Acta Cryst. (1984). A40, 24–31

Treatment of Secondary Extinction and Multiple Scattering in Polarized Neutron Scattering: An Improved Method. II. Application to Nickel

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(*Received* 18 *May* 1983; *accepted* 2 *August* 1983)

Abstract

The flipping ratios for polarized neutron scattering from the first six reflections in Ni have been measured on a series of samples of varying thickness and perfection and at a number of wavelengths. The results were corrected for secondary extinction on a point-by-point basis, using the measured absolute reflectivities, and multiple scattering was detected using conservation of neutrons. No adjustable parameters were used, and all data, except those from a rather perfect specimen which showed both primary and secondary extinction, agree to within the experimental accuracy after extinction correction. A diffuse scattering process with spin dependence was also detected, and the flipping ratios corrected for this. The corrected values differ somewhat from the values given by Mook [*Phys. Rev.* (1966), **14B**, 495–501].

1. Introduction

In the previous paper (Yelon, van Laar, Kaprzyk & Maniawski, 1984), hereafter I, we presented a new method for treating secondary extinction and multiple scattering in polarized neutron diffraction. Traditionally, two different methods have been used to treat secondary extinction. In one, based on the Zachariasen (1967) model, an extinction parameter is calculated from the integrated intensities measured for a set of reflections in a single specimen. For the other, either the thickness of the sample is varied, or the wavelength is varied for a single sample and the results are extrapolated to zero diffracting power, where extinction is zero. The former method relies on assumptions, not always fulfilled, about the form of the mosaic distribution function, and makes a number of approximations in the solution of the intensity transfer equations (Darwin, 1922). The latter method is, in principle, less bound to untested assumptions, but requires either a set of specimens of varying thickness but otherwise uniform properties or the availability of a variable-wavelength polarized-neutron-beam spectrometer. The latter method, in either form, is also very time consuming since several measurements are made for each reflection. All methods have tested for multiple scattering by observing the diffracted intensity as the specimen is rotated around the scattering vector (Ψ scan). If the intensity does not vary, then multiple scattering is assumed to be absent.

The new method presented in I, while making use of the same theoretical base, approaches both problems in a unified way. Unlike other methods, both the diffracted and transmitted intensities are measured. Lack of conservation of neutrons is taken as evidence of multiple scattering. In multiple-scattering-free geometries, the reflectivity, r, is determined and the extinction-free values calculated from r with no further parametrization.

In this paper, application of the method to nickel with several samples and at differing wavelengths will be presented. A new set of values for the flipping ratio for the first six reflections for nickel will also be given.

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0108-7673/84/010024-08$01.50

2. Experimental

To test the method, a number of samples of Ni were prepared. All were cut perpendicular to a $[01\bar{1}]$ axis from the same ingot. One sample ($A1$) was simply cut and polished and had a rather high degree of perfection. Three others, of varying thickness, were cut and mechanically deformed according to previously established procedures (Kwiatkowska, Maniawski, van Laar & Kaprzyk, 1982). They were subsequently pressed flat, polished smooth and annealed ($A2$, $A18$, $A19$). The mosaic widths of these three samples were quite large, and it is assumed that the resolution requirements for the application of the 'R-on-reflectivity' method were met. Eventually these samples will be examined in detail with γ-ray diffraction to confirm this assumption.

The samples were all glued to 1 mm thick quartz disks which could be simply mounted in the neutron spectrometers used in the study. The beam was defined to be smaller than the sample either by apertures on the exit of the guide-field collimator, or by Cd masks glued directly over the samples onto the quartz disks. The final thicknesses of the four samples $A1$, $A2$, $A18$ and $A19$ are: 0·36, 0·425, 0·132 and 0·243 mm.

Measurements were performed on the polarized neutron diffractometer COPOL at the HFR, Petten, with neutron wavelength 1·08 Å, and at the variable-wavelength diffractometer D5 at the ILL, Grenoble, at 0·84, 0·60, 0·50 and 0·42 Å. The flipping ratio was determined for the first six reflections, 111, 200, 220, 311, 222 and 400, on the thickest ($A2$) and thinnest ($A18$) specimens at Petten, while the first two reflections were studied on all three deformed specimens at Petten, and on the $A2$ specimen at all wavelengths. Only the 111 reflection was investigated on the $A1$ sample. In all of the Petten measurements at least 10^6 counts were collected at every point in the rocking curve for the summed beam, $I_B + I_T$, for both spin-up and spin-down states. Since the direct beam at Petten was $\sim 1{\cdot}5 \times 10^4$ ns^{-1} (on an area of about $\frac{1}{6}$ cm^2), only about 1 min collection of the direct beam is necessary to reach this level. In many cases, however, the diffracted beam was measured for considerably longer times to improve the statistical accuracy in the determination of R. At present one detector is used to measure the two components of the beam sequentially, but ideally a second detector permanently monitoring the transmitted beam will be used. Rocking curves were measured in 0·2° steps over the range of appreciable intensity while 1° steps were used for an additional 5° of background on each side of the peak. Typically 51–56 steps were made over the scan. The majority of data were collected in symmetric Laue geometry, but in a few cases asymmetric geometries were used when multiple scattering contaminated the data in the highly symmetric geometry (220).

