The Wavelength Dependence of Secondary Extinction Effects

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The wavelength dependence of extinction effects in X-ray and neutron diffraction predicted by recent theories is considered and compared with the results obtained for recent accurate diffraction measurements. It is shown that it is not usually possible to determine reliable values of the domain radius and mosaic spread parameters separately from data measured at only one or two conventional wavelengths. The most significant experimental test of the wavelength dependence is at present that for secondary extinction in a spherical crystal arising from neutron diffraction measurements for SrF_2 at three different wavelengths. These have been analysed on both the Cooper–Rouse and the Becker–Coppens formalisms, both of which predict a simple form for the wavelength dependence. Although both these formalisms give excellent agreement with the data when those for different wavelengths are analysed separately the results indicate, in both cases, that the wavelength dependence is not accounted for adequately by the theory.

Introduction

In the past the majority of X-ray and neutron diffraction studies of single crystals have been carried out using one, or possibly two, fairly short wavelengths (~ 1 Å) for a particular material. Although a number of authors have considered the derivation of reliable extinction corrections for such measurements, very little attention has been paid to the dependence of such corrections on the wavelength. However, consideration of the wavelength dependence would seem to be important at the present time, particularly in view of the increasing number of studies being carried out with longer wavelength neutrons ($2 \rightarrow 10$ Å) for which extinction effects will be greater and also of the increasing use of extended-wavelength neutron sources such as the Harwell LINAC. In the latter case it is obviously vital to be able to account for the wavelength dependence of extinction effects over the whole range of wavelengths involved in the measurements.

It is the purpose of the present paper, therefore, to consider in particular the wavelength dependence predicted by recent extinction theories and the results of a number of recent X-ray and neutron diffraction experiments which can be used to test the theoretical predictions. It should be noted, however, that neutron diffraction measurements have a number of advantages over X-ray diffraction measurements in this respect. Neutron scattering lengths are essentially independent of angle so that significant extinction effects are not restricted to small Bragg angles. The absorption of neutrons in the sample is usually small and extinction is usually predominantly secondary in nature which simplifies the form of the necessary corrections. Furthermore the Maxwellian spectrum of the reactor enables a number of wavelengths over an extended range to be selected conveniently using a crystal monochromator. Consequently we have placed particular

emphasis on the results of a series of accurate neutron diffraction measurements carried out recently at Harwell in order to study anharmonic thermal vibrations in a number of materials with simple structures. In order to provide confidence in the corrections applied to the experimental data these measurements were made at a number of wavelengths for each crystal and the results can therefore be used to study the wavelength dependence of the observed extinction effects. We shall therefore consider, in particular, the form of the extinction theories appropriate to these measurements, *i.e.* for spherical crystals in which the effects of primary extinction are small.

Zachariasen and Cooper–Rouse theories

Recent attempts to make accurate corrections for extinction effects in X-ray and neutron diffraction measurements originate from the theory given by Zachariasen (1967). The Zachariasen theory for a real crystal consisting of small spherical domains in which primary extinction can be ignored can be summarized by the following equations:

$$F_c^2 = F_k^2 y, \tag{1}$$

$$y = (1 + 2x)^{-1/2}, \tag{2}$$

$$x = r^* Q \lambda^{-1} \bar{T}, \tag{3}$$

$$r^* = r/[1 + (r/\lambda g)^2]^{1/2}, \tag{4}$$

where F_c is the calculated extinguished structure factor, F_k is the theoretical kinematical structure factor, y is the extinction factor, r is the domain radius, g is the mosaic spread parameter, Q is the conventional crystallographic quantity proportional to $F^2 \lambda^3 \, \mathrm{cosec} \, 2\theta$ and $\bar{T}$ is the mean path length through the crystal.

The Zachariasen theory has two major shortcomings; it ignores the angle dependence of the effective path length through the crystal and it over-estimates

the value of y for large x, since equation (2) is an approximation which is only valid for small x (<1). The present authors (Cooper & Rouse, 1970) therefore extended the Zachariasen theory to avoid these shortcomings by replacing equation (2) by analytical functions of the form:

$$y=f[x, \sin \theta] . \qquad (5)$$

Functions were chosen for spherical and cylindrical crystals to give an approximation to the theoretical dependence on $\sin \theta$ and to give an approximation to the dependence on x which is valid to a much larger value of x (~ 12) on the basis of accurate neutron diffraction measurements from crystals of CaF_2 and SrF_2 obtained at three different wavelengths in each case.

