

The XTAL system and the concepts on which it is based have recently been used under the sponsorship of NRCC to develop a portable multiple isomorphous replacement program. A discussion of this project and its wider implication can be found in Robinson (1980).

References

- HALL, S. R., STEWART, J. M., NORDEN, A., MUNN, R. J. & FREER, S. (1980). *The XTAL System of Crystallographic Programs: Programmer's Manual*. Report TR-873. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- KERNIGHAN, B. W. & PLAUGER, P. J. (1976). *Software Tools*. Reading, Mass.: Addison-Wesley.
- MUNN, R. J. & STEWART, J. M. (1978). *RATMAC: Kernighan and Plauger's Structured Programming Language*. Report TR-675. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- MUNN, R. J. & STEWART, J. M. (1979). *RATMAC: A Primer*. Report TR-804. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- ROBINSON, A. (1980). *Science*, **207**, 746.
- STEWART, J. M. (1976*a*). The XRAY system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- STEWART, J. M. (1976*b*). *Crystallographic Computing Techniques*, pp. 433–443. Copenhagen: Munksgaard.
- STEWART, J. M. & MUNN, R. J. (1978). In *Computing in Crystallography*. Delft Univ. Press.

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On Formalism of Extinction Correction within the Validity Limits of the Mosaic Model

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Abstract

The results of an investigation of the polarization coefficient of X-ray radiation diffracted in real crystals are given. The form of the angular dependence of the polarization coefficient in the range of the Bragg reflection is found to be qualitatively different in the cases of primary and secondary extinction. It allows the unambiguous identification of the type of extinction in the crystal. On the basis of the experimental data analysis of the polarization coefficients for silicon and germanium crystals with different dislocation densities, it is shown that the mosaic model of a crystal is suitable for describing X-ray scattering in real crystals if the dislocation density is higher than 10^4 mm^{-2} and in practice only primary extinction is present in mosaic crystals. An expression is given for the primary extinction factor for the mosaic crystal, obtained on the basis of the solution of the Takagi-Taupin equations for finite crystals. This expression was used for the analysis of the LiF and NaF structure factors measured by different authors. The effective size which was obtained for the domains appeared to be physically reasonable and to be directly connected with the value of the dislocation density in the crystal.

1. Introduction

Extinction in X-ray crystallography is described in most cases in terms of the Darwin (1914) mosaic block model. Zachariasen (1967) developed the formalism of the extinction theory on the basis of the Darwin energy transfer equations and applied it in the analysis of X-ray data for a number of substances (Zachariasen, 1968*a,b*). The Zachariasen theory greatly renewed interest in extinction. Coppens & Hamilton (1970) generalized the Zachariasen approach in the case of extinction anisotropy. It was established by many authors that the Zachariasen formalism significantly improved the agreement between the calculated and corrected-for-extinction experimental structure factors. This formalism was refined by Cooper & Rouse (1970) and more strictly reconsidered by Becker & Coppens (1974*a*, 1975). At the same time, different authors pointed out the shortcomings of the indicated formalism. Its main limitation is the kinematical approach (Werner, 1969), for it is based on the transfer differential equations, which take no account of coherence, since they involve only the intensities of the beams. This method does not appear to be suitable for correcting for severe primary

extinction (Lawrence, 1972). The formalism of extinction which was considered was discussed (Lawrence, 1977; Becker, 1977) both from the point of view of the applicability of the models and the physical sense of its parameters.

Comparison of block sizes, obtained in the refinement of the extinction parameters, with dislocation densities (Michell, Smith & Sabine, 1969; Killean, Lawrence & Sharma, 1972; Sharma, 1974) showed that the Zachariasen theory gave physically unrealistic results. The block size obtained in the refinement of the theoretical parameters is an order or two less than the distance between dislocations in the crystal under study. The problem of the physical sense of the block sizes is closely connected with that of the relation between primary and secondary extinction (Lawrence, 1974; Becker & Coppens, 1974*a,b*). Following Zachariasen, primary extinction is assumed to be absent in most cases. However, experiments on the variation of extinction with beam path length in a crystal (Denne, 1972; Lawrence, 1972, 1973) showed this assumption to be unjustified and the primary extinction effect to be essential.