Because of the limited time available at ILL fewer counts were taken in the total beam ($\sim 3 \times 10^5$) and short scans over the peak were made (17–25 steps). As a result, somewhat higher correlation between background and R was observed than in the Petten data.

At both facilities the direct-beam intensity was measured as a function of thickness of sets of plexiglass attenuators and the data were fitted to determine direct-beam strength and the dead-time constants using a model including both paralyzable and non-paralyzable dead-time effects (Evans, 1969). The attenuation coefficients were also determined but were not subsequently used for other measurements. At ILL these measurements were repeated at each wavelength.

All data were corrected for dead time, but no correction to the direct beam for $\lambda/2$ or fast-neutron contamination was made since it has been shown in I that these effects should have negligible influence on the final values of the extinction corrections.

Data were treated with the R-on-reflectivity program which tests for multiple scattering, and fits unaffected data to either the Bragg or the Laue model with the R factor and background as refinable parameters. The transmitted intensity data are used both for the test for multiple scattering and in the determination of r, the reflectivity. For comparison, in a number of cases the same data were fitted using the R-on-rocking program in which R, background and the extinction parameter G were adjustable parameters. The transmitted intensities were not used at all for these determinations and no direct tests for multiple scattering were carried out.

3. Results

3.1. *Multiple scattering*

Multiple scattering was observed in many of the experimental settings, and various remedies were found to provide unaffected data. Measurements on the $\bar{1}\bar{1}1$ were initially performed with one [022] axis vertical. However, all of the reflections measured this way were found to have significant multiple scattering which was shown by a continuous decrease of R_T as a function of rocking angle (Fig. 1a). It is interesting that in this case the multiple scattering is very broad and thus might not be seeen in a Ψ scan. The flipping ratio $R(\bar{1}\bar{1}1)$ calculated is $\sim 1{\cdot}56$, significantly less than the value determined on a thin crystal with negligible extinction and multiple scattering. When the crystal was remounted so that the $\bar{1}11$ reflection was in symmetric Laue geometry (around [211]) no multiple scattering is visible and $R(\bar{1}11)$ agrees well with the thin-crystal data (Fig. 1b).

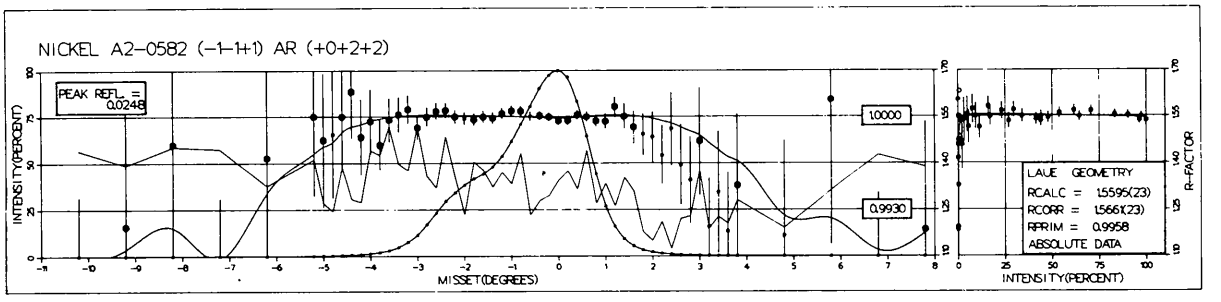
The 200 family showed multiple scattering for rotations around the [200] axis, but with [022] vertical

unaffected data were collected. In spite of the multiple scattering, which affected only some of the data, reasonable values for $R(200)$ could be extracted from two of the four symmetry equivalents with [200] vertical. Nevertheless, this geometry was excluded in the final data analysis.

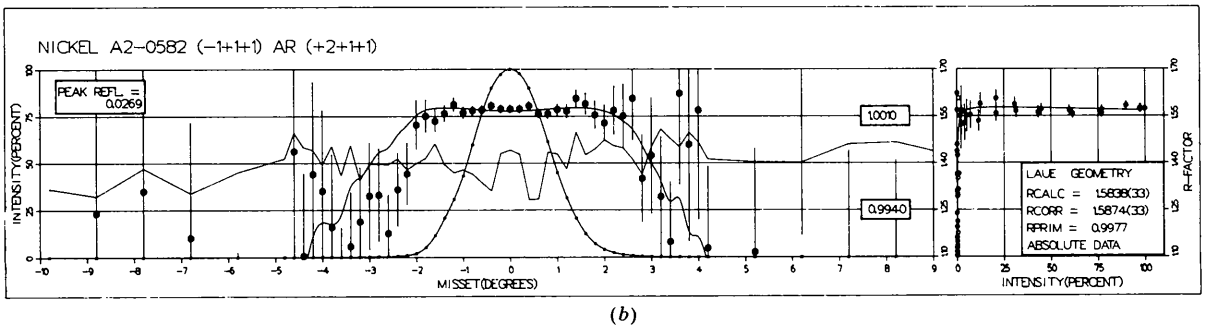
With the 222 family of reflections a different problem is encountered. Measurement with [211] vertical shows a strong dip in R_T centered directly at the peak position and the data are considered not usable. At $\lambda = 1{\cdot}08$ Å with crystals cut perpendicular to $[0\bar{1}1]$ no other orientation is available since the setting with [022] vertical puts the $22\bar{2}$ and its symmetry equivalents into highly asymmetric settings. For one pair of reflections the surface of the crystal is along the direct-beam direction, while for the other pair it is along the diffracted-beam direction. The difference in path length for transmitted and diffracted beams is so great that absorption corrections cannot be reliably made, and the reflectivity cannot be properly defined. We therefore measured in the original setting after rotating by $\sim 5°$ in ψ. While multiple scattering is still present, more of the data points are usable and $R(222)$ determined from these data agrees well with the value determined on the thinner crystal. Unfortunately a greater ψ offset was not possible, but would probably have improved the results still further.

