comments are offered concerning possible effects of primary extinction and the magnitude of instrumental broadening is estimated.

We are grateful to Dr J. R. Schneider for helpful correspondence and also to our colleagues, Drs S. L. Mair and S. W. Wilkins, for critical comment and discussion.

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On Freedom from Extinction and the (Universal) Kinematical Limit

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Abstract

Examination of the limiting relation of extinction and diffraction makes it clear that *extinction is only zero, in an absolute sense, when diffracted power is identically zero*. This latter condition is the proper operational identifier for the attainment of the kinematical limit and is valid irrespective of the state of perfection of the crystal medium. At the limit of zero diffracted power, the kinematical (single-scattering or first Born) approximation is asymptotically exact so that experiment and theory become strictly compatible. Experimental structure-factor values which are free from extinction effects can therefore be derived in this limit. In practice, the advantages of this approach have to be gained by greater attention to data collection. Typically, the method involves (i) determination of integrated reflectivity at a series of levels of interaction (attained by controlled variation of a suitable physical parameter) and (ii) extrapolation of an appropriate function of the measurements to zero level of interaction as identified by zero diffracted power. Various possible procedures for effecting this approach are discussed here in general terms. The approach proposed here has advantages over the earlier prescription of the kinematical limit [Bragg, Darwin & James (1926). *Philos. Mag.* **1**, 897–922] based on the state of the crystal medium ('ideally imperfect'). It avoids any need for the necessarily approximate assumptions inherent in the Darwin–Zachariasen treatment of extinction. It also avoids dealing with the complications arising from idiosyncratic or anisotropic extinction effects since it refers all cases to zero level of interaction. The kinematical limit, as defined here, is a universal limit.

Introduction

The conventional (Darwin–Zachariasen) approach to treating the problem of extinction in real crystals is deficient in a number of important respects, namely: (i) The equations involved are usually limited by the assumption of the Darwin energy-transfer equations (see Becker & Coppens, 1975). (ii) The theoretical models of the inner morphology of the crystal involve severe approximations which do not accord with experimental evidence (*e.g.* Lehmann & Schneider, 1977; Lawrence & Mathieson, 1977). (iii) Invocation of calculated structure-factor values to assess the degree of extinction influences the final model of the electron-density distribution because extinction corrections and the electron-density distributions are highly correlated statistically.

In view of these shortcomings, it is not surprising that a juridical comment has been made recently in relation to the conventional approach that 'there exists some as yet improperly accounted for source of error' (USA National Research Council, 1976). My view is that this residuum of error is, at least in part, due to

the deficiencies inherent in the conventional approach to the problem of extinction.

To overcome such defects, an alternative and more fundamental approach to extinction is required. An important feature must be that it avoid any reliance on *theoretical estimates of structure-factor values* in estimating the degree of extinction, or indeed on *theoretical estimates of the extinction corrections*. To be soundly based in a physical sense, any such approach must deal, instead, only with experimentally measurable quantities (see Bridgman, 1936).

Recent studies (Mathieson, 1976, 1977*a,b*; Lawrence & Mathieson, 1977) have indicated the possibility of a practical, operational approach of this type, based on the exact limiting relationship between the process of diffraction and its *Doppelgänger* – extinction. This particular approach focuses attention on certain critical questions which have not previously been posed in an explicit manner in the study of extinction. These questions are: (*a*) What precisely does one mean by data which are free of extinction? (*b*) How would one attain such data? (*c*) How does one know, *in an operational sense*, that an extinction-free measurement has, indeed, been achieved?

The present paper outlines an approach to answering these questions and explores some of its logical consequences for the problem of extinction.

Definition of freedom from extinction

The starting point for this analysis lies in a careful consideration of the process of the scattering of radiation, and of the level of interaction between the radiation and the crystal medium. Our concern here is essentially with the exact relationship between diffraction and extinction in the limit of zero diffracted power.