The wavelength dependence of y is determined by equations (3) and (4) and measurements with at least two wavelengths are necessary to determine the individual extinction parameters r and g. The exact form of the wavelength dependence will depend on the relative magnitude of r and λg and Zachariasen classified the extreme cases as follows:

Type I crystals $r \gg \lambda g$, so that
$$r^* = \lambda g \text{ and } x = gQ\bar{T} . \qquad (6)$$

Type II crystals $r \ll \lambda g$, so that
$$r^* = r \text{ and } x = rQ\lambda^{-1}\bar{T} . \qquad (7)$$

If primary extinction is not negligible then equation (3) must be replaced by:

$$x = \tfrac{3}{2}Q\lambda^{-1}[r^2 + (\tfrac{2}{3}\bar{T}-r)r^*] . \qquad (8)$$

It should be noted, however, that the term in r^2, which corresponds to the primary extinction, has the same form as that for type II secondary extinction with $\tfrac{3}{2}r^2$ replacing $r\bar{T}$ and furthermore if $r \ll \lambda g$ then $r^* = r$ and x has the value given by equation (7), as before. Thus equation (7) is still valid in this case, even when primary extinction is not negligible. We should note, however, that if r is much less than $\bar{T}$ secondary extinction will be more important than primary.

For a type I crystal $r \gg \lambda g$, $r^* = \lambda g$ and if $r \ll \bar{T}$ equation (8) becomes:

$$x = \tfrac{3}{2}Q\lambda^{-1}(r^2 + \tfrac{2}{3}\bar{T}\lambda g) \qquad (9)$$

and the primary extinction term may then be significant. However, a plot of r^* determined from equation (3) against wavelength would then have a slope of value g and an intercept at $\lambda = 0$ of $3r^2/(2\bar{T})$, the latter thus indicating the relative importance of the primary extinction.

X-ray diffraction measurements

Zachariasen carried out a series of experiments with Mo and Cu X-radiation in order to test the predictions of his theory. The crystals studied were spheres of quartz, hambergite, LiF, CaF_2 and phenakite

(Zachariasen, 1969) and the values obtained for the extinction parameters are given in Table 1.

Table 1. *Extinction parameters derived from Zachariasen's analyses*

| | $r^* \times 10^4$ cm | | r | $\dfrac{g}{\times 10^{-4}}$ | |
	Mo	Cu	$\times 10^4$ cm	rad^{-1}	Type
LiF	0·022	0·045	0·11	0·03	I
Quartz	0·47	0·46	0·46	>0·7	II
Phenakite	0·69	1·00	1·2	1·2	–
Hambergite	0·98	1·54	2·0	1·6	–
CaF_2	2·5	3·0	3·2	5·7	–

Unfortunately Zachariasen gives no indication of the accuracy with which individual values of r and g can be determined from these measurements and the results are therefore somewhat misleading. In order to demonstrate this we have considered in particular the experimental results obtained for LiF (Zachariasen, 1968) and have re-analysed these using a least-squares fitting procedure, assuming an accuracy of 1% in individual measured intensities, as indicated by Zachariasen. The best fit obtained for the Mo $K\alpha$ data, which consist of 23 reflexions, gave a weighted R for the structure factors of 0·74%, a value of $r^*=0·44$ (6) $\times 10^{-5}$ cm and temperature factors of $B_{Li}=1·07$ (3) and $B_F=0·72$ (2) Å^2. These compare with Zachariasen's values of $R_F=0·8\%$, $r^*=0·22 \times 10^{-5}$ cm, $B_{Li}=0·90$ (4) and $B_F=0·63$ (1) Å^2. Although the overall agreement is not significantly better the temperature factors are in much better agreement with recent accurate experimental values (Merisalo & Inkinen, 1968; Howard & Khadake, 1974) and with the theoretical values of Merisalo & Inkinen (1966).