3.2. *R-on-rocking vs R-on-reflectivity*

Our experience with the R-on-rocking method (van Laar, Maniawski & Kaprzyk, 1979) is that in certain instances the extinction correction resulting from this method is larger for a weaker reflection than for a stronger one. This is clearly an unphysical result which appears to be caused by a high correlation between the extinction parameter G and the extinction-free flipping ratio R. In the R-on-reflectivity method such a situation cannot arise, but it would be disappointing if the quality of the fit were much worse with this method than with the R-on-rocking method, especially in those cases where multiple scattering is absent. On the contrary, it is found that the quality of fit measured by the χ^2 test is only slightly worse for the new method. Results of a comparison of the two methods on a number of reflections are given in Table 1. Figs. 2 and 3 show data for two reflections, one strong and one weak, analyzed by both methods. Since some data points are rejected by the R_T test the number of points fitted is generally



(*a*)



(*b*)

Fig. 1. Comparison of two 111 reflections measured in different geometries. (*a*) the $\bar{1}\bar{1}1$ reflection rocked around [022], which shows multiple-scattering effects. (*b*) The $\bar{1}11$ reflection rocked around [211], which is apparently free of multiple scattering. In this and subsequent figures the intensity distribution I^+ is shown on a relative scale with the peak normalized to 100% (left-hand frame). The flipping ratio $R_{obs} = I^+_{obs}/I^-_{obs}$ is shown, with error bars, as a function of the misset angle ω. The scale for R_{obs} is on the right side. The thin solid line zig-zagging across the frame connects the values of R_T at each rocking angle. The scale (acceptance range) for this curve is given in the boxes on the right of the left frame. If $R_T(\omega)$ lies within the acceptance range, the points $R_{obs}(\omega)$ are accepted and shown double sized. The solid line through $R_{obs}(\omega)$ is the fit to equation (I-7) or (I-8) (depending on the geometry) using only the accepted points. In the right frame, the calculated flipping ratio is shown as a solid line *versus* I^+ along with the accepted experimental data. The extinction-corrected flipping ratio RCALC is given as well as this value corrected for diffuse scattering RCORR. The average value of R_T for the accepted points RPRIM is also given. The decrease in R_T with ω in (*a*) is taken as evidence of multiple scattering.

Table 1. *Comparison of results corrected for extinction using the R-on-rocking and R-on-reflectivity methods*

				R-on-reflectivity				*R*-on-rocking				
Sample	*HKL*	*hkl*	λ (Å)	*R*	BKG	χ^2	*N*	*R*	*G* (×10³)	BKG	χ^2	*N*
A2	$\bar{1}11$	[211]	1·08	1·5838(33)	0·075(10)	38·0	56	1·5628(88)	−0·236(210)	0·069(9)	33·9	56
A2	$\bar{1}11$	[211]	0·84	1·5903(27)	0·388(82)	3·39	16	1·5891(129)	0·040(248)	0·340(140)	6·06	17
A2	$\bar{1}11$	[211]	0·60	1·5903(36)	0·453(105)	4·87	17	1·5976(132)	0·190(247)	0·500(135)	4·74	17
A2	$\bar{1}11$	[211]	0·50	1·5991(67)	0·585(203)	9·65	17	1·5886(249)	−0·180(499)	0·512(268)	9·53	17
A2	200	[022]	1·08	1·5060(15)	0·055(8)	15·1	48	1·4982(39)	−0·051(106)	0·055(8)	17·19	51
A2	$2\bar{2}0$	$[\bar{1}11]$	1·08	1·2962(42)	0·119(36)	27·5	48	1·2850(106)	−0·452(540)	0·102(33)	27·6	51
A2	$20\bar{2}$	$[\bar{1}11]$	1·08	1·2920(25)	0·064(19)	19·5	45	1·2953(55)	0·393(248)	0·088(17)	20·9	51
A2	$02\bar{2}$	$[\bar{1}11]$	1·08	1·2916(25)	0·127(25)	21·3	45	1·2907(56)	0·242(269)	0·121(25)	24·6	51
A2	$3\bar{1}\bar{1}$	[233]	1·08	1·2037(27)	0·188(33)	18·2	45	1·2076(72)	0·401(413)	0·102(29)	20·7	51
A19	$\bar{1}11$	[211]	1·08	1·5887(50)	0·076(15)	19·6	49	1·5700(121)	−0·328(294)	0·069(14)	19·2	51
A19	$\bar{2}00$	[022]	1·08	1·5031(48)	0·077(14)	25·9	55	1·4938(131)	−0·227(352)	0·075(14)	27·1	56
A18	$1\bar{1}\bar{1}$	[211]	1·08	1·5967(50)	0·138(18)	19·7	51	1·5984(124)	0·155(266)	0·129(17)	21.9	56
A18	$\bar{2}00$	[022]	1·08	1·5245(66)	0·162(43)	27·8	44	1·5307(145)	0·247(354)	0·171(35)	21·6	51

