather than the reflectivity formula of (7a). In the DeMarco work, the largest reflectivity was ~13% and the approximations were probably valid. In the Suortti study of Be, however, reflectivities appear to be sufficiently high that the approximations are questionable. In any case, with the availability of a simple closed-form expressions for this special geometry, there is no need to rely on any such approximate solutions.

In polarized neutron diffraction it is not single intensities which are measured, but rather the ratio of the scattered intensities for spin-up and spin-down neutrons. Extinction affects both intensities although each to a different degree. Expressions (5) and (7) can be used individually to correct the intensity for each spin state, but it is possible to simplify further if the ratio is expressed as a function of r^+, the reflectivity for the spin-up state. With (5) taken for each spin state and the substitution $R_B = I^+/I^-$ made, the extinction-affected flipping ratio in symmetric Bragg geometry as a function of R, the true (kinematic) flipping ratio, becomes

$$R_B(\varepsilon) = R + (1-R)r^+(\varepsilon) \tag{8a}$$

or

$$R = \frac{R_B(\varepsilon) - r^+(\varepsilon)}{1 - r^+(\varepsilon)}. \tag{8b}$$

R_B is the experimental flipping ratio corrected for background and is derived from $R_{\rm obs} = I^+_{\rm obs}/I^-_{\rm obs}$ in the following way:

$$R_{\rm obs} = \frac{R_B(\varepsilon)r^+(\varepsilon)}{r^+(\varepsilon) + r_{\rm BKG}(\varepsilon)[R_B(\varepsilon) - 1]}. \tag{9}$$

The background, $r_{\rm BKG}$, is assumed to be spin independent.

It is convenient to define the reduced quantity

$$R_R = \frac{R_B - 1}{R - 1}, \tag{10}$$

which is a measure of the relative difference in true and extinction-affected magnetic structure factors. From (8) it is found quite simply that

$$R_R = 1 - r^+(\varepsilon). \tag{11}$$

Thus, in Bragg geometry R_R is a universal quantity depending only on the reflectivity r^+.

In symmetrical Laue geometry, the analogous expressions are derived from (7) and are given as

$$R_B(\varepsilon)=\frac{2r^+(\varepsilon)}{1-[1-2r^+(\varepsilon)]^{1/R}} \qquad (12a)$$

$$R=\frac{\ln[1-2r^+(\varepsilon)]}{\ln[1-2r^+(\varepsilon)/R_B(\varepsilon)]}. \qquad (12b)$$

No simple expression for R_R is available in the Laue case, but in Fig. 2 R_R is plotted for two values of R in the Laue geometry as well as for the Bragg case. The range of validity of the linear (in r^+) model is easily seen here, as well as the fact that for Laue geometry R_R may be taken as a universal quantity to $r\simeq 0{\cdot}2$, which is probably adequate in most cases.

Fig. 3 shows a similar plot in terms of $\sigma^+\bar{T}$ rather than r^+. As expected, the dependence of R_R on $\sigma^+\bar{T}$ is quite weak for $\sigma^+\bar{T}$ large and the use of this formulation is quite problematical.

Although R-on-reflectivity is based on the same model as the R-on-rocking method, the advantage of the new method is quite apparent from Fig. 2. Experimental data across a rocking curve will typically range in reflectivity from 0 to $\leq 0{\cdot}1$ and will have significant statistical error, as well as possible systematic errors such as multiple scattering *etc.* If r^+ is known, the slope of the curve of R_B *vs* I is very well determined in spite of those errors. In principle, with the R-on-reflectivity method it is necessary to measure only one point on the rocking curve (normally the peak for statistical purposes) but in practice it is found to be advantageous to measure the full rocking curve. This will be discussed further in the next section.

Measurement of the reflectivity is especially straightforward in large non-absorbing specimens in Laue geometry, since the transmitted and diffracted intensities I_B can be summed to give the direct beam I_0. For samples in symmetric Laue geometry the effect of absorption may be neglected since the path lengths for the diffracted and transmitted beams are equal and reflectivity may be defined as

$$r=I_B/(I_B+I_T)=I_B/I_0. \qquad (13)$$

Thus the ideal geometry for the method is symmetric Laue, using an instrument with a χ circle allowing the measurement of any reflection on the plane of a plate-like sample. In other geometries one must be concerned with the situation in which the transmitted and diffracted beams have significantly different path lengths and absorptions. The effects of errors in the reflectivity determination due either to absorption or to errors in the determination of the direct beam are easily examined (assuming the validity of the Zachariasen solutions). Assuming the linear model (8*b*) the relative error in R_B as a function of the error in reflectivity Δr^+ is found, to first order, to be

$$\frac{\Delta R}{R-1}\simeq(\Delta r^+)r^+. \qquad (14)$$

If the reflectivity is approximately known, it is easy to define the accuracy needed in the direct-beam determination to match the required precision of an experiment. If reflectivity is kept small ($r\leq 0{\cdot}1$) the demands on this determination are quite modest and the effects of absorption can usually be neglected for materials with moderate absorption (or absorption corrections made with good confidence).

