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The Absolute Measured Value of $f(220)$ for Cu – The Importance of Extrapolation to Zero Extinction

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Abstract

A method of deriving an extinction-free estimate of an X-ray structure-factor value is outlined. The method is based on the availability of experimental estimates of the level of extinction from the mosaic distribution of the crystal. A plot of the diffracted intensity or its corresponding structure factor (uncorrected or nominally corrected for extinction) against the percentage extinction effect yields an extinction-free value in the limit on extrapolation to zero level. Such a procedure can also reveal any inadequacy in the correction procedures by lack of internal consistency. An illustration of the potential of this procedure is given using the set of 11 experimental values of f for the 220 reflexion of Cu derived by Schneider [*Acta Cryst.* (1977), A**33**, 235–243] from γ-ray diffractometry. Use of the experimental estimates of the level of extinction together with the nominally corrected f data indicates the presence of systematic residual error. Linear extrapolation of these f values to zero extinction yields an estimate of $f(220)$ in the region of 16·77. A value in this region is more in accord with a Hartree–Fock value than with the band-structure value, which was favoured by Schneider's original estimate of 16·46.

Introduction

The derivation of an absolute value of an X-ray structure factor from measurements of diffracted intensity requires that it corresponds to the condition of zero extinction, a condition which is only defined exactly when the diffracted power is zero (Mathieson, 1978). It follows that an absolute value of a structure factor is only attainable with a procedure which allows extrapolation to the condition of zero diffracted power. One line of approach involves a series of measurements of intensity on a single specimen with controlled change of a suitable physical variable, so that the ratio of measured intensity to an appropriately chosen function of the variable tends to a non-zero limiting value at the limit of zero diffracted power (Mathieson, 1979). This type of null-power measurement provides a clear-cut operational limit to the extrapolation.

This paper deals with an alternative but less definitive procedure which involves a series of measurements with different specimens whose internal morphologies differ significantly one from the other, and for which a numerical estimate of the magnitude of the extinction effect can be derived *from experimental measurements.* Extrapolation to (nominal) zero extinction of either the original or the corrected values of the integrated intensity (or the corresponding derived structure factor) should yield an extinction-free value in the limit. By contrast with the single-specimen null-power procedure, the definition of the extrapolated limit may not be as clear-cut, since it is dependent on the theoretical basis of the numerical estimate of the magnitude of the extinction effect.

An illustration of the potential of this latter procedure and of its significance with respect to obtaining structure-factor values is given here, based on a reinterpretation of some recent careful studies of the 220 reflexion of Cu with γ-ray diffractometry by Schneider (1976, 1977), chosen because these experimental data are, in our view, of the highest quality.

The original data and conclusions

The data, reported on by Schneider, related to careful measurement on 11 different volume elements of a single-crystal specimen of Cu, and demonstrate dramatically the path-dependent character of extinction (see also Lawrence & Mathieson, 1977). Interpreting the scan profiles as giving a direct estimate of the probability density function, W, for the orientation of the reflecting crystallites, Schneider applied point-by-point corrections for secondary extinction, based on Darwin's energy-transfer equations, to the individual curves and derived a series of nominally absolute estimates, f, of $f(220)$. The 11 values of f were presented in graphical form together with values of p_2. The latter was an estimate of the degree of extinction for each volume element derived from the uncorrected measured integrated intensity, R_m, and a value of R_{kin} based on a value f_{ref} for $f(220)$ chosen by Schneider. Equation (1), which defines p_2, is effectively the same as that in Schneider (1976, p. 399). It also

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defines f_m, the atomic scattering factor uncorrected for extinction, a quantity not given numerically by Schneider.

$$p_2 = 1 - \frac{R_m}{R_{\text{kin}}} = 1 - \frac{f_m^2}{f_{\text{ref}}^2}. \qquad (1)$$

In assessing the validity of the 11 values for f, Schneider made a subjective decision that, for volumes 10 and 11, 'extinction was significantly under-estimated for these two measurements which will be excluded from all further consideration'. The remaining nine experimental values were quoted to be 'significantly smaller than the Hartree–Fock free-atom value and (to) oscillate around a theoretical value which is the average of the two different values obtained from band calculations by Arlinghaus (1967) and by Wakoh & Yamashita (1971)'. The data for these nine were therefore treated as subject only to random errors and the mean value deduced for $f(220)$ was 16·46 ± 0·02, where the quoted error is one standard deviation of the mean.