Taking the most general view, the process of diffraction removes energy from an X-ray beam (Bragg, 1914, Fig. 10; Calvert, Killean & Mathieson, 1976). This is the essential feature whatever the level of multiple (*i.e. n-*) scattering or the balance of coherent/incoherent interaction.* Therefore, under diffraction conditions, just as the *transmitted beam* is extinguished (Darwin, 1914) so also is the *diffracted beam* (Darwin, 1922; Bragg, Darwin & James, 1926). This is true, in an absolute sense, however weak the level of interaction of the diffraction process. In other words, *any measurement with a finite diffracted intensity is afflicted by extinction* (statement 1). In fact, diffraction

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* In respect of *n*-scattering, the components progressively decrease in magnitude with increase in *n*, either coherently (wave flow ≡ 'primary extinction') or incoherently (energy flow ≡ 'secondary extinction') or any in-between situation involving partial coherence.

and extinction are indissolubly linked and are simply two aspects of the process whereby X-radiation interacts with matter. We may therefore conclude, in principle, that *extinction is only identically zero when diffracted power is zero* (statement 2). This then constitutes a *proper definition of zero extinction or freedom from extinction*. It establishes a precisely defined operational condition which constitutes an *exact identifier for the condition of freedom from extinction*.

One could re-phrase statement 2 as 'extinction is only identically zero when the level of interaction is zero' – but this form has no direct *operational* significance.

The kinematical approximation and the kinematical limit

Let us examine the consequences of our definition of 'freedom from extinction' for the validity of the kinematical approximation.

The usually expressed attitude to the kinematical (*i.e.* single-scattering or first Born) approximation is that it is, by its very nature, an approximate theory in respect of measurement of diffracted intensity and the resultant derived structure-factor values. As Kato (1974) has observed in this context: 'Extinction effects are unavoidable as "theoretical impurities"'. Our contention in the present paper is that Kato's statement is not necessarily universally true but that, under certain circumstances, while the 'impurities' remain, their effects can be 'refined out' and the theory becomes exact.

The kinematical approximation, as specified in *International Tables for X-ray Crystallography* (1959), requires that 'the intensity of the X-ray beam passing through a crystal is not affected by the process of diffraction' and that this 'is only true if the crystal is composed of small parts that scatter independently'. It is clear that these conditions cannot be strictly satisfied where there is extraction (and return) of energy relative to the transmitted beam, by any diffraction process (including single scattering) leading to finite diffracted intensity.

These difficulties with the kinematical approximation both disappear in the (kinematical) limit as the diffracted power tends to zero; at the limit the following conditions hold: (*a*) The total energy of the system is manifestly conserved. (*b*) The usual relationship between integrated intensity and structure factor becomes exact. (*c*) As shown previously (Hirsch & Ramachandran, 1950; Mathieson, 1977*b*), the limit attained is independent of the state of the crystal, whether near ideally perfect, near ideally imperfect or in any intermediate condition.

In other words, the zero-power diffraction condition is where the kinematical theory is exact and the derived

formulae are exact. There also, theory and experiment are in exact accord so that the resultant data are no longer specimen-specific but are simply structure-specific.

The zero-power diffraction condition therefore allows a *precise and operationally determinate prescription for attaining the kinematical limit*. Since it is independent of the state of the crystal, we can refer to it, under this prescription, as a universal limit.

Attainment of the extinction-free limit

Having established an operational definition of freedom from extinction and shown that it accords with an exact relationship between theory and experiment within the kinematical theory, let us explore its significance for the determination of extinction-free data.

It is evident from statement 1 that, in a strict sense, extinction-free data cannot be attained by *any single measurement of finite diffracted intensity*. Clearly also, the only single measurement which would be physically significant would involve null intensity. So the only way in which extinction-free data can be obtained is from *a series of measurements involving a controlled range of a suitable physical variable by taking a limit identified by the diffracted power going to zero*. Either the integrated intensity (integrated diffracted power), p, may approach a finite (non-zero) limit or, in those cases where $p \to 0$, the ratio of p to some appropriately chosen function of the physical variable approaches such a limit.

