space groups using convergent-beam electron diffraction, and that this method could be applied to any enantiomorphous space-group problem for substances stable in the electron beam. The relative lack of sophistication needed is emphasized in this particular determination, since all the diffraction pictures which gave the necessary evidence were taken by indirect photography (*i.e.* from outside the vacuum) of a fluorescent screen within an ion-pumped diffraction camera, and are of poorer than conventional quality and resolution.

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Extinction-Free Measurements with Plane-Polarized X-rays

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A means of obtaining single-crystal data from which the effects of extinction have been eliminated is described. The method involves the use of plane-polarized X-rays diffracting in the π mode from a crystal plane. Measurements of integrated intensity are made over a range of 2θ on either side of $2\theta = 90°$. A suitably chosen function of the intensities is plotted against a function of 2θ and extrapolated to the limit, $2\theta = 90°$. The prerequisite for this procedure is a source of plane-polarized X-rays of wavelength selectable over a range such as 5 to 0·5 Å, a facility previously difficult to establish but now feasible with synchrotron radiation. The method is discussed in relation to symmetrical Bragg reflexion from an extended-face crystal but is relevant to other cases such as the transmission (Laue) technique or a small crystal bathed in the X-ray beam.

Introduction

In a recent paper, I discussed one experimental procedure (method I) for obtaining single-crystal diffraction data free from extinction, using asymmetric reflexion from extended-face crystals (Mathieson, 1976). While that procedure requires a relatively large crystal specimen and may involve its being shaped and polished, nevertheless the requirements in respect of diffraction equipment are simple.

Further consideration of the basic physical principles underlying the occurrence of extinction has led to the recognition of a second practicable experimental procedure (method II) which is capable of controlled variation so that, in the limit, it yields extinction-free data. Method II involves the use of plane-polarized X-rays diffracting in the π mode (Compton & Allison, 1935) and extrapolation of an appropriate function of the measured intensities to $2\theta = 90°$.

In contrast to method I, method II requires somewhat specialized conditions which, in the past, would have been rather difficult to set up. Now, however, a synchrotron source can provide the necessary prerequisite, namely plane-polarized X-rays of wavelength selectable over a wide range (see, for example, Codling, 1973).

From the discussion which follows, it will be evident that this second method is not as restrictive as the first in terms of size, and especially shape, of the crystal specimen. Hence method II may prove useful in circumstances where method I is not applicable.

Comment on the kinematical theory and extinction

Before dealing with the method, it may be as well to clarify the approach to the question of extinction.

In the literature, one finds that the discussion of kinematical theory varies sufficiently from author to author, depending upon the specific aspect which he wishes to treat, that it would appear advisable to present an explicit statement as to the viewpoint adopted here, namely that the formulae associated with the

kinematical theory, such as that given in equation (1) below, which is widely used as applicable for small structure factors (*e.g.* Weiss, 1966; Warren, 1969), is only strictly true in the limit of zero interaction.

To be specific, equation (1) is based on the assumption that energy abstraction from the incident beam is due only to normal absorption, the magnitude of which is indicated by the attenuation coefficient, $\mu_0(\lambda)$. On this basis, the existence of multiple scattering and of attenuation of the primary beam by single scattering is excluded, so that the theoretical integrated intensity. ϱ_0', given by equation (1), is by definition free of (secondary) extinction, as specified by the subscript. Because it does not take account of the energy abstracted by diffraction and hence the requirement of energy balance, the formula is strictly correct and applicable only when the diffracted energy is zero. This being so, the attainment of extinction-free data can only be achieved in such a limit.

In general, the approach to extinction in the past has been that its effect should be *reduced* by choice of experimental procedure so that the process of applying corrections was assisted. All such approaches depended upon the selection of a suitable physical model by which the appropriate form of correction could be determined. A summary of such approaches is given in Weiss (1966, p. 49).

The present approach is somewhat different in that we seek to establish experimental procedures with which extrapolation can achieve exact matching of the physical conditions corresponding to the basic assumptions underlying the formulae associated with the kinematical limit (exemplified here for the extended-crystal case) so that the effect of extinction is *eliminated.*

Method II

Method I (Mathieson, 1976) depends upon extrapolation to the kinematical limit for integrated intensity using the special conditions associated with asymmetric reflexion when the asymmetry angle, α, tends to $+\theta$ or to $-\theta$, θ being the Bragg angle for the reflexion under consideration.

