References

ABRAHAMS, S. C., ALEXANDER, L. E., FURNAS, T. C., HAMILTON, W. C., LADELL, J., OKAYA, Y., YOUNG, R. A. & ZALKIN, A. (1967). *Acta Cryst.* **22**, 1.

BATTERMAN, B. W., CHIPMAN, D. R. & DEMARCO, J. J. (1961). *Phys. Rev.* **122**, 68.

COCHRAN, W. (1969). *Acta Cryst.* A**25**, 95.

COOPER, M. J. (1970). *Thermal Neutron Diffraction*. Ed. B. T. M. WILLIS. Oxford University Press.

COOPER, M. J. & PANKE, D. (1970). *Acta. Cryst.* A**26**. In the press.

COOPER, M. J. & ROUSE, K. D. (1968). *Acta Cryst.* A**24**, 405.

COOPER, M. J. & ROUSE, K. D. (1970*a*). To be published.

COOPER, M. J. & ROUSE, K. D. (1970*b*). *Acta Cryst.* A**26**, 214.

COOPER, M. J., ROUSE, K. D. & WILLIS, B. T. M. (1968). *Acta Cryst.* A**24**, 484.

COPPENS, P. (1968). *Acta Cryst.* A**24**, 253.

DAWSON, B., HURLEY, A. C. & MASLEN, V. W. (1967). *Proc. Roy. Soc.* A**298**, 289.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

MACKENZIE, J. K. & MASLEN, V. W. (1968). *Acta Cryst.* A**24**, 628.

POWELL, M. J. D. (1965). *Computer J.* **7**, 303.

ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558.

ZACHARIASEN, W. H. (1968*a*). *Acta Cryst.* A**24**, 425.

ZACHARIASEN, W. H. (1968*b*). *Acta Cryst.* A**24**, 421.

ZACHARIASEN, W. H. (1969). *Acta Cryst.* A**25**, 276.

Acta Cryst. (1970). A**26**, 214

Extinction in X-ray and Neutron Diffraction

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Accurate neutron-diffraction measurements from crystals suffering from severe extinction have been used to test the recent general theory of extinction of Zachariasen (*Acta Cryst.* (1967). **23**, 558). Analysis of these measurements indicates that certain of the approximations made in the theory are not generally valid and result in systematic deviations between theory and experiment, namely a marked angle-dependent effect and an inadequacy of the theory for strong extinction. The original theory is therefore extended to take these factors into account and to give agreement with the observed data.

Introduction

Theoretical formulae for the Bragg intensities of diffracted X-rays or neutrons have been derived rigorously only in the limiting cases of an ideally perfect crystal (the dynamical theory) and an ideally imperfect crystal (the kinematical theory). In general a given crystal will lie somewhere between these two extreme cases and modification of the kinematical theory is necessary to take into account the degree of perfection of the crystal. The treatment is normally based on the mosaic model for which the crystal is assumed to consist of a number of small perfect crystal domains, each slightly misoriented with respect to its neighbours.

Zachariasen (1967) has recently described a general theory of X-ray diffraction in crystals, based on an approximate treatment of the coupling between incident and diffracted beams. In this theory he derives a general formula for the intensity diffracted by a finite perfect crystal and hence the intensity diffracted by a finite mosaic crystal. Because of the complexity of the problem a number of approximations are introduced and the ultimate test of this theory is therefore, as Zachariasen states, a test of its agreement with experiment. Zachariasen himself has carried out a number of experimental tests using X-ray diffraction data (see Zachariasen, 1968*a*, *b*, *c*, 1969) and has obtained excellent agreement for the crystals studied: lithium fluoride, quartz, phenakite, hambergite and calcium fluoride. In addition, other experimental X-ray diffraction tests have provided good agreement with the theory (see *e.g.* Chandrasekhar, Ramaseshan & Singh, 1969).

The Zachariasen formulae have also been applied to accurate neutron diffraction measurements on several crystals. These include barium fluoride (Cooper, Rouse & Willis, 1968) and strontium fluoride and calcium fluoride (Cooper & Rouse, 1970). For barium fluoride only limited strongly extinguished data were collected but the theory held up to a level of extinction of about 16 per cent in intensity (at $\lambda = 1{\cdot}038$ Å). For calcium fluoride complete two-dimensional *hkk* data were collected initially at a wavelength of 0·877 Å and a preliminary analysis gave a value of r^* [see equations (16)] comparable to that obtained by Zachariasen (1968*b*). However, once again the theory did not correct the strongest intensities adequately and so a more extensive study was undertaken. Complete two-dimensional neu-

tron *hkk* data were collected from two crystals in which the extinction is quite severe, a sphere of strontium fluoride of diameter 3 mm and a cylinder of calcium fluoride of diameter 3 mm and length 7 mm. Measurements were made at three wavelengths in each case, in order to provide a more stringent test of the theory. However, one set of data for strontium fluoride showed anomalous background effects and was therefore not used in the extinction analysis; these effects will be discussed elsewhere (Cooper & Rouse, 1970).

Analysis of these neutron measurements indicated that certain of the approximations made in the theory are not generally valid, although the resultant discrepancies are not generally so large for X-ray diffraction measurements. However, the limitations of the theory are indicated, to some extent, by an analysis of recent X-ray diffraction measurements on single crystals of calcium fluoride (see Cooper, 1970). It is the purpose of this paper, therefore, to demonstrate the shortcomings of the Zachariasen theory and to extend it to account for the observed neutron diffraction measurements.

Zachariasen theory

In order to form a basis for our development the relevant parts of the Zachariasen theory are outlined below.

(*a*) *Small perfect crystal*

If I_0 and I are the intensities of the incident and diffracted beams respectively, then the fundamental equations which these quantities must satisfy are

$$\frac{\partial I_0}{\partial t_1} = -\sigma I_0 + \sigma I \qquad (1a)$$

$$\frac{\partial I}{\partial t_2} = -\sigma I + \sigma I_0 , \qquad (1b)$$

where t_1 and t_2 represent the depth below the crystal surface measured along the two propagation directions (see Zachariasen, 1967, Fig. 1) and σ is the diffracting power.

A function $\varphi(\sigma)$ is introduced such that the total power of the diffracted beam $P(\varepsilon_1)$ is

$$P(\varepsilon_1) = \int \frac{\partial I}{\partial t_2} \, \mathrm{d}v = \mathscr{I}_0 v \sigma \varphi(\sigma) , \qquad (2)$$

where ε_1 is the direction of the incident beam, $\mathscr{I}_0$ is the incident intensity and v is the irradiated crystal volume.