3. Multiple scattering

Multiple scattering arises when two or more diffraction spots (in addition to the origin) lie on the sphere of reflection (Fig. 4). The effects of such a situation have been described by Moon & Shull (1964) and we follow their description here. The intensity observed in the spot of interest H_{01} with reflectivity r_{01} is modified in several ways by the presence of an extra spot. The second spot H_{02} with reflectivity r_{02} removes primary-beam intensity, reducing the beam available to be diffracted by reflection H_{01}. It also provides a

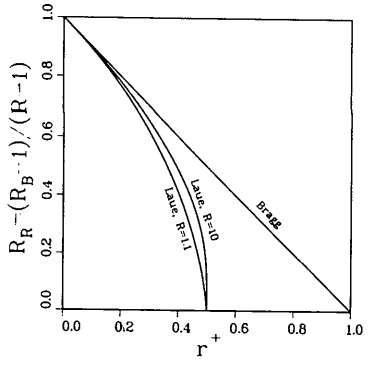


Fig. 2. The reduced quantity $R_R=(R_B-1)/(R-1)$ for the Bragg case and for the Laue case for $R=1{\cdot}1$ and $R=10$ *versus* the reflectivity.

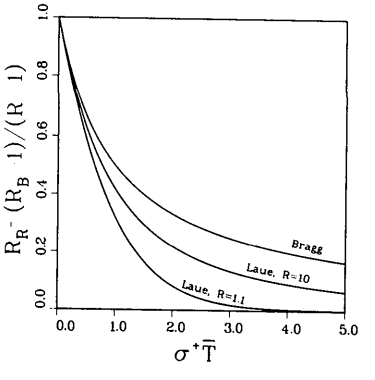


Fig. 3. The same quantity R_R as in Fig. 2 plotted as a function of $\sigma\bar{T}$ rather than r.

new channel into which the once-diffracted beam can be rediffracted with reflectivity r_{12}. These two processes reduce the observed intensity (*Aufhellung*). Opposing this is a process whereby the diffracted intensity increases through a second scattering of the second beam $r_{02} \times r_{21}$, known as *Umweganregung* or detour radiation. The presence of these processes makes the measurement of $r(\varepsilon)$ unreliable. To avoid this, usually rotations about the scattering vector (ψ scans) are performed to find regions where the peak intensity is not changing. These regions are assumed to be free of multiple scattering and the intensity (or flipping ratio) is measured. However, in a crystal with broad mosaic, it may be quite difficult to define a suitable region for measurement.

Furthermore, the change in reflectivity Δr_{01} to second order is given by (Schneider 1975):

$$\frac{\Delta r_{01}}{r_{01}} = \frac{1}{2}\left(-r_{02} - r_{12} + \frac{r_{02} r_{21}}{r_{01}}\right). \qquad (15)$$

Since both *Aufhellung* and *Umweganregung* processes occur simultaneously Δr_{01} may be quite small for some cases where the individual terms in (15) are themselves non-negligible. This will normally occur for only one spin state (since $r^+_{hk} = r^-_{hk}$) and the flipping ratio will be incorrectly measured. If the ψ scan looks at the variation in R rather than in r^+ this may be avoided, but the sensitivity in this case is somewhat poorer.

In the R-on-reflectivity method a simple and reliable test for multiple scattering, based on the conservation of neutrons, is possible. If only one reflection is on the sphere of reflection, then the sum of diffracted intensity I_B and intensity transmitted through the sample I_T, corrected for absorption, will equal the intensity of the direct beam I_0 (Fig. 5*a*). If a second spot lies on the sphere of reflection some intensity will be directed into the directions H_{02} and H_{12} regardless of the relative strengths of the terms in (15). Thus the sum $I_B + I_T < I_0$. If this is found to be true for some points along the rocking curve, those data may be eliminated from the determination of R (Fig. 5*b*).