Whilst the value of r^* for the Mo $K\alpha$ data is reasonably well determined ($\sigma \sim 15\%$) it should be noted that the extinction is not at all severe, only seven reflexions being reduced in intensity by more than 1%. Furthermore, in order to be able to determine reliable values for r and g individually it is necessary to be able to determine a fairly precise value of r^* for the Cu $K\alpha$ data. This is clearly impossible in the present case since only four reflexions were measured at this wavelength and a minimum of two parameters, r^* and the scale factor, must be determined. Consequently the value of r^* for Cu $K\alpha$ will necessarily have a very large uncertainty and any values derived therefrom for r and g will be ill-determined.

In fact, using the temperature factors obtained from the analysis of the Mo $K\alpha$ data the best fit to the Cu $K\alpha$ data gave a value of $r^*=0·37 \times 10^{-5}$ cm and of R_F 0·76%. The latter is significantly better than the R_F value of 1·33% obtained by Zachariasen and the result for r^*_{Cu} contrasts strongly with that obtained by Zachariasen in being smaller rather than larger than the value of r^*_{Mo}. Our analysis therefore leads us to the conclusion that the crystal is of type II rather than type I. This again is in contrast to Zachariasen's

conclusion that the crystal tended towards type I, but we may note that Killean, Lawrence & Sharma (1972) have obtained a similar result from recent measurements on a LiF sphere.

In this case absorption in the crystal is small and so $\bar{T}$ is equal to $\frac{3}{4}R$ where R is the radius of the crystal (0·03 cm). Hence $r \ll \bar{T}$ and it can be seen from equation (8) that the extinction is therefore predominantly secondary in nature.

Neutron diffraction measurements

The X-ray diffraction measurements referred to in the previous section involved the use of two wavelengths only. Recently we have carried out a series of accurate neutron diffraction measurements on spherical crystals of SrF_2 (Cooper & Rouse, 1971), ZnS and ZnTe (Cooper, Rouse & Fuess, 1973) and a cubic crystal of KCl (Cooper & Rouse, 1973). Extinction in the SrF_2 crystal was significantly anisotropic at long wavelengths (>2 Å). However, this anisotropy was less at shorter wavelengths and all measurements were carried out in such a way that the resultant intensities could be analysed using an isotropic model for the extinction. No significant anisotropy was observed in the other crystals. Although the KCl crystal was not a sphere the absorption and extinction were both small enough for a spherical approximation to be used. Except in the case of ZnTe, these measurements involved the use of three different wavelengths and so provide a more sensitive test of the wavelength dependence of the extinction parameters, even though the range of wavelengths covered is somewhat less. In each case data for the different wavelengths were analysed separately to give the best values of the effective domain radius r^* and the results of these analyses are summarized in Table 2.

Table 2. *The results of analyses of neutron diffraction measurements*

	λ	y_{min}	r^* (10^{-5} cm)	R_I (%)
SrF$_2$	0·746	0·26	9·26 (40)	1·76
(sphere)	0·865	0·21	11·98 (46)	2·14
	1·077	0·14	16·49 (105)	4·58
ZnS	0·873	0·88	1·19 (4)	1·30
(sphere)	0·945	0·85	1·34 (7)	0·74
	1·146	0·82	1·67 (18)	0·94
ZnTe	0·945	0·89	1·18 (14)	1·96
(sphere)	1·143	0·92	1·40 (68)	3·24
KCl	0·948	0·90	0·62 (10)	0·87
(cube)	1·142	0·87	0·80 (10)	1·34
	1·346	0·84	0·81 (9)	0·80

The values of r^* obtained for the different wavelengths were then used to derive values of r and g from equation (4) with the results given in Table 3.

These results indicate that the SrF_2 and ZnS crystals are both type I and that the ZnTe and KCl crystals also tend towards type I. However, the large uncertainties associated with r and g values determined from so few r values mean that except for the crystals which are definitely type I the type is not well determined. This is particularly true for ZnTe for which measurements were made at two wavelengths only because of limitations arising from the near equality of the scattering lengths of zinc and tellurium.

