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Experimental Determination of the Extinction Factor by the use of Polarized X-Rays

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The problem of estimating the extinction factor by the use of polarized X-rays has been re-examined in the light of the theory of X-ray diffraction in real crystals developed recently by Zachariasen. Expressions are given for deriving the extinction-free structure factors in terms of the observed integrated intensities for perpendicular and parallel polarizations. A simple attachment to a diffractometer for analysing the polarization of the diffracted beam is described. Measurements on quartz are presented; the extinction-free structure factors so obtained are in excellent agreement with Zachariasen's calculated values based on new f curves.

Theory

The theory of X-ray diffraction in real crystals developed recently by Zachariasen (1967, 1968) provides a basis for evaluating large extinction effects to a greater precision than has been possible so far. According to the theory, the integrated intensity of reflexion from a symmetrically shaped crystal of volume v, assumed to consist of nearly spherical domains of radius r, is given by

$$P = P_k y \tag{1}$$

for unpolarized X-rays, where

$$P_k \text{ (the kinematical value)} = I_0 v A Q_0 \left(\frac{1+\cos^2 2\theta}{2}\right). \tag{2}$$

y (the extinction factor)

$$= \frac{(1+2x_0)^{-\frac{1}{2}} + \cos^2 2\theta (1+2x_0 \cos^2 2\theta)^{-\frac{1}{2}}}{1+\cos^2 2\theta}. \tag{3}$$

$$x_0 = Q_0 \lambda^{-1} T r^*, \tag{4}$$

$$Q_0 \lambda^{-1} = \left|\frac{e^2 \lambda F}{mc^2 V}\right|^2 \Big/ \sin 2\theta,$$

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

$$T = -\frac{1}{A}\frac{dA}{d\mu} = \frac{1}{A^*}\frac{dA}{d\mu}.$$

I_0 is the incident intensity, $A^* = A^{-1}$ the absorption factor, g the factor determining the disorientation of the perfect domains in the crystal, and the other symbols have their usual meanings. We shall show in this paper that the extinction factor can be determined experimentally by the use of polarized X-rays.

That the polarization factor of a reflexion depends critically on the state of perfection of the crystal was demonstrated experimentally for the first time by Ramaseshan & Ramachandran (1953, 1954). A method of applying a first order correction for extinction errors using polarized X-rays was developed by Chandrasekhar (1956, 1963). We reconsider this method in the light of Zachariasen's new formulae. For perpendicular polarization (1)–(4) give

$$P_\perp = P_{k\perp} y_\perp \tag{5}$$

where

$$P_{k\perp} = I_0 v A Q_0$$

and

$$y_\perp = (1+2x_0)^{-\frac{1}{2}}.$$

For parallel polarization

$$P_\parallel = P_{k\parallel} y_\parallel \tag{6}$$

where

$$P_{k\parallel} = P_{k\perp} \cos^2 2\theta$$

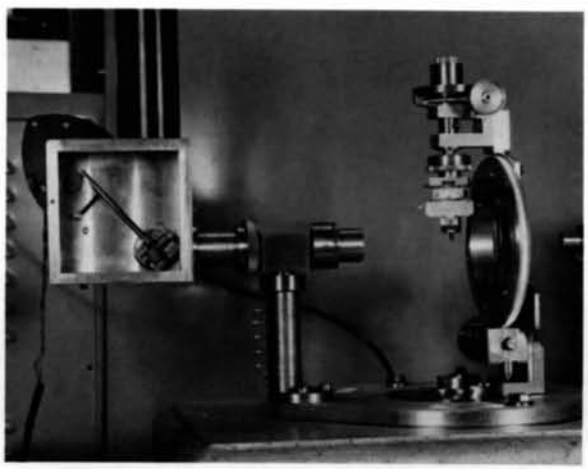
$$y_\parallel = (1+2x_0 \cos^2 2\theta)^{-\frac{1}{2}}.$$

From (5) and (6)