This method may be used for any type of scattering experiment, X-ray, electrons, *etc.*, providing absorption corrections can be made. For polarized neutrons

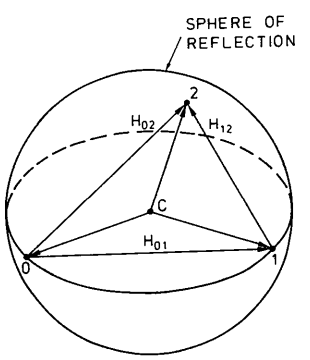
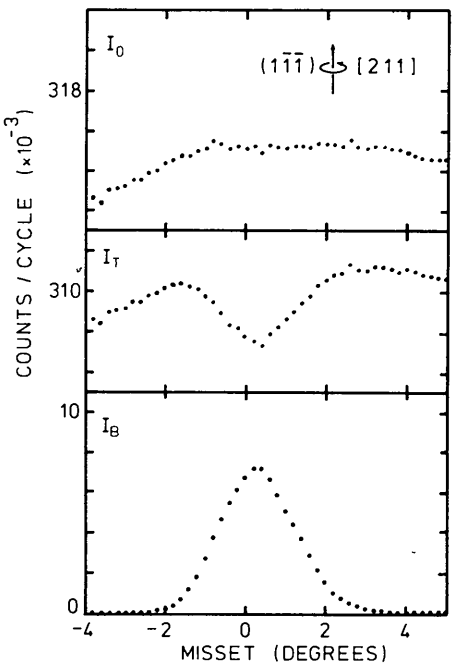


Fig. 4. The sphere of reflection showing two diffraction spots 1 and 2 as well as the origin 0 in the sphere (after Moon & Shull, 1964).



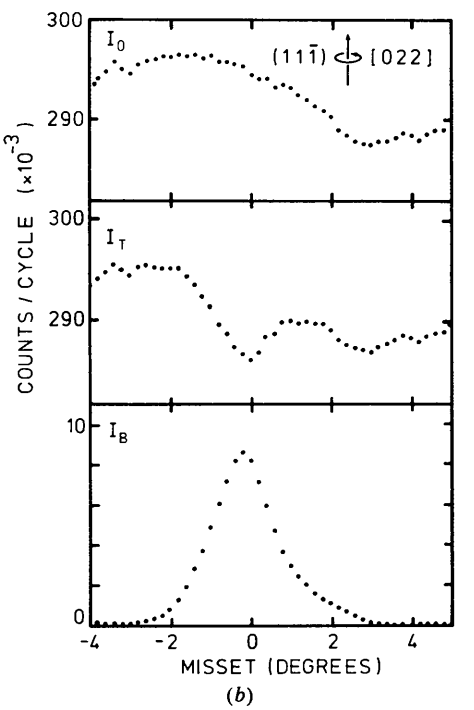


Fig. 5. Diffracted intensity I_B, transmitted intensity I_T and the total intensity I_0(*a*) for $(1\bar{1}\bar{1})$ rocked around [211] showing no multiple scattering at the peak; (*b*) for $(11\bar{1})$ rocked around [022] showing multiple scattering across most of the rocking curve.

a further degree of sophistication is possible, since I_B and I_T can be measured for both spin states. If only a single spot is on the sphere, the ratio

$$R_T = (I_B^+ + I_T^+)/(I_B^- + I_T^-) \tag{16}$$

will (ideally) equal 1. If multiple scattering is present, however, the reflectivities r_{hk}^+ will differ from r_{hk}^- and in general more intensity will be lost for one spin state than for the other and the ratio R_T will become different from 1 (Fig. 6), and data can be rejected on the basis of this determination.

While this test is exact for non-absorbing specimens, the effect of absorption on R_T is easily seen. If the transmitted beam has transmission t_1 and the diffracted beam t_2 (owing to differing path lengths), the ratio R_T is

$$R_T \simeq \frac{1 - r^+(1 - t_2/t_1)}{1 - (r^+/R)(1 - t_2/t_1)} \simeq 1 - \frac{r^+}{R}(R-1)(1 - t_2/t_1), \tag{17}$$

where r^+ is the reflectivity for spin-up neutrons. Thus, if absorption is moderate and the geometry is not extremely asymmetric ($t_2 \simeq t_1$), or if the reflectivity r^+ is small, then absorption may be neglected in testing for multiple scattering. Nevertheless, the ideal geometry is symmetric Laue, for in that case $t_2 = t_1$.

