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A Procedure for Measuring X-ray Attenuation Coefficients

BY J. L. LAWRENCE

Department of Physics, University of St. Andrews, North Haugh, St. Andrews, Scotland KY16 9SS

AND A. MCL. MATHIESON

Division of Chemical Physics, CSIRO, P. O. Box 160, Clayton, Victoria, Australia 3168

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An alternative to the standard absorber-in/absorber-out procedure for the measurement of X-ray attenuation coefficient, μ, is proposed. The method is based on systematic variation of the length of the absorbing path by tilt of a parallel-sided plate of the material under study. The procedure allows for the incorporation of in-built checks. The method is illustrated for LiF using Mo $K\bar{\alpha}$ radiation. The precision capability of the technique is discussed.

Introduction

In *International Tables for X-ray Crystallography* (1974), the general comment is offered that the ultimate accuracy of X-ray structure factors determined by intensity measurements may depend upon the accuracy with which the attenuation coefficient, μ, is known. More specifically, Inkinen (1969), in allocating error magnitudes to various sources in powder intensity measurements, has judged those due to the 'absorption coefficient' and the 'attenuation factor' to be dominant. In respect of single-crystal intensity measurements also, the role of μ in establishing accurate structure factors is of concern, particularly in Bragg-type measurements with extended-face crystals. There, the direct dependence on the precision of μ is obvious from the form of the relation used, $E\omega/I = Q/2\mu$ (James, 1948).

The 'state of the art' in establishing values of μ from published measurements is indicated in the recent compilation of μ/ϱ for Be to Zn by Stiglich, Weiss & Hansen (1974). The values are derived by an interpolation procedure and the error estimates range from a few percent up to the region of 10%. Similarly, the precision of the compiled values in *International Tables* (1974) is placed within four categories with envelopes of uncertainty ranging from ± 2 to $\pm > 15\%$. Under these circumstances, an alternative to the standard experimental procedure for determining μ warrants consideration.

The attenuation coefficient, μ, is defined by

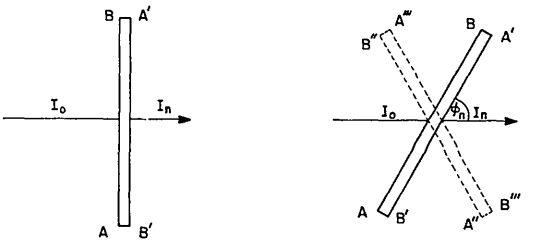
$$I = I_0 \exp[-\mu(\lambda_0)t] \qquad (1)$$

and the normal experimental method is to measure the intensity of the incident beam, I_0, of wavelength λ_0, that of the transmitted beam, I, and determine the specimen thickness, t. While apparently straightforward, the absorber-in/absorber-out procedure is not without its problems (see *International Tables*, 1974).

An alternative procedure potentially capable of improved precision is to vary t systematically on a single specimen by use of the angle-setting capability of the modern diffractometer. This procedure has the advantage of allowing incorporation of certain internal checks.

Method

If a single-crystal parallel-sided plate specimen of thickness, t, is mounted on a diffractometer, then appropriate values of path, nt, can be established by suitable adjustment of diffractometer angle, φ (say). Thus, with $\omega = 0°$ and $\chi = 90°$, φ may be set so that $n = 1/\cos\varphi$. $\varphi = 0°$ corresponds to $n = 1{\cdot}0$, *i.e.* the specimen is normal to the X-ray beam (Fig. 1*a*). For $n = 1{\cdot}0$, there are only two positions, 0 and 180°. For values other than 1·0, Fig. 1(*b*), there are four equivalent settings, φ, $-\varphi$, $180° + \varphi$ and $180° - \varphi$. The concordance of the four transmitted intensities provides an estimate of path uniformity while the mean of the four provides a more precise estimate for I for the path nt. With a diffractometer having a χ full circle, a further set of four measurements can be made at $\chi = 270°$ as well as the original four at $\chi = 90°$. The values of n which we have used in practice were 1·0 to 5·0 in steps of 0·5.



(*a*) (*b*)

Fig. 1. The relation of the X-ray beam and the parallel-sided plate (*a*) for $\varphi = 0$ and 180°, (*b*) for the four general positions with equal path length, $\pm\varphi$ and $180° \pm \varphi$.

