A Crystal Structure Refinement from Laue Photographs taken with Synchrotron Radiation

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Abstract

The crystal structure of α-AlPO$_4$ (berlinite; $P3_121$) has been refined from Laue photographs taken with synchrotron radiation at the SRS Daresbury Laboratory. The refinement led to an R factor of 0·19 for the integrated intensities (measured by microdensitometer) of 175 non-symmetry-equivalent Laue spots. The refinement program includes explicitly the overlapping diffraction orders and uses an experimentally determined instrument function to describe the incident-beam intensity and the film response as functions of wavelength. The values of the eight positional parameters obtained in this preliminary assessment of the Laue method are in good agreement with those previously determined by conventional single-crystal X-ray diffractometry (*e.g.* the mean Al–O and P–O bond lengths correspond to within 0·025 Å) suggesting that accurate structure refinements should be obtainable. By using the Laue method large amounts of data can be collected with exposures of only a few seconds. A number of applications for the technique are suggested.

1. Introduction

Although the Laue method formed the basis of the earliest crystal structure determinations, it is now generally considered unsuitable for structure solution and refinement. With conventional laboratory X-ray sources it does indeed seem to offer few advantages over monochromatic methods [see, for example, Amorós, Buerger & Amorós (1975, p. 119)], especially as the white radiation available from an X-ray tube is usually orders-of-magnitude weaker than the characteristic lines. With synchrotron sources, however, white-radiation methods offer considerable gains as they make efficient use of the whole spectrum of the incident radiation. Mainly for this reason, there has been a resurgence of interest in recent years in energy-dispersive X-ray diffraction with both single-crystal and powder specimens [see, for example, Laine & Lähteenmäki (1980) for a bibliography of the energy-dispersive method].

For single-crystal diffraction, however, the detectors required must have high spatial resolution as well as energy resolution and are thus complex and difficult to construct. We therefore decided to investigate the possibility of refining crystal structures from Laue photographs. Although X-ray film has effectively no energy resolution it still offers far better spatial resolution than other position-sensitive detectors. Provided that the space group of the crystal is known, the superposition of the diffraction orders in the data presents no fundamental problem for the refinement. In this paper we describe a preliminary refinement of the crystal structure of α-AlPO$_4$ (berlinite) from Laue photographs taken at the SRS at Daresbury Laboratory. The refined positional parameters are in good agreement with those determined by conventional single-crystal X-ray diffraction.

2. The intensity formula

Assuming an ideally imperfect mosaic crystal in the kinematical approximation the integrated intensity of a diffracted order in a Laue photograph is given by

$$I(hkl) = I_0(\lambda) \, V_c N_c^2 |F_c(hkl)|^2 \, \lambda^4 \, \text{Lp}, \qquad (1)$$

where V_c = crystal volume, N_c = number of unit cells per unit volume, $F_c(hkl)$ = structure factor and Lp = Lorentz and polarization factor [see, for example, Buras & Gerward (1975)]. Equation (1) refers to an ideal experiment. In practice, the formula

$$I(hkl) \propto I_0(\lambda) \, \lambda^4 \, \eta(\lambda) \, O(\lambda,\mathbf{r}) A_c(\lambda,\mathbf{r}) A_a(\lambda,\mathbf{r}) A_w(\lambda,\mathbf{r})$$

$$\times |F_c(hkl)|^2 \, \text{Lp}(\mathbf{r}) \qquad (2)$$

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applies, where η is the film response, A_c, A_a and A_w are the absorption of the crystal, the air and the film wrapping respectively, and O is the film obliquity factor. The notation $(\lambda,\mathbf{r})$ denotes a possible dependence on wavelength and diffracted-beam direction respectively. Equation (2) may be written as

$$I(hkl) \propto \chi(\lambda,\mathbf{r})\, O(\lambda,\mathbf{r})\, A_c(\lambda,\mathbf{r})\, |F_c(hkl)|^2\, \mathrm{Lp}(\mathbf{r}), \quad (3)$$

where $\chi(\lambda,\mathbf{r}) = I_o(\lambda)\,\lambda^4\,\eta(\lambda)\,A_a(\lambda,\mathbf{r})\,A_w(\lambda,\mathbf{r})$, is a function of the source and camera used. The intensity of a Laue spot may then be calculated from

$$I(\text{calc.}) = \sum_n I(nh,nk,nl),$$

where n denotes the order of the reflection.