Finally, there arise the questions of the applicability limits of the mosaic model itself and of the assessment of the dislocation density range in a crystal where this model could make sense physically. There are cases when the extinction formalism, based on the mosaic block model, is applied for the analysis of the experimental data obtained for weakly distorted crystals, and satisfactory agreement is achieved between the corrected and calculated structure factors. This suggests that a formally achieved agreement of structure factors without an estimation of the physical significance of the extinction parameters cannot give evidence on the validity of physical model of X-ray scattering in real crystals which has been used.

A study of the polarization ratio of the Bragg reflections for crystals with different dislocation densities showed (Olekhovich, Rubcov & Schmidt, 1975; Olekhovich & Schmidt, 1977; Olekhovich, Kaspei & Markovich, 1978) the limited range of applicability of the Darwin transfer equations and of the mosaic model itself for describing X-ray diffraction in real crystals. Some progress in the solution of the extinction problem can probably be made by studying the angular dependence of the polarization coefficient of the Bragg reflections (Olekhovich & Markovich, 1978).

The aim of the present paper is: to carry out an analysis of the angular dependence of the polarization coefficient of the Bragg reflection for a mosaic crystal block model in the case of primary and secondary extinctions; estimation of the lower limit of dislocation density in a crystal, above which the mosaic crystal model can be applied; investigation of the nature of extinction and finding an approach for its description in

the case of mosaic crystals; and an illustration of the possibilities of the approach found for the analysis of the experimental structure factors of NaF and LiF for which the extinction effect has been studied carefully by many investigators.

2. Polarization coefficient and extinction type identification

Let $R_\sigma(\varepsilon)$ and $R_\pi(\varepsilon)$ be the reflected powers for a crystal at the given diffraction angle $\varepsilon = \theta - \theta_B$ for the σ and π polarization components of the unpolarized incident beam. Then the polarization coefficient of the diffracted radiation can be defined as:

$$P_R = \frac{R_\pi(\varepsilon)}{R_\sigma(\varepsilon)}. \quad (1)$$

This is a differential characteristic of the scattered radiation determining the polarization ratio at each point of the Bragg reflection curve. As in the case of the ideal mosaic crystal the scattering curve profiles for the π and σ polarizations are identical; the polarization coefficient for such a crystal has a constant value of $\cos^2 2\theta_B$ (θ_B is the Bragg angle) over the whole Bragg reflection curve.

We now consider the character of the angular dependence of the polarization coefficient for real mosaic crystals.

The case of primary extinction

If the crystal is composed of independent mosaic blocks the polarization coefficient can be expressed as:

$$P_R = \frac{\int_{-\infty}^{\infty} w(\alpha) R_\pi^b(\varepsilon + \alpha) d\alpha}{\int_{-\infty}^{\infty} w(\alpha) R_\sigma^b(\varepsilon + \alpha) d\alpha}. \quad (2)$$

Here R_π^b and R_σ^b are diffracted powers for the mean mosaic block at the $\varepsilon + \alpha$ angle for π and σ polarizations, respectively, and $w(\alpha)$ is the angular distribution function of the crystal blocks. As was shown by a calculation (Olekhovich, 1978) based on the solution of the Takagi-Taupin (Takagi, 1969) equations for different shapes of finite crystals in the range of the principal maximum, the scattering curve profiles had practically the same shape for both polarizations. If these data are taken into account, it follows from (2) that the angular dependence of P_R for the crystals with the type of mosaic considered is a function close to the Π -shaped one, *i.e.* it is in the larger part of the Bragg reflection curve (Fig. 1*a*), it has a constant value exceeding $\cos^2 2\theta_B$, and on passing into the range of the reflection tails the value of the polarization coefficient sharply decreases up to the

kinematical limit (Fig. 1*b*, curve 1). Angular dependence of the polarization coefficient does not depend on the character of the angular distribution of the block. The P_R value in the plateau range depends directly on the block size. If its size is much less than the extinction length then the value of the polarization coefficient is $\cos^2 2\theta_B$.