fewer for the *R*-on-reflectivity method. Taking this into account it is seen that no significant loss in goodness-of-fit occurs with *r*-on-reflectivity with only two adjustable parameters (*R* and BKG) compared to *R*-on-rocking with three (*R*, *G* and BKG). Furthermore, the standard deviation on *R* is reduced by at least a factor of 2 in all cases, and in some cases by a factor of ~4. This is related to the strong correlation between *R* and *G* which is found to be greater than 0·9. For the same reason *G* is poorly defined; in most cases the refined value is smaller than its standard deviation and in many cases *G* is negative, an unphysical result. Correlation between *R* and BKG, on the other hand, is quite small (~0·1) except in a few cases where the data do not cover a sufficient intensity range to define BKG independently.

3.3. *Diffuse scattering*

In I it was stated [equation (I-15)] that R_T should equal 1 within the statistical accuracy of the measurement if no multiple scattering were present. We have observed, however, that, even when sharp multiple-scattering processes are absent, the average value of R_T (R_{prim}) is less than 1, although statistical variation is present and some individual values exceed 1. The deviation from 1 appears to increase as the effective thickness of sample increases. Measurements of the beam with no sample present give $I_0^+ / I_0^- = 1$ to within the statistical accuracy of the measurements.

Table 2 gives $1 - R_{\text{prim}}$ for the first six reflections in Ni for two samples, at 1·08 Å. The standard deviation (statistical) on all values is ~0·0003. All of the

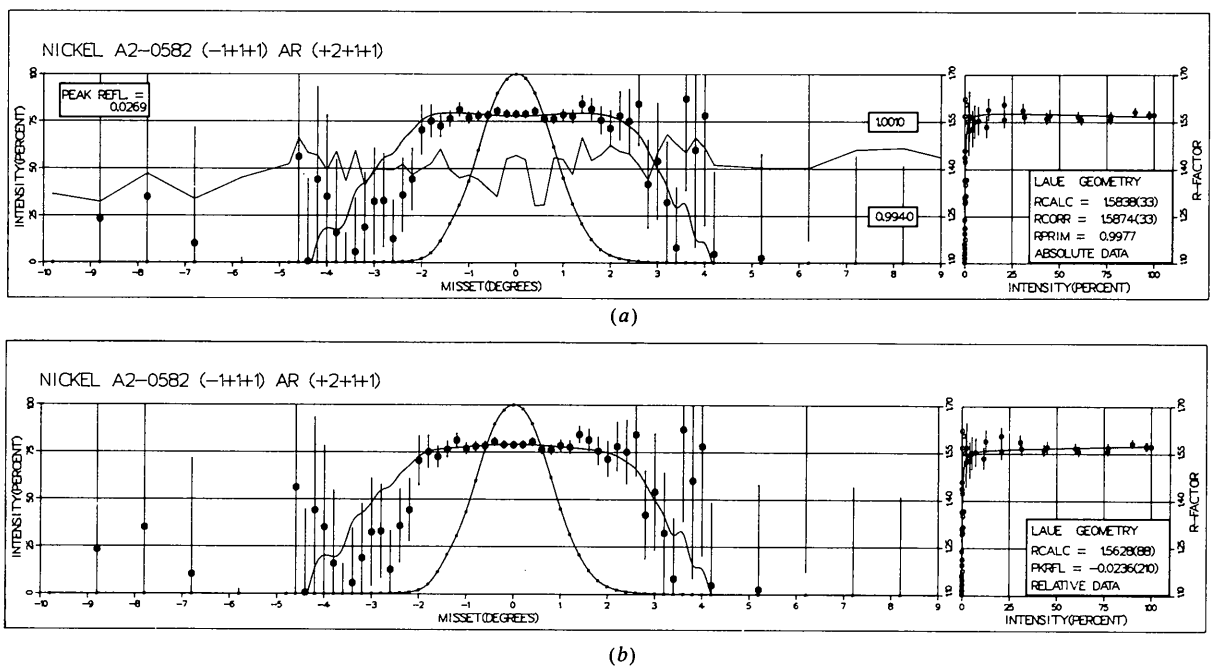


Fig. 2. Data for $\bar{1}11$ rocked around [211]. (*a*) The data are fitted using the measured reflectivities (*R*-on-reflectivity method). (*b*) The data are fitted with the extinction treated as an adjustable parameter (*R*-on-rocking). In this case all data are used and R_T is not calculated. The calculated value PKRFL, the peak reflectivity, is 100 times the extinction parameter *G* in the text and can be directly compared with the measured peak reflectivity in (*a*). The negative value for PKREL is an unphysical result and the extinction is badly underestimated.

