

- KOPTSIK, V. A. & KOTZEV, J. N. (1974*b*). *Commun. Joint Inst. Nucl. Res., Dubna, USSR*, P4-8068.
- KOSTER, G. F., DIMMOCK, J. O., WHEELER, R. G. & STATZ, H. (1963). *Properties of the Thirty-two Point Groups*. Cambridge, MA: MIT Press.
- LITVIN, D. B., KOTZEV, J. N. & BIRMAN, J. L. (1982). *Phys. Rev. B*, **26**, 6947–6970.
- NEUNHAM, R. E. (1974). *Am. Mineral.* **59**, 906–918.
- NEUNHAM, R. E. & CROSS, L. E. (1974*a*). *Mater. Res. Bull.* **9**, 927–933.
- NEUNHAM, R. E. & CROSS, L. E. (1974*b*). *Mater. Res. Bull.* **9**, 1021–1031.
- NEUNHAM, R. E. & CROSS, L. E. (1976). *Ferroelectrics*, **10**, 269–276.
- NEUNHAM, R. E. & SKINNER, D. P. JR (1976). *Mater. Res. Bull.* **11**, 1723–1284.
- NYE, J. F. (1964). *Physical Properties of Crystals*. Oxford: Clarendon Press.
- OPECHOWSKY, W. (1980). *Match: Commun. Math. Chem.* **9**, 51–64.
- SHUBNIKOV, A. V. & KOPTSIK, V. A. (1974). *Symmetry in Science and Art*. New York: Plenum.
- TENENBAUM, J. (1966). *Proc. Indian Acad. Sci.* **64**, 74–83.
- WADHAWAN, V. K. (1979). *Acta Cryst.* **A35**, 629–633.

Acta Cryst. (1984). **A40**, 261–263

Secondary Extinction and Absolute Structure Factors in X-ray Diffraction: Determination by Polarization Variation

BY W. B. YELON*

Joint Research Center, Petten Establishment, PO Box 2, 1755 ZG Petten, The Netherlands

AND B. VAN LAAR

Netherlands Energy Research Foundation, ECN, PO Box 1, 1755 ZG Petten, The Netherlands

(Received 13 June 1983; accepted 21 November 1983)

Abstract

If a rocking curve is measured in symmetric Laue geometry for two different X-ray polarizations, and the incident beam meets the geometrical conditions for diffraction, *i.e.* the incident beam is much less divergent than the sample mosaic, then the intensity ratio R_{obs} , for the intensities measured with each polarization, will depend upon the reflectivity at each point on the rocking curve. From the variation of R_{obs} vs the observed intensity, I_{obs} , the absolute reflectivities and secondary extinction can be determined. If absorption is properly treated, then all data taken in this geometry should lie on a single curve of R_{obs} vs I_{obs} . Failure to fit this curve is evidence that the sample has other processes occurring such as multiple scattering or primary extinction.

Introduction

A major advantage of high-intensity synchrotron X-ray sources, which have recently been constructed or will soon become operational, is the ability to vary the polarization of a monochromatic beam falling on a diffracting sample, while still keeping sufficient intensity for easy data collection. One use to which the polarization dependence can be put is in the study

of primary extinction (Suortti, 1982*a, b*), since the extinction length is inversely proportional to the polarization. A second advantage of the synchrotron source is the high intensity available in a very narrow angular and wavelength band. Unlike conventional X-ray sources, with synchrotrons it should be possible to restrict the divergence of the beam in both angle and energy, so that the divergence of the beam is less than that of the sample (for all but the most perfect specimens), while preserving reasonable intensity on the sample.

In two recent papers (Yelon, van Laar, Kaprzyk & Maniawski, 1984; Yelon, van Laar, Maniawski & Kaprzyk, 1984) it has been shown that absolute reflectivity measurements with a beam meeting the above divergence conditions could give good secondary extinction corrections in polarized neutron scattering, free from any parametrization or fitting. In the present paper we propose an inverse method in which measurement of the intensity ratio for X-ray scattering with two different beam polarizations can be used to determine the absolute reflectivity as well as to give the secondary extinction corrections for a measured rocking curve.