Method II also depends upon extrapolation to the kinematical limit but invokes a different physical operation. In this case, use is made of plane-polarized X-rays diffracting in the π mode from the crystal plane (Fig. 1). By choice of a series of wavelengths, the corresponding intensities for reflexion from one crystal plane, (*hkl*), are measured over a range of 2θ encompassing 90°, say from 74 to 106°. Extrapolation of a suitably chosen function of the measured intensities to $2\theta=90°$, both from lower and higher angles, defines a limiting value which does not involve multiple scattering or attenuation of the primary beam by single scattering, and which is therefore free from extinction and can be related exactly to the kinematical formula of the π component.

The method will be outlined by reference to the case of symmetrical Bragg reflexion from an extended-face crystal. Extension to other cases is relatively straightforward.

To establish that the relevant condition is fulfilled in the limit, $2\theta=90°$, for both primary and secondary extinction (and hence for any combination of the two), we shall consider the two cases individually.

Primary extinction

In this case the situation relating to the perfect crystal can be considered. For structure factors $|F|$ which are small, it has been shown (*e.g.* Warren, 1969, p. 333) that the corresponding integrated intensity ϱ tends to that for an ideally imperfect crystal ϱ_0', given for the case of unpolarized X-rays by equation (1).

$$\varrho_0' = \frac{E\omega}{I} = \frac{Q}{2\mu_0(\lambda)} = \frac{1}{2\mu_0(\lambda)} \times \frac{1}{\sin 2\theta}\left[\frac{Ne^2}{mc^2} \times |F|\right]^2 \times \lambda^3\left[\frac{1+\cos^2 2\theta}{2}\right]. \quad (1)$$

E is the diffracted intensity, I the incident energy and ω the scan rate. Q is the reflectivity per unit volume, $\mu_0(\lambda)$ is the attenuation coefficient at wavelength λ, and θ is the Bragg angle for the reflexion under consideration.

The approximation $\varrho \to \varrho_0'$ improves as Q becomes small but the relationship $\varrho=\varrho_0'$ only holds exactly in the limit $Q \to 0$, as is evident from consideration of Fig. 117 in James (1948) or Fig. 4 in Hirsch & Ramachandran (1950). For unpolarized X-rays, the integrated intensity ϱ is the sum of the σ component, ϱ_σ, and the π component, ϱ_π. In the region near to applicability of equation (1), we may provisionally equate ϱ_σ', ϱ_π' to the corresponding components $Q_\sigma'/2\mu_\sigma'$ and $Q_\pi'/2\mu_\pi'$ respectively, where μ_σ', μ_π' are effective attenuation coefficients associated with the two polarization components. If we consider only the π component Q_π', it is of such a form [see equation (2)] that, irrespective of the magnitude of $|F|$, the cos 2θ factor is capable of adjustment so that $Q_\pi' \to 0$, and a practical procedure to approach the kinematical limits is evident.

$$Q_\pi' = \frac{1}{\sin 2\theta}\left[\frac{Ne^2}{mc^2} \times |F|\right]^2 \lambda^3 \cos^2 2\theta\,. \quad (2)$$

Secondary extinction

Here it is obvious that cos 2θ can be brought into

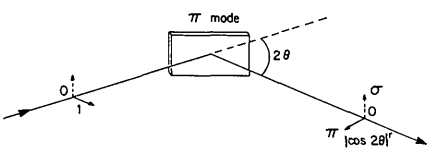

Fig. 1. Diffraction in the π mode with X-rays plane-polarized in the diffraction plane. With an incident component of magnitude unity, the diffracted component is proportional to $|\cos 2\theta|^r$. In the case of theoretical kinematical diffraction, r is 2. In the case of theoretical dynamical diffraction, $r=1$.

a region where Darwin's (1922) approximation for μ', namely $\mu' = \mu_0(\lambda) + g_1 Q - g_2 Q^2 + \ldots$ *etc.*, is valid. Whether Q is regarded as the kinematical value or a smaller, effective value, Q', it is clear that as Q (or Q') $\rightarrow 0$, $\mu' \rightarrow \mu_0(\lambda)$, and again the kinematical formula holds exactly in the limit.