3. Experimental details

All data were collected on CEA Reflex 15 single-coated film using a Pye–Unicam S25 oscillation camera, with a 3 cm radius cylindrical film holder. The SRS ran at an energy of 2·0 GeV throughout the experiment. The camera was placed at about 55 m from the source and aligned so that the film axis was vertical, *i.e.* perpendicular to the polarization direction of the incident X-rays.
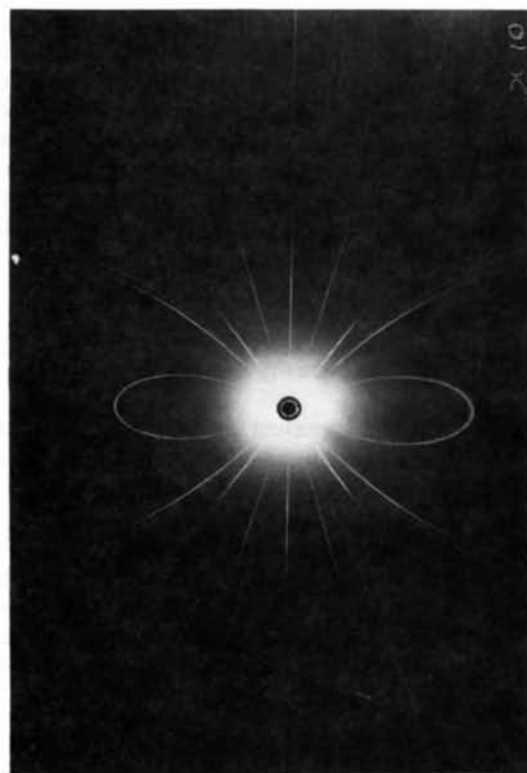
Fig. 1. Rotation photograph of a small silicon crystal taken on the SRS, running in single-bunch mode. Exposure 3 min.

3.1. *Determination of the instrument function*

The instrument function was determined from a white-radiation rotation photograph of a small (0·15 mm linear dimensions) single crystal of silicon set so as to rotate about [001]. With the SRS running in single-bunch mode with a beam current of ~3 mA a 3 min exposure was required. The resulting photograph is shown in Fig. 1. A densitometer trace of one of the 111 streaks, measured using the Joyce–Loebl MDM-6 flat-bed microdensitometer of the SERC Micro-densitometer Service (Daresbury Laboratory), is shown in Fig. 2. The data are corrected for Lorentz and polarization factors assuming a 100% horizontally polarized beam. The discontinuity of the trace at 0·92 Å is due to the bromine absorption edge in the AgBr emulsion. Also shown in Fig. 2 are empirical functions fitted by least squares to the data above and below this absorption edge. These take the form

$$i = 3014 - 9825\lambda + 8047\lambda^2$$

for $0\cdot62 < \lambda < 0\cdot91995$ Å, and

$$i = 1716 \sin(-4\cdot92 + 4\cdot63\lambda - 0\cdot36\lambda^2) + 1727$$

for $0\cdot91995 < \lambda < 2\cdot4$ Å.

We assume that the function $\chi(\lambda,\mathbf{r})$ is given by the above formula. This approximation ignores variations in the film obliquity (calculated to change by less than 3% along the streak). The third-order harmonic contamination is negligible below 2·0 Å (the maximum wavelength used) and there is no second order since $|F(222)_{Si}| = 0$. We have also assumed that the absorption of the two crystals (Si and AlPO$_4$) is sufficiently similar to allow the factor $A_c(\lambda,\mathbf{r})$ to be incorporated into the instrument function. For crystals of the size used, the ratio $e^{-\mu t}$ varies by about 25% over the range from 0·7 to 1·6 Å, which is acceptable for the
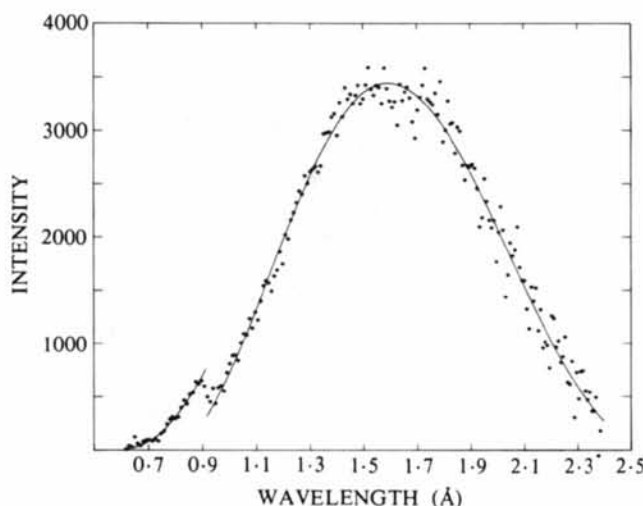
Fig. 2. Densitometer trace of a 111 streak from silicon. The full lines show fits of the data to empirical functions.