The need for reinterpretation

If the correction procedure for volumes 10 and 11 was incomplete, there appears to be no objective reason why a similar deficiency should not apply to volumes 1 to 9.

If one allows the possibility that the correction procedure applied by Schneider was incomplete due to partial breakdown of the assumptions involved, then the corrected data for all volumes, 1 to 11, would still retain residual errors due to extinction, to an extent dependent on the original magnitude of the extinction. Under these circumstances, there is no *a priori* reason to treat 10 and 11 as different from 1 to 9. Rather one should consider all volumes on an equal footing.

The original stimulus for the present enquiry was a plot of f against p_2, which appeared to indicate a simple functional relationship and therefore the possibility of extrapolation. However, further thought persuaded us that, while this possibility remained, the use of p_2 was misleading because, among other reasons, f_{ref} is to some extent arbitrary, so that the origin of p_2 is equally arbitrary and the end point of the extrapolation ill-defined. An estimate of the percentage extinction effect more closely related to the experimental measures was obviously necessary and this was made feasible since Schneider recorded W in full detail for the 11 volumes.

An appropriate measure of extinction (Robinson, 1933)* in each volume is

$$p_1 = 1 - y = 1 - (f_m/f)^2. \qquad (2)$$

For each volume the value of p_1 depends only on an integration over the actual profile to obtain f_m and over the point-by-point corrected profile to obtain f; assumptions concerning 'expected' values of $f(220)$, of either experimental or theoretical origin, are avoided. While Schneider carried out this process of correction, we have no record of the values of p_1 he may have obtained.† However, the values of both p_1 and f_m can be reconstructed using Schneider's published data and this is done below.

Reinterpretation

The graphical information presented by Schneider was carefully measured and the resulting numerical values for various quantities are given in Table 1. The reading accuracy (and probably the plotting accuracy) was about ±0·007 for f, ±0·07 for p_2 and ±1% for the density function W. In accordance with the theory

* In this classic work on the measurement of one order of anthracene at two wavelengths using 18 crystals, Robinson used the technique of profile correction for extinction. His method was potentially iterative rather than the one-step procedure used by Schneider.

† Reference to Table 2 shows that for volumes 1 to 9 the values of p_1 are almost constant and about 4%. It is easily shown that such constancy of p_1 implies that a plot of f against p_2 should be nearly linear and so extrapolation using p_2 is of little physical significance.

Table 1. *Input data read and computed from Schneider's figures*

			Density integrals				Fitted double Gaussian gives			
Volume	f	p_2 (%)	$W_2 \times 10^{-3}$	$W_3 \times 10^{-6}$	$W_4 \times 10^{-9}$	$W_{\max}$	$W_4 \times 10^{-9}$	g	τ_1	τ_2
1	16·491	3·15	0·3650	0·2496	0·2198	1120·0	0·2229	0·2088	0·326	4·502
2	16·500	2·91	0·3445	0·1841	0·1207	880·0	0·1240	0·1798	0·416	3·919
3	16·341	4·73	0·3404	0·1890	0·1250	864·0	0·1302	0·2336	0·509	4·473
4	16·364	4·03	0·3167	0·1535	0·0877	752·0	0·0909	0·2176	0·585	4·434
5	16·557	2·01	0·3226	0·1400	0·0702	688·0	0·0719	0·1337	0·511	3·611
6	16·565	2·50	0·3713	0·2136	0·1474	864·0	0·1484	0·2540	0·571	4·028
7	16·465	4·32	0·4390	0·3217	0·2783	1048·0	0·2797	0·3303	0·545	4·233
8	16·448	3·73	0·3532	0·1820	0·1096	736·0	0·1094	0·2918	0·794	4·187
9	16·457	3·55	0·3452	0·1599	0·0853	704·0	0·0865	0·1571	0·585	3·440
10	16·150	11·07	0·7460	0·8334	1·0449	1520·0	1·1505	0·3985	0·489	2·047
11	16·213	10·27	0·7260	0·7468	0·8486	1344·0	0·8525	0·4972	0·630	2·642