Table 3. *Extinction parameters derived from neutron diffraction data*

	$r \times 10^5$ cm	$g \times 10^{-3}$ rad^{-1}	Type
SrF$_2$	$\propto$	13·4 (3·5)	I
ZnS	$\propto$	1·39 (0·36)	I
ZnTe	4·1 (59·7)	1·3 (1·6)	$\rightarrow$ I
KCl	1·3 (0·9)	0·77 (0·27)	$\rightarrow$ I

For both SrF_2 and ZnS equation (4) gave negative values of $1/r^2$, *i.e.* $-0·34 \times 10^{10}$ cm^{-2} for SrF_2 and $-0·96 \times 10^{10}$ cm^{-2} for ZnS. These are clearly not meaningful and the values of g have therefore been determined for these crystals by setting $1/r^2 = 0$. However this result clearly indicates a significant deviation from the predictions of equation (4), particularly in the case of SrF_2 for which the extinction is fairly severe and so provides a more exacting test of the wavelength dependence.

This analysis has so far ignored the possible effect of primary extinction. However, although a plot of r^* against λ gave a good fit to a straight line this also resulted in a significant negative intercept at $\lambda = 0$, which from equation (9) indicates that the primary extinction is negligible and confirms that the wavelength dependence of the secondary extinction is not adequately accounted for.

If we re-write equation (4) in the form:

$$1/r^{*2} = 1/r^2 + 1/(\lambda g)^2 \qquad (10)$$

we see that a plot of $1/r^{*2}$ against $1/\lambda^2$ should be linear with an intercept at $1/\lambda^2 = 0$ of $1/r^2$. The experimental values of $1/r^{*2}$ are therefore plotted in Fig. 1 which clearly demonstrates the negative value of $1/r^2$ which is obtained by assuming equation (10) to be valid. It also shows clearly that the experimental points lie on a curve rather than a straight line. In both cases the best curve would appear to be one with a very small positive intercept at $1/\lambda^2 = 0$, as shown by the solid curve for the SrF_2 results. Such a curve is consistent with the need for a positive value of $1/r^2$. A similar plot for the KCl values show that these would also be fitted better by a similar curve, although in this case it would result in a significantly large positive value of $1/r^2$.

The neutron diffraction measurements on these materials therefore indicate that the wavelength dependence given by equation (10) is not correct and that a

higher order term in $1/\lambda$ is necessary. An expression which fits the experimental results is given by:

$$1/r^{*2} = 1/r^2 + a/(\lambda g)^2 + b/(\lambda^2 g)^2 \qquad (11)$$

with $b \simeq 2a$ (Å^2).

Becker–Coppens theory

More recently Becker & Coppens (1974a) have derived a more rigorous theory of extinction for spherical crystals. This theory again predicts a secondary extinction correction to the Bragg intensities which is given by equations (1) and (5) but removes an approximation retained in both the Zachariasen and Cooper–Rouse formalisms† by replacing the domain radius r by $r \sin 2\theta$. However, these authors retained an ambiguity in the possible form of the domain mosaic orientation function, presenting results for both Gaussian and Lorentzian distributions. The Becker–Coppens extinction correction for spherical crystals can thus be written as:

$$F_c^2 = F_k^2 y_s , \qquad (12)$$

$$y_s = f[X, \sin \theta] , \qquad (13)$$

$$X = r^* \sin 2\theta Q \lambda^{-1} \bar{T} , \qquad (14)$$

where r^* for a Gaussian distribution is given by:

$$r_G^* = r/[1 + \tfrac{2}{3}(r \sin 2\theta/\lambda g)^2]^{1/2} \qquad (15)$$

and r^* for a Lorentzian distribution is given by:

$$r_L^* = r/(1 + r \sin 2\theta/\lambda g) . \qquad (16)$$

The function $f[X, \sin \theta]$ is tabulated for values of X and $\sin \theta$ for these two cases and analytical approximations to equation (13) are also given.

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† It should be emphasized that the Cooper–Rouse theory correctly replaced t_2 by t_2' in Zachariasen's (1967) equation (14) and Becker & Coppens (1974a) are therefore in error in stating that the former only partially corrects the wrong variation with θ by the introduction of an angle dependent term.
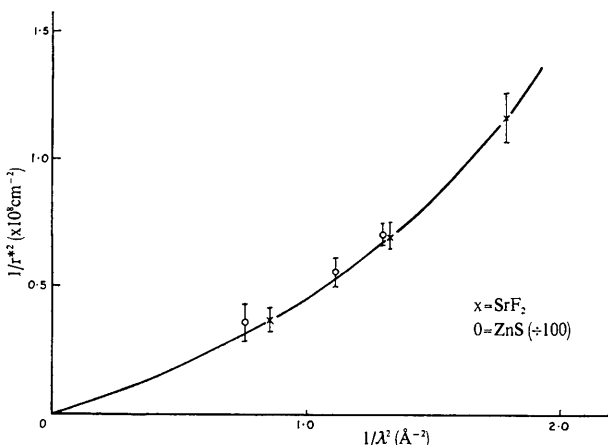
For the two extreme cases we have, provided that $\sin 2\theta$ is not too small:

Type I crystals $r \gg \lambda g$, so that

$$r_G^* = \tfrac{8}{9}\lambda g/\sin 2\theta \text{ and } X_G = \tfrac{8}{9}gQ\bar{T} \qquad (17)$$

$$r_L^* = \lambda g/\sin 2\theta \text{ and } X_L = gQ\bar{T} . \qquad (18)$$

Type II crystals $r \ll \lambda g$, so that

$$r_G^* = r_L^* = r \text{ and } X_G = X_L = r \sin 2\theta Q \lambda^{-1} \bar{T} . \qquad (19)$$

The additional factor of $\sin 2\theta$ does not therefore occur in the formalism for type I crystals and will have a negligible effect for crystals which tend towards type I. For example the smallest values of $\sin 2\theta$ which occur for the SrF_2 data referred to earlier are 0·22, 0·26 and 0·32 at the three wavelengths, so that the type I relations given by equations (17) and (18) for $r \gg \lambda g$ are still valid. Thus for spherical crystals of type I the Becker–Coppens and Cooper–Rouse formalisms for secondary extinction are identical except for the exact form of the function $f[X, \sin \theta]$ and the ambiguity in the relation between r^* and g in the Becker–Coppens formalism.

Primary extinction is included by replacing equation (12) by:

$$F_c^2 = F_k^2 y_s y_P \qquad (20)$$

where y_P has a similar form to y_s [equation (13)] but with X given by:

$$X_P = \tfrac{3}{2}Qr^2 \sin 2\theta/\lambda . \qquad (21)$$

Consequently the primary extinction will be appreciably less than the secondary extinction if $r^2 < \tfrac{2}{3}r^*\bar{T}$.

It should be noted, however, that neither this formalism, nor the more realistic one subsequently suggested by Becker & Coppens (1975), in which X_S is replaced by $y_P(X_P)$. X_S, is entirely correct since it does not give the right behaviour for r comparable in magnitude with $\bar{T}$, when primary extinction will predominate.

Tests of the Becker–Coppens theory

Becker & Coppens (1974b) have applied their formalism to the neutron diffraction measurements for SrF_2 referred to in the previous section and conclude that these support the validity of their formalism. It is therefore instructive to consider the results which they obtained in some detail. Their results for separate analyses of the data for the different wavelengths are summarized in Table 4. These results were obtained using a Lorentzian mosaic spread distribution, the fit being poorer for a Gaussian distribution. The original study of SrF_2 (Cooper & Rouse, 1971) did in fact include simultaneous least-squares refinements on the scale, temperature and extinction parameters for the different wavelengths which may therefore be compared with the Becker–Coppens results. These were not

Fig. 1. Plot of $1/r^{*2}$ against $1/\lambda^2$ for SrF_2 and ZnS.

Table 4. *Results of Becker–Coppens analyses of* SrF_2 *Data*

	Type I			Mixed type
	λ_1 (0·746 Å)	λ_2 (0·865 Å)	λ_3 (1·077 Å)	λ_3 (1·077 Å)
U_{Sr} (Å^2)	0·00803 (28)	0·00742 (16)	0·00763 (28)	0·00689 (13)
U_F (Å^2)	0·01075 (30)	0·01069 (19)	0·01122 (31)	0·01017 (15)
$r \times 10^5$ cm	–	–	–	9·6 (7)
$g \times 10^{-4}$	1·64 (11)	1·75 (09)	2·35 (18)	1·50 (16)
R	0·014	0·016	0·013	0·006
R_2	0·022	0·026	0·023	0·013

published in the earlier paper since they were used at that time only to provide values of the temperature factors for subsequent analyses. However, the results of these refinements are summarized in Table 5 in a form suitable for direct comparison with the Becker–Coppens results. These results do not differ significantly from those obtained by Becker & Coppens using our formalism. However, we have used a computer program (*TAILS*) which minimizes an agreement factor based on the intensities rather than F or F^2 (see Cooper & Rouse, 1971) and uses the search algorithm of Powell (1965) rather than a conventional least-squares algorithm. These factors presumably account for small differences in the final values of the refined parameters. We may note in particular, however, that the values of g are in agreement within their standard deviations and that the ratios are essentially identical.