The experimental realization of the null-intensity (kinematical) limit

The practical realization of such procedures may be divided into two classes. One is of more general applicability, being dependent on the functional form of Q, the reflectivity per unit volume, which enters into the various experiment-specific intensity relationships. The second is of more specific applicability, being dependent on the particular experimental arrangement.

In the following, some particular experimental configurations for achieving zero extinction are discussed in general terms.

General class

The formula for Q_π, the π-polarization component, is given by

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

From this relationship it is evident that for any given value of $|F|$ there are two variables which can be controlled so as to make Q_π approach zero, namely $\cos^2 2\theta$ and λ. While they are not completely independent, variation of $\cos^2 2\theta$ about zero involves only limited variation of λ for a given reflexion plane, so that it may be treated as a case distinct from that of $\lambda \to 0$.

The case for variation of $\cos^2 2\theta$ has been examined (Mathieson, 1977a), and with a synchrotron source is eminently feasible. It is possibly the most generally applicable technique in that it can be used for both reflexion and transmission methods with large crystals and also for diffraction from small crystals.

The case of variation of λ is not clear-cut. For reflexion from extended-face crystals, the evidence of Wooster & MacDonald (1948) suggests that convergence of dynamical and kinematical limits lies towards longer wavelengths while for transmission and for small crystals the limit would be $\lambda = 0$. Although general comments on this possibility of extrapolation have appeared, *e.g.* Weiss (1966), evidence of any practical exploration of its potential is limited.* In the process of data collection and reduction for an international intensity project, Grant, Killean, Lawrence, Senol & Sharma (1972) explored the possibility of extrapolation against λ. The work of Maier-Leibnitz and Schneider (see Schneider, 1974) used radiation of such short wavelengths (γ-rays) that there was initially a tendency to believe that extinction was vanishingly small. However, in accord with statement 1 above, since they were measuring finite diffracted power, extinction was still present and, in fact, proved to be appreciable. Their derivation of structure-factor values from such data required the assumption that the

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* Bragg & Azaroff (1962) have made measurements on a Si single crystal at five wavelengths. Their purpose, however, was to establish a measure of the crystallite disorientation and not of the structure factor. From these results (their Fig. 4), it is clear that the wavelength range was not large enough to define the curves sufficiently near to the point of zero interaction.
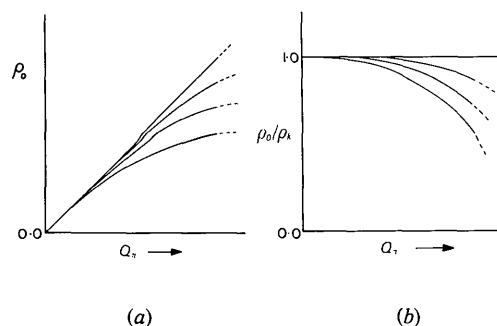

(a)   (b)

Fig. 1. (a) The relationship between p_o and Q_π for different levels of interaction, due (say) to different structure-factor values. (b) The corresponding relationships for the normalized intensity, p_o/p_k.

corrections made for extinction were exact. That this may not have been so has been suggested by Mackenzie & Mathieson (1979), who offer an alternative procedure for attaining nominally extinction-free structure-factor values from the γ-ray data for $f(220)$ of Cu from Schneider (1976, 1977). This procedure is, however, less powerful than those involving the zero-power criterion.

To illustrate this general class, Fig. 1(a) shows schematically the possible variation of ρ_0 with Q_π as the latter goes to zero, for a number of specific levels of interaction (cf. Fig. 1 in Bacon, 1951). Fig. 1(b) shows the corresponding variation of the normalized intensity, ρ_0/ρ_k.