The case of secondary extinction

The calculation of the polarization coefficient of the diffracted radiation for a mosaic crystal, consisting of incoherently connected blocks (there is no primary extinction), can be carried out on the basis of the solution of the energy transfer equations (Zachariassen, 1967). For instance, the solution of these equations for Bragg diffraction in a thick crystal gives, in the symmetrical case, the following expression for the integrated intensity (Olekhovich & Schmidt, 1977):

$$\rho = \frac{1}{2\mu} \int_{-\infty}^{\infty} \frac{\bar{\sigma}(\varepsilon) d\varepsilon}{[1 + \bar{\sigma}(\varepsilon)/\mu]^{1/2} [1 + 2\bar{\sigma}(\varepsilon)/\mu]^{1/4}}. \quad (3)$$

The polarization coefficient will therefore be:

$$P_R = \cos^2 2\theta_B \frac{[1 + \bar{\sigma}_o(\varepsilon)/\mu]^{1/2} [1 + 2\bar{\sigma}_o(\varepsilon)/\mu]^{1/4}}{[1 + \bar{\sigma}_\pi(\varepsilon)/\mu]^{1/2} [1 + 2\bar{\sigma}_\pi(\varepsilon)/\mu]^{1/4}}. \quad (4)$$

Here $\bar{\sigma}(\varepsilon)$ is the effective value of the reflected power per unit volume of the crystal (Becker & Coppens, 1974*a*), μ is the absorption coefficient, and

$$\bar{\sigma}_\pi = \bar{\sigma}_o \cos^2 2\theta_B.$$

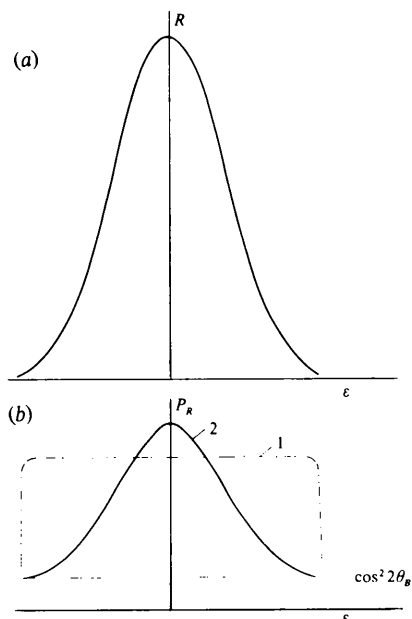


Fig. 1. (a) Rocking curve of the Bragg reflection for the mosaic crystal, and (b) the angular dependence of the polarization coefficient. Curve (1) is the case of primary extinction, curve (2) of secondary extinction.

The calculations performed for the case of secondary extinction show the angular-dependence curve of the polarization coefficient to be similar to the rocking curve of the Bragg reflection (Fig. 1*b*, curve 2). The character of the angular dependence P_R in the case considered does not depend on the approximations used in the calculations, *i.e.* on the angular distribution function of blocks and their shape. It should be noted that the calculation of the polarization coefficient on the basis of the dynamical-theory approach developed by Kato (1976) is impossible, since the theory does not determine the angular dependence of the introduced correlation parameter. With primary and secondary extinction appearing in the crystal, the polarization coefficient will be described by the curve, which is some superposition of curves (1) and (2) in Fig. 1(*b*).

Thus the analyses performed show that the type of extinction in a crystal can be accurately identified by the observed angular dependence of the polarization coefficient.

3. Experiment

Investigations of the polarization coefficient were carried out on single crystals of silicon (Olekhovich & Markovich, 1978) and germanium with different dislocation densities. The character of the angular dependence P_R is found to change with increasing dislocation density. With a dislocation density higher than 10^5 mm^{-2} , one can observe a plateau on the curve of the angular dependence of the polarization coefficient. The plateau covers practically the whole angular range of the Bragg reflection (Fig. 2). Only on the tails of the rocking curves, where the intensity is about 20 times weaker than at the maximum, does the jump of the polarization coefficient occur. The value of the polarization coefficient on the plateau decreases with increasing dislocation density. The decrease of dislocation density from 10^5 to 10^4 mm^{-2} results in a gradual degeneration of the plateau in the angular dependence of the polarization coefficient. When the dislocation density is lower than 10^4 mm^{-2} , the curve of the angular dependence of P_R (Fig. 3) gradually approaches the curve corresponding to the perfect crystal.

Mathieson, Calvert & Killean (1974), while studying the polarization ratio of the graphite-crystal monochromator, observed a plateau in the angular dependence of the polarization coefficient for the Bragg reflection 0002. The crystal investigated by them seems to be highly defective as its rocking curve is rather wide.