The extinction factor y, the ratio of the diffracted integrated intensity to that calculated on the kinematical theory, is then

$$y = Q^{-1} \int \sigma \varphi(\sigma) \mathrm{d}\varepsilon_1 , \qquad (3)$$

where Q is the well known crystallographic quantity, which for X-rays is

$$Q = \left| \frac{e^2 FK}{mc^2 V} \right|^2 \lambda^3 \operatorname{cosec} 2\theta , \qquad (4)$$

where F is the structure factor, K is the polarization factor and the other symbols have their usual meaning.

Power series solution of equations (1) can be obtained for a perfect crystal of any shape totally immersed in the incident beam and the result for $\partial I/\partial t_2$ is

$$\frac{\partial I}{\partial t_2} = \sigma \mathscr{I}_0 \sum_n \frac{(-\sigma)^n}{n!} t^{(n)} \qquad (5a)$$

$$t^{(n)} = \sum_j \binom{n}{j} t_1^{n-j} t_2^j . \qquad (5b)$$

For a crystal of arbitrary shape

$$\varphi(\sigma) = \sum_n \frac{(-\sigma)^n}{n!} \overline{t^{(n)}} \qquad (6a)$$

where

$$\overline{t^{(n)}} = v^{-1} \int t^{(n)} dv \qquad (6b)$$

Zachariasen gives the formulae for $\varphi(\sigma)$ for a sphere for small scattering angles as

$$\varphi(\sigma) = 1 - \sigma \bar{t} + \tfrac{16}{15}(\sigma \bar{t})^2 - \tfrac{80}{81}(\sigma \bar{t})^3 + \ldots \qquad (7a)$$

and for the backward scattering direction as

$$\varphi(\sigma) = 1 - \sigma \bar{t} + \tfrac{64}{45}(\sigma \bar{t})^2 - \ldots \qquad (7b)$$

with $\bar{t} = \frac{3}{2}r$, where r is the radius of the sphere.

He then assumes that it is normally true that $\sigma \bar{t} \ll 1$ at large scattering angles and that the following equation is a good approximation for $\varphi(\sigma)$ at any scattering angle when $\sigma \bar{t}$ is small:

$$\varphi(\sigma) = \frac{1}{1 + \sigma \bar{t}} . \qquad (8)$$

Expressions similar to equation (7*a*) are also given for various other crystal shapes and it is concluded that equation (8) is, in general, a reasonable approximation for any crystal shape.

In order to derive a simple expression for y from this equation an approximate form for the scattering power is used, *viz.*

$$\sigma(\varepsilon_1) \simeq \frac{\frac{4}{3}Q\alpha}{1 + \left(\frac{4\pi}{3} \alpha \varepsilon_1\right)^2} \qquad (9)$$

with $\alpha = t_\perp/\lambda$ and $t_\perp$ the mean thickness of the crystal normal to the incident beam.

Equations (3), (8) and (9) then give

$$y = (1 + 2x)^{-1/2} \qquad (10)$$

with

$$x = \tfrac{2}{3} Q \alpha \bar{t} . \qquad (11)$$

Because of the approximations involved in equations (8) and (9) two other closed forms for y are sug-

gested, *viz.* $\tanh \sqrt{3x}/\sqrt{3x}$ and $\tan^{-1} \sqrt{3x}/\sqrt{3x}$. These cannot be distinguished from equation (10) for small x but do differ significantly for $x \gg 1$.

(*b*) *Real crystal*

It is assumed that a real crystal consists of a large number of small perfect domains whose misalignment obeys an isotropic Gaussian distribution law, *i.e.*

$$W(\Delta) = \sqrt{2}g \exp(-2\pi g^2 \Delta^2) \qquad (12)$$

where Δ measures the angular deviation from the mean orientation.

The analysis of § (*a*) is then repeated replacing σ by $\bar{\sigma}$, the mean diffracting power of the whole crystal, t_1 and t_2 by T_1 and T_2, the corresponding paths in the whole crystal, and α by α', where

$$\alpha' = \alpha/\sqrt{1+(2\alpha/3g)^2}\,. \qquad (13)$$

Equation (11) is then replaced by

$$x = \tfrac{2}{3} Q\alpha' \bar{T}\,. \qquad (14)$$

If $\bar{t}$ is not negligible compared with $\bar{T}$ we must write

$$x = \tfrac{2}{3} Q\alpha[\bar{t} + (\bar{T}-\bar{t})/\sqrt{1+(2\alpha/3g)^2}]\,. \qquad (15)$$

However, in the present paper we shall assume that $\bar{t} \ll \bar{T}$ and that we can use equation (14). We shall also ignore absorption and polarization effects, both of which are detailed in Zachariasen's paper.

Experimental test of the Zachariasen theory

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:

$$F_c^2 = F_k^2 y \qquad (16a)$$

$$y = (1+2x)^{-1/2} \qquad (16b)$$

$$x = r^* Q \lambda^{-1} \bar{T} \qquad (16c)$$

$$r^* = r/[1+(r/\lambda g)^2]^{1/2} \qquad (16d)$$

where F_c is the calculated extinguished structure factor, F_k is the theoretical kinematical structure factor and r is the domain radius.

For the neutron diffraction experiments on calcium fluoride and strontium fluoride $\bar{T}$ is a constant for all measured reflexions and we can therefore write

$$x = CF_k^2 \operatorname{cosec} 2\theta \qquad (17)$$

where C is a constant, proportional to r^*, and it is then convenient to consider $1/y$ as a function of F_k^2 cosec 2θ.

The experimental intensities were corrected for thermal diffuse scattering using the isotropic approximation (Cooper & Rouse, 1968) and the observed structure factors, averaged over equivalent reflexions, were compared with those calculated according to equations (16) and (17), adjusting C and the scale factor