Specific classes

(i) Extended-face (Bragg) reflexion

With this technique, an additional experimental variable which can be introduced is asymmetry. In a formal sense, this technique also introduces the absorption coefficient, μ, but this factor is not to be regarded as a variable which is controllable and capable of independent extrapolation to an appropriate limit (see Wooster & MacDonald, 1948). The case of asymmetric reflexion in relation to single crystals has been explored by Mathieson (1976, 1977b) while the case for the perfect crystal has been subjected to a full theoretical treatment in a study by Wilkins (1978). So far as powder specimens are concerned, the practical possibilities are at present speculative, but there seems to be no obvious reason why the technique of asymmetric reflexion with properly prepared specimens should not prove useful. This aspect is under investigation.

The appropriate schematic diagrams to illustrate this situation are given in Fig. 2. The vertical coordinate in Fig. 2(a) is the measured integrated intensity, while that in (b) has been corrected for asymmetry and normalized (see Mathieson, 1977b). Fig. 2(a) and (b) constitutes an elaboration of Fig 6(a) and (b) in Mathieson (1977b).

(ii) Transmission (Laue) reflexion

In this case, the additional variable is path length. This technique was originated by Bragg, James & Bosanquet (1921a,b). They prepared a series of plates of different thicknesses, t, measured the transmitted integrated intensities, ρ_0, plotted $\ln(\rho_0/t)$ versus t and extrapolated to $t = 0$. This was a key experiment. Unfortunately, apart from studies by Sakisaka (1927) and Bragg & West (1928), this technique has been largely ignored [see, however, Göttlicher (1968) and Göttlicher & Kieselbach (1976)]. At the time, it was noted by Bragg, James & Bosanquet that not all

measurements fell on the curve fitted to the majority of measurements. So they, and also Darwin (1922), were understandably troubled by this evidence of idiosyncratic behaviour. Recently Lawrence & Mathieson (1977) have modified the procedure to use only one specimen and have shown that the variation is indeed not exceptional but is natural and to be expected because of the different beam paths through a specimen in which the crystallite distribution is non-uniform. As
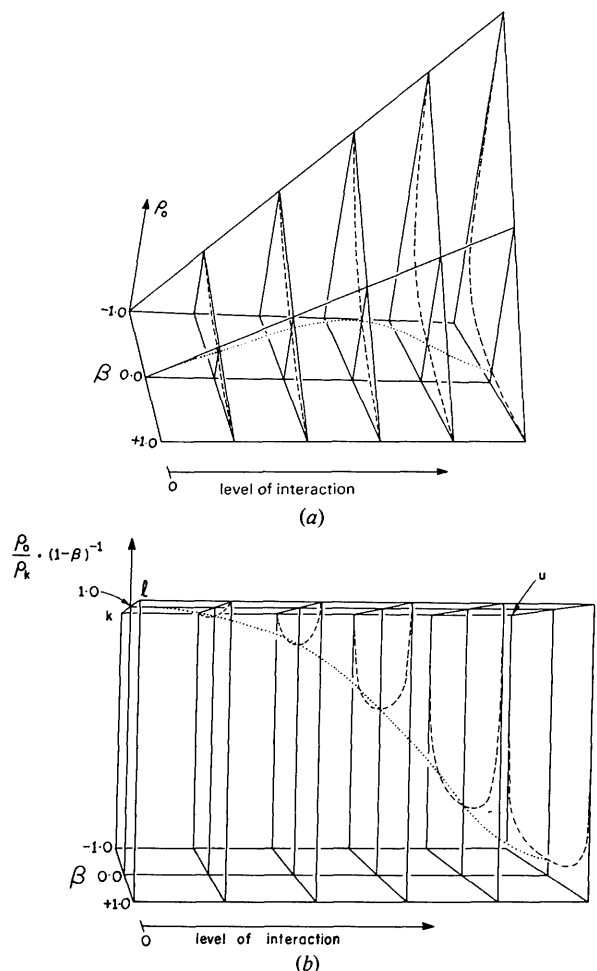