Thus a comparison of the experimental and theoretical data on the angular dependence of the polarization coefficient for radiation diffracted by a real crystal leads to the following conclusion. In describing X-ray diffraction in real crystals the mosaic crystal

model appears to make physical sense when the dislocation density (N_d) is higher than 10^4 mm^{-2} . With $N_d > 10^5 \text{ mm}^{-2}$ the structure mosaic is such that the separate domains of the crystal scatter X-rays independently, *i.e.* secondary extinction is practically absent

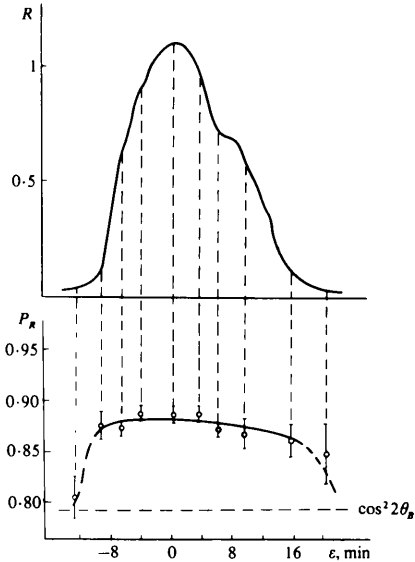


Fig. 2. The angular dependence of the polarization coefficient P_R and the rocking curve R for the reflection 111 of Ge with dislocation density $3 \times 10^5 \text{ mm}^{-2}$.

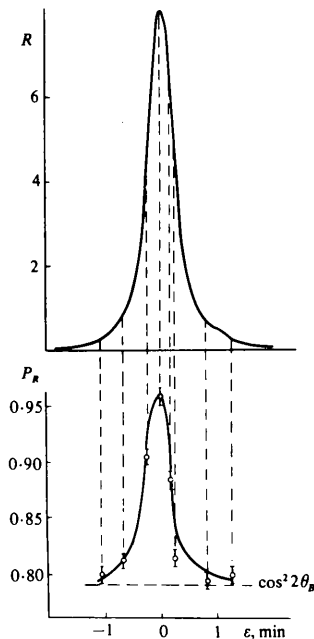


Fig. 3. Angular dependence of the polarization coefficient P_R and the rocking curve R for the reflection 111 of Ge with dislocation density $1.2 \times 10^3 \text{ mm}^{-2}$.

and the scattering mechanism is described by the primary extinction effect in individual blocks. When the dislocation density is less than 10^5 mm^{-2} some coherent relation appears between the individual domains of the crystals in the process of X-ray scattering. If N_d decreases below 10^4 mm^{-2} this coherent relation becomes so essential that some crystal domains lose their individuality in X-ray scattering.

Primary extinction for such crystals obviously depends on path lengths (until now extinction dependence on path length was considered to be due to secondary extinction).

Let us consider the extinction correction for mosaic crystals with a small coherent relation between the individual domains in them. Extinction for imperfect crystals, the diffraction in which could not be described in terms of the mosaic model, will be considered elsewhere.

4. The extinction factor for mosaic crystals

As follows from the analysis of the above-mentioned experimental data on the angular dependence of the polarization coefficient, X-ray scattering in mosaic crystals is practically concerned with the primary extinction effect in individual blocks. The primary extinction for a perfect crystallite can be calculated on the basis of the solution of the Takagi-Taupin equations. The solution of these equations for finite crystals in the forms of a cylinder and a parallelepiped (Oleknovich & Oleknovich, 1978, 1980) showed that the primary extinction factor for a crystal block is determined by its average size (τ) in the diffraction plane expressed in extinction length units:

$$\tau = \frac{r r_0 \lambda |F| C}{V} \quad (5)$$

Here r is the geometrical size of the block, $V/r_0 \lambda |F| C$ the extinction length, V the unit-cell volume, r_0 the classical electron radius, λ the wavelength, F the structure factor, and $C = 1$ or $\cos 2\theta$.

If the above is taken into account, then for the applicability limits of the mosaic model it is sufficient to consider the case when τ does not exceed 1.5. Within this range of τ change, the primary extinction factor of the crystal blocks does not depend on the Bragg angle and can be accurately estimated by the following expression:

$$y = \frac{\exp(-\tau_0^2/4) + C^2 \exp(-\tau_0^2 C^2/4)}{1 + C^2} \quad (6)$$

When the monochromator is used the extinction factor is given as:

$$y = \frac{\exp(-\tau_0^2/4) + k_M C^2 \exp(-\tau_0^2 C^2/4)}{1 + k_M C^2} \quad (7)$$

where k_M is the polarization ratio for the crystal monochromator used, $\tau_\sigma = rr_0 \lambda |F|/V$.