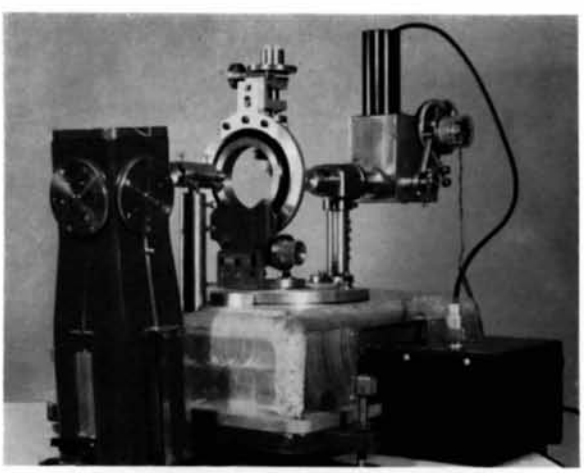
$$P_{k\perp}^2 = \frac{P_\perp^2 P_\parallel^2 (1-\cos^2 2\theta)}{P_\perp^2 \cos^4 2\theta - P_\parallel^2 \cos^2 2\theta} \tag{7}$$

and

$$x_0 = \tfrac{1}{2}[(P_{k\perp}/P_\perp)^2 - 1]. \tag{8}$$



(*a*)



(*b*)

Fig. 1. The analysing attachment to the diffractometer set to measure the parallel component. (*a*) The top lid has been removed to show the germanium crystal and cam arrangement. (*b*) Back view showing the motor drive.

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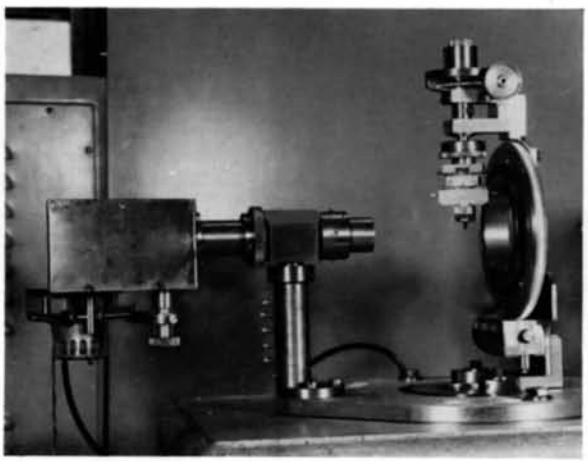
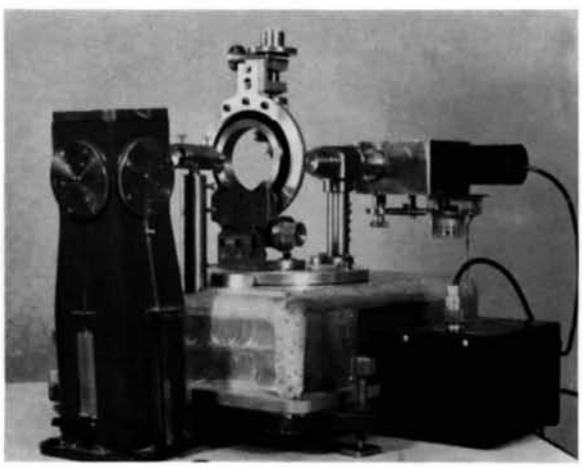


(*a*)



(*b*)

Fig. 2. The analysing attachment to the diffractometer, set to measure the perpendicular component.

A measurement of $P_\perp$ and $P_\parallel$ directly yields $P_{k_\perp}$ (or $|F|^2$) and x_0, provided θ is not too close to 0°, 45°, or 90°. Now, we observe from (4) that a plot of x_0/Q_0 *versus* T (for different reflexions) gives a straight line of slope $r^*\lambda^{-1}$ passing through the origin. This graph may be used to obtain the extinction-free structure factors for those reflexions for which (7) and (8) become ill-conditioned. The value of x_0/Q_0 corresponding to any T may be read off from the straight line and, assuming that the data are on an absolute scale, this gives $x_0/P_k=\alpha$, say. Substitution in (5) and simplification leads to the relation:

$$P_{k_\perp}=P_\perp[\alpha P+(\alpha^2P+1)^{-\frac{1}{2}}] \qquad (9)$$

from which $|F|^2$ may be evaluated.

The equations in their present form assume that r and g are isotropic, an assumption which may not be valid in all crystals. However in this paper we discuss only the isotropic case.

A polarization attachment to a diffractometer

In all previous experiments using polarized X-rays (Ramaseshan & Ramachandran, 1953, 1954; Chandrasekhar, 1960; Chandrasekhar & Phillips, 1961) the incident beam was polarized. However, exactly the same results could be obtained by using an incident unpolarized beam and analysing the polarization of the diffracted beam.† We have designed a simple attachment to a diffractometer for this purpose.