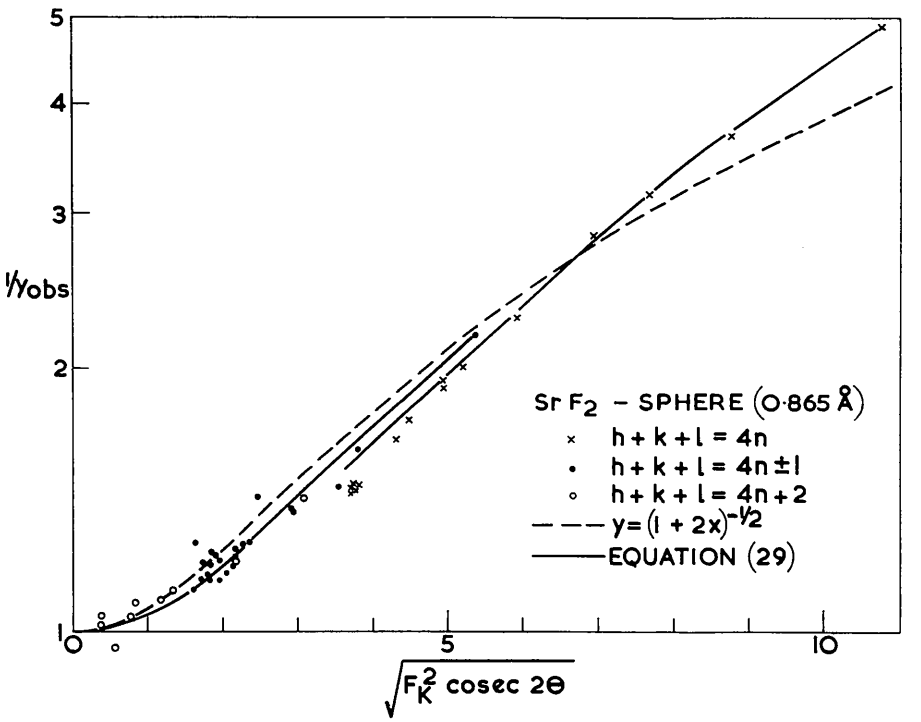

Fig. 1. $1/y_{obs}$ as a function of $\sqrt{F_k^2 \operatorname{cosec} 2\theta}$ for strontium fluoride at $\lambda = 0{\cdot}865$ Å. The broken curve represents the function for $1/y$ predicted by the Zachariasen theory such that agreement with experiment is obtained for the $4N$ data near $\theta = 45°$. The solid curves are the functions predicted by equation (29).

to give agreement over the less severely extinguished reflexions. These reflexions were used to refine the values of the thermal parameters and a consistent set of data was obtained for each crystal with the values for different wavelengths on approximately the same scale. Fixed values of the scattering lengths were used for calcium ($0{\cdot}488\times10^{-12}$ cm) and fluorine ($0{\cdot}560\times10^{-12}$ cm). That for strontium, which has been less well established, was refined giving a final value of $0{\cdot}690\ (\pm0{\cdot}012)\times10^{-12}$ cm, in excellent agreement with the value of $0{\cdot}683\ (\pm0{\cdot}007)\times10^{-12}$ cm obtained recently by Loopstra & Rietveld (1969). The final thermal parameters were $B_{Sr}=0{\cdot}546$ and $B_F=0{\cdot}820$ Å^2 for strontium fluoride and $B_{Ca}=0{\cdot}330$ and $B_F=0{\cdot}505$ Å^2 for calcium fluoride. Further analyses with various values of the thermal parameters showed that the expressions derived for the extinction are independent of these parameters. This will be discussed in more detail elsewhere (Cooper & Rouse, 1970). The values of C and the range of values of y obtained from this preliminary analysis are given in Table 1. These figures indicate the severity of the extinction: for the calcium fluoride crystal all reflexions were at least 25% extinguished and the strongest were almost 90% extinguished.

Table 1. *Preliminary extinction parameters for neutron diffraction data from* CaF_2 *and* SrF_2

	λ	C	y_{min}	y_{max}
	0·877 Å	0·444	0·11	0·75
CaF_2	1·077	0·625	0·11	0·71
	1·339	0·789	0·11	0·72
	0·746	0·052	0·23	0·99
SrF_2	0·865	0·068	0·21	0·99
	1·077	0·148	0·15	0·99

Systematic deviations from the Zachariasen theory were observed in each set of data, as can be seen from Figs. 1 and 2 where $1/y$ is plotted as a function of $\sqrt{F_k^2}\ \mathrm{cosec}\ 2\theta$ for one set of data from each crystal. A marked angle dependent effect is observed, particularly in the calcium fluoride data (Fig. 2). For the

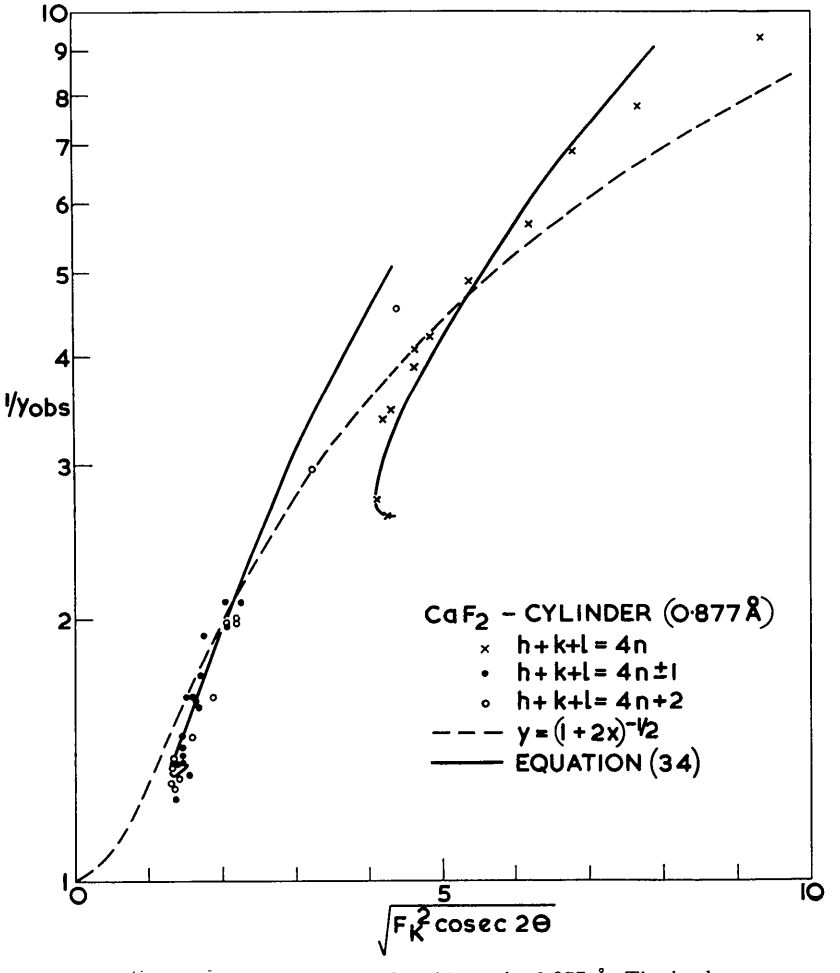

Fig. 2. $1/y_{obs}$ as a function of $\sqrt{F_k^2}\ \mathrm{cosec}\ 2\theta$ for calcium fluoride at $\lambda=0{\cdot}877$ Å. The broken curve represents the function for $1/y$ predicted by the Zachariasen theory such that agreement with experiment is obtained for the $4N$ data near $\theta=45°$. The solid curves are the functions predicted by equation (34).

fluorite structure the reflexions can be separated into three groups depending on the index sum $(h+k+l)$ and there is then a direct correlation between angle and intensity for reflexions within a particular group. Deviation from the Zachariasen theory occurs at the higher angle (lower intensity) end of each group. In addition a further deviation from the theory also occurs for the very strong reflexions.