The error in flipping ratio caused by an unobserved multiple scattering process with reflectivity r_{lm} is found from (15) and will be of order

$$\Delta R \simeq r_{lm}\left(1 - \frac{1}{R_{lm}}\right) \tag{18a}$$

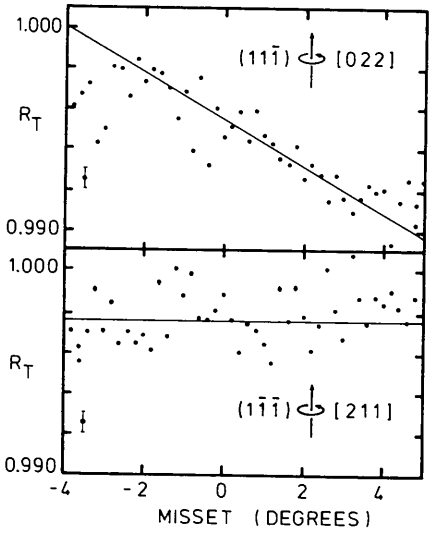


Fig. 6. $R_T = (I_B^+ + I_T^+)/(I_B^- + I_T^-)$ for the two cases plotted in Fig. 5. R_T clearly shows the multiple scattering effects which are also seen in Fig. 5.

$$\frac{\Delta R}{R-1} \simeq \frac{r_{lm}}{R_{lm}} \frac{R_{lm} - 1}{R - 1}, \tag{18b}$$

where R_{lm} is the flipping ratio for reflection H_{lm}. Equations (18*a*) and (18*b*) can be used to define the statistical precision needed in the measurement of R_T to define multiple-scattering-free regions. In most practical cases $\sim 10^6$ summed counts should be sufficient to ensure results within the desired experimental accuracy. Since the experimental data have statistical errors, an acceptance range

$$1 - \varepsilon \le R_T \le 1 + \varepsilon \tag{19}$$

can be chosen as a criterion for the rejection of data experiencing multiple scattering.

4. Discussion

Treatment of secondary extinction within the framework of the Zachariasen formalism has usually used integrated intensity data collected for many reflections (weak and strong). Connection is made with the reflecting power and kinematical cross sections through a series of steps. These include determination of a scale factor, assumption of the form and homogeneity of the mosaic distribution function, as well as a series of mathematical approximations needed to arrive at integral solutions to the Zachariasen model. The method we propose avoids all of these problems, but assumes instead that the geometrical condition for diffraction is satisfied equally for all parts of the divergent incident beam at any point on the rocking curve, and that the reflectivity measured at a given point is the true, and not an average, reflectivity. This implies the mosaic to be broad relative to the beam divergence. While this is not normally the case for as-grown specimens and normally prepared beams, many materials can be treated to broaden their mosaic. It will also be necessary in most cases to reduce the beam divergence, which will, in turn, increase the measuring times, but with modern high-flux neutron and X-ray sources this appears to be a reasonable prospect. In general, it will be necessary also to test the validity of the assumption of 'broad mosaic' by means of γ-ray diffraction to characterize the mosaic structure.

Other experimenters have made measurements on an absolute scale, but re-examination of the Zachariasen solutions has shown that formulation of the extinction problem in terms of reflectivity rather than as a function of the cross section leads to simple closed-form solutions for both symmetric Bragg and Laue cases for plane parallel plates, and gives confidence that a linear model can be used for asymmetric geometries provided that reflectivity is not too large ($<0{\cdot}1$). The simplicity of the result is remarkable and it is quite surprising that only limited attention has

been given to reflectivity measurements. Treatment of flipping-ratio data within this method is particularly attractive since errors in I_0 affect R in a weaker way than in the case of absolute structure-factor measurements and direct-beam measurements also provide a simple and reliable test for multiple scattering at the same time that the flipping ratio is determined. Primary extinction is not treated by this method, but meeting the resolution requirements previously mentioned usually requires alteration of sample microstructure in such a way that primary extinction is likely to be quite small. The effect of absorption has essentially been neglected here, and it has been pointed out by several authors (Werner, 1974; Borie, 1982) that the separation of diffraction and absorption in the treatment by Zachariasen is essentially incorrect, and that the approach is only valid for small absorption in the general case. In symmetric Laue geometry the Zachariasen solutions may be used, however, since diffracted and transmitted beams (including multiply scattered beams) have the same path lengths and absorptions. This is clearly the preferred geometry, but several specimens will normally be needed to measure enough zones of interest. It would seem, however, that for experiments in which high accuracy is essential, such as spin-density determination, and where the cost of measuring is high (any neutron or synchrotron study), the value of such a set of specimens would be quite high compared to the cost of their preparation.

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