It is concluded therefore that, for both primary and secondary extinction (and any combination), measurement in the π mode and extrapolation of $\varrho_\pi'/\cos^2 2\theta$ to $2\theta = 90°$ will lead to a value for Q_π given by

$$Q_\pi = \frac{\lambda^3}{2\mu_0(\lambda)}\left[\frac{Ne^2}{mc^2} \times |F|\right]^2 = \lim_{2\theta \rightarrow 90°} \varrho_\pi'/\cos^2 2\theta\,, \quad (3)$$

which is completely consistent with that for a theoretical ideally imperfect crystal and hence is free from extinction. Of course, in a strict practical sense, the diffraction intensity ϱ_π' is then zero. This does not exclude the possibility of obtaining significant and accurate values by extrapolation to this limit, provided it can be done in a systematic and controlled manner and provided the extrapolation function is chosen appropriately.

To put this method into operation requires the measurement of absolute integrated intensity (a process perfectly feasible with extended-face crystals) at a series of wavelengths which would diffract from the particular crystal plane under investigation at values of 2θ ranging from 74 (say) to 106° (say) at suitably small angular intervals. Care would have to be taken to avoid the intrusion of simultaneous diffraction but even such an event is likely to reveal itself by its outlier character in the series of measurements. Since λ is being varied, it would at first seem reasonable to incorporate the factor $\mu_0(\lambda)/\lambda^3$ in the function of ϱ_π to be plotted, since it seems likely to change rapidly with λ. However, it has been shown (Stiglich, Weiss & Hansen, 1974) that $\mu_0(\lambda)/\lambda^{2\cdot73}$ is virtually constant over a limited range of λ so that concern over the factor $\mu_0(\lambda)/\lambda^3$ may be provisionally laid aside in respect of extended-face measurements. So the simpler function, $\varrho_\pi'/\cos^2 2\theta$, may be used and plotted against some function of 2θ, such as $\cos^2 2\theta$. Alternatively, a plot of $\log(\varrho_\pi'/\cos^2 2\theta)$ against $|\cos 2\theta|$ may warrant trial. Practical and theoretical considerations may, under later investigation, show alternative functional forms which would improve the extrapolation procedure. Convergence occurs, of course, both from below and above the limit, $2\theta = 90°$. It will be noted that, even if the plane-polarized source contains a small residual σ component (Fig. 1), the magnitude of that component can be determined at $2\theta = 90°$ (since the π component there is zero) and an appropriate correction made before the extrapolation function is calculated. Since the magnitude of the extinction effect on the σ component does not alter rapidly near $2\theta = 90°$ and measurements are available on either side of 90°, correction should be relatively straightforward and exact.

Given that an extrapolated value of $\varrho_\pi'/\cos^2 2\theta$ of high accuracy has been obtained, the precision of the structure-factor value $|F|$ derived by equation (3), will depend upon the accuracy of the value of $\mu_0(\lambda)$ at the wavelength where $2\theta = 90°$ (*cf. International Tables for X-ray Crystallography*, 1974). This value may be available from compilations (Stiglich, Weiss & Hansen, 1974; *International Tables for X-ray Crystallography*, 1974) but their precision may not be adequate (see Calvert, Killean & Mathieson, 1975) and it would be advisable to establish a value experimentally. An improved procedure for the measurement of attenuation coefficients has recently been presented by Lawrence & Mathieson (1976).

To illustrate the range of wavelength required in a practical case, the wavelengths for (200), (400) and (600) planes of LiF are listed in Table 1 over the 2θ range 74 to 106°. The range of wavelengths required does not pose any problem for a synchrotron source (*cf.* Marr, 1974; Codling, 1973), nor does the possible requirement of measurement in vacuum for part of the range. The earlier practical experience of Parratt (1932) up to 5 Å shows that there is no intrinsic difficulty. Combination of a monochromator crystal as dispersing agent together with a solid-state detector of high resolving power would provide, over the wavelength range 5 to 0·5 Å, the necessary basis for measurement with a synchrotron source.