Figs. 1(*a*) and (*b*) show the unit mounted on the counter arm of the diffractometer, set to measure the parallel components of the integrated intensity. The diffracted beam enters a collimating system and gets reflected by a germanium crystal at $2\theta=90°4'$ into the counter. The germanium was a highly perfect crystal plate cut parallel to the (111) face and surface etched. The 333 reflexion ($2\theta=90°4'$ for Cu $K\alpha_1$) was used. The crystal was oscillated 120 times a minute over a range of about 2° by means of a cam [seen in Fig. 1(*a*)] driven by a synchronous motor. The specimen under investigation was oscillated at $\frac{1}{8}°$ per minute. Typically the width of the reflexion was about $\frac{1}{4}°$ and hence the germanium crystal oscillated about 240 times as the specimen swept once through the reflexion. The rate and range of oscillation of the germanium were found to be large enough to achieve integration of the diffracted beam, as will be seen from the data discussed in the next section.

Figs. 2(*a*) and (*b*) show the analyser turned through 90° about an axis collinear with the diffracted beam. At this setting it measures the perpendicular component of the integrated intensity.

† The advantage of using a monochromator (polarizer) between the specimen and the counter have been discussed by A. McL. Mathieson (1968) in a paper dealing with different types of monochromator settings for diffractometers. A similar arrangement has also been considered by Z. Barnea (private communication).

The X-ray set was a stabilized Philips unit (PW 1010); the input power supply was also stabilized so that the X-ray intensity was quite constant throughout the experiment.

Measurements on quartz

Measurements were made on quartz mainly to see whether the polarization method would lead to results similar to those arrived at by Zachariasen (1968) on the basis of his new formulae. A piece of quartz cut from a large, perfect, optically homogenous crystal was ground into a cylinder of radius $1{\cdot}81\times10^{-2}$ cm with its axis parallel to [010] (to within 10′ of arc). Table 1 gives the observed intensities *on an arbitrary scale* for perpendicular, parallel and 45° settings of the analyser. Each observed value represents the mean of 10 readings. Since

$$N_{45°}=N_\perp\cos^2 45°+N_\parallel\sin^2 45°=\tfrac{1}{2}(N_\perp+N_\parallel)$$

the agreement between the last two columns of the Table confirms that the germanium does integrate the diffracted beam in the desired manner.

Table 1. *Experimental data on quartz cylinder*

Cylinder axis [010]. Radius=0·181 mm.

hkl	$N_\perp$	$N_\parallel$	$\frac{1}{2}(N_\perp+N_\parallel)$	N_{45}
100	4440	4100	4270	4300
101	7550	6600	7075	7010
$10\bar{1}$	12300	10800	11500	11640
102	4170	2800	3485	3520
$10\bar{2}$	1240	770	1005	985
203	8800	1990	5395	5305
$20\bar{3}$	3550	600	2075	2125
$30\bar{1}$	7400	1510	4455	4390

Table 2. *Structure factors*

hkl	*y*	F_{obs} (Corrected)	F_c (Zachariasen, 1968)
100	0·5815	15·75 (18·72)	16·17
101	0·4421	26·01 (26·42)	26·19
$10\bar{1}$	0·3058	39·91 (35·75)	40·09
102	0·6863	17·76	17·76
$10\bar{2}$	0·8937	8·49	8·43
203	0·5399	31·43	30·95
$20\bar{3}$	0·7991	16·40	16·22
$30\bar{1}$	0·5964	27·37	27·18

Substitution of $N_\perp$ and $N_\parallel$ in (7) gives the extinction-free structure factors. These have been scaled appropriately and are shown in Table 2 along with Zachariasen's (1968) calculated values based on new scattering factors. The agreement is seen to be excellent for the given higher angle reflexions. For two of the lower angle reflexions (the values for which are shown in brackets in the Table)the agreement is not so good; this is not surprising since (7) is ill-conditioned for small θ and the uncertainties in F_0 may be expected to be correspondingly greater. More precise extinction corrections were evaluated for these reflexions in the manner outlined earlier (equation 9). Fig. 3 shows the

plot of x_0/Q_0 *versus* $T = RdA^*/A^*d(\mu R)$ where R is the radius of the cylinder. A^* and T were obtained from *International Tables for X-ray Crystallography* (1962). The points for the higher angle reflexions fall quite well on the theoretically expected straight line passing through the origin. The extinction-free structure factors deduced from the graph also agree closely with the F_c's. The excellent overall agreement is gratifying especially since the crystal is subject to severe extinction effects. For example the observed intensity for the $10\bar{1}$ reflexion is only about 30% of the kinematical value. In principle, the graph may be used to derive the extinction correction for all other reflexions from this specimen.