present preliminary study. In general, however, the function $\chi(\lambda,\mathbf{r})$ as determined above must be corrected for the factor $A_{\mathrm{Si}}(\lambda,\mathbf{r})$ and a separate sample absorption correction introduced into the calculation.

3.2. The film obliquity correction

Diffracted X-rays striking the film at oblique incidence produce an enhanced blackening because of their longer path lengths in the emulsion. For a cylindrical single-coated film with normal-beam geometry $O(\lambda,\mathbf{r})$ takes the form

$$O(\lambda,\mathbf{r}) = \{1 - \exp\left[-\mu(\lambda)\,t\,\sec\,v\right]\}/\{1 - \exp\left[-\mu(\lambda)\,t\right]\}$$

[see *International Tables for X-ray Crystallography* (1962, p. 140)] where $\mu(\lambda)$ and t are the absorption and thickness of the film emulsion and v is the angle between the diffracted beam and the equatorial plane. The effective thickness of the emulsion (assumed to be pure AgBr) was found by making a number of absorption measurements in the range $0\cdot5$ to $1\cdot0$ Å, giving a value of $0\cdot003$ g cm^{-3} for ρt (ρ = density). The value of μ/ρ was then computed as a function of wavelength using Victoreen's formula [*International Tables* (1962, p. 161)].

3.3. Data collection from AlPO₄

For convenience in indexing the pattern, the AlPO₄ crystal, of linear dimensions $0\cdot2$ mm, was set with [001] parallel to the axis of the film. Several sets of Laue photographs were taken and those with the incident beam parallel to [210] (*i.e.* parallel to the vertical mirror plane) were chosen for analysis. Three films were measured with exposures of 20, 10, and 2 s respectively (SRS operating at 2 GeV and approximately 200 mA). Single exposures were used rather than a film pack to eliminate the problem of differential absorption present if multiple-film methods are used. A Laue photograph similar to those used, but with an exposure of 30 s, is shown in Fig. 3. Integrated intensities were obtained using a Joyce–Loebl MDM-6 flat-bed microdensitometer. An area of $0\cdot5 \times 0\cdot5$ mm around each spot was integrated in 25 μm steps using a 25×25 μm aperture in the densitometer. An additional 'picture frame' of width $0\cdot1$ mm was scanned to determine the local background. The small size and sharpness of the Laue spots presents difficulties in densitometry and the procedure used – constant spot and raster size – will not lead to very accurate measurements. Use of a more sophisticated densitometer control program, especially if combined with oscillation or vibration of the crystal to increase the spot size, may well produce an improvement in the R factors.
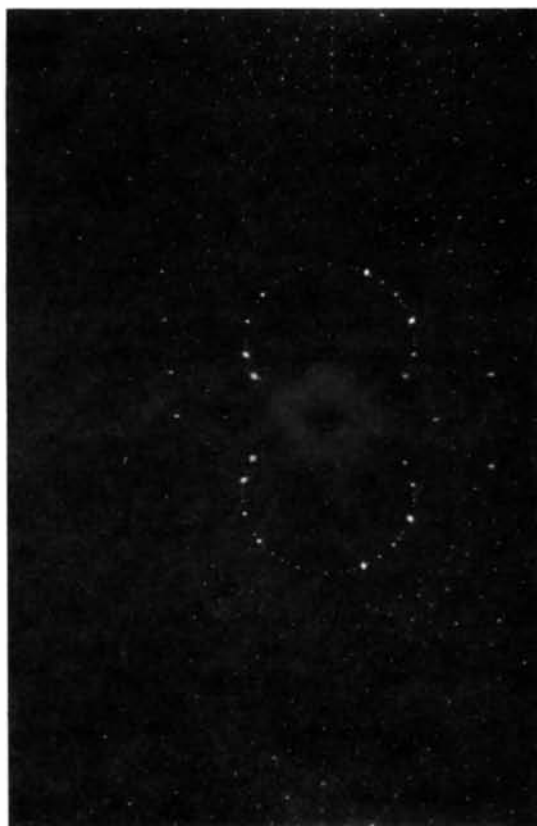

Fig. 3. Laue photograph of AlPO₄ taken on the SRS running in multi-bunch mode. Exposure 30 s. Incident-beam direction [210], [001] vertical.