It was thus concluded from this analysis that there are two major shortcomings of the Zachariasen theory; it does not provide for any angle dependence in the magnitude of the extinction as a function of intensity and it is not adequate for severe extinction ($x \gg 1$). These shortcomings arise from some of the approximations introduced into the theory and in the following sections we shall show how they can be overcome to account for the observed neutron data.

Extension of the theory

(*a*) *Angle dependence*

Comparison of equations (*7a*) and (*7b*) indicates that unless $\sigma\bar{t} \ll 1$ the expression for $\varphi(\sigma)$ may have a significant angle dependence. This will be particularly important for neutron data since scattering lengths are essentially independent of angle so that strong reflexion of neutrons can occur over the entire range of angle. On the other hand the rapid decrease in the X-ray scattering factors tends to restrict the strongest X-ray reflexions to small scattering angles so that any angle dependence will be less apparent. This is illustrated in Fig. 3, which shows $1/y$ as a function of θ for the calcium fluoride crystals used in the X-ray and neutron experiments (see Cooper, 1970, and Table 5).

Calculation of $\overline{t^{(n)}}$ from equations (*5b*) and (*6b*) for a spherical domain and various values of the scattering angle θ lead to expressions which decrease with increasing θ, giving for $\theta = 90°$:

$$\varphi(\sigma) = 1 - \sigma\bar{t} + \tfrac{32}{45}(\sigma\bar{t})^2 + \ldots . \qquad (18)$$

This is clearly in contradiction with equation (*7b*), and with the observed experimental data, which indicate that $\varphi(\sigma)$ should increase with increasing θ. However, it would appear that this is due to the fact that equation (*5b*) is only valid for $\theta = 0$ and in general we should consider the functions

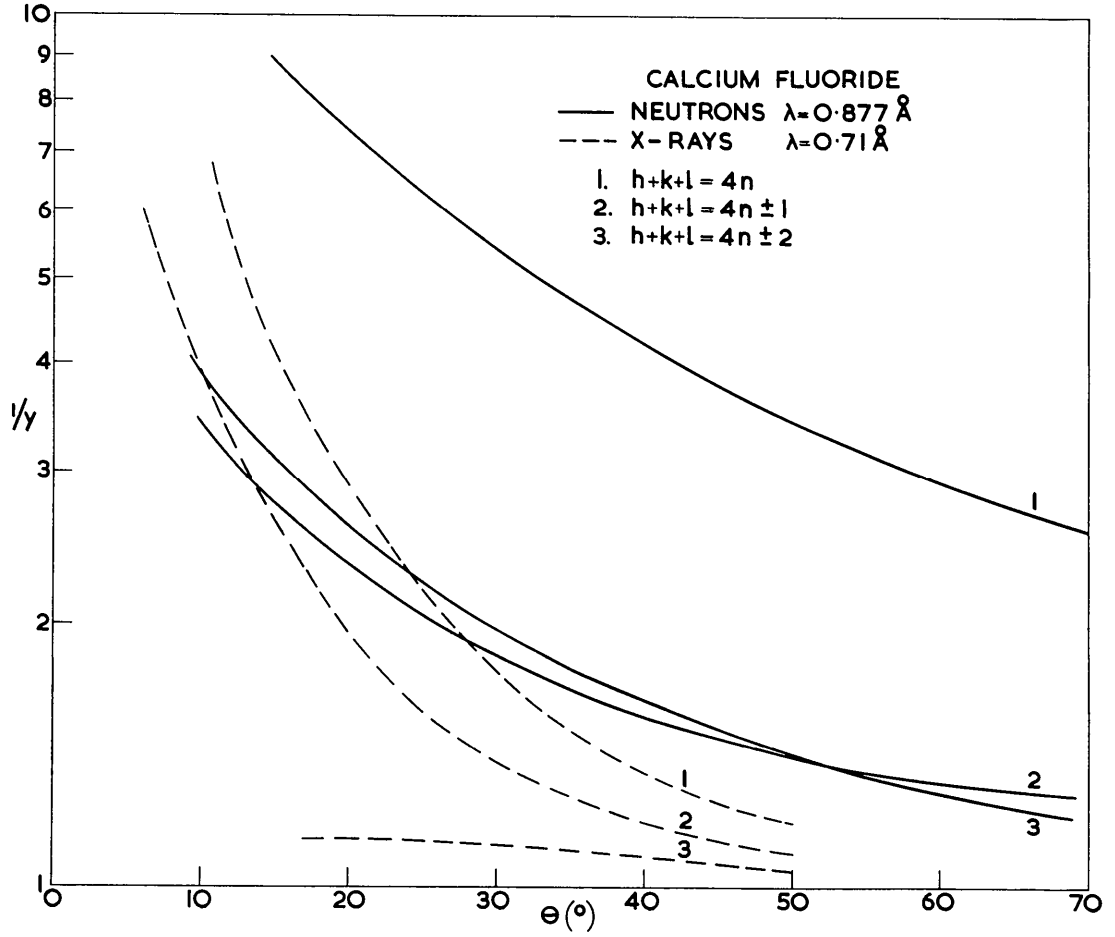

Fig. 3. $1/y_{obs}$ as a function of the scattering angle θ for neutrons ($\lambda = 0{\cdot}877$ Å) and for X-rays ($\lambda = 0{\cdot}71$ Å) for the crystals of calcium fluoride used in the two sets of experiments.

$$\overline{t^n} = v^{-1} \int (t_1 + t_2')^n \, dv \qquad (19)$$

(see Zachariasen, 1965) where t_2' is the path length of the diffracted beam from the point of diffraction to the emergent surface. Equations (5*b*) and (19) are equivalent for $\theta = 0$.

In order to determine the angle dependence of $\varphi(\sigma)$ we have calculated $\overline{t^n}$ for $n = 1$ to 10 and for $\theta = 0$ to 90° in steps of 10°. To a first approximation, for $\sigma\bar{t}$ not too large, we can consider $t^n(\theta)$ in the following form:

$$\overline{t^n}(\theta) = \overline{t^n}(0)\,[f_n(\theta)] \qquad (20a)$$

with

$$f_n(\theta) \simeq [f(\theta)]^{n-1} \quad \text{for } n > 1 \qquad (20b)$$

$$f_0(\theta) = f_1(\theta) = 1 \qquad (20c)$$

and

$$f(\theta) = f_2(\theta) \simeq 1 + \tfrac{1}{3} \sin^{2\cdot5} \theta \, . \qquad (20d)$$

The function $f(\theta)$ is given in Table 2 together with the corresponding values of $1 + \frac{1}{3} \sin^{2\cdot5} \theta$. For convenience we have used the latter function in our analyses. Equation (20*b*) underestimates $f_n(\theta)$ increasingly for large n but is likely to be a valid approximation unless $\sigma\bar{t}$ is very large at large θ.