Table 2. *Relative reduction in the primary beam for neutron spin-up and neutron spin-down at different symmetric Laue reflection settings for two crystals*

HKL around [*hkl*]		$1-R_{prim}$ *A*2	*A*18
111	[$\bar{2}$11]	0·0023	0·0009
200	[022]	0·0022	0·0005
220	[002]	0·0037	0·0015
311	[$\bar{2}$33]	0·0026	0·0009
222	[$\bar{2}$11]	0·0048	0·0018
400	[022]	0·0071	0·0026

Table 3. *Measurements of R*(311) *in several different settings*

R is the extinction-corrected flipping ratio, R_{corr} is further corrected for diffuse scattering

Sample	*HKL* around [*hkl*]		*R*	R_{corr}	σ
*A*2	3$\bar{1}$1	[022]	1·1983	1·2041	21
*A*2	3$\bar{1}\bar{1}$	[233]	1·2037	1·2066	27
*A*2	$\bar{3}$11	[233]	1·2041	1·2073	26
*A*18	311	[233]	1·2074	1·2085	38
*A*18	$\bar{3}\bar{1}\bar{1}$	[233]	1·2074	1·2084	28

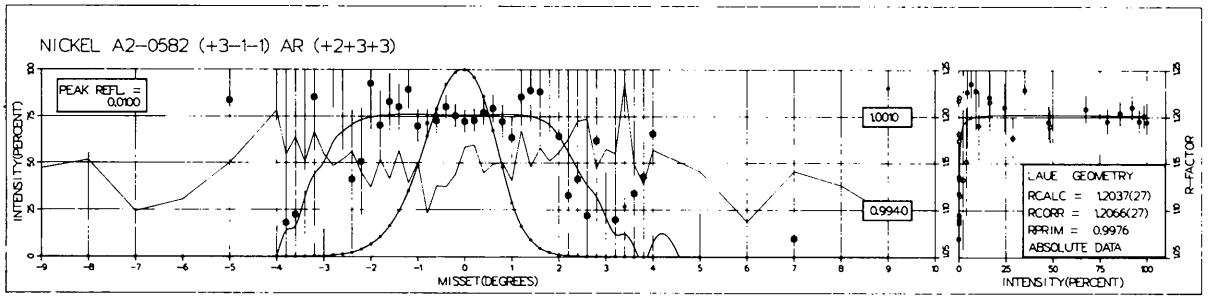
$\Delta R = 0{\cdot}0091$
$\Delta R_{corr} = 0{\cdot}0044$

data are from symmetrical Laue geometry and the 220 result is badly contaminated by multiple scattering. The *A*2 sample (0·425 mm) is about 3·2 times thicker than the *A*18 sample (0·132 mm) and the deviation from 1 scales in about the same ratio.

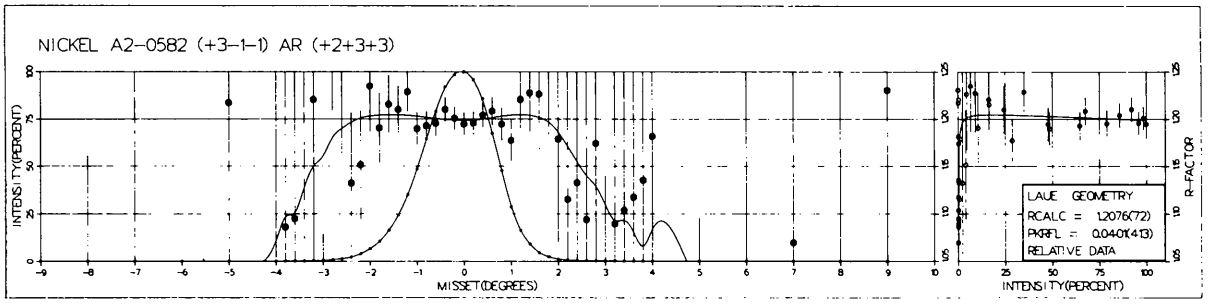
Apparently, more neutrons in the spin-up state are removed from the beam than in the spin-down state and some of these removed neutrons do not appear in the diffracted beam. While multiple scattering behaves this way, the constant value of R_T across most scans and the smooth variation with thickness, independent of sample orientation, suggests that multiple scattering is not the cause. It is more likely that these scattering processes are non-Bragg and diffuse in nature.

The effect of this diffuse scattering is to reduce the effective direct-beam strength in the spin-up state relative to the spin-down state. It is necessary to take this into account in calculating a final flipping ratio, R_{corr}, by dividing the extinction-free flipping ratio *R* by R_{prim}. This consistently improves the agreement between equivalent reflections measured either on crystals of different thickness or on a single crystal measured in different geometries. It appears to help, also, with the variable-wavelength data, but the statistical accuracy was not sufficient to test this rigorously. Table 3 shows five measurements of the 311 family of reflections on two crystals. After extinction correction the maximum variation between results was 0·0091, which is outside the statistical uncertainty in the results. After further correction for diffuse scattering the variation is reduced to 0·0044, which is within the calculated statistical accuracy.

The experimental conditions here ($\lambda = 1{\cdot}08$ Å, sample thickness $\leq 0{\cdot}5$ mm) are not at all extreme and it is quite likely that these effects are present in many other experiments. We know of no reports of this correction being made, and no other technique capable of revealing and measuring the effect.



(*a*)



(*b*)

Fig. 3. Data for the 3$\bar{1}\bar{1}$ reflection rocked around [233]. All explanations are the same as for Fig. 4. In this case, however, the peak reflectivity PKRFL in (*b*) is larger than the true reflectivity and the extinction is overestimated.