This approach to extinction estimation appears to be valid for an analysis of the measured structure factors in many cases of X-ray crystallography, since here small crystal samples with a rather high dislocation density are used (high dislocation density is generated in the process of cutting or polishing). The value of the block size found in correcting for the extinction of experimental X-ray data will characterize the mean distance between dislocations. However, if the dislocation density is within the range of values in which the domains of the crystal are not completely independent as regards scattering ($N_d < 10^5 \text{ mm}^{-2}$), then one can find an effective block size which varies slightly with X-ray wavelength. This variation is because the increasing wavelength comes to have an increasing coherent relation between the domains in a crystal.

The possibilities of the approach described above and its physical validity were tested on a number of LiF and NaF experimental data sets which will be briefly analysed below.

5. Sodium fluoride

Howard & Jones (1977) carried out a precise measurement of the structure factors (F_o^2) for NaF on a single crystal $0.096 \times 0.074 \times 0.076 \text{ mm}$ using Ag $K\alpha$, Mo $K\alpha$, Cu $K\alpha$ and Co $K\alpha$ radiations. Their comparison of the F_o^2 values with the calculated structure factors (F_c^2) showed that integrated intensities of strong reflections are affected by extinction, depending on the wavelength. The data obtained at four wavelengths by Howard & Jones (1977) were reanalysed by Cooper (1979) using both the Cooper–Rouse and the Becker–Coppens extinction formalisms in order to study the wavelength dependence of extinction in NaF. Cooper concluded that the wavelength dependence of the integrated intensity can be accounted for on the basis of the secondary extinction effects, taking the crystal to be intermediate between type I and type II according to the Zachariasen classification.

We carried out an analysis of the experimental data of Howard & Jones on the basis of our primary

extinction approach to mosaic crystals described above. The only fit parameter to be refined was the effective size of the crystal domain r related to the extinction factor by (6). The value of the extinction parameter r was determined by the least-squares method by minimizing the value used by Cooper:

$$S = \sum_i w_i (I_{oi} - I_{ci})^2. \quad (8)$$

Here Cooper's notation is used:

$$I_o = \overline{F_o^2} \text{ cosec } 2\theta_B, \quad (9)$$

$$I_c = sy |F_c|^2 \text{ cosec } 2\theta_B, \quad (10)$$

where s is the scale factor, and y the extinction factor, which has the form given by (6).

The calculation of the structure factors $|F_c|^2$ was carried out using the atomic scattering factors of the AM2 model (Aikala & Mansikka, 1972) and the value of the temperature factor determined by Cooper ($B = B_F = B_{Na} = 0.915 \text{ \AA}^2$).

The level of agreement between the measured and calculated intensities was estimated by the value of the weighted discrepancy index according to Cooper

$$R_w = \frac{\sum_i w_i |I_{oi} - I_{ci}|}{\sum_i w_i I_{oi}}. \quad (11)$$

The analysis of the experimental data for each wavelength was made independently and the size of the effective domain was found.

Table 1 gives the results of the analysis performed with our primary extinction approach and the results obtained by Cooper (1979) using the Cooper–Rouse (C–R) and Becker–Coppens (B–C) secondary extinction formalisms.

As can be seen from Table 1, our primary extinction approach and the C–R, B–C formalisms give close values for the weighted discrepancy index. The effective domain sizes obtained using the primary extinction approach and the C–R, B–C formalisms have a different order of values.

The effective domain size found from the primary extinction approach decreases slightly with the increase

Table 1. Results of the analysis of the NaF experimental data obtained by Howard & Jones

	Ag $K\alpha$	Mo $K\alpha$	Cu $K\alpha$	Co $K\alpha$	Extinction Formalism
λ (Å)	0.56	0.71	1.54	1.79	
$r \times 10^3$ (mm)	5.5 ± 0.3	5.6 ± 0.3	5.0 ± 0.2	5.1 ± 0.3	
R_w (%)	1.14	1.28	0.83	0.94	Present work
τ_{200}	0.49	0.65	1.16	1.34	
$r \times 10^4$ (mm)	1.00	1.00	1.00	1.00	Cooper (C–R)
R_w (%)	1.18	1.30	1.06	0.93	
$r \times 10^4$ (mm)	2.3	2.3	2.3	2.3	Cooper (B–C)
R_w (%)	1.18	1.29	1.55	0.59	

of the wavelength. This is because the dislocation density ($N_d = 3.2 \times 10^4 \text{ mm}^{-2}$) estimated in terms of the effective domain size lies in the range of values at which there is some coherent relation between the individual crystal ranges, increasing with the wavelength. However, the coherent relation effect between domains for the dislocation density obtained is rather small as r_{Cu} is close to r_{Mo} . The values of the effective domain size obtained are smaller than 1.5 of the extinction length of the strongest 200 reflection for all wavelengths used (τ_{200} , Table 1), and thus are in the applicability range of the relations (6, 7). The relation between τ_{200} and r follows from (5): $\tau_{200} = rr_0 \lambda |F_{200}| / V$.