Table 2. *Values of $f(\theta)$ and $1 + \frac{1}{3} \sin^{2\cdot5}\theta$ for various values of θ*

θ	$f(\theta)$	$1 + \frac{1}{3} \sin^{2\cdot5} \theta$
0°	1·0000	1·0000
10	1·0068	1·0042
20	1·0254	1·0228
30	1·0636	1·0589
40	1·1124	1·1104
50	1·1703	1·1712
60	1·2302	1·2326
70	1·2832	1·2853
80	1·3200	1·3208
90	1·3333	1·3333

We shall therefore take as a reasonable approximation:

$$\varphi(\sigma) = 1 - \sigma\bar{t} + \tfrac{16}{15}(\sigma\bar{t})^2 f(\theta) - \tfrac{80}{81}(\sigma\bar{t})^3 [f(\theta)]^2 + \tfrac{15}{19}(\sigma\bar{t})^4 [f(\theta)]^3 - \tfrac{5}{9}(\sigma\bar{t})^5 [f(\theta)]^4 + \tfrac{21}{61}(\sigma\bar{t})^6 [f(\theta)]^5 - \ldots \qquad (21)$$

corresponding to equation (7*a*) for $\theta = 0$.

If we assume, as in the derivation of equation (10*a*) from equation (7*a*), that $\sigma\bar{t}$ is small, then equation (21) gives

$$y' = \left[1 - \frac{1}{f(\theta)}\right] + \frac{1}{f(\theta)} [1 + 2x \, . \, f(\theta)]^{-1/2} \, . \qquad (22)$$

This equation should therefore be used instead of equation (10*a*) and may be expected to be valid for $x < 1$.

Extension of this theory to the case of a real crystal is given, as before, by using the expression for x as given by equation (14) or equation (15).

(*b*) *Severe extinction*

The expression for y given by Zachariasen has been derived by approximating the infinite series expression for $\varphi(\sigma)$ by a closed form. This approximation is only valid for small $\sigma\bar{t} (< 1)$ and hence the wrong form of y is predicted for large x, as shown by the experimental measurements.

If we retain the expression for $\sigma(\varepsilon_1)$ in the form given for a parallelepiped, *viz.*

$$\sigma(\varepsilon_1) = Q\alpha \, \frac{\sin^2 \pi\alpha\varepsilon_1}{(\pi\alpha\varepsilon_1)^2} \, , \qquad (23)$$

we can retain $\varphi(\sigma)$ in its series form and evaluate the corresponding series form for y from equation (3), integrating term by term. This requires the evaluation of integrals of the form

$$S_n = \frac{1}{\pi} \int_{-\infty}^{\infty} \left(\frac{\sin X}{X} \right)^n dX \qquad (24)$$

and we have therefore determined values of S_n for $n = 1$ to 20, as listed in Table 3 (values for n odd are included for completeness).

Table 3. *Values of* $S_n = \frac{1}{\pi} \int_{-\infty}^{\infty} \left(\frac{\sin X}{X} \right)^n dX$

n	S_n
1	1·000000
2	1·000000
3	0·750000
4	0·666667
5	0·598958
6	0·550000
7	0·511024
8	0·479365
9	0·452921
10	0·430418
11	0·410963
12	0·393926
13	0·378844
14	0·365371
15	0·353239
16	0·342240
17	0·332208
18	0·323009
19	0·314534
20	0·306693

The resultant series for y is

$$y = 1 - x + \tfrac{4}{3}x^2 - \tfrac{8}{5}x^3 + \tfrac{12}{7}x^4 - \tfrac{5}{3}x^5 + \tfrac{10}{7}x^6 - \ldots \qquad (25)$$

and the final problem is then to determine a closed form approximation which can be used over a reasonably large range of x.

Zachariasen has suggested the three forms:

$$y = \tanh \sqrt{3x} / \sqrt{3x} = 1 - x + \tfrac{6}{5}x^2 - \tfrac{51}{35}x^3 + \ldots \qquad (26a)$$

$$y = (1 + 2x)^{-1/2} \quad = 1 - x + \tfrac{3}{2}x^2 - \tfrac{5}{2}x^3 + \ldots \qquad (26b)$$

$$y = \tan^{-1} \sqrt{3x} / \sqrt{3x} = 1 - x + \tfrac{9}{5}x^2 - \tfrac{27}{7}x^3 + \ldots \qquad (26c)$$

These functions cannot be distinguished when x is small but differ appreciably when $x \gg 1$. For example, the values for $x=10$, quoted by Zachariasen, are $y=0{\cdot}183$, $0{\cdot}218$ and $0{\cdot}254$ for equations (26*a*), (26*b*) and (26*c*) respectively.

In order to allow for the angle dependence, discussed in (*a*) above, we must replace x in equations (26) by $x \,.\, f(\theta)$ and, as in equation (22), replace y by y', where

$$y' = \left[1 - \frac{1}{f(\theta)}\right] + \frac{1}{f(\theta)}\, y \,. \qquad (27)$$

Values of y'_{calc} from equations (26) and (27) were compared with values of $y_{\text{obs}} = F_0^2/F_k^2$ for the neutron data and although good agreement could be obtained for $x < 1$ all these functions deviated from the observed values for large x. A number of other functions can

Table 4. *Values of* $1/y_{\text{obs}}$, $1/y'_{\text{calc}}$, $1/y_{\text{Zach}}$ *and* $f(\theta)$ *for strontium fluoride*