4. Comparison of equivalent reflections

If the samples (and beams) satisfy the geometrical conditions for diffraction, and primary extinction is absent, then all measurements of a particular family of reflections, free from multiple scattering, should give the same corrected flipping ratio, within the statistical accuracy of the experiment. The results of our measurements on Ni are given in Table 4. Altogether 51 independent measurements were made on six different reflections. The results are grouped by *HKL* with the mean given after each group. Omitted from the calculation of the mean is the result for the *A*1 crystal, which suffers from primary extinction, and data which show significant multiple scattering are also omitted. Two means for the 111 family are given, including and excluding the one experimental point (not showing multiple scattering) which lies more than 2σ from the mean. The 111 and 200 data are also plotted in Fig. 4. No trends, with thickness or with wavelength, are apparent in these data, and the overall agreement between equivalents appears to be within the range expected from the statistics. The relative uncertainty $\Delta R/(R-1)$ is $\leq 1\%$ for all but the weakest reflection (400).

Data taken at ILL on the specimens used in the present study were treated for extinction by means of a fit of the form

$$I^{\pm} \sim (F_N \pm F_M)^2[1 - \alpha\lambda^2(F_N \pm F_M)^2],$$

i.e. a first-order approximation in λ^2, based on the observed wavelength dependence of R (Schweizer,

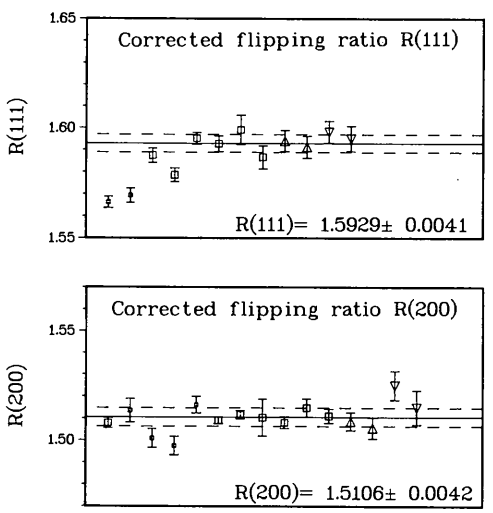


Fig. 4. Flipping ratios corrected for extinction for the 111 and 200 reflections. The points given by □ are data on the *A*2 specimen, the △ are for *A*18 and ▽ are for *A*19. Data at all wavelengths are included, and the points from left to right are in the same order as in Table 4. The data points with half-sized symbols have significant multiple scattering and are omitted from the calculation of the mean. The weighted means and standard deviations are shown on the curve and given in the lower right corners.

Table 4. *Summary of results for the flipping ratios of* Ni *corrected for extinction and diffuse scattering*

Weighted means are given for each family of reflections, excluding only data for which multiple scattering is observed.

Sample	*HKL*	[*hkl*]	λ (Å)	r_{max}	R_{corr}	Comments
*A*1	111	[$\bar{2}$11]	1·08	0·054	1·364 (70)	(*A*)
*A*2	$\bar{1}\bar{1}$1	[022]	1·08	0·025	1·5662(26)	(*B*)(*D*)
*A*2	11$\bar{1}$	[022]	1·08	0·029	1·5693(33)	(*B*)(*D*)
*A*2	$\bar{1}$11	[211]	1·08	0·027	1·5874(33)	
*A*2	1$\bar{1}\bar{1}$	[211]	1·08	0·023	1·5786(31)	(*C*)
*A*2	$\bar{1}$11	[211]	0·84	0·0074	1·5952(27)	
*A*2	$\bar{1}$11	[211]	0·60	0·0046	1·5927(36)	
*A*2	$\bar{1}$11	[211]	0·50	0·0033	1·5991(67)	
*A*2	$\bar{1}$11	[211]	0·42	0·0025	1·5866(52)	
*A*19	1$\bar{1}\bar{1}$	[211]	1·08	0·020	1·5940(49)	
*A*19	$\bar{1}$11	[211]	1·08	0·014	1·5912(50)	
*A*18	1$\bar{1}\bar{1}$	[211]	1·08	0·010	1·5981(50)	
*A*18	$\bar{1}$11	[211]	1·08	0·007	1·5950(58)	
R(111) = 1·5910(64)						
R(111) = 1·5929(41)(*C*)						
*A*2	$\bar{2}$00	[022]	1·08	0·021	1·5079(23)	
*A*2	020	[200]	1·08	0·034	1·5136(54)	(*B*)(*D*)
*A*2	00$\bar{2}$	[200]	1·08	0·023	1·5010(43)	(*B*)(*D*)
*A*2	002	[200]	1·08	0·016	1·4975(42)	(*B*)(*D*)
*A*2	0$\bar{2}$0	[200]	1·08	0·050	1·5162(38)	(*B*)(*D*)
*A*2	200	[022]	1·08	0·015	1·5091(15)	
*A*2	$\bar{2}$00	[022]	1·08	0·015	1·5117(19)	
*A*2	200	[022]	0·84	0·0031	1·5104(84)	
*A*2	200	[022]	0·60	0·0021	1·5081(27)	
*A*2	200	[022]	0·50	0·0015	1·5148(41)	
*A*2	200	[022]	0·42	0·0014	1·5111(32)	
*A*19	200	[022]	1·08	0·018	1·5086(41)	
*A*19	$\bar{2}$00	[022]	1·08	0·011	1·5056(48)	
*A*18	$\bar{2}$00	[022]	1·08	0·0068	1·5250(66)	
*A*18	200	[022]	1·08	0·0085	1·5149(78)	
R(200) = 1·5106(42)						
*A*2	0$\bar{2}\bar{2}$	[200]	1·08	0·010	1·3003(64)	
*A*2	022	[200]	1·08	0·0078	1·2939(41)	
*A*2	$\bar{2}\bar{2}$0	[$\bar{1}$11]	1·08	0·012	1·3007(42)	(*D*)
*A*2	$\bar{2}$0$\bar{2}$	[$\bar{1}$11]	1·08	0·023	1·2988(25)	(*D*)
*A*2	02$\bar{2}$	[$\bar{1}$11]	1·08	0·016	1·2996(27)	(*D*)
*A*2	220	[$\bar{1}$11]	1·08	0·0062	1·2940(37)	(*D*)
*A*2	202	[$\bar{1}$11]	1·08	0·014	1·2016(26)	(*D*)
*A*2	0$\bar{2}$2	[$\bar{1}$11]	1·08	0·024	1·3000(25)	(*D*)
*A*18	022	[200]	1·08	0·0037	1·2944(56)	
*A*18	0$\bar{2}\bar{2}$	[200]	1·08	0·0058	1·3018(63)	
R(220) = 1·2986(29)						
*A*2	3$\bar{1}\bar{1}$	[022]	1·08	0·011	1·2041(21)	(*D*)
*A*2	3$\bar{1}\bar{1}$	[233]	1·08	0·010	1·2066(27)	
*A*2	$\bar{3}$11	[233]	1·08	0·0073	1·2073(26)	
*A*18	311	[$\bar{2}$33]	1·08	0·0044	1·2085(38)	
*A*18	$\bar{3}\bar{1}\bar{1}$	[$\bar{2}$33]	1·08	0·0033	1·2084(28)	
R(311) = 1·2067(19)						
*A*2	$\bar{2}$22	[211]	1·08	0·0090	1·1808(41)	(*B*)
*A*2	2$\bar{2}\bar{2}$	[211]	1·08	0·0080	1·1871(69)	(*B*)
*A*2	$\bar{2}$22	[211]	1·08	0·0066	1·2044(56)	(*E*)
*A*18	$\bar{2}$22	[211]	1·08	0·0023	1·2086(43)	
*A*18	2$\bar{2}\bar{2}$	[211]	1·08	0·0038	1·2077(54)	
R(222) = 1·2071(22)						
*A*2	$\bar{4}$00	[022]	1·08	0·0073	1·1019(21)	
*A*18	400	[022]	1·08	0·0031	1·1036(55)	
*A*18	$\bar{4}$00	[022]	1·08	0·0019	1·0997(42)	
R(400) = 1·1017(17)						