(a)

(b)

Fig. 2. (a) A schematic representation of the integrated intensity, ρ_0, against the level of interaction (Q_k or ρ_k) with variation of asymmetry, β. The symmetrical reflexion position is represented by the section with $\beta = 0$. The dotted curve in this section corresponds to a variation of ρ_0 (for the symmetrical reflexion) with change of level of interaction. The dashed curves represent the variation with asymmetry at given levels of interaction. For $\beta = +1$, ρ_0 goes to zero while at $\beta = -1$, the specific intensity (per unit surface area of the crystal) goes to zero (see Mathieson, 1976, 1977b). (b) The corresponding representation for the intensity normalized and corrected for asymmetry, $\rho_0(1 - \beta)^{-1}/\rho_k$. Dotted and dashed curves here correspond to those in (a). Here the 'universal' kinematical limit is represented by the surface $ukls$ which can be attained at uk, kl and ls by appropriate extrapolation.

the interaction level drops, the intensity variation contracts and vanishes completely at the limit of zero interaction.

The work of Lawrence & Mathieson (1977) was exploratory and clearly established that, for relatively high interaction levels and hence non-linear log plots [contrast with the results of Göttlicher (1968) and Göttlicher & Kieselbach (1976)], it would be necessary to approach the $t = 0$ limit (in the case of LiF and Mo $K\alpha$ radiation) more closely than ≈ 1 mm, the minimum dimension in the experiments of Lawrence & Mathieson (1977). This aspect is also receiving further attention.

For this case, the appropriate schematic is given in Fig. 3, which shows the form of variation of ρ_o/t with t.

For the transmission case asymmetry is also a possible variable, but here its use would start from a fixed minimum-extinction situation and approach a maximum-extinction condition asymptotically. Hence it would appear to be of little value in approaching an extinction-free limit.

(iii) *Small crystals*

For such specimens, the additional variable is the volume of the crystal, V. (Note that, at zero interaction, the detailed shape of the crystal is not relevant.) Cochran (1953) used measurements with a number of crystals to show the trend with diminishing volume. His procedure assumed that the data from the smallest crystal for the 10 strongest reflexions were correct. Later Tulinsky, Worthington & Pignataro (1959) used the device of extrapolation to zero volume of the derived F_o values. The technique of extrapolation of ρ_o/V does not appear to have been investigated although it should be noted that Robinson (1933), in attempting to establish an absolute value for one order of anthracene with 18 crystals, compared corrected intensity with crystal volume over an extended range.
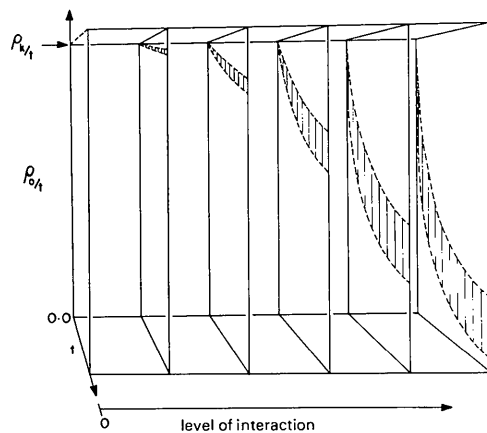

Fig. 3. Schematic representation of the ratio of integrated intensity, ρ_o, to path traversed, t, *versus* t, for various levels of interaction.

The appropriate schematic for this case is similar to that for the Laue case.

Commentary

At this late stage in the history of the subject, a re-examination of the exact meanings of freedom from extinction and the kinematical limit may appear to be an academic exercise. That it is, in fact, of practical concern is evident when one recognizes that the procedures for measuring physically significant structure-factor values are dictated by the definitions adopted. Indeed the possibility of achieving improved accuracy (not merely precision*) in the establishment of structure-factor values is very much linked to the operational capability of the definition chosen.