	$\lambda = 0{\cdot}865$ Å				$\lambda = 1{\cdot}077$ Å			
$h\ k\ l$	$1/y_{\text{obs}}$	$1/y'_{\text{calc}}$	$1/y_{\text{Zach}}$	$f(\theta)$	$1/y_{\text{obs}}$	$1/y'_{\text{calc}}$	$1/y_{\text{Zach}}$	$f(\theta)$
0 2 2	4·866	4·777	3·644	1·007	6·955	–	5·241	1·016
4 0 0	3·660	3·651	3·025	1·016	5·199	5·308	4·338	1·028
4 2 2	3·146	3·093	2·693	1·027	4·510	4·375	3·859	1·047
0 4 4	2·813	2·738	2·468	1·039	3·986	3·794	3·541	1·067
4 4 4	2·277	2·295	2·167	1·064	3·198	3·097	3·130	1·111
8 0 0	2·002	2·023	1·967	1·092	2·862	2·702	2·884	1·159
8 2 2	1·930	1·923	1·890	1·106	2·703	2·570	2·807	1·184
0 6 6	1·897	1·923	1·890	1·106	2·666	2·570	2·807	1·184
4 6 6	1·748	1·770	1·767	1·136	2·440	2·406	2·750	1·236
8 4 4	1·653	1·711	1·717	1·152	2·427	2·379	2·796	1·263
0 8 8	1·465	1·558	1·588	1·218				
8 6 6	1·469	1·538	1·573	1·235				
12 0 0	1·455	1·527	1·567	1·253				
4 8 8	1·445	1·527	1·567	1·253				
12 2 2	1·449	1·527	1·574	1·270				
1 1 1	2·174	2·198	2·011	1·002	3·059	3·147	2·739	1·003
3 1 1	1·616	1·644	1·589	1·010	2·116	2·183	2·075	1·018
1 3 3	1·453	1·551	1·524	1·020	1·868	1·891	1·853	1·035
5 1 1	1·376	1·387	1·376	1·031	1·732	1·739	1·732	1·054
3 3 3	1·361	1·393	1·381	1·031	1·715	1·750	1·742	1·054
5 3 3	1·421	1·283	1·282	1·056	1·578	1·561	1·582	1·096
7 1 1	1·268	1·257	1·259	1·069	1·555	1·524	1·551	1·119
1 5 5	1·261	1·254	1·255	1·069	1·530	1·517	1·544	1·119
3 5 5	1·251	1·239	1·242	1·083	1·519	1·500	1·533	1·143
7 3 3	1·243	1·217	1·221	1·097	1·489	1·457	1·507	1·168
5 5 5	1·142	1·183	1·188	1·112	1·401	1·410	1·457	1·193
9 1 1	1·207	1·179	1·184	1·127	1·445	1·419	1·476	1·219
9 3 3	1·153	1·153	1·159	1·158	1·405	1·443	1·508	1·273
1 7 7	1·191	1·155	1·161	1·158	1·415	1·448	1·515	1·273
7 5 5	1·220	1·170	1·176	1·158	1·476	1·484	1·558	1·273
3 7 7	1·223	1·159	1·166	1·174	1·478	1·555	1·656	1·301
11 1 1	1·147	1·139	1·146	1·207				
5 7 7	1·258	1·125	1·131	1·207				
9 5 5	1·113	1·124	1·130	1·224				
11 3 3	1·193	1·139	1·147	1·242				
7 7 7	1·145	1·153	1·162	1·259				
1 9 9	1·157	1·150	1·160	1·295				
13 1 1	1·170	1·190	1·204	1·313				
11 5 5	1·221	1·209	1·224	1·313				
3 9 9	1·197	1·207	1·222	1·313				
2 0 0	1·416	1·433	1·412	1·003	1·759	1·814	1·768	1·005
2 2 2	1·208	1·226	1·225	1·011	1·458	1·435	1·444	1·020
6 0 0	0·917	1·088	1·091	1·045	1·246	1·181	1·197	1·077
2 4 4	1·122	1·088	1·091	1·045	1·295	1·181	1·197	1·077
6 2 2	1·089	1·069	1·072	1·057	1·239	1·146	1·161	1·099
6 4 4	1·082	1·036	1·037	1·099	1·150	1·084	1·095	1·171
2 6 6	1·043	1·029	1·030	1·114	1·121	1·120	1·081	1·197
10 0 0	0·753	–	1·016	–	1·025	1·054	1·061	1·277
10 2 2	0·961	–	1·013	–	0·982	1·059	1·067	1·305
6 6 6	0·543	–	1·013	–	0·974	1·059	1·067	1·305
10 4 4	1·015	1·007	1·007	1·226				
2 8 8	1·049	1·007	1·007	1·226				
R^* (%)		2·68	6·35			2·22	6·55	

* $R = \Sigma|1/y_{\text{obs}} - 1/y'_{\text{calc}}|/\Sigma 1/y_{\text{obs}}$ or $\Sigma|1/y_{\text{obs}} - 1/y_{\text{Zach}}|/\Sigma 1/y_{\text{obs}}$.

be considered which are similar for small x but tend to different values at large x, such as

$$y' = \left[1 - \frac{1}{f(\theta)}\right] + \frac{1}{f(\theta)} \left[\frac{\sinh^{-1}\sqrt{\frac{3}{2}x \,.\, f(\theta)}}{\sqrt{\frac{3}{2}x \,.\, f(\theta)\,[1+\frac{3}{2}x \,.\, f(\theta)]}}\right], \quad (28a)$$

$$y' = \left[1 - \frac{1}{f(\theta)}\right] + \frac{1}{f(\theta)} \left[\left(\frac{3}{2x \,.\, f(\theta)}\right)^2 \times \left\{\sinh^{-1}\left(\tfrac{1}{2}\sqrt{\frac{3}{2x \,.\, f(\theta)}}\right) - \ln \sqrt{\frac{3}{2x \,.\, f(\theta)}}\right\}\right]. \quad (28b)$$

In the above theory we have considered firstly a spherical domain and then extended this to a real crystal by replacing t by $\bar{T}$. The theory is therefore valid for a spherical real crystal, but may require modification for a crystal of any other shape. We shall therefore consider the two cases for which we have experimental data, a spherical crystal and a cylindrical crystal, separately.

(*i*) *Spherical crystal*

A least-squares fitting was carried out on the groups of $1/y_{obs}$ values, varying the scale factor and the value of C [equation (17)] at each wavelength, for the various functions of $1/y'_{calc}$ as given from equations (26) and (28). No single function gave a satisfactory fit and combinations of the various functions were therefore used. The final expression adopted to provide a good fit for the strontium fluoride data is:

Table 5. *Values of* $1/y_{obs}$, $1/y'_{calc}$, $1/y_{Zach}$ *and* $f(\theta)$ *for calcium fluoride*