Comments:
(*A*) Strong primary extinction.
(*B*) Multiple scattering, omitted.
(*C*) Omitted from second mean.
(*D*) Non-symmetric geometry.
(*E*) ψ rotation by 5°, multiple scattering still visible.

1983). The extinction-corrected flipping ratios using the ILL programs are somewhat lower for the 111 (0·006) and for the 200 (0·007) reflections on the *A*2 crystal than ratios measured at the same wavelengths and corrected by the present method. However, the ILL method gives a reasonable value for the 111

Table 5. *Corrected flipping ratios for* Ni

	This method			ILL data ILL method	
hkl	Petten	Petten +ILL	Mook (1966)	*A*2	*A*1
111	1·604(4)	1·609(6)	1·615(3)	1·608(6)	1·618(5)
200	1·519(4)	1·524(6)	1·529(3)	1·521(5)	
220	1·304(3)		1·309(2)		
311	1·210(2)		1·213(2)		
222	1·209(2)		1·206(2)		
400	1·103(2)		1·099(2)		

flipping ratio for the *A*1 crystal, whereas the present method breaks down completely owing to the presence of primary extinction and the inability to satisfy the divergence conditions for the beam.

Table 5 gives the nickel results corrected for beam polarization, flipper efficiency and other instrumental effects. In the first column only the data taken at Petten are included, while in the second column the ILL data, analyzed with the present method, have also been included. The correction for flipper efficiency to the ILL data is relatively large (~0·01 for 111), while for the Petten data it is small (~0·001). Since the instrumental corrections will be overestimated if the analyzer crystals used to determine the polarization, and the crystal used to determine the flipper efficiency in the ILL case, are not ideal, but will never be underestimated, it is preferable to use the data for which the total instrumental correction is smallest. The possibility of an overestimation in the ILL data is supported by the observation of a small shift between the Petten and ILL results after these corrections, although no wavelength dependence is apparent. For this reason we consider the Petten results alone to be more reliable than the combined results.

The results of Mook (1966) on Ni as well as the results of the ILL experiments on the same specimens using the ILL analysis are also given in Table 5. The quoted uncertainty in the data in Table 5, for the present method, is determined from the weighted means of all the data collected, but is primarily determined by the counting statistics. For the ILL method the larger error bars represent poorer counting statistics owing to very short counting terms.

5. Discussion

Although absolute measurements have been used in X-ray and γ-ray diffraction and occasionally in neutron scattering, it is usually argued that since flipping ratios are the quantity of interest in polarized-neutron scattering, absolute measurements are of no special value in this technique. We have found, on the contrary, that absolute measurements including determination of the transmitted (undiffracted) beam provide a surprising amount of valuable information.