Table 2. *Values of p_1, f_m and p_{2est} derived from Schneider's data for f and W*

Volume	f	$R \times 10^3$	p_1 (%)	$= W_2 R$	$-\frac{2}{3}W_3R^2$	$+\frac{1}{3}W_4R^3$	f_m	p_{2est}	p_2	$p_{2est}-p_2$
1	16·491	0·12242	4·233	4·469	−0·249	0·013	16·138	3·261	3·15	0·111
2	16·500	0·12255	4·045	4·222	−0·184	0·007	16·163	2·966	2·91	0·056
3	16·341	0·12020	3·917	4·092	−0·182	0·007	16·018	4·700	4·73	−0·030
4	16·364	0·12054	3·674	3·818	−0·149	0·005	16·061	4·190	4·03	0·160
5	16·557	0·12340	3·843	3·981	−0·142	0·004	16·236	2·089	2·01	0·079
6	16·565	0·12352	4·378	4·586	−0·217	0·009	16·198	2·539	2·50	0·039
7	16·465	0·12203	5·055	5·357	−0·319	0·017	16·043	4·394	4·32	0·074
8	16·448	0·12178	4·128	4·301	−0·180	0·007	16·105	3·660	3·73	−0·070
9	16·457	0·12192	4·055	4·209	−0·158	0·005	16·120	3·481	3·55	−0·069
10	16·150	0·11741	8·049	8·758	−0·766	0·056	15·486	10·918	11·07	−0·152
11	16·213	0·11833	7·941	8·591	−0·697	0·047	15·556	10·116	10·27	−0·154

presented later, the nth powers of these curves were integrated to give the tabulated values of W_n; the estimated value of W_1 was unity to better than 1% when scaled to radian measure (3438′ = 1 rad). The remaining columns in Table 1 refer to the constants for a double-Gaussian approximation. This is used, as described below under *Theory*, to estimate limits for the effect of deconvolution of the density functions for the finite angular resolving power of the apparatus. The required values of p_1 and of f_m were computed by means of the theory given later and are listed in Table 2.

The derived uncorrected measurements f_m are plotted as full circles in Fig. 1 against the derived estimates p_1 of the magnitude of the (secondary) extinction effect. Values for volumes 1 to 9 are closely bunched together over a relatively limited range of p_1 so that we may take these as representing the experimental spread of f_m for $p_1 \sim 4\%$. Volumes 10 and 11 correspond to $p_1 \sim 8\%$ and unfortunately constitute a more restricted sample. Linking the centres of these two groups and extrapolating linearly* to $p_1 = 0$ yields a nominally zero-extinction-limit value of 16·77.

The corrected values are likewise plotted as open circles in Fig. 1 and the same extrapolation procedure leads to almost the same limit value. This is to be expected since the theory shows that the correction is dominated by the first term in equation (12) and so is almost proportional to p_1.

If the correction procedure for deriving f from f_m were complete, the same values of f would be obtained (within the experimental error) for the two groups and the extrapolating line for f would be nearly horizontal. It is therefore evident from Fig. 1 that the correction procedure was incomplete and indeed went only half way, indicating that the assumptions involved require closer examination.

Of the assumptions made by Schneider (1976, p. 399), we treat the one relating to deconvolution in a crude numerical fashion and offer some comments about the possibility of primary extinction.