	$\lambda = 0{\cdot}877$ Å				$\lambda = 1{\cdot}077$ Å			
h k l	$1/y_{obs}$	$1/y'_{calc}$	$1/y_{Zach}$	$f(\theta)$	$1/y_{obs}$	$1/y'_{calc}$	$1/y_{Zach}$	$f(\theta)$
0 2 2	10·111	–	8·037	1·008	9·818	–	7·444	1·014
4 0 0	8·493	9·392	6·628	1·019	8·247	8·237	6·192	1·033
4 2 2	7·526	7·634	5·875	1·032	7·334	6·599	5·541	1·054
0 4 4	6·180	6·508	5·368	1·046	6·077	5·584	5·119	1·077
4 4 4	5·358	5·114	4·690	1·077	5·193	4·382	4·601	1·128
8 0 0	4·614	4·278	4·242	1·110	4·583	3·712	4·348	1·184
8 2 2	4·472	3·975	4·072	1·128	4·286	3·491	4·314	1·213
0 6 6	4·262	3·975	4·072	1·128	4·108	3·491	4·314	1·213
4 6 6	3·795	3·518	3·812	1·164				
8 4 4	3·710	3·344	3·718	1·183				
0 8 8	2·998	2·927	3·634	1·262				
8 6 6	2·863	2·895	3·756	1·283				
1 1 1	4·003	4·476	3·303	1·002	4·080	4·117	3·066	1·004
3 1 1	2·988	2·930	2·455	1·012	2·982	2·700	2·308	1·020
1 3 3	2·287	2·431	2·165	1·024	2·291	2·262	2·056	1·040
5 1 1	2·298	2·166	2·004	1·038	2·254	2·039	1·922	1·063
3 3 3	2·155	2·185	2·017	1·038	2·166	2·056	1·934	1·063
5 3 3	2·093	1·850	1·795	1·067	1·944	1·787	1·759	1·112
7 1 1	1·887	1·779	1·748	1·083	1·827	1·741	1·733	1·139
1 5 5	1·738	1·766	1·738	1·083	1·723	1·729	1·723	1·139
3 5 5	1·753	1·729	1·716	1·100	1·676	1·718	1·726	1·166
7 3 3	1·778	1·665	1·669	1·117	1·666	1·687	1·710	1·195
5 5 5	1·522	1·564	1·586	1·134	1·512	1·626	1·664	1·224
9 1 1	1·612	1·560	1·588	1·152	1·605	1·681	1·732	1·255
9 3 3	1·499	1·494	1·535	1·190				
1 7 7	1·491	1·501	1·542	1·190				
7 5 5	1·561	1·554	1·592	1·190				
3 7 7	1·495	1·532	1·576	1·210				
11 1 1	1·503	1·498	1·553	1·249				
5 7 7	1·506	1·444	1·498	1·249				
9 5 5	1·349	1·467	1·526	1·270				
11 3 3	1·452	1·584	1·654	1·290				
2 0 0	4·950	5·511	3·879	1·003	4·796	5·075	3·597	1·006
2 2 2	3·242	3·704	2·923	1·014	3·276	3·400	2·740	1·023
6 0 0	2·187	2·320	2·129	1·054	2·257	2·191	2·059	1·090
2 4 4	2·192	2·320	2·129	1·054	2·156	2·191	2·059	1·090
6 2 2	2·158	2·116	1·997	1·069	2·085	2·027	1·956	1·115
6 4 4	1·780	1·739	1·732	1·119	1·685	1·762	1·782	1·199
2 6 6	1·602	1·659	1·670	1·137	1·583	1·728	1·765	1·228
10 0 0	1·426	1·497	1·539	1·192				
10 2 2	1·506	1·464	1·511	1·212				
6 6 6	1·394	1·464	1·511	1·212				
10 4 4	1·483	1·427	1·484	1·272				
2 8 8	1·415	1·427	1·484	1·272				
R (%)		5·91	10·75			7·76	13·87	

$$y' = \left[1 - \frac{1}{f(\theta)}\right] + \frac{1}{5f(\theta)} \times \left[\frac{4\sinh^{-1}\sqrt{\frac{3}{2}x \cdot f(\theta)}}{\sqrt{\frac{3}{2}x \cdot f(\theta)}\,[1+\frac{3}{2}x \cdot f(\theta)]} + \frac{\tanh\sqrt{3x \cdot f(\theta)}}{\sqrt{3x \cdot f(\theta)}}\right] \quad (29)$$

The final values of $1/y_{obs}$ and $1/y'_{calc}$ are given in Table 4, together with the values of $f(\theta)$ and the values of $1/y_{Zach}$ calculated from equation (26*b*), fitted to $1/y_{obs}$ for the 511 reflexion. The inadequacy of the Zachariasen theory is readily apparent. The values of $1/y'_{calc}$ given by equation (29) for the 0·865 Å data are also shown in Fig. 1. Data collected at 0·746 Å were not used in the final analysis because of the anomalous effects mentioned previously. The largest $1/y_{obs}$ value (6·955) at 1·077 Å was also omitted.

(ii) *Cylindrical crystal*

None of the functions given in equations (28) or (29) gave a satisfactory fit for the calcium fluoride data for large x and we must therefore reconsider the expressions for $\varphi(\sigma)$ and y appropriate to this crystal shape.

For a cylindrical crystal $\bar{T} = (16/3\pi)\,R$, where R is the radius and $\bar{T}$ is the mean path length in the plane perpendicular to the cylinder axis. The coefficients of the equations

$$\overline{T^n} = A_n R^n \quad (30)$$

will be different from those for a spherical crystal (see Zachariasen, 1965) and $\varphi(\sigma)$ then has the form:

$$\varphi(\sigma) = 1 - \sigma\bar{T} + \tfrac{2}{2}\tfrac{5}{4}(\sigma\bar{T})^2 f(\theta) - \tfrac{2}{2}\tfrac{5}{7}(\sigma\bar{T})^3[f(\theta)]^2 + \tfrac{4}{6}\tfrac{5}{4}(\sigma\bar{T})^4[f(\theta)]^3 - \tfrac{6}{1}\tfrac{5}{3}(\sigma\bar{T})^5[f(\theta)]^4 + \tfrac{1}{4}\tfrac{1}{1}(\sigma\bar{T})^6[f(\theta)]^5 - \ldots \quad (31)$$

resulting in a series for y (for $\bar{T} \gg \bar{t}$):

$$y = 1 - x + \tfrac{9}{7}x^2 f(\theta) - \tfrac{3}{2}x^3[f(\theta)]^2 + \tfrac{2}{1}\tfrac{3}{5}x^4[f(\theta)]^3 - \tfrac{1}{1}\tfrac{8}{3}x^5[f(\theta)]^4 + \tfrac{3}{3}\tfrac{9}{5}x^6[f(\theta)]^5 - \ldots \quad (32)$$

We would therefore expect a different closed form to be more suitable in this case and we have found that a reasonable closed-form approximation for equation (32), ignoring the angle dependence, is

$$y = \left[\frac{\sqrt{\pi}}{2}(\operatorname{erf}\sqrt{3x})/\sqrt{3x}\right]^{5/4}. \quad (33)$$

This approximation is valid for all x and the corresponding expression for y', *viz*:

$$y' = \left[1 - \frac{1}{f(\theta)}\right] + \frac{1}{f(\theta)} \times \left[\frac{\sqrt{\pi}}{2}[\operatorname{erf}\sqrt{3x \cdot f(\theta)}]/\sqrt{3x \cdot f(\theta)}\right]^{5/4}, \quad (34)$$

was found to give a better fit to the observed data than any other of the functions used.