Equation (1) may be recast as

$$\ln I_n = \ln I_0 - \mu(\lambda_0)nt\,. \qquad (2)$$

The slope of the plot of $\ln I_n$ *versus* n is $-\mu t$. From the measurement of t, $\mu(\lambda_0)$ can be established. The intercept at $n=0$ yields a value of I_0. Comparison of this value with the direct measurement of I_0 provides a check on the essential consistency of the set of measurements. If the value for I_0 by direct measurement is significantly larger than that obtained by extrapolation, the presence of spectral component(s) with $\lambda > \lambda_0$ is indicated. Spectral components with $\lambda < \lambda_0$ have a different effect on the measurements, showing up in the slope of the log plot. This effect can be identified by deliberately modifying the ratio $I_{\lambda<\lambda_0}/I_{\lambda_0}$ (see below).

Results

The procedure is illustrated for a specimen of LiF using Mo $K\bar{\alpha}$ radiation, monochromated using a pyrolytic graphite crystal. The specimen, of dimensions $20 \times 20 \times 1{\cdot}283$ (2) mm, was mounted on a Siemens diffractometer. The φ axis was used to establish the tilt of the plate, χ being set at 90°. The results, the average of the four $\ln I_n$ values, are listed in Table 1. From a least-squares fit, one obtains $\mu = 3{\cdot}12$ (2) cm^{-1}, the value in brackets representing the estimated standard deviation. For LiF and Mo $K\bar{\alpha}$, the value calculated from the latest values of μ/ϱ in *International Tables* (1974) is 3·1986. Given that the values listed for Li and F belong to the highest category with an envelope of uncertainty of ±2%, this corresponds to a range of 3·26 to 3·14. No critical comparison is offered here because the spectral composition of the radiation used was not sufficiently monoenergetic to satisfy the requirements for highest accuracy (see below). The measurements were carried out to establish the feasibility of the method.

Table 1. *Values of the average of the four values of* $\ln I_n$ *against* n

The four measurements of I_n correspond to tilt angles $\pm\varphi$, $180° \pm \varphi$.

n	$\ln I_n$	
1·0	8·602	
1·5	8·423	$\ln I = 9{\cdot}10$ (1)$-0{\cdot}400$ (2)n
2·0	8·182	$I_0 = 8185$ (80)
2·5	8·004	$t = 0{\cdot}1283$ (2) cm
3·0	7·797	$\mu = 3{\cdot}12$ (2) cm^{-1}
3·5	7·610	
4·0	7·405	
4·5	7·212	
5·0	7·006	

Operational requirements

A number of aspects of this technique require careful consideration. These are dealt with under the following headings:

(*a*) *Specimen.* The specimen must be shaped to have the main faces accurately parallel and planar. To establish the thickness with precision, the finish should preferably be optically flat on both entrance and exit faces. It may be advantageous to make the faces slightly offset with respect to any major Bragg plane. Then, in the event of a Bragg reflexion occurring, the effect of the asymmetry will be revealed by an inequality of the transmitted intensities (*cf.* James, 1948). The specimen thickness, t, should be measured by a method not involving direct physical contact, *e.g.* by an optical procedure or with an air-pressure gauge.

(*b*) *Specimen orientation of diffractometer.* It is advantageous to tilt the specimen slightly in the plane of its main face so that no major crystallographic axis is parallel to the φ axis of the diffractometer. Ideally one should calculate the occurrence of Bragg reflexion coincidences to ensure that only simple absorptive processes operate.

A critical step is the establishment of φ_0, *i.e.* the value of φ for which the X-ray beam is exactly normal to the specimen surface and so t is at its minimum. The procedure used was to adjust to a value of $+\varphi$ where the effective thickness is $\simeq 5t$ (say), measure the transmitted-beam intensity, then repeat the procedure at the nominally equivalent $-\varphi$ setting. Adjust this latter $-\varphi$ setting until the beam intensity is equal to that at $+\varphi$. The mean of $+\varphi$ and $-(\varphi+\Delta\varphi)$ is φ_0. Measurements at $180°+\varphi$ and $180°-(\varphi+\Delta\varphi)$ will confirm the result. An alternative procedure would be to use an optical method, but the method given above is probably more direct and relevant to the actual experiment.