Table 5. *Results of Cooper–Rouse analyses of* SrF_2 *data*

	λ_1 (0·746 Å)	λ_2 (0·865 Å)	λ_3 (1·077 Å)
U_{Sr} (Å^2)	0·00769 (18)	0·00715 (14)	0·00739 (42)
U_F (Å^2)	0·01072 (36)	0·01061 (16)	0·01129 (44)
$r \times 10^5$ cm	–	–	–
$g \times 10^{-4}$	1·28 (9)	1·36 (6)	1·65 (18)
R	0·014	0·013	0·021
R_2	0·022	0·020	0·042

We have now repeated the analysis of our data using the Becker–Coppens formalism in the *TAILS* computer program. The results obtained for type I and mixed-type extinction are summarized in Table 6. The analyses for a type I crystal again reproduce the results of Becker & Coppens fairly closely but with small differences resulting from the different method of analysis. Introduction of the particle size in the refinement for λ_3 gives a slight improvement, with R_2, the reliability index based on intensities, reduced from

2·7 to 2·1%. It is only when primary extinction is allowed for as well that our results for a mixed-type crystal compare with those given by Becker & Coppens, but even then R_2 is only reduced to 2·0%. These analyses confirmed the very high correlation between r and g (0·92 for λ_3), as would be expected from the theory, but give more realistic values for the standard deviations of the parameters, *i.e.* about twice those obtained by Becker & Coppens, which were unreasonably small. This would appear to support a preference for the type of algorithm used in the *TAILS* program.

A detailed comparison of our analyses for a type I crystal show that the agreement obtained is better for the two shorter wavelengths with the Cooper–Rouse formalism and is better with the Becker–Coppens formalism for the longest wavelength only. Moreover, although the Becker–Coppens mixed-type formalism appears to give an improved fit for the angle dependence of the λ_3 data for intermediate θ values it results in very large differences for some of the smaller angle reflexions for which the sin 2θ term becomes important. As reported previously by Becker & Coppens the results obtained with their type I formalism show a significant increase in g_I† with λ, although it should be emphasized that this increase is inconsistent with the theory. However, statistical tests indicate that this increase is significant at a confidence level of 99·9%.

The different angle-dependent function in the Becker–Coppens formalism results in different absolute values of g_I, but these are consistently about 25% higher than those given by the Cooper–Rouse formalism at each wavelength. Hence the same wavelength dependence considerations apply in both cases, and in fact the increase with wavelength is slightly larger for the Becker–Coppens formalism. Moreover, examination of the theories shows that these considerations are

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† We shall use g_I to denote an effective value of g derived from a Type I analysis.

Table 6. *Results of re-analysis of* SrF_2 *data using the Becker–Coppens formalism*

	Type I			Mixed type	
	λ_1 (0·746 Å)	λ_2 (0·865 Å)	λ_3 (1·077 Å)	Secondary only	Primary + Secondary
U_{Sr} (Å^2)	0·00790 (29)	0·00734 (16)	0·00753 (31)	0·00738 (27)	0·00637 (29)
U_F (Å^2)	0·01073 (43)	0·01053 (19)	0·01111 (37)	0·01102 (30)	0·00977 (28)
$r \times 10^5$ cm	–	–	–	33·6 (9·3)	9·3 (1·3)
$g \times 10^{-4}$	1·56 (14)	1·68 (10)	2·22 (20)	2·66 (25)	1·57 (30)
$R(F)$	0·015	0·016	0·014	0·011	0·009
$R_2(I)$	0·026	0·026	0·027	0·021	0·020

not altered by the introduction of a primary extinction contribution which can only lead to a decrease of g_I with increase in wavelength.