Theory

The present method is based on the Zachariasen (1967) solutions to the intensity transfer equations (Darwin, 1922) in symmetric Laue geometry, which

* On leave from the University of Missouri Research Reactor, Columbia, Missouri 65211, USA, now returned.

is the only case for which the Zachariasen solution is valid if absorption is non-negligible. The extinction parameter $\varphi(\varepsilon)$ (where ε is the rotation angle) for a large parallel-plate sample in that geometry was given by Zachariasen as

$$\varphi(\varepsilon) = \frac{1 - \exp[-2\sigma(\varepsilon)\bar{T}]}{2\sigma(\varepsilon)\bar{T}} \quad (1)$$

where $\sigma(\varepsilon)$ is the macroscopic cross section and \bar{T} is the effective thickness of the slab sample ($= T/\cos\theta_B$). This expression can be given in terms of the reflectivity $r(\varepsilon)$ (Schneider, 1976; Yelon, Van Laar, Kaprzyk & Maniawski, 1984; Yelon, van Laar, Maniawski & Kaprzyk, 1984)

$$\varphi(\varepsilon) = -2/\ln(1-2r) \quad (2)$$

and

$$\sigma(\varepsilon)\bar{T} = -\frac{1}{2}\ln(1-2r). \quad (3)$$

These expressions have meaning, however, only if the sample diffracts all components of the incident beam (wavelength and angle) equally well at any given setting. This, in turn, leads to the requirement that $\sigma(\varepsilon)$ be homogeneous throughout the sample and that the beam divergence be much less than the sample mosaic. This latter condition is rarely met with conventional X-ray sources, but with synchrotrons it appears to be feasible to meet this requirement.

If the diffraction experiment is performed with two beams with different polarization factors C_1 and C_2 , one can define a kinematical ratio of diffracted intensities.

$$R_K = \frac{(C_1)^2}{(C_2)^2}. \quad (4)$$

The observed intensity ratio will depend on extinction and will be

$$R_B = R_K \varphi_1 / \varphi_2, \quad (5)$$

which, from (2), is found to be

$$R_B = \frac{2r_1}{1 - (1 - 2r_1)^{1/R_K}}. \quad (6)$$

The observed ratio R_B varies from $R_B = R_K$ at $r_1 = 0$, the kinematic limit, to 1 at $r_1 = 0.5$, the maximum reflectivity in the Laue case. A reduced quantity

$$R_R = \frac{R_B - 1}{R_K - 1} \quad (7)$$

is shown in Fig. 1 for $R_K = 1.1$ and $R_K = 10$. From (6) it is seen that a determination of R_K can give the reflectivity and extinction corrections at all points on the rocking curve.

The effect of unequal beam strengths and absorption (in symmetric Laue geometry where all path lengths are equal) can easily be taken into account,

and the observed intensity ratios will be

$$R_{\text{obs}}(\varepsilon) = R_0 \frac{2HI_1(\varepsilon) e^{-\mu\bar{T}}}{1 - [1 - 2HI_1(\varepsilon) e^{-\mu\bar{T}}]^{1/R_K}}, \quad (8)$$

where $R_0 = I_{01}/I_{02}$, the relative incident beam strengths, $H = 1/I_{01}$ and μ is the effective linear absorption coefficient. All of the variables in this expression can (in principle) be determined independently so that again $r_1 = HI_1 e^{-\mu\bar{T}}$ can be used in (3) to correct for extinction without parametrization. This expression is valid for all reflections on a given specimen in this geometry as well as for all points in a given rocking curve and so a large number of data points can be used to determine any of the variables not independently measured. Furthermore, an ideally diffracting crystal free from multiple scattering and primary extinction can be used to determine all the variables except μ .

Once μ is known for a particular sample, all R_{obs} vs r_1 can be plotted on a universal curve. Deviation of the measured points from this curve is evidence of other processes such as multiple scattering or primary extinction. A simple χ^2 test should be sufficient to define those reflections which are affected by one or more of these processes.

Discussion

With the new synchrotron X-ray sources, it should be possible to prepare beams with divergences which are much smaller than the mosaic widths of most normally prepared specimens. If, in addition, the polarization factor is varied, then it is likely that significant improvement can be made in the collection of high-precision data.

With the method presented in this paper, measurement with two different polarizations allows the data

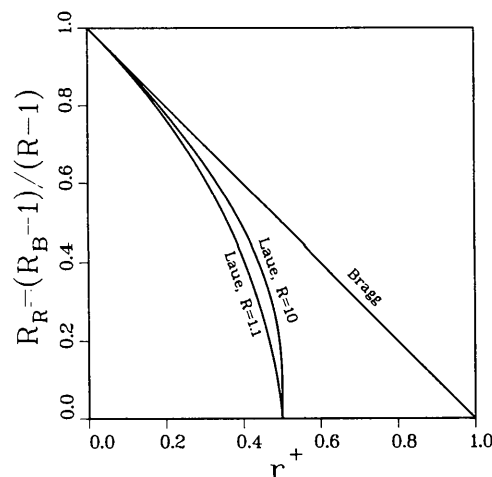


Fig. 1. Variation of the reduced quantity $(R_B - 1)/(R_K - 1)$, where R_B is the observed intensity ratio and R_K is the kinematical ratio ($= C_1^2/C_2^2$) versus r_1 , the reflectivity for polarization C_1 , for $R_K = 1.1$ and $R_K = 10$.