Final values of $1/y_{obs}$ and $1/y'_{calc}$ are given in Table 5, together with the values of $f(\theta)$ and the values of $1/y_{Zach}$ calculated from equation (26*b*) fitted to $1/y_{obs}$ for the 155 reflexion. The inadequacy of the Zachariasen theory is again readily apparent. The values of $1/y'_{calc}$ given by equation (34) for the 0·877 Å data are also shown in Fig. 2. Because of the severity of the extinction and the limited amount of data collected at $\lambda = 1{\cdot}339$ Å, measurements at this wavelength were not included in the analysis. The 022 reflexion ($1/y \simeq 10$) was also omitted at the other wavelengths.

Discussion

It appears that the Zachariasen theory of extinction is reasonably adequate for a crystal of general shape for $x < 1$, that is for extinction up to a level of about 40% reduction in intensity ($y = 0{\cdot}6$). Above this value it underestimates the extinction and the neglect of the angle dependence becomes increasingly important. In addition the form of the extinction correction becomes increasingly dependent on the crystal shape.

The major problem in extending the theory for $x > 1$ is that both $\varphi(\sigma)$ and y can be determined as power series which can be approximated readily by closed forms only for $x < 1$. However, we may note that, although the coefficients of the power series for y initially increase, they then decrease with increasing power of x so that convergence is also obtained at large x. Nevertheless, because of this behaviour it is extremely difficult to determine a suitable closed form approximation.

A series of accurate neutron diffraction measurements has enabled us to find closed form expressions for y which account for the observed extinction in a spherical and a cylindrical crystal, up to levels of over 80% extinction in each case. These expressions are given in equations (29) and (34), and although we have considered only the case for which primary extinction can be neglected, the theory can readily be extended to take this into account also, by retaining the terms in $\bar{t}$ in equation (15) and considering spherical domains as before.

Extensions of the Zachariasen theory to an anisotropic treatment have been considered (see, *e.g.* Hamilton, 1969) in terms of an anisotropic Gaussian distribution of orientation and an ellipsoidal particle shape. Hamilton has found that in general this extension results in a significant improvement in the R factor, while the tensors in most cases refine to the correct symmetry even though this is not necessarily constrained. However, we should like to emphasize that the introduction of anisotropic extinction parameters should be treated with great care since they may correlate with other parameters of the system and other anisotropic effects may be misinterpreted. Moreover, anisotropic extinction can arise from variations in the state of perfection within the crystal, since when extinction is severe the intensity is very critically dependent on the domain size and orientation. This effect was readily apparent in the strongest intensities measured for cal-

cium fluoride at the longest wavelength (1·339 Å) which are given in Table 6. The standard deviations of these intensities calculated from counting statistics are 0·1 % and their true accuracy is estimated to be about 0·25 %. In spite of this high accuracy of measurement, which was confirmed by the reproducibility, large differences were observed between the intensities of equivalent reflexions; that between 044 and $0\bar{4}\bar{4}$ being as much as 8·6 %. Further measurements rejected non-uniformity of the beam as a possible cause and similar measurements on the strontium fluoride crystal gave excellent agreement between equivalents. These observations are therefore attributed to anisotropy in the extinction for the calcium fluoride crystal. However, since these differences occur between 180° related reflexions they must arise from variation in the perfection within the crystal and not from anisotropy of the domain shape. In order to overcome this effect one must therefore average the intensity over a suitable set of equivalent reflexions, as was done in the present analysis, and consider mean values for the domain radius and the mosaic spread parameter.

Table 6. *Neutron diffraction data for 4N reflexions from calcium fluoride at* $\lambda = 1{\cdot}339$ Å

$h\ k\ l$	Intensity	$(I-\bar{I})/\bar{I}$
0 2 2	251,964	+2·6%
$0\ \bar{2}\ \bar{2}$	239,378	−2·6%
4 0 0	202,006	−1·0%
$\bar{4}$ 0 0	206,155	+1·0%
4 2 2	184,138	0
$\bar{4}$ 2 2	190,903	+3·7%
$4\ \bar{2}\ \bar{2}$	179,637	−2·4%
$\bar{4}\ \bar{2}\ \bar{2}$	181,636	−1·3%

Table 6 (*cont.*)

$h\ k\ l$	Intensity	$(I-\bar{I})/\bar{I}$
0 4 4	199,922	+4·3%
$0\ \bar{4}\ \bar{4}$	183,570	−4·3%
4 4 4	239,224	0
$\bar{4}$ 4 4	245,883	+2·8%
$4\ \bar{4}\ \bar{4}$	232,935	−2·6%
$\bar{4}\ \bar{4}\ \bar{4}$	238,470	−0·3%

Finally, we should like to emphasize that although we have obtained good agreement between the theory and experiment it is likely that some further improvement could be made in the exact form of the closed-form expressions used. It is therefore desirable that further experimental tests of this theory be carried out.

References

CHANDRASEKHAR, S., RAMASESHAM, S. & SINGH, A. K. (1969). *Acta Cryst.* A**25**, 140.
COOPER, M. J. (1970). *Acta Cryst.* A**26**, 208.
COOPER, M. J. & ROUSE, K. D. (1968). *Acta Cryst.* A**24**, 405.
COOPER, M. J. & ROUSE, K. D. (1970). To be published.
COOPER, M. J., ROUSE, K. D. & WILLIS, B. T. M. (1968). *Acta Cryst.* A**24**, 484.
HAMILTON, W. C. (1969). *Acta Cryst.* A**25**, 102.
LOOPSTRA, B. O. & RIETVELD, H. M. (1969). *Acta Cryst.* B**25**, 787.
ZACHARIASEN, W. H. (1965). *Trans. Amer. Cryst. Ass.* **1**, 33.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558.
ZACHARIASEN, W. H. (1968*a*). *Acta Cryst.* A**24**, 425.
ZACHARIASEN, W. H. (1968*b*). *Acta Cryst.* A**24**, 324.
ZACHARIASEN, W. H. (1968*c*). *Acta Cryst.* A**24**, 212.
ZACHARIASEN, W. H. (1969). *Acta Cryst.* A**25**, 102.

Acta Cryst. (1970). A**26**, 223

Absolute Measurement of Structure Factors Using a New Dynamical Interference Effect

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A new method of determining X-ray scattering factors by dynamical interference is described. The theoretical background to the interference effect is discussed in detail and an expression for relating the fringe period to the structure factor is developed. The method relies on anomalous transmission and is therefore most suitable for measurements on nearly perfect crystals of high atomic weight. It also has the attractive property of being insensitive to slowly varying lattice strains. Applying the method to the 220 reflexion of silicon a value of $8{\cdot}487 \pm 0{\cdot}017$ for the atomic scattering factor has been obtained using Mo $K\alpha_1$ radiation. This value is in excellent agreement with the author's previous results using the Pendellösung method.

1. Introduction

In recent years several attempts have been made to improve the accuracy of absolute structure factor determinations with a view to comparing the results with the values predicted by the different theoretical scattering models. With adequately precise measurements the reduction of X-ray structure factors to atomic scat-