We have also repeated simultaneous refinements on all data sets and these again essentially confirm the results given by Becker & Coppens. However, the overall agreement obtained from such analyses depends critically on how the various data sets are weighted relative to one another and the results can therefore be misleading. In particular they conceal the fact that the apparent improvement in overall agreement given by the Becker–Coppens formalism results solely from the improvement obtained for the λ_3 data and that the agreement for the λ_1 and λ_2 data sets is significantly worse. Moreover, although a single model for the extinction can be fitted for both theories, in both cases this forces a particular wavelength dependence of r^* and a significantly better fit would be obtained for all wavelengths if a model were used which allowed for the wavelength dependence of g_I indicated by the separate analyses.

We have also repeated our analysis of the Zachariasen LiF X-ray data using the Becker–Coppens extinction formalism in the *TAILS* computer program. In view of the limited Cu $K\alpha$ data we have again fixed the thermal parameters from analysis of the Mo $K\alpha$ data and refined only the extinction parameters for the Cu $K\alpha$ data. The results of our analyses for various extinction models are summarized in Table 7, which for completeness includes the results obtained using the Cooper–Rouse formalism discussed earlier. Because of the limited Cu $K\alpha$ data no standard deviations are given for the extinction parameters at this wavelength. However, further analyses were carried out for these data with all thermal and extinction parameters fixed at the values obtained from the Mo $K\alpha$ data and the resultant reliability index value, wR_2', is also given.

It is clear from a study of these results that all models give a reasonably good fit to the Mo $K\alpha$ data (wR_2 values in the range 1·35 to 1·40%) but that the only single model which gives good agreement for both sets of data simultaneously is the Cooper–Rouse type II model ($wR_2' = 2·15\%$). As indicated previously this model could equally well allow for primary extinction, but since $r \ll \bar{T}$ this will be much less than the secondary extinction in this case. In contrast, none

of the Becker–Coppens models give good agreement for both sets of data simultaneously, although the best fit to the Cu $K\alpha$ data is given by the type II model, including primary extinction. These results conflict with the earlier results obtained by Becker & Coppens (1974*b*) for their analysis of a different set of LiF X-ray data from which they concluded that the extinction is primary in nature. However, this conclusion is not physically acceptable in this case, since $r \ll \bar{T}$.

Further details of our analyses of these SrF$_2$ and LiF data will be given elsewhere.

Conclusions

The increasing use of long-wavelength and extended-wavelength neutron sources for diffraction studies demands an adequate formalism for the wavelength dependence of extinction effects. However, recent theories of extinction and experimental tests of these have been concentrated almost entirely at providing formalisms which are acceptable for data measured at a single wavelength only and the wavelength dependence has received little attention. In particular Becker & Coppens (1974*b*, 1975) have presented results of analyses of data for six different materials (SrF$_2$, LiF, LiTbF$_4$, αDOX, TCNE and LiOH.H$_2$O) using their recent extinction formalism but only two of these (SrF$_2$ and LiF) involve data collected at more than one wavelength. Their analyses of the data for SrF$_2$ and LiF are, however, misleading although they were presented as evidence for the validity of the new formalism.

Recent theories of extinction in spherical crystals predict a simple wavelength dependence of the effective domain radius or the effective mosaic spread parameter on the wavelength. However, this dependence is such that it is not usually possible to determine reliable values of the domain radius and mosaic spread parameters separately from data measured at one or two conventional wavelengths only. Even for data measured recently at three wavelengths the theories are only tested to any significant extent by those for a spherical crystal of SrF$_2$ which we have therefore re-analysed using both the Cooper–Rouse and the Becker–Coppens formalisms. In addition we have re-analysed, again using both formalisms, X-ray data obtained by Zachariasen (1968) for a spherical crystal