Using Schneider's estimate of 0·5′ for the full width of his angular resolution and the method outlined in the following section, we have made crude estimates of upper and lower limits for the effect of deconvolution. The lower limit leads to estimates of f which scatter about the dotted curve in Fig. 1; this curve has a limit value of 16·71, while the upper limit is indicated by the dashed curve with a limit value of 16·60. If the upper limit were a valid estimate of the effect of deconvolution the correction procedure would be effectively complete. However, it seems to us likely that deconvolution only accounts for part of the remaining correction and that other factors may be significant.

In respect of primary extinction, Schneider estimated that, for the 220 reflexion of Cu and γ-rays of 0·0302

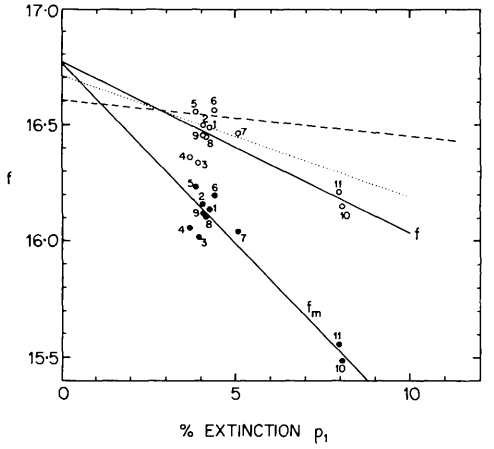

Fig. 1. Plots of atomic scattering factors f for Cu against an experimental estimate of the secondary-extinction effect. The solid circles are for raw measured values and the open circles are corrected for secondary extinction for all of 11 volume elements. The dotted and dashed curves represent two extreme estimates of the effect of correcting for a finite angular resolution of the apparatus.

* Consideration of equation (12) shows that, provided a theory leading to the Darwin energy-transfer equations is applicable, a linear relationship should hold for small levels of extinction. Failing the validity of such a theory, linear dependence is the simplest possibility although, with only two coherent groups of points, there is no direct experimental evidence for this failure.

Å, the extinction length is 92 μm. It can be shown that for a perfect sheet crystal of thickness one tenth of the extinction length, the estimated dynamical intensity is ~3% less than that estimated for the kinematical intensity (Wilkins, personal communication). Hence, if there are effectively perfect regions of the order of 9 μm, then primary extinction could introduce an apparent error of about $1\frac{1}{2}$%.

If there is in fact a significant contribution from primary extinction, then a correction based on the Darwin energy-transfer equation is no longer well founded. In particular, p_1 is no longer a valid estimate for the extent of extinction and the zero of extinction does not necessarily correspond to $p_1 = 0$.

Theory

The following theory makes the same assumptions as in Schneider (1977) and uses a notation similar, but not identical, to his.

Assuming the validity of the Darwin transfer equations the measured reflectivity per unit of angle, $r_m(\omega)$, when corrected for linear absorption, is given for the symmetric Laue case by

$$r_m(\omega) = \tfrac{1}{2}\{1 - \exp[-2\sigma(\omega)t/\cos\theta_B]\}, \quad (3)$$

where θ_B is the Bragg angle, t is the thickness of the specimen and $\sigma(\omega)$ is the scattering power per unit of angle per unit of path. If, further, the scattering power is entirely due to secondary extinction

$$\sigma(\omega) = W(\omega)Q, \quad (4)$$

where W is the probability density (per radian) of the reflecting crystallites and

$$Q = |F|^2(r_0/V)^2\lambda^3\frac{1 + \cos^2 2\theta_B}{2\sin 2\theta_B}, \quad (5)$$

where F is the structure factor of a unit cell of volume V at the temperature of the measurement. Since there are four atoms per unit cell in Cu, the atomic scattering factor corrected for thermal motion is given by

$$f = F/(4e^{-M}). \quad (6)$$

The analysis of the limited experimental data presented in Schneider's papers is facilitated by defining the corrected reflecting power, $r(\omega)$, and its integral R by the relations

$$r(\omega) = \frac{\sigma(\omega)t}{\cos\theta_B} = W(\omega)R. \quad (7)$$

Thus, equation (3) can be written

$$r_m(\omega) = \tfrac{1}{2}\{1 - \exp[-2\,r(\omega)]\} \quad (8)$$

and

$$R = Cf^2 = 4{\cdot}502 \times 10^{-7}f^2, \quad (9)$$

where in (5), (6) and (7) we have used the values t = 0·82 cm, e^{-M} = 0·9125 nominated by Schneider and the values $r_0 = e^2/mc^2 = 2{\cdot}8178 \times 10^{-13}$ cm, a = 3·615 Å and λ = 0·030105 Å obtained respectively from Cohen & DuMond (1965, p. 590), *Landolt–Börnstein* (1971, p. 7), and Muller, Hoyt, Klein & DuMond (1952, p. 790).

