Increasing the size of search fragments for use in Patterson method calculations – the partial fragment rotation function. Erratum.
By C. C. WILSON, *Neutron Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, England*

Abstract

Equations given by Wilson [*Acta Cryst.* (1988) A44, 478–481] are corrected. There are misplaced brackets in equations (1) and (3) and an incorrect lower summation limit in equation (3).

Equation (1) should read

$$\sigma(\theta_1, \theta_2, \theta_3)$$
$$= \sum_{\mathbf{h}} |F_{\mathbf{h}}^s|^2 \left[\left(\sum_i \cos 2\pi \mathbf{h} \cdot \mathbf{r}_i \right)^2 + \left(\sum_i \sin 2\pi \mathbf{h} \cdot \mathbf{r}_i \right)^2 \right] \quad (1)$$

and equation (3) should read

$$\sigma(\theta_1, \theta_2, \theta_3, \theta_p)$$
$$= \sum_{\mathbf{h}} |F_{\mathbf{h}}^s|^2 \left[\left(\sum_{i=1}^{n_1} \cos 2\pi \mathbf{h} \cdot \mathbf{r}_i \right)^2 + \left(\sum_{i=1}^{n_1} \sin 2\pi \mathbf{h} \cdot \mathbf{r}_i \right)^2 \right]$$
$$+ \sum_{\mathbf{h}} |F_{\mathbf{h}}^s|^2 \left[\left(\sum_{j=n_1+1}^{n_2} \cos 2\pi \mathbf{h} \cdot \mathbf{r}_j \right)^2 \right.$$
$$\left. + \left(\sum_{j=n_1+1}^{n_2} \sin 2\pi \mathbf{h} \cdot \mathbf{r}_j \right)^2 \right]. \quad (3)$$

All relevant information is given in the *Abstract*.

Synchrotron X-ray diffraction on a CaF₂ microcrystal with 2·2 cubic micrometres volume.
By WOLFGANG RIECK, HARALD EULER and HEINZ SCHULZ, *Institute for Crystallography and Mineralogy, University of Munich, D-8000 Munich, Federal Republic of Germany,* and WILFRIED, SCHILDKAMP, *Cornell High Energy Synchrotron Source, Cornell University, Ithaca, NY 14853, USA*

Abstract

The photon flux generated by the six-pole wiggler at CHESS combined with a focusing mirror and a focusing monochromator allowed diffraction experiments at 1·56 Å wavelength with a 2·2(5) μm^3 CaF₂ single crystal. The crystal was oriented by means of a multiwire proportional area counter. Reflection profiles and Bragg intensities were collected with a scintillation counter. The Bragg intensities were used for a structure refinement. The results demonstrate that crystals composed of light elements with volumes down to only 0·5 μm^3 can be mounted and used for single-crystal X-ray diffraction experiments. Until now such crystals have been considered as powder grains. Besides the possibility of applying single-crystal methods to materials of which larger crystals are not available the essentially extinction-free data from microcrystals allow a high-precision determination of electron densities and vibrational amplitudes.

Synchrotron radiation allows experiments on very small single crystals because of the low divergence and high brilliance of the beam. This feature stimulated experiments with a 200 μm^3 CaF₂ microcrystal (Bachmann *et al.*, 1983) and an 800 μm^3 zeolite microcrystal (Eisenberger, Neusam, Leonowicz & Vaugham, 1984). Rocking curves and reflec-

tion intensities have been recorded for these microcrystals. The Bragg intensities measured from the 200 μm^3 CaF₂ crystal have also been used for structure refinements and analyses of the mosaic spread of the crystal (Bachmann, Kohler, Schulz & Weber, 1985; Höche, Schulz, Weber, Belzner, Wolf & Wulf, 1986). Microcrystals of about 10^4 μm^3 volume have been used recently for diffraction experiments with macromolecular materials (Andrews, Papitz, Blake, Helliwell & Harding, 1988).

From the viewpoint of an X-ray scattering experiment the size of a crystal provides only a very rough estimate of the expected scattering effect, which is a function of the scattering power of a single crystal. The scattering power may be defined for an ideally imperfect crystal as

$$S = (F_0/V_e)^2 V_c \lambda^3 \quad (1)$$

where F_0 is the number of electrons per elementary cell, V_e and V_c are the volumes of the elementary cell and of the crystal, and λ is the wavelength. Usually crystals with $S = 10^{16} - 10^{17}$ are used for standard structure investigations. The above-mentioned CaF₂ (Bachmann *et al.*, 1983) and zeolite (Eisenberger *et al.*, 1984) microcrystals had scattering powers of $1·45 \times 10^{14}$ and $1·85 \times 10^{15}$, respectively.