Table 7. *Results of analyses of LiF data*

	Cooper–Rouse ($r^* = r$)	General	Becker–Coppens (Lorentz) Primary	Type I	Type II
B_{Li} (Å²)	1·07 (3)	1·08 (3)	1·08 (3)	1·08 (3)	1·08 (3)
B_F (Å²)	0·72 (2)	0·72 (2)	0·73 (2)	0·72 (2)	0·73 (2)
$r_{Mo} \times 10^5$ cm	0·44 (6)	3·3 (5·5)	62 (5)	–	1·4 (4)
$r_{Cu} \times 10^5$ cm	0·37	14·3	38	–	0·58
$g_{Mo} \times 10^{-4}$	–	9 (10)	–	15 (2)	–
$g_{Cu} \times 10^{-4}$	–	47	–	32	–
wR_2(Mo) (%)	1·37	1·37	1·35	1·40	1·36
wR_2(Cu) (%)	1·75	1·89	2·91	2·24	3·24
wR_2'(Cu) (%)	2·15	8·86	9·72	8·84	8·62

of LiF. Our conclusions from these analyses together with a detailed consideration of the theories are as follows:

(1) Extinction in the SrF_2 crystal is essentially type I secondary whereas that in the LiF crystal is essentially type II secondary.

(2) For spherical crystals of type I the Becker–Coppens and Cooper–Rouse formalisms for secondary extinction are identical except for the exact form of the angle-dependent function $f[X, \sin\theta]$ for y and an additional factor of $\frac{8}{9}$ multiplying the value of g in the Becker–Coppens formalism if the mosaic spread function is Gaussian rather than Lorentzian.

(3) Type I analyses of individual SrF_2 data sets give values of g_I which are about 25% larger for the Becker–Coppens formalism as a result of the different angle dependent function, but the wavelength dependence of g_I is essentially the same in both cases.

(4) In both cases the increase of g_I with wavelength is significant, although the theories predict that g_I should be independent of wavelength for type I extinction and decrease with wavelength for other types of extinction.

(5) The different angular-dependent functions result in better agreement being obtained for the Becker–Coppens formalism for the long wavelength data but better agreement for Cooper–Rouse formalism for the data at the two shorter wavelengths.

(6) The Becker & Coppens (1974b) analysis is misleading since it conceals the wavelength dependence of g_I by analysing all data sets simultaneously with a single model for the extinction. However, it is clear that a significant improvement in the overall agreement could be obtained if a model were used which allowed for the wavelength dependence indicated by the separate analyses.

(7) The Cooper–Rouse formalism gives excellent agreement for the LiF data at both wavelengths. In contrast the Becker–Coppens formalism gives comparable agreement for data at one wavelength only.

(8) The Becker–Coppens formalism is not correct unless $r \ll \bar{T}$. Furthermore, primary extinction cannot predominate if $r^2 \ll r^*\bar{T}$. Thus for a type II crystal primary extinction cannot predominate if $r \ll \bar{T}$.

Our basic conclusions from the analyses presented by Becker & Coppens (1974b, 1975) and our own analyses are thus that, provided $r \ll \bar{T}$, both extinction formalisms give good agreement for data collected at a single wavelength but that neither formalism accounts correctly for the wavelength dependence of the secondary extinction. The formalisms are very similar for type I secondary extinction and in both cases the wavelength dependence for this type can be allowed for by introducing an additional wavelength dependent term in g. Although good agreement could be obtained for the Zachariasen LiF data at both wavelengths using the Cooper–Rouse formalism similar agreement

could not be obtained using the Becker–Coppens formalism. This appears to indicate a further shortcoming in the latter.

In view of the shortcomings which these analyses demonstrate so conclusively it is interesting to note that Niimura, Tomiyoshi, Takahashi & Harada (1975) have recently carried out neutron time-of-flight measurements on a crystal of CuCl over an extended wavelength range and report 'good' agreement using the Becker–Coppens type I formalism. However, the extinction is considerably smaller in this crystal than in the SrF_2 crystal discussed previously and for wavelengths below about 1·5 Å appears to be significant only for the 111 and 222 reflexions. Furthermore, some deviation from the theory appears to occur for these reflexions at the shorter wavelengths. The good agreement obtained at longer wavelengths is in fact perfectly consistent with our earlier conclusions since Fig. 1 shows that the existing formalisms which give a linear dependence of $1/r^{*2}$ on $1/\lambda^2$ or of $1/r^*$ on $1/\lambda$ could well be valid for wavelengths greater than 1·5 Å.

Obviously further studies involving data collected over an extensive range of wavelengths will be necessary in order to establish the detailed wavelength dependence of extinction effects with confidence. A series of measurements is therefore being undertaken on the same SrF_2 crystal in order to extend the range of wavelengths to both longer and shorter values.

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