Since $W_{max} \sim 1000$ for most of Schneider's samples and $f \sim 16{\cdot}5$, his reflecting power, $r(\omega)$, has a maximum of about 0·15 and so a few terms of the series expansion of $\exp[-2r(\omega)]$ suffice in equation (8). Thus, on integration and using the definition of R in (7), the integral R_m of the measured reflecting power is given by

$$R_m = R - W_2R^2 + \tfrac{2}{3}W_3R^3 - \tfrac{1}{3}W_4R^4, \quad (10)$$

where

$$W_n = \int W^n(\omega)\,d\omega, \quad (11)$$

and $W_1 = 1$ on account of the normalization of the probability density W. Referring all quantities to the final values of f by means of (9)

$$p_1 = 1 - (f_m/f)^2 = W_2R - \tfrac{2}{3}W_3R^2 + \tfrac{1}{3}W_4R^3, \quad (12)$$

where f_m is the value corresponding to R_m and (10) has been used.

The use of (10) to express R in terms of R_m is numerically equivalent to Schneider's procedure and since, in the present case, each term in (10) is less than 10% of the preceding term (see Table 2), the main effect of secondary extinction is determined by the value of W_2 and the correction is nearly proportional to R.

The actual numerical procedure for reconstructing the required values of p_1 and f_m, for testing the consistency of this reconstruction with Schneider's values of p_2 and for estimating the effect of deconvolution will now be indicated.

Having read off the values of f and $W(\omega)$ (see Fig. 2) for one of the eleven volumes, the first step is to calculate the values of the power integrals W_n in

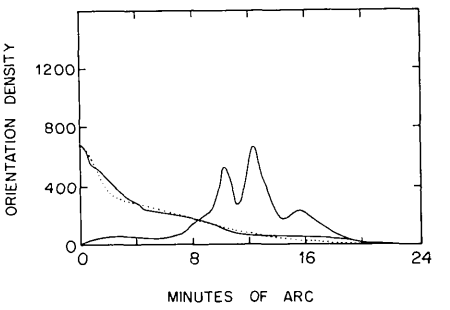

Fig. 2. The middle full-line curve is a reproduction of Schneider's orientation density function for his volume 5. The left-hand full-line curve is a sideways transfer of this curve into a single peak. The dotted curve is a double-Gaussian approximation to this curve.

accordance with equation (11). The values so obtained, renormalized so that $W_1 = 1$, are given in Table 1. Starting with a value of f, equation (9) determines R and then p_1 and f_m follow using equations (12), (10) and (9) in turn. These values are given in Table 2.

Unfortunately, we do not know exactly the values Schneider used either for the constant $C(4{\cdot}502 \times 10^{-7})$ in equation (9) or for f_{ref} and so we cannot be certain that we have recovered exactly his original implicit values of R and p_1. He does, however, give values for f, W and p_2 and these can be subjected to a consistency test for proposed values of C and f_{ref}.