Microcrystals with diameters smaller than the extinction length L behave as ideally imperfect crystals. The extinction

length is given by

$$L = V_e/(r_0 F_{hkl}\lambda),$$

where $r_0 = e^2/(mc^2)$ is the electron radius. L is about 3 μm even for the strongest structure amplitudes F_{hkl}. Diffraction data collected from crystals much smaller than 3 μm are free from primary extinction effects. Furthermore, the influence of secondary extinction and of absorption are so low, even in the worst case, that these systematic errors can be neglected. It follows that the diffraction data from very small crystals can be analysed with the simple kinematical diffraction theory and the errors in the Bragg intensities can be exactly calculated from the counting statistics. Such data should allow study of the details of electron densities with high precision. The above-mentioned microcrystals (Bachmann et al., 1983; Eisenberger et al., 1984) did not generate such ideal experimental conditions. Therefore we focused our efforts on crystals in the 1 μm region.

A micromanipulator and a specially designed microscope of the Leitz Company were used for mounting the crystal. The objective lens of the microscope is placed below the working plate, which is made of glass. This working plate is fixed and the objective lens can be moved relative to the fixed glass plate. In this way a very short distance between objective lens and crystal can be used without restrictions for the manipulator operations.

The crystals were mounted on Lindemann-glass tubes with a diameter of 80 μm. The closed ends of the tubes were broken off such that a sharp tip was generated. This tip was covered with a thin layer of epoxy glue (XW 396/397 Ciba Geigy Company).

For our experiment we selected a CaF_2 crystal of 2·2(5) μm³ volume with linear dimensions $1·8 \times 2·0 \times 0·6$ μm (Fig. 1). From (1), its scattering power is $S = 7·1 \times 10^{12}$.

The most difficult and time-consuming step in diffraction work with microcrystals is the search for the first reflections to set up the orientation matrix. This is particularly true for structures with small lattice constants and with an F-centred unit cell, like CaF_2. To find reflections in an unknown orientation requires a 'strong' beam, low background, and a low-background area detector.

The powerful beam was provided by the A1 beamline at CHESS. Its source is a six-pole wiggler within the Cornell Electron Storage Ring (CESR) operated at 5·3 GeV with typical currents of 50 mA. The X-rays are horizontally focused by a cylindrically bent germanium(111) monochromator and a vertically bent total reflection mirror. The flux on the sample amounts to approximately 10^{12} photons mm^{-2} s^{-1} at 8 keV.

The background is mainly due to air scattering. Therefore, a collimator of 0·3 mm diameter was used and the path length of the primary beam through air was restricted to about 30 mm. No background contribution of the glass tip and the glue was observable.

A 30×30 cm multiwire proportional counter (Multiwire Laboratories Ltd) with a pixel size of 1×2 mm and maximum total count rate of 40 kHz was used to find {111}-type reflections. With a gas mixture of 90% Ar and 10% CO_2 the detector efficiency was 15% at 8 keV. Reciprocal space was explored by φ scans at 0·05° s^{-1} integrated over 5 s. After background reduction each frame was visually inspected, and within 12 h five reflections were

unambiguously identified. Typical peak intensities were 50 counts at a background of 15 counts per pixel. The identified reflections were recentred to a better precision in typical four-circle geometry using an NaI scintillation counter.

Data collection was carried out with a normal scintillation counter by measuring an ω scan over 0·7° divided into 101 (non-equidistant) steps. 57 reflections were measured. The maximum peak count rate was equal to 3600 counts s^{-1}. The degree of polarization of the beam was not monitored. Its value was assumed to be constant and equal to the theoretical value of 68% during the whole measurement. This value and its stability against instabilities of the electron beam are due to the focusing optics. The intensity decay of the primary beam was followed by a monitor and the reflection intensities were correspondingly corrected. These reflections were averaged to nine symmetrically non-equivalent reflections. This corresponds to a complete data set up to $(\sin \theta)/\lambda = 0·45$ Å^{-1}. Data could not be collected at higher values owing to hardware limitations. The internal agreement of the intensities was calculated as

$$R(I) = \sum_{m,n} |I_{mn} - I_m|/\sum I_{mn} = 0·16.$$

I_{mn} and I_m are the single intensity measurements and the intensity averaged over symmetrically equivalent reflections, respectively.

Typical rocking curves are shown in Figs. 2 and 3. The full width at half maximum is about 0·05°. Besides symmetric reflection profiles (Fig. 2), non-symmetric reflection profiles were observed (Fig. 3), indicating that the mosaic spread of the crystal strongly deviates from an isotropic distribution. This shows that a microcrystal of 1 μm³ is still composed of a number of mosaic blocks.