(*c*) *Radiation.* The spectral purity of the radiation used is probably the most important single factor in experiments of this type. It is essential therefore that (i) a crystal monochromator is used, (ii) the generator should be kept below the excitation voltage for $\lambda_0/2$ radiation,* and (iii) for the initial experiment, set the beam intensity at a convenient level by use of the X-ray set controls. Avoid the use of absorbers for this purpose since it tends to accentuate short wavelength components. When the first set of data has been collected, it is advisable to insert deliberately in the beam path an absorber to decrease the λ_0 component much more than the $\lambda_0/2$ component, and hence accentuate the ratio $I_{\lambda_0/2}:I_{\lambda_0}$. Then repeat the measurements. If the slope is now significantly lower than the earlier result then a $\lambda_0/2$ component (or, in general terms, a component of wavelength shorter than λ_0) is contributing to the original value of μ. If the effect is small, a correction may be made. Alternatively, experimental conditions may be changed until the short wavelength components are sufficiently small to satisfy the test above.

* While the nominal voltage reading may suggest that no $\lambda_0/2$ radiation is being excited, much depends on the actual circuitry of the generator. It is advisable to determine the operational spectrum with care, particularly in the region $\lambda_0/2$.

(*d*) *Divergence*. The divergence of the main beam will introduce slight differences in the path length through the crystal. However, provided the profile of the main beam is uniform, a divergence of 0·3° will affect the average path length by less than 0·1 % for values of $n < 5$.

Estimation of precision requirements

The present results are given as an illustration of the method and are not intended to demonstrate its full capability. The actual wavelength band, $\Delta\lambda$, from the pyrolytic graphite monochromator using Mo radiation was somewhat too broad to warrant aiming for the highest precision (*cf.* use of plane-polarized Cu $K\alpha_1$ X-rays by Calvert, Killean & Mathieson, 1975). However, it is evident that, in addition to high spectral purity, establishment of a value of μ to an accuracy of 0·1 % (say) requires the precision of the various components of equation (2), namely I, n and t to be individually superior to that figure. For the sake of future applications, it is worth while to draw attention to the basic requirements for such precision.

In the case of a specimen with t of the order of 1 mm, the dimension requires to be established over the length of the specimen involved, *i.e.* at least 5 mm, to rather better than 10^{-3} mm (< 10 000 Å). Hence, one may conclude that over the length of the specimen, the maximum deviation permitted would be of the order of one optical fringe. For a specimen of thickness 10^{-1} mm, the corresponding requirement would be < 1000 Å.

The error in n, Δn, is dependent on the error in $\varphi, \Delta\varphi$. For $n = 5$, an error of 0·01° in setting φ would produce a 0·1 % error in n. Hence, while an individual reading would verge on the practical limit of precision for a standard diffractometer, the process of averaging four (or eight) readings will ensure adequate precision in n.

For the measurement of the intensities I_n, total counts, corrected for dead time and background, will require to reach a level where precision is better than 0·1 %, *i.e.* well above 10^6 counts will be necessary.

Discussion

Some use of limited tilt to fractionally increment μt has been made by Bearden (1966) in measurement of attenuation coefficients, but systematic application in the present manner was not proposed. Measurement of the effective absorption coefficient, μ', with systematic variation of t by tilt has been carried out on a specimen of pyrolytic graphite (Calvert, Killean & Mathieson, 1976). For that material, being a turbostratic structure, the μ' pattern is complex, but the study indicated the appropriate choice of tilt region for the determination of the mass attenuation coefficient of μ/ϱ for carbon (Calvert, Killean & Mathieson, 1975). In Calvert, Killean & Mathieson (1976), attention was drawn to the advantages of using single-crystal material in the accurate determination of μ. Indeed for single-crystal materials, provided due recognition is made of coincidence of Bragg reflexions, measurements of μ by systematic variation of beam path would appear to be eminently practicable for many inorganic materials available in large crystalline plates and of sufficient hardness that parallel plates can be prepared by standard polishing techniques. This method would also appear suitable for application to selected organic materials where these can be obtained as moderate-sized crystals and where the technique of preparing parallel-sided specimens of relatively soft materials has been developed.

As noted in the *Introduction*, lack of precision in the establishment of attenuation coefficients places a definite limit on the accuracy of structure factors. It is indeed evident from the discussion above why the usual method involving one measurement on one specimen is liable to have low precision [*cf.* equation (1)]. While one may increase counts to any required limit, the estimation of t for a foil of thickness *ca* 10^{-2} cm to better than 1000 Å, and testing for parallelism, pose a rather intractable problem.

Because of the capability of internal checking and averaging, the method proposed here would appear to be capable of achieving the level of accuracy for μ necessary to subsume a 0·1 % accuracy in structure factors.

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