Discussion

In the case of method I (Mathieson, 1976) the disposition and condition of the specimen surface relative to the reflexion plane must be established rather critically. With method II the situation is markedly different. Since the interaction between the incident beam and the crystal (and also with the diffracted beams)

Table 1. *Tabulation of X-ray wavelengths* (Å) *required for diffraction of* 200, 400 *and* 600 *of* LiF *over the range* 74 *to* 106°(2θ)

	74	76	78	80	82	84	86	88	90°
200	2·4235	2·4793	2·5343	2·5885	2·6420	2·6946	2·7464	2·7974	2·8475
400	1·2118	1·2397	1·2672	1·2943	1·3210	1·3473	1·3732	1·3987	1·4238
600	0·8078	0·8264	0·8448	0·8628	0·8806	0·8982	0·9155	0·9325	0·9492
	92	94	96	98	100	102	104	106°	
200	2·8968	2·9451	2·9926	3·0392	3·0848	3·1296	3·1733	3·2161	
400	1·4484	1·4726	1·4963	1·5196	1·5424	1·5648	1·5867	1·6081	
600	0·9656	0·9817	0·9975	1·0131	1·0283	1·0432	1·0577	1·0720	

is low (zero in the limit), the specific condition of the various parts of the specimen is not relevant. In other words, the extinction length is great and the specimen behaves effectively as if uniform in respect of its scattering capability. Because this is so the technique may be readily extended beyond the case of Bragg reflexion to encompass the Laue (*i.e.* transmission) case or the case of a small crystal bathed in the X-ray beam. These latter two cases are dependent on the beam path t through the specimen ($\varrho = Qte^{-\mu t}$) and on the volume V of the specimen ($\varrho = QVA_c$) respectively.* One may therefore conclude that method II is not sensitive with respect to specimen shape so that it is capable of wider application than method I for the establishment of extinction-free values of structure factors.

Earlier attempts to obtain reliable structure-factor values using plane-polarized X-rays involved measurement of both σ and π components at one wavelength. Since it operated within the extinction region, the method was dependent on the differing magnitudes of extinction associated with the two components, σ and π, over the range of 2θ covered by the observational data. The reduction of the data to structure-factor values involved a correction procedure which was based on assumptions as to the trend of intensity with extinction and was limited to low levels of extinction. Chandrasekhar discussed the possibility of this method (Chandrasekhar, 1956) and then treated certain applications (Chandrasekhar, 1960). Later Chandrasekhar, Ramaseshan & Singh (1969) attempted to integrate measurements of that type with the theoretical models of extinction developed by Zachariasen (1967, 1968). The capabilities of plane-polarized X-rays in the last case have been critically appraised by Dawson (1975).

Suggestions have been made earlier concerning the use of plane-polarized X-rays adjacent to $2\theta = 90°$ (*e.g.* Weiss, 1966; Warren, 1969), but these have been proposed to reduce extinction errors. Deliberate elimination of the effect of extinction does not appear to have been proposed as a practical procedure for structure factors of any size or for crystals extending over the range from highly perfect to highly imperfect.

While the establishment of extinction-free values of intensity and hence of structure factors is of prime importance, it should also be appreciated that one may use methods I and II in reverse to explore experimentally the region of extinction in a more controlled manner and consequently on a sounder physical basis than previously possible. In terms of experimental measurements, the extinction region has been sadly neglected for the very obvious reason that the diagnostic – intensity – is dependent on a range of physical variables [*cf.* equation (1)]. In the past, the reference value, namely the kinematical-limit value, was not experimentally available. Hence reliance was placed on theoretical estimates which were themselves based on theoretical models of atomic shape whose ultimate validity depended on the accuracy (not precision) of the experimental intensities. So one was involved in a circular argument with no clear experimental reference point. With method II, one has the potential of controlling precisely one variable, 2θ, and hence exploring the magnitude of the extinction for a series of $|F|$ values. Combination of the two methods, by the use of plane-polarized X-rays in the study of asymmetric reflexion, would allow a detailed mapping of the extinction region.

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* For details of the formulae and their components, such as the absorption correction A_c, see *International Tables for X-ray Crystallography* (1959).

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