The extinction effect in NaF was investigated by Sharma (1974). As a result of the analysis of the structure factors measured from a spherical crystal of approximate radius 0.10 mm with Mo $K\alpha$ radiation and the Zachariasen formalism Sharma came to the conclusion that 'the Zachariasen theory of extinction is physically meaningless' since the value of the block size $(5.6 \pm 0.4) \times 10^{-5} \text{ mm}$ obtained by him does not agree with the dislocation density (10^4 mm^{-2}). We reanalysed the structure factors measured by Sharma on the basis of the primary extinction approach. The structure factors F_c were calculated using atomic scattering factors of the AM2 model (Aikala & Mansikka, 1972) and taking into account dispersion corrections (Cromer & Liberman, 1970). The parameters to be refined were the temperature factors B_{Na} and B_F and the domain radius r . To determine temperature and scale factors the 200, 220, 400, 420, 440, 442 and 600 reflections were excluded from the least-squares refinement. The size of the effective domain r was determined by minimizing the value used by Sharma:

$$\sum_i (F_{oi}^2 - y |F_{ci}|^2)^2. \quad (12)$$

The level of agreement between the calculated and experimental data was determined by the value of the discrepancy index

$$R_2 = \frac{\sum_i |F_{oi}^2 - y |F_{ci}|^2|}{\sum_i F_{oi}^2}. \quad (13)$$

The y value in (12) and (13) was related to r by (6). The results of the analysis are given in Table 2.

Table 2. Results of the analysis of the NaF structure factor measured by Sharma

	Present work	Sharma
$B_{Na} (\text{\AA}^2)$	0.853	0.860
$B_F (\text{\AA}^2)$	0.866	0.880
$R_2 (\%)$	2.2	—
$r (\text{mm})$	$(7.9 \pm 0.3) \times 10^{-3}$	$(5.6 \pm 0.4) \times 10^{-5}$
τ_{200}	0.89	—

Our temperature factors and those of Sharma are close to each other, but they are less than the value obtained by Cooper (1979). This is because the structure factors measured by Sharma were not corrected for thermal diffuse scattering. Application of the primary extinction approach developed above for the analysis of the experimental data is found to give better agreement between the observed and calculated structure factors than that of the Zachariasen formalism. The dislocation density estimated using the value obtained for the effective domain size is $1.6 \times 10^4 \text{ mm}^{-2}$ and agrees with the measured value given by Sharma. The effective domain size in the crystal investigated does not exceed the extinction length for the 200 reflection ($\tau_{200} = 0.89$).

6. Lithium fluoride

The extinction effects in lithium fluoride have been studied by many investigators. Zachariasen (1967) measured the structure factors for LiF from a sphere of radius 0.299 mm, using Mo $K\alpha$ and Cu $K\alpha$ radiations, and carried out the extinction analysis on the basis of the theory developed by him. Killean, Lawrence & Sharma (1972) (KLS hereafter) repeated measurements of F_o for LiF to test the results obtained by Zachariasen. They showed that the mean radius of the mosaic domains is physically unreal. The Zachariasen experimental data were reanalysed by Cooper & Rouse (1976) on the basis of the C-R and B-C formalisms, and the KLS data were analysed by Becker & Coppens (1974a,b) in terms of primary extinction.