In the past, there has been, as we will show, a lack of precision in the relevant definition(s) which has given to the search for absolute (or extinction-free) structure-factor values a measure of vagueness or uncertainty which has been screened from full recognition by the traditional reliance upon *theoretical estimates* of structure-factor values. A serious consequence of the deficiency in definition has been a lack of precision in the interpretation of experimental results, especially in those cases where it has been assumed that the specimen effectively accords with the classical definition, namely in the case of powdered specimens or very small crystals.

Consider the definition of the 'upper limit' by Bragg, Darwin & James (1926). To avoid misunderstanding, let us quote the original statement from p. 906 of that reference: 'In this paper, the ideally imperfect crystal is regarded as the standard, and the integrated intensity is supposed to be lowered below this standard by two phenomena which are called primary and secondary extinction...'.

This definition of the 'upper limit' has tended to be identified in the literature with the 'kinematical limit'. For reasons which will become obvious, we will not assume that they are identical and will retain their separate identity in the following.

The definition of the 'upper limit' contains certain serious defects. For one, it invokes the phenomenon of extinction as part of the definition. The defects are more evident, however, when one seeks to visualize setting up appropriate experiments to attain the limit. These defects are associated with two components in the definition: (a) it depends upon a prescription for a

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* The term 'precision' is used to note the level of reproducibility achieved by repeated measurement using one technique. The term 'accuracy' refers to the degree of approximation to the absolute value. The distinction between 'precision' and 'accuracy' used here has similarities to the distinction between the criterion of internal consistency and the criterion of external consistency introduced by Birge (1932).

crystalline state – the 'ideally imperfect' or 'mosaic' crystal; and (b) it implies the measurement of finite diffracted intensity. In respect of measurement of intensity, what the definition by Bragg, Darwin & James specified was a *maximum integrated reflectivity* which was to be sought as representing the 'upper limit' corresponding to the 'ideally imperfect' crystal. No clear-cut operational guide was offered, either in 1926 or subsequently, as an identifier of when the true maximum had been attained or how close one could come to its attainment in practice. So, even from the earliest quantitative measurements of diffracted intensity, all experimental estimates of structure-factor values have been bedevilled by this uncertainty as to how much they fell short of the 'standard' of ideal imperfection. Indeed, it is clear that it was this very uncertainty that led to the introduction of the traditional procedure of relying on *theoretical estimates* of structure-factor values (see Bragg, Darwin & James, 1926, p. 909) and to continued reliance on this procedure.

The second component of the definition – which, from a cursory inspection, might appear to offer some guide as to how to proceed experimentally – was the nomination of an 'ideally imperfect' state. The difficulty in relation to this part of the definition is that a proper meaningful prescription for a reference physical state can present difficulties not necessarily evident in the wording. Thus it is paradoxical that the state of being 'perfect' [which was used in relation to the 'lower limit' by Bragg, Darwin & James, (1926)], so far as a crystal is concerned, can be defined fairly readily and is, for a few selected materials, almost attainable, whereas the state of being 'ideally imperfect' as a description of a real physical entity which would yield an intensity corresponding to the 'upper limit' is difficult or may be impossible to specify. Hart (1974) has put the point succinctly in the following: 'Whereas the mathematical description (either) of a perfect crystal (or a liquid or a gas) is recognizable in its time-averaged structure, the mathematical prescription for an ideally imperfect crystal is not recognizable in its structure. In fact, the usual prescription is internally inconsistent'. It is evident that, as a consequence of the unphysical nature of the term 'ideally imperfect', this component also does not provide an operational guide as to how to attain the 'upper limit'.