4. Structure refinement and results

The refinements were carried out on the NAS 7000 computer at Daresbury Laboratory using a program constructed from the Cambridge Crystallography Subroutine Library (Matthewman, Thompson & Brown, 1982). The function minimized in the refinement was

$$M = \sum_i w_i \left[I_i(\text{obs.}) - \frac{1}{c} I_i(\text{calc.}) \right]^2. \qquad (4)$$

Since anomalous scattering was not considered in the calculation, the intensities of the Bijvoet pairs observed on the film were averaged. Those pairs whose intensities differed by more than $\pm15\%$ of the mean (probably due to incorrect integration by the densitometer or to multiple diffraction) were excluded. These amounted to about 20% of the data measured. A total of 175 reflections, with fundamental wavelengths less than $2\cdot0$ Å, were used in the refinement. Their standard deviations, σ, were estimated roughly as

$$\sigma(I) = [I + (I_1 - I)^2]^{1/2},$$

where I is the average intensity of the Bijvoet pair and I_1 the intensity of one of its components. The weights

Table 1. *Atomic parameters for* AlPO$_4$ (*berlinite*)

Space group $P3_121$. Origin as in *International Tables for X-ray Crystallography* (1969).

		Present work*	Thong & Schwarzenbach (1979)†
Al	x	0·4661 (6)	0·46643 (5)
	y	0	0
	z	1/3	⅓
	U_{11}	0·0041 (9)	0·00754 (7)
	U_{22}	0·0044 (12)	0·00586 (7)
	U_{33}	−0·0011 (33)	0·00633 (7)
	U_{23}	0·0002 (14)	−0·00030 (8)
P	x	0·4667 (5)	0·46685 (4)
	y	0	0
	z	5/6	⅚
	U_{11}	0·0029 (7)	0·00775 (6)
	U_{22}	0·0003 (8)	0·00544 (7)
	U_{33}	−0·0039 (27)	0·00627 (6)
	U_{23}	0·0003 (10)	−0·00030 (6)
O(1)	x	0·4126 (18)	0·4163 (1)
	y	0·2947 (14)	0·2922 (1)
	z	0·4007 (9)	0·39770 (4)
	U_{11}	0·028 (4)	0·0179 (2)
	U_{22}	0·013 (2)	0·0123 (2)
	U_{33}	0·013 (4)	0·0117 (1)
	U_{23}	−0·010 (3)	−0·0049 (1)
	U_{13}	−0·007 (3)	−0·0031 (1)
	U_{12}	0·018 (3)	0·0100 (2)
O(2)	x	0·4128 (15)	0·4156 (1)
	y	0·2572 (16)	0·2576 (1)
	z	0·8816 (9)	0·88365 (4)
	U_{11}	0·016 (3)	0·0175 (2)
	U_{22}	0·009 (2)	0·0117 (2)
	U_{33}	0·020 (6)	0·0129 (1)
	U_{23}	−0·006 (2)	−0·0053 (1)
	U_{13}	−0·001 (3)	−0·0042 (1)
	U_{12}	0·010 (2)	0·0101 (2)

* $R(I) = \sum |I_o - I_c| / \sum I_o = 0{\cdot}19$; $R_w(I) = \sum w|I_o - I_c| \sum wI_o = 0{\cdot}18$.
† $R(F) = 0{\cdot}022$; $R_w(F^2) = 0{\cdot}044$.

used in (4) were taken as $1/\sigma^2$. The refined values of the positional and thermal parameters are shown in Table 1, together with those from a recent very accurate conventional single-crystal structure refinement.*