We carried out an analysis of the experimental structure factors measured by Zachariasen, as well as those by KLS, using only the above-mentioned primary-extinction approach. The structure factors were calculated both for NaF and LiF using the AM2 model (Aikala & Mansikka, 1972), taking into account dispersion corrections (Cromer & Liberman, 1970). The temperature factors were determined by least-squares refinement using the F_o factors set for Mo $K\alpha$ radiation, excluding the 200, 220, 222, 400, 420, 422, 440, 111, 311 reflections. Then, minimizing

$$\sum_i w_i (F_{oi}^2 - sy |F_{ci}|^2)^2, \quad (14)$$

the scale factor and the effective domain size of the mosaic blocks were found for both wavelengths. The level of agreement between the calculated and experimental structure factors was determined by the value of the weighted discrepancy index,

$$R_{2w} = \frac{\sum_i w_i |F_{oi}^2 - y |F_{ci}|^2|}{\sum_i w_i F_{oi}^2}. \quad (15)$$

Table 3. *Results of the analysis of the LiF data measured by KLS*

	Present work		KLS, formalism Z	Becker & Coppens formalism B-C
	Mo $K\alpha$	Cu $K\alpha$		
B_{Li} (\AA^2)	1.01	1.01	0.96	0.912
B_F (\AA^2)	0.69	0.69	0.66	0.538
R_{2w} (%)	1.6	1.6	—	2.7
$r \times 10^3$ (mm)	(7.1 ± 0.3)	(3.8 ± 0.2)	0.015	1.9
τ_{200}	0.80	0.88	—	—

Table 4. *Results of the analysis of the LiF data measured by Zachariassen*

	Cooper-Rouse					
	Present work		Formalism C-R		Formalism B-C	
	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	Cu $K\alpha$
B_{Li} (\AA^2)	1.06	1.06	1.07	1.07	1.08	1.08
B_F (\AA^2)	0.69	0.69	0.72	0.72	0.73	0.73
R_{2w} (%)	1.4	2.3	1.37	1.75	1.36	3.24
$r \times 10^3$ (mm)	(10.0 ± 1.8)	(6.0 ± 0.9)	0.044	0.037	0.14	0.058
τ_{200}	1.13	1.38	—	—	—	—

The results of the analysis of the structure factors measured by KLS and Zachariassen are given in Tables 3 and 4 respectively.

The parameters of the analyses obtained by the above-mentioned authors are also given in the tables for comparison.

As can be seen from the tables, the R_{2w} values obtained on the basis of the primary extinction approach are close to the values derived from the C-R formalism, but are slightly less than those given by the B-C formalism. It should be noted that the standard deviation for the effective domain size r , calculated using the Zachariassen data, is 15–18% of the value determined, and in the case of the KLS data it is about 5%. This difference in the accuracy of the r determination is because the Zachariassen structure factors were measured with larger standard deviations.

Unlike other formalisms, the primary extinction approach gives physically real values of the effective domain size, correlating with dislocation density. However, it should be noted that the effective domain size obtained in the case of the LiF crystal for Cu $K\alpha$ radiation is considerably smaller than that for Mo $K\alpha$ radiation, though $\tau_{200} < 1.5$. This difference indicated that in the crystal under study there is an appreciable coherent relation between domains in the scattering process. In fact, the dislocation density in the given crystals is about 10^4 mm^{-2} (Sharma, 1974), below which the mosaic crystal model is inappropriate. The primary extinction refinement of Zachariassen's measurements on LiF made by Cooper & Rouse

(1976) gave domain sizes, which are of the same order as that from our refinement.

Conclusion

Analysis of a number of NaF and LiF experimental data sets shows that the new primary extinction approach given in § 4 allows the integrated intensity, measured on crystals with a dislocation density (higher than 10^4 mm^{-2}) for which the applicability condition of the mosaic crystal model is satisfied, to be accounted for. The effective domain size determined by this approach for a mosaic crystal has a real physical sense and, consequently, the dislocation density can be estimated using the extinction factor. The analyses of the NaF and LiF data were performed in terms of an isotropic extinction factor, *i.e.* the anisotropy of extinction in the crystal investigated, as pointed out by the authors, was negligible. However, in the general case the extinction effect is anisotropic, *i.e.* it depends on two sizes of domain in the scattering plane. The anisotropic factor of the primary extinction can be calculated by the solution of the Takagi-Taupin equations for finite crystals of the given form. If the dislocation density is less than 10^5 mm^{-2} the partial coherent relation between the domains in the scattering is revealed in some change with wavelength of the effective domain size. It will probably result in a primary extinction change of path lengths of the whole crystal.

The primary extinction approach considered can be used for the analysis of the diffraction data, measured on polycrystals, if the dislocation density in a crystal grain satisfies the applicability condition of the mosaic model.