By contrast, starting from a definition of freedom from extinction based on level of interaction, our prescription for the *kinematical limit* is an operational one, *i.e.* it can be converted into experimental procedures so that experiment and theory are consistent and compatible at the limit of zero level of interaction, a limit which is identified in a practical sense by attaining zero diffracted power.

The substitution of the original definition of the 'upper limit' by our prescription for the 'kinematical limit' based on level of interaction and only attainable by extrapolation makes it clear that the specification of the physical state of the crystal medium in respect of this latter limit is, in fact, an unnecessary qualification. A prescription which is dependent only on level of interaction at the zero limit is applicable to the whole range of real crystals from near ideally perfect to powders (see Hirsch & Ramachandran, 1950; Mathieson, 1977b; Wilkins, 1978). In this sense, it is a *universal* limit.

It may be instructive to use a heuristic device, Fig. 4, to illustrate the trend of level of interaction to zero for a range of crystal states. The level of interaction, which we have been discussing in general terms, may be equated, for example, with g^{-1} where g is as given in equation (2) of Hirsch & Ramachandran (1950), and is dependent on such variables as asymmetry and polarization factor, which can be varied to change the level of interaction and so allow
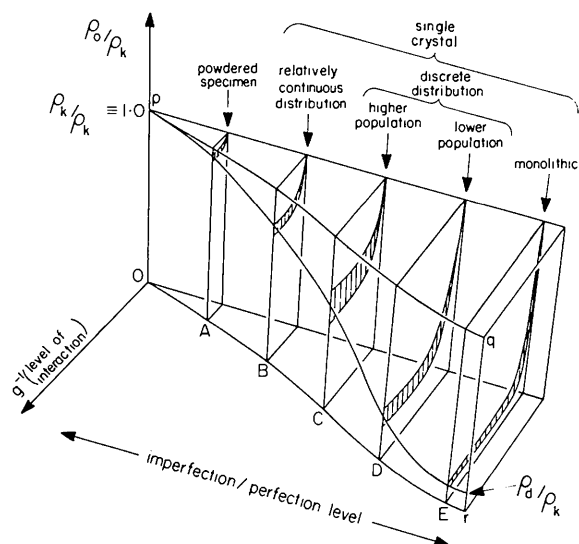

Fig. 4. A schematic representation of the relationship of normalized intensity ρ_o/ρ_k, against the level of interaction for various levels of imperfection/perfection between the nominal limits of 'ideally imperfect' and 'ideally perfect'. The level of interaction is parameterized, here as g^{-1}, where g is as given in equation (2) of Hirsch & Ramachandran (1950). The state of the crystal specimens is represented by various vertical sections: A is that of a powder specimen and E is that of a nearly perfect specimen. B, C and D correspond to single-crystal specimens of different characteristic population distributions of crystallite size and misorientation spanning the region between A and E. Surface $Opqr$ corresponds to the equivalent level of interaction for the various specimens (say) for a given value of a structure factor. The actual shape of surface $Opqr$ is not definitive but indicates the general trend. The intensity measure for each specimen is not represented as single-valued but has a spread which recognizes the more realistic specimen-specific situation associated with variation of beam paths and intercepted crystallite population. As the level of interaction tends to zero, so the normalized intensity for all specimens and for all different paths tends to the universal kinematical limit.

extrapolation to the required level of zero interaction. In operational terms, the level of interaction for a specific crystal and a particular reflexion H at a setting angle ω can be judged, *e.g.* by the reflectivity ratio, $P_H(\omega)/P_0$, where P_0 is the incident power and $P_H(\omega)$ the diffracted power. Reference to the reflectivity allows a more general definition, independent of a specific experimental procedure (see Wilkins, 1978). Each specimen type, with a particular degree of crystal perfection, is represented by a vertical section in Fig. 4. Instead of simple integrated intensity as vertical coordinate, ρ_o/ρ_k is used where ρ_o is the measured, *i.e.* extinguished, intensity and ρ_k the corresponding theoretical kinematical intensity. Note that the extinction-free situation is when $\rho_o/\rho_k = 1\cdot0$. In this diagram, the non-uniqueness of the value for each specimen state, A to E, is indicated by the vertical spread which is associated with different potentially possible beam paths in the specimen (see Lawrence & Mathieson, 1977).