The nine averaged structure amplitudes F were used for structure refinements, and the result is listed in Table 1. Three parameters (two isotropic temperature factors and a scale factor) were refined. The reliability factors were

$$R = \sum |\Delta F|/\sum F = 0·063$$

$$wR = [\sum w(\Delta F)^2/\sum wF^2]^{1/2} = 0·049.$$

Weights w were calculated from the counting statistics. The thermal mean-square amplitudes showed (surprisingly high) values of $\overline{u^2}(Ca) = 0·019(6)$ and $\overline{u^2}(F) = 0·033(10)$ Å². Expected values are 0·0073 Å² for Ca and

549nm
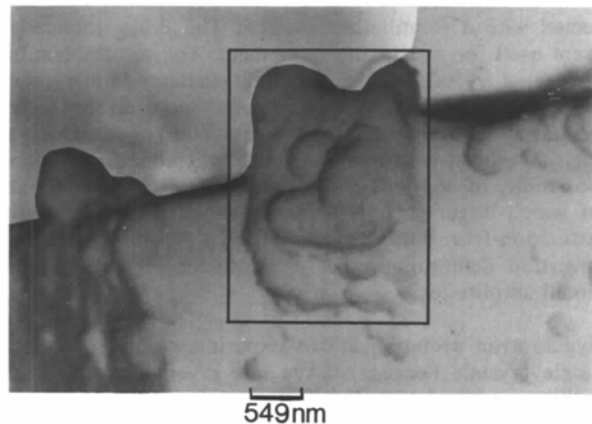
Fig. 1. Scanning-electron-microscope photograph of the 2·2 μm³ crystal mounted on a glass tip.

0·010 Å² for F [Fig. 4 of Bachmann, Kohler, Schulz & Weber (1985)]. From the size of the crystal, it can be expected that the data are completely free from extinction effects.

Because no experimental information on the degree of polarization was available, the refinements of the temperature factors were repeated under the assumption of various degrees of polarization. Within the region between 30 and 90% of polarization the temperature factors varied from 0·015 (6) to 0·023 (6) Å² for Ca and from 0·030 (9) to 0·037 (9) Å² for F. They did not reach the above-mentioned expected values.

Our experiments allow an extrapolation to the present limitations for diffraction experiments on microcrystals. The crystal mounting as described above can handle crystals down to 0·5 μm in diameter if blue light is used. Such crystals appear only as an unsharp spot. An ideal counter for work with microcrystals is a wire detector. Its intrinsic background is zero and it allows the registration of single counts. The relatively low maximum count rate of these area detectors corresponds well to the relatively weak diffracted intensities. It is necessary to reduce the background intensity to an acceptable signal-to-noise ratio. The background level could be reduced by at least one order of magnitude compared with our experiments if air scattering is avoided. It follows that microcrystals down to about 0·2 μm³ could be used for X-ray diffraction experiments, following the experimental procedure described in this paper. Further reductions of the crystal size should be
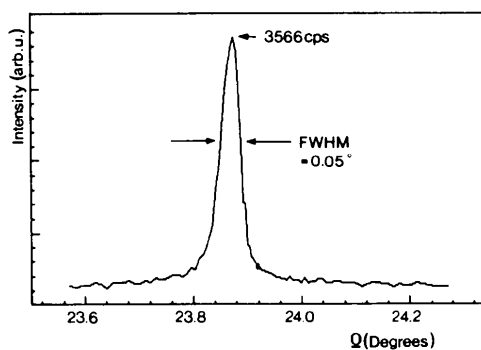
Table 1. F(hkl) values

h	k	l	F (obs.)	F (calc.)	σ (F)
0	0	2	6·356	4·045	5·14
0	0	4	60·621	58·092	3·30
0	2	2	89·789	86·463	1·77
0	2	4	14·853	11·444	2·39
1	1	1	60·499	61·078	1·17
1	1	3	37·069	41·602	1·76
1	3	3	31·137	31·379	3·15
2	2	2	17·643	10·075	4·11
2	2	4	41·784	42·829	2·35

possible if the peak search is carried out with computer control.

Such experiments may lead to large progress in several fields of solid-state research for the following reasons: (a) A detailed description of the atomic arrangements and vibrational properties of a solid is best achieved by crystals which can be described by the kinematic theory of X-ray diffraction. However, frequently diffraction intensities are biased by absorption and extinction effects. Diffraction experiments on very small single crystals do not suffer from these shortcomings, and one can obtain an unbiased data set for crystal structure analysis. (b) Frequently newly synthesized compounds can only be grown to crystal sizes of about 1 μm in diameter. Such compounds can now be investigated by single-crystal diffraction methods, if synchrotron radiation is used. (c) Crystals in special environments may be limited in size by experimental conditions. This holds especially for single crystals in high-pressure cells in the pressure range above 10^{10} Pa.

These considerations lie precisely on a line for future experiments proposed in the foundation-phase report of the European Synchrotron Radiation Facility (1987) (the so-called 'red book'). Diffraction experiments on sample sizes of (200 Å)³ or short-time diffraction experiments with 1 μm³ crystals in 1 μs are considered in this report.

Fig. 2. ω scan (rocking curve) of the 220 reflection; peak intensity ~3600 counts s⁻¹.

Fig. 3. ω scan of the 202 reflection; peak intensity ~2400 counts s⁻¹.

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