Determination of the reflectivity automatically gives the secondary-extinction correction free from any parametrization. The technique is especially applicable to data collected in a symmetric Laue geometry where the effects of absorption may be ignored and consequently the Zachariasen solution to the intensity transfer equations is valid. However, for small reflectivity ($r \leq 0{\cdot}1$) it appears to apply more generally, if absorption is moderate, and we have found no significant differences in corrected flipping ratios in symmetric or asymmetric Laue or Bragg geometries in the case of Ni.

Multiple scattering is conveniently observed with this method as well, since the presence of an extra spot on the sphere of reflection leads to non-conservation of neutrons in the total of primary diffracted beam plus transmitted beam. Testing for this is done by comparing the summed beams for both spin states, a method which appears to be sufficiently sensitive to multiple scattering and relatively insensitive to absorption effects in moderately asymmetric geometries. In an ideal instrument the direct beam would be measured simultaneously with the diffracted beam, and the required number of counts ($\sim 10^6$) could be collected in the same amount of time as is normally spent counting the diffracted beam only.

The presence of (apparently) non-Bragg scattering processes in Ni has also been revealed by this technique, since it is found that the total beam ($I_B + I_T$) for spin-down neutrons is (on average) stronger than for spin-up neutrons. Two possible causes for this phenomena may be suggested. Firstly, the scattering may be due to magnetic defects and would presumably be at small angles. If all of the scattering is at low q (form factor $\simeq 1$) at least 1·5% of the beam must be scattered outside $q = (4\pi \sin\theta/\lambda) \simeq 0{\cdot}3$ Å^{-1}, the acceptance of our detector. This scattering must also be rather flat or else a significant amount would be accepted by the detector. If this were to occur, then the correction for diffuse scattering would be underestimated, since those neutrons, while accepted by the detector, are none-the-less unavailable to be diffracted. Within the accuracy of our measurements no evidence for this is found, but small-angle scattering studies will be carried out on these samples.

A second explanation may be found in the magnetovibrational (inelastic) scattering which has been observed by Steinsvoll, Moon, Koehler & Windsor (1981). This has the correct dependence on magnetic field to explain our observations, but we do now know if the total cross section for this process is large enough to explain our results. In any case, the effect is sufficiently large to require correction in many experiments and we know of no other method to reveal its presence.

There is a small but significant difference in the extinction correction performed with the ILL system and with the present method (on the same specimen) and also between different specimens of different quality (*A*1 and *A*2) corrected with the ILL system.

We believe this is due to the necessity of assuming the functional form of the wavelength dependence in the ILL method. Since both primary and secondary extinction may be present (as well as diffuse scattering), each with different wavelength dependence, the assumed function may not be correct, but can still give a good fit with data over a limited wavelength range. In fact, for the *Al* specimen it was necessary to exclude the 0·84 Å data to reach a satisfactory fit. In principle, however, a wavelength-dependent method should successfully extrapolate to the true flipping ratio as the wavelength decreases and the scattering power tends toward zero in all cases, while the present method is only applicable to specimens which are free from primary extinction and divergent compared to the beam.

The Petten results differ somewhat from those of Mook, for which approximately comparable accuracy is claimed. A possible explanation for the difference is that in Mook's data the size of the extinction correction was fixed by essentially one measurement, the 111 intensity on a very thin (38 μm) crystal. Any error in that measurement will propagate through the data. In our case the extinction correction for each reflection is done independently and with no adjustable parameters. The good agreement for different wavelength, thickness and reflectivity gives us confidence in the present results.

In some cases, the maximum reflectivity for a sample will be small enough ($\leq 0{\cdot}001$) that extinction and multiple scattering can be neglected. Once this has been determined (through knowledge of the direct-beam strength), it would appear that the best strategy in data collection is to measure the peak intensities only, for which the highest statistical accuracy can be achieved. Over a wide range of reflectivity ($0{\cdot}5 > r > 0{\cdot}001$), however, the advantage of this technique, which requires scanning the entire rocking curve, is appreciable. In most cases data collection will be two to three times longer than with the usual method of determining peak and background only plus performing a ψ scan for multiple scattering, because of the larger number of points measured, but, compared to preparing many samples or measuring at several wavelengths, it is actually faster.

Perhaps the greatest remaining problems concern the availability of suitable samples. Preparation of metal alloys with the required geometry, and mechanical treatment to eliminate primary extinction and satisfy the resolution requirements for the *R*-on-reflectivity method, appears to be possible. However, many compounds such as magnetic insulators cannot easily be deformed, and others such as rare-earth transition-metal intermetallics have not been grown in large enough ingots to allow preparation of suitable plate samples. For the former group of samples, some other treatment to introduce defects (such as radiation treatment, liquid-N_2 quenching *etc.*) may be useful. For the latter group absolute measurements (with reduced accuracy) may still be made by measuring flux density and sample volume. However, treatment of multiple scattering and diffuse scattering in this case becomes much more problematical.

Despite these reservations a great many materials of interest can be prepared to meet the demands of this technique. Its application could lead to significantly more reliable spin density maps than are now available.

The authors would like to acknowledge J. Schweizer, ILL, Grenoble, for making the D5 diffractometer available to them and for his kind assistance during the measurements performed on this apparatus. We would also like to acknowledge several useful discussions with E. Frikkee, ECN. One of us (WBY) thanks the University of Missouri Research Reactor for support during his sabbatical leave.

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