In the surface, $Opqr^*$, the spread of values narrows as one tends towards the extremes of the physical state of the specimen, namely powdered and monolithic. This is in accord with the practical observation that values of structure factors derived from such specimens tend to fall within a more restricted range than those derived from imperfect single crystals such as B, C, or D. It is also indicated by section A that for any real powdered specimen the measurement of finite diffracted intensity will not coincide exactly with the zero-extinction limit.

As the level of interaction is reduced, the normalized intensity increases for all specimens, A to E; further, the spread of values for each specimen contracts, so that all measurements tend towards the same limit. In this limit, the normalized intensity is equal to unity, and is a universal limit, independent of the state of the crystal.

Conclusion

The approach to extinction outlined in this paper necessarily influences one's attitudes towards experimental intensity-measurement procedures for the derivation of structure factors. It shows how the usual one-off measurement procedure must ultimately rely, *via* theoretical estimates of extinction correction factors, on simplified parameterization to mimic the variation of extinction effect across the scan of the reflexion. By contrast, we here stress the need for extrapolation under controlled variation of some chosen physical variable if one is to avoid being

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* The surface, $Opqr$, which represents the functional relations, for different crystalline states for (say) a given value of structure factor, is not exactly defined in shape. That depicted here is simply to illustrate the trend with change of crystalline state.

influenced by such theoretical estimates. Extrapolation with control has an additional advantage in that it allows for the capability of internal experimental checks without reference to any theoretical estimates. It can therefore arrive at some proper estimate of experimental accuracy and not merely of experimental precision.

One message which is very clearly spelled out by this approach is that accuracy can only be gained by care in the design of an experiment and care in implementing it. As one tends towards the zero level of interaction, the reflectivity decreases so that one must increase the time of measurement to maintain the same level of statistical precision. This makes it very obvious that one must trade time for accuracy, a feature which is basic to the derivation of accurate structure factors whether from measurement of intensity or of fringe separation (see Aldred & Hart, 1973). For measurements of the former type (*e.g.* Mathieson, 1977*a*) a source of high intensity, such as that afforded by a synchroton, is clearly advantageous.

The proper resolution of the problem of extinction has considerable bearing on the accuracy, and hence on the physical reality, of electron density distributions from intensity measurements, particularly as attention is directed towards higher acuracy (say) of the order of 1 to 0·1% and better. It is in relation to this level of accuracy (see *Introduction*) that the approach to extinction outlined in this paper is of relevance. It offers neither an easy solution nor a numerical substitute for reality. It refocuses attention on the vital importance of experiment, an aspect of the study of extinction which has been very much overshadowed by enthusiasm for the conventional theoretical approach.

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A Comparison of the Least-Squares and Maximum-Likelihood Estimators for Counts of Radiation Quanta which follow a Poisson Distribution

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Abstract

The weighted least-squares method cannot correctly be used when measurements have errors given by counting statistics. The usual procedure results in bias in the values and errors in the calculated variances of the parameters. The maximum-likelihood method requires only a minor change in the least-squares equations and is generally thought to have more desirable properties for its estimates.

Introduction

Suppose a functional relationship exists between two measurable quantities y_0 and x given by

$$y_0 = f(\theta_0, x), \qquad (1)$$

where the θ_0 are the true, but unknown, parameters, and suppose we have a list of measurements $y(x)$ of $y_0(x)$ at various values of the independent variable x. We assume the x's to be measured precisely but the y's to be imprecise.

$$\mathbf{y} = \mathbf{y_0} + \mathbf{\varepsilon},\dagger \qquad (2)$$

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† Vector and matrix notation used throughout.