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References

- AIKALA, O. & MANSIKKA, K. (1972). *Phys. Kondens. Mater.* **14**, 105–110.
- BECKER, P. (1977). *Acta Cryst.* **A33**, 243–249.
- BECKER, P. J. & COPPENS, P. (1974a). *Acta Cryst.* **A30**, 129–147.
- BECKER, P. & COPPENS, P. (1974b). *Acta Cryst.* **A30**, 148–153.
- BECKER, P. & COPPENS, P. (1975). *Acta Cryst.* **A31**, 417–425.
- COOPER, M. J. (1979). *Acta Cryst.* **A35**, 176–180.
- COOPER, M. J. & ROUSE, K. D. (1970). *Acta Cryst.* **A26**, 214–223.
- COOPER, M. J. & ROUSE, K. D. (1976). *Acta Cryst.* **A32**, 806–812.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- DARWIN, C. C. (1914). *Philos. Mag.* **27**, 315–340.
- DENNE, W. A. (1972). *Acta Cryst.* **A28**, 192–201.
- HOWARD, C. J. & JONES, R. D. G. (1977). *Acta Cryst.* **A33**, 776–783.
- KATO, N. (1976). *Acta Cryst.* **A32**, 453–466.
- KILLEAN, R. C. G., LAWRENCE, J. L. & SHARMA, V. C. (1972). *Acta Cryst.* **A28**, 405–407.
- LAWRENCE, J. L. (1972). *Acta Cryst.* **A28**, 400–404.
- LAWRENCE, J. L. (1973). *Acta Cryst.* **A29**, 208–210.
- LAWRENCE, J. L. (1974). *Acta Cryst.* **A30**, 454–455.
- LAWRENCE, J. L. (1977). *Acta Cryst.* **A33**, 232–234.
- MATHIESON, A. MCL., CALVERT, L. D. & KILLEAN, R. C. G. (1974). *Annual Report (1973–1974)*, pp. 24–26. Division of Chemical Physics, CSIRO, Clayton, Australia.
- MICHELL, D., SMITH, A. P. & SABINE, T. M. (1969). *Acta Cryst.* **B25**, 2458–2460.
- OLEKHNOVICH, N. M. (1978). *Dokl. Akad. Nauk B. SSR*, **22**, 506–509.
- OLEKHNOVICH, N. M., KARPEI, A. L. & MARKOVICH, V. L. (1978). *Krist. Tech.* **13**, 1463–1469.
- OLEKHNOVICH, N. M. & MARKOVICH, V. L. (1978). *Kristallografiya*, **23**, 658–661.
- OLEKHNOVICH, N. M. & OLEKHNOVICH, A. I. (1978). *Acta Cryst.* **A34**, 321–326.
- OLEKHNOVICH, N. M. & OLEKHNOVICH, A. I. (1980). *Acta Cryst.* **A36**, 22–27.
- OLEKHNOVICH, N. M., RUBCOV, V. A. & SCHMIDT, M. P. (1975). *Kristallografiya*, **20**, 796–802.
- OLEKHNOVICH, N. M. & SCHMIDT, M. P. (1977). *Isv. Akad. Nauk B. SSR, Fiz. Mat. Nauk*, **1**, 118–122.
- SHARMA, V. C. (1974). *Acta Cryst.* **A30**, 278–280.
- TAKAGI, S. (1969). *J. Phys. Soc. Jpn.* **26**, 1239–1253.
- WERNER, A. S. (1969). *Acta Cryst.* **A25**, 639.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.
- ZACHARIASEN, W. H. (1968a). *Acta Cryst.* **A24**, 212–216.
- ZACHARIASEN, W. H. (1968b). *Acta Cryst.* **A24**, 324–325.

Acta Cryst. (1980). **A36**, 996–1001

Anomalous Dispersion of Small-Angle Scattering of Horse-Spleen Ferritin at the Iron K Absorption Edge

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Abstract

Small-angle scattering experiments of horse-spleen ferritin solutions have been performed at various wavelengths near the K absorption edge of iron, using synchrotron radiation from the storage ring DORIS. The anomalous dispersion of the atomic form factor f as described by f' and if'' has been monitored by the

dependence of the radius of gyration R and the absorption coefficient μ respectively. There is a 4% increase of R at the absorption edge. The relative full half width of this peak of 0.0016 corresponding to 11 eV of the energy scale reflects the drastic variation of f' by 7 electrons. The predictable relation between R and μ has been verified by the Kramers–Kronig relation. As small-angle scattering is primarily influenced by f' , best