For a given value of C and a particular f, equations (9) and (12) determine R, p_1 and f_m in turn. Finally, using a value for f_{ref}, the estimated value, p_{2est}, can be calculated from (1) and this can be compared with Schneider's value of p_2. The results of these calculations are given in Table 2 for $C = 4{\cdot}502 \times 10^{-7}$ and $f_{ref} = 16{\cdot}408$. While the agreement obtained between p_2 and p_{2est} is not unreasonable, the value used for f_{ref} is not compatible with Schneider's statement that he used the average of two theoretical values obtained by means of band-structure calculations. This average is about 16·48 and his plotted value agrees with this value. Since $f \simeq f_{ref}$ it is easily shown that the effect of a change in the values of C and f_{ref} on the above calculation of p_{2est} is given by

$$\Delta p_{2est} \simeq \frac{2\Delta f_{ref}}{f_{ref}} + p_1 \Delta C/C. \qquad (13)$$

Thus, although the calculated value of p_{2est} is insensitive to a change in the value of C, a change in f_{ref} by 0·4% would change p_{2est} by 0·8%, and this is not in agreement with any reasonable reading of Schneider's graphs.

In order to estimate crudely the possible effects of deconvolution each density function W was replaced by a single-peak representation W_{eq}.

A typical variation of W (that for volume 5) is shown as the curve with multiple peaks in the centre of Fig. 2. The solid curve, W_{eq}, to the left has the same maximum value and gives the same values for the integrals W_n. As in Lebesgue integration, for each subdivision of the (vertical) density range, W_{eq} takes values in this subdivision for the same total angular range as does W; the original curve has been shifted sideways to give a single peak while at the same time maintaining the values of the integrals. This last curve has been fitted so as to give the same values of W_{max}, W_2, W_3 by a double-Gaussian variation,

$$W_{eq}(\omega) \simeq \frac{g}{\sqrt{(2\pi)}\tau_1} \exp\left(\frac{-\omega^2}{2\tau_1^2}\right) + \frac{(1-g)}{\sqrt{(2\pi)}\tau_2} \exp\left(\frac{-\omega^2}{2\tau_2^2}\right), \qquad (14)$$

and the resulting values of g, τ_1, and τ_2 are given in Table 1; the adequacy of this procedure was checked by calculating the W_4 integral from W_{eq}.

The double-Gaussian approximation is shown as the dotted curve in Fig. 2 and this representation is used to estimate the effect of deconvolution. Clearly the effect of this sideways shifting of W is to give a main peak with a half-width τ_1 greater than that of the narrowest of the individual peaks in W. In fact, in the extreme case where W is composed of m identical and isolated Gaussian peaks of half-width τ, the value of τ_1 is equal to $m\tau$. Now for a Gaussian apparatus function of half-width τ_0, the relation between the 'true' and observed values is

$$\tau^2 = \tau_1^2 - \tau_0^2. \qquad (15)$$

The half-width of Schneider's apparatus was about 0·25′ and so a lower bound to the effect of deconvolution can be found by using this value for τ_0 and recomputing first the deconvoluted values of W_2, W_3, W_4 and then the resulting values of f. This gives the dotted curve in Fig. 1. On the other hand, a rough estimate of the greatest expected effect of deconvolution can be found by taking $\tau_0 = b\tau_1$ and the dashed curve in Fig. 1 was derived in this way using $b = 0{\cdot}8$.

Summary

When the level of secondary extinction can be estimated experimentally, it can be combined with the corresponding measured integrated intensity to yield valuable information as summarized below.

(1) A plot of either the integrated intensity or the derived structure factor, before or after the correction for the effect of extinction, against the corresponding value of the level of extinction can show whether the corrections lead to internally consistent results or whether a residual error remains.

(2) Irrespective of whether the correction to the structure factor or intensity is complete or not, graphical extrapolation can yield in the limit a value of the structure factor which is essentially free of secondary extinction, provided the estimate of the level of extinction is at least correct proportionately.

(3) An illustration of the application of this procedure is given in relation to the value of $f(220)$ for Cu, based on experimental data for 11 samples measured with γ-rays by Schneider (1976, 1977).

(4) The result of re-examination of Schneider's data with this procedure is to show that the absolute value is ~2% higher than that nominated by Schneider.

(5) The existence of residual error, even for low levels of extinction and short wavelengths, indicates that the correction procedure based on the Darwin energy-transfer equations was not complete. Hence the assumptions accepted by Schneider were in practice not wholly validated. In relation to these assumptions,

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

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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

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