5. Discussion

As can be seen from Table 1, the positional parameters agree well with those determined by Thong & Schwarzenbach (1979). Of the eight fractional coordinates six lie within 2σ of the values previously determined and only one, $z[O(1)]$, lies outside 3σ. Particularly remarkable is the determination in a pseudosymmetric structure of the Al and P x coordinates to within one standard deviation of the literature values. The temperature factors, however, are less well determined,

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* Details of the refinement cycles and a list of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38513 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

although it should be noted that they are of roughly the correct magnitude and are similar for the chemically equivalent ions despite the fact that no constraints were used in the refinement. We may therefore conclude that even in the present crude form the Laue method used with synchrotron radiation is capable of giving accurate fractional coordinates. The errors in the temperature factors probably reflect their greater sensitivity to the neglect of absorption and extinction, the omission of the anomalous scattering, and other systematic errors such as multiple diffraction and twinning. Both extinction and multiple diffraction are likely to be significant in a hard material such as AlPO$_4$. While we have no real basis for comparison the R factors appear to be much higher than those normally quoted in conventional single-crystal refinements, although it must be remembered that they refer to intensities rather than to $|F|$. In addition, they reflect the bias of the data towards short d spacings and the omission of systematic errors from the model.

The work presented in this paper was intended as a preliminary investigation of the Laue method with synchrotron radiation. It is clear that the technique offers considerable promise. We see no reason why a more refined experimental technique and better corrections for the systematic aberrations should not lead to results approaching the accuracy of conventional single-crystal work. Even the determination of space groups is possible provided that principal zones can be examined with an energy-resolving solid-state detector. The main advantage of the Laue method is that it is capable of collecting large amounts of data extremely rapidly – the present experiment, for example, involved exposures of only a few seconds. There are therefore a number of areas in which it may make a novel contribution:

(i) Time-dependent phenomena, *e.g.* studies of reaction kinetics, or of crystals which decompose rapidly. Short-lived excited states in solids may be studied provided that a stroboscopic technique can be employed. By using the synchrotron in single-bunch mode, with a phase-locked light source, the crystal may be examined with a variable delay time after excitation from about 1 to 300 ns. In this mode data can be collected in a few (~ 10) minutes.

(ii) Studies of small specimens, *e.g.* mineral grains in thin sections of rocks. The synchrotron beam allows a high degree of collimation with a small beam size and high intensity. In principle, studies of crystals approximately 10 μm in size could be attempted. Measurable spots on the photograph can be produced by oscillating the crystal through a very small angle (this integration procedure would also be advantageous with larger crystals).

(iii) Twinned materials in which the Laue topographs obtained may help to identify the twinning mode and allow separation of the intensity components.

(iv) Diffraction from specimens in controlled environments (*e.g.* pressure cells) with restricted apertures in which the time taken to collect data conventionally may be excessive. The forward-scattered beams in the Laue method tend to be of very short wavelengths (on the SRS wiggler beam the short wavelength cut-off will be 0·2 Å) and hence are only weakly absorbed by the sample container.

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Chlorite Polytypism.
I. OD Interpretation and Polytype Symbolism of Chlorite Structures

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Abstract

In order to establish identification criteria for chlorites, all their polytypes with maximum degree of order (MDO polytypes, identical with 'standard', 'regular' or 'simple' polytypes) have been derived. There are 164 di-dioctahedral, 44 tri-dioctahedral and 20 tri-trioctahedral MDO polytypes. The geometrical analysis leading to their derivation was based on the idealized model of the chlorite structures which can be interpreted as an order–disorder (OD) structure. This made it possible to apply consistently the apparatus of the OD theory. Individual polytypes are described by fully descriptive symbols – a comparison with the symbols of other authors is also given.

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† Deceased 27 July 1981.

1. Introduction

This paper is a continuation of a series dealing with polytypism of sheet silicates from the point of view of the theory of order–disorder (OD) structures (Dornberger-Schiff, 1964, 1966, 1979; Dornberger-Schiff & Fichtner, 1971). Practical applications of the results to these substances appeared, for example, in the papers of Mikloš (1975), Weiss & Mikloš (1979), Weiss & Ďurovič (1980). The important definitions and concepts of the OD theory (as applied to sheet silicates) were given in some detail by Dornberger-Schiff & Ďurovič (1975*a*), to which the reader who is not familiar with these ideas is particularly referred. A unified system of fully descriptive polytype symbols for the main types of sheet silicates has also been worked out (Ďurovič & Dornberger-Schiff, 1979).