Table 3. *Structure factor ratios*

	Present experiment Uncorrected	Present experiment Corrected	Pendellösung data Yamamoto *et al.* (1968)
$\frac{F(101)}{F(10\bar{1})}$	0·7830	0·6518	0·6575
$\frac{F(102)}{F(10\bar{2})}$	1·834	2·091	2·029
$\frac{F(203)}{F(20\bar{3})}$	1·575	1·916	1·936

Table 3 gives the structure factor ratios obtained in the present experiment along with those due to Yamamoto, Homma & Kato (1968) from Pendellösung measurements. Again the values are most satisfactory.

The accuracy of the results indicates that although many simplifying assumptions have had to be made in Zachariasen's theory, his formulae for the real crystal are valid to a very good approximation in the isotropic case, and may be used for determining the extinction factor experimentally by the use of polarized X-rays.

We thank Mr N. Narayana Iyer and Mr R. V. Ramani of NAL for the construction of the four circle diffractometer and the oscillating analysing device, Mr C. Balasingh for the help he rendered in setting up the diffractometer, Mr M. S. Madhava and Mr R. Sashidhar for checking the calculations. We are also indebted to Dr A. Jayaraman (Bell Telephone Laboratory), Dr A. K. Ramdas (Purdue University) and Dr G. Sadasiv (RCA Research Laboratory) for sending us perfect crystals of germanium.

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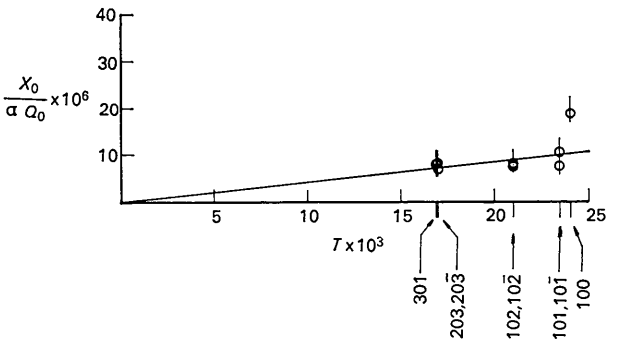

Fig. 3. Plot of x_0/Q_0 *versus* T.

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DISCUSSION

LADELL: The polarization factor for a perfect monochromator crystal should be $\frac{1}{2}(1 + |\cos 2\theta|)$, while for an ideally mosaic crystal it should be $\frac{1}{2}(1 + \cos^2 2\theta)$. In most cases the factor to be used should be between the two.

CHANDRASEKHAR: Yes.

ZACHARIASEN: In my equation it is impossible to get all r and g, except by using two different wavelengths, because r^* appears in the equations at this point if the domain radius is not negligible compared with the crystal radius.

CHANDRASEKHAR: The only assumption we made was that $t = 3r/2$, where t is the mean path-length within the domain and r is the domain radius.

MATHIESON: I can confirm that it is a considerable advantage to have the polarizing monochromator on the counter arm since the monochromator and counter move as one unit. (*Rev. Sci. Instrum.* 1968).

LANG: I want to make a general plea. In certain X-ray crystallographic studies, including some of the most recent ones, such as those presented at this conference, the plane which has long been recognized as structurally and morphologically the major rhombohedron is given the index of the minor rhombohedron. The history of this confusion, and a mnemonic for the correct orientation of the Miller–Bravais axes with respect to the structure has been published (A. R. Lang, '*The Orientation of the Miller–Bravais Axes of Alpha Quartz*', *Acta Cryst.* **19**, (1965), 290).

MEGAW: Dr Lang has asked that anyone working with quartz should use the original morphological axes, which were also those used by Bragg in his structure determination. I would like to support that, and also to point out that Wyckoff's use, in *Crystal Structures* is not only different but internally inconsistent. The description is of a right-handed crystal, the drawing (with the normal axial convention) of a left-handed one. Moreover, if low quartz has spacegroup $P3_12$, the high quartz produced by the transition is $P6_42$ not 6_22, which would involve a change of hand.