to be corrected for secondary extinction and to be transferred from a relative scale to an absolute scale without reference to any specific model of the mosaic distribution function or to any approximate solution for the integral of the Zachariasen solution. The technique also has a number of possibilities for cross checking. All of the parameters of (8) can be determined by direct measurement rather than by fitting diffraction data. The intensity ratio I_{01}/I_{02} will normally be determined with reasonable accuracy using the ionization chambers which monitor the beam, while I_{01} will be determined only to within the calibration of the chambers. In addition, all of the parameters except μ can be fixed by measuring on different specimens, especially prepared for calibration. The agreement of the various methods should provide a measure of confidence for the entire procedure. It should be particularly noted that this method preserves a constant diffraction geometry and that unlike methods which involve wavelength variation to change scattering power, no corrections for anomalous scattering are necessary. It can also be seen from Fig. 1 that a large change in polarization is not necessary to have reasonable sensitivity for this method. Failure of the experimental data to fit (8) is evidence that the sample does not meet the conditions which were defined in setting up the model. Among the possible causes of the failure are: 1. multiple scattering; 2. primary extinction; 3. inhomogeneous sample; and 4. insufficiently narrow beam divergence.

The effect of multiple scattering is likely to be manifested in only some of the data on the rocking curve and thus recognizable, while primary extinction will cause all points on a rocking curve to deviate from the ideal behavior. Even when the functional form of primary extinction mimics that of secondary extinction the absolute measurement of reflectivity with this method should make it possible to recognize its presence. For an inhomogeneous sample (widely varying grain size, *etc.*) the deviations from (8) are likely to be less regular than for the previous effects. Wavelength, as well as polarization variation, should provide a good way to distinguish between these effects and to arrive at optimum measuring conditions. Multiple scattering processes should show rapid change with wavelength while primary extinction will vary only slowly. However, it should be possible to select a short wavelength and polarization for which primary extinction is negligible, since the extinction length (Zachariasen, 1945) is inversely proportional to λ and C . The agreement of the data to (8) will help to define this point. In some specimens it may not be possible to reach this limit (such as

perfect Si, *etc.*). It is not clear that any present method is capable of treating such samples, unless they are perfect enough for a purely dynamical treatment. Inhomogeneous samples will, of course, give problems at all wavelengths and polarizations, at least until the reflectivity (and secondary extinction) has been reduced to extremely small values.

It should also be noted that while this discussion has focused on measurements in the symmetric Laue geometry, only one point on a given rocking curve can be in exactly symmetric geometry. If, however, one works with short-wavelength radiation, so that the Bragg angles are small, then the deviation of the effective paths for diffracted and transmitted beams can be kept to a minimum and the solution treated as valid at all points. For this reason, also, samples should have mosaic widths which are not too broad. The quality of the samples and the validity of the divergence conditions should be tested either with γ -ray diffraction or with a test beam especially tailored for this purpose.

It is clearly not practical, in the general case, to make all measurements in symmetric Laue geometry with plate samples larger than the beam. It should be possible, however, to measure the most intense reflections in this geometry (as well as a variety of weak reflections to permit scaling of the data sets) and then to collect a full data set in the conventional way. This would appear to be a reasonable strategy in that only a few samples in Laue geometry need be prepared to reach the principal zones. For example, in a simple cubic system only two plates (with [001] and [110] axes) are needed to reach the first 12 reflections. The final results of such a procedure are likely to be more satisfactory than the conventional method alone, since the scale factor will be fixed and not refined, and those reflections which have the greatest extinction will be corrected independently of the semi-empirical fitting which characterizes the usual extinction treatments.

References

- DARWIN, C. G. (1922). *Philos. Mag.* **49**, 800–824.
 SCHNEIDER, J. R. (1976). *J. Appl. Cryst.* **9**, 394–402.
 SUORTTI, P. (1982a). *Acta Cryst.* **A38**, 642–647.
 SUORTTI, P. (1982b). *Acta Cryst.* **A38**, 648–656.
 YELON, W. B., VAN LAAR, B., KAPRZYK, S. & MANIAWSKI, F. (1984). *Acta Cryst.* **A40**, 16–23.
 YELON, W. B., VAN LAAR, B., MANIAWSKI, F. & KAPRZYK, S. (1984). *Acta Cryst.* **A40**, 24–31.
 ZACHARIASEN, W. H. (1945). *Theory of X-ray Diffraction in Crystals*. New York: Wiley.
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.