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Structure Investigation of a 6 μm CaF_2 Crystal with Synchrotron Radiation

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Abstract

Two data sets containing altogether 131 Bragg intensities have been collected from a CaF_2 crystal of 200 μm^3 volume, which corresponds to a cube of about 6 μm edge length. The scattering power S of this crystal amounts to $1{\cdot}3\times10^{14}$. It is the smallest crystal ever used for an X-ray diffraction experiment. Crystal orientation and data collection were carried out at the storage ring DORIS II, HASYLAB, DESY, Hamburg, with the wavelength $\lambda = 0{\cdot}91$ Å. For the first data set all reflections up to $\sin\theta/\lambda = 0{\cdot}58$ $Å^{-1}$ were collected, for the second only those reflections considered as observed by a prescan were measured up to $\sin\theta/\lambda = 0{\cdot}78$ $Å^{-1}$. The refinements, carried out as a function of the degree of polarization K, converged to $R_w(F) = 0{\cdot}005$ for $K = 0{\cdot}93$ and $R_w(F) = 0{\cdot}031$ for $K = 0{\cdot}94$ for the first and second data set, respectively. For comparison, a 90 μm sphere was investigated with synchrotron radiation [$\sin\theta/\lambda \leq 0{\cdot}91$ $Å^{-1}$, $R_w(F) = 0{\cdot}020$, $K = 0{\cdot}50$] and with a normal X-ray tube [Mo $K\alpha$ $R_w(F) = 0{\cdot}013$]. The intensities are strongly affected by secondary extinction, in contrast to the 6 μm crystal. The following isotropic temperature factors were obtained for the 6 μm, 90 μm (synchrotron) and 90 μm (X-ray tube) data: $B(\mathrm{Ca}) = 0{\cdot}38\,(5)$, $0{\cdot}64\,(3)$, $0{\cdot}610\,(6)$; $B(\mathrm{F}) = 0{\cdot}83\,(4)$, $0{\cdot}92\,(3)$, $0{\cdot}812\,(8)$ $Å^2$. The TDS correction increased only the temperature factors from the data set measured with the X-ray tube owing to the difference in FWHM (0·03° for synchrotron radiation, 0·210° for the X-ray tube).

Introduction

Synchrotron radiation allows diffraction experiments on very small crystals because of the low divergence and high brightness of the beam. Such experiments will lead to major advances in several fields of solid-state research for the following reasons.

(1) Frequently, crystals cannot be grown to sizes which permit single-crystal diffraction with conventional X-ray sources. These sources require crystals of about 100 μm in diameter.

(2) Crystals in special environments may not surpass a certain size because of experimental limitations. This holds especially for single crystals in high-pressure cells in the pressure range above 10 GPa.

(3) Under normal laboratory conditions diffraction data are very frequently affected by absorption, thermal diffuse scattering and, particularly, extinction. Diffraction experiments on very small crystals reduce these systematic errors because they depend among other things on the crystal size or beam divergence.

From the viewpoint of an X-ray scattering experiment the size of a crystal is only a very rough estimate of the expected scattering power, which may be defined for an ideally imperfect crystal in the following way.

$$S = (F_{000}/V_e)^2 V_c \lambda^3, \qquad (1)$$

F_{000} is the number of electrons/elementary cell, V_e is the volume of the elementary cell, V_c is the volume of the crystal, λ is the wavelength.

Each set of equipment for X-ray diffraction can be characterized by a smallest S. This S_{min} allows the calculation of the minimum size for a crystal with a given composition and for a given wavelength. Usually crystals with $S = 10^{16}$–10^{17} are used for standard structure investigations.

The most serious systematic error in measuring the intensities of Bragg reflections is caused by extinction. Crystals usually do not follow exactly either the kinematical or the dynamical diffraction theory, but the diffracted intensities lie between the upper and lower intensity limits predicted by these theories. Extinction can be corrected only in an approximate way. The correction depends on the structure model and consequently the parameters of the extinction correction are correlated with the parameters of the structure model (Zachariasen, 1963, 1968*a*, 1969; Coppens & Hamilton, 1970; Becker & Coppens, 1974*a*, *b*, 1975; Cooper & Rouse, 1970). Therefore, extinction-free Bragg intensities would greatly simplify the interpretation of these data.

The extinction is divided into primary extinction (size of mosaic crystallites) and secondary extinction (angular spread of mosaic crystals). There are two cases where extinction is reduced or even eliminated:

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(1) Primary extinction is reduced strongly if the diameter of the crystal is equal or smaller than the extinction length L (*e.g.* Schneider, 1977):

$$L = \frac{1}{r_0}\frac{V_e}{F\lambda}, \qquad (2)$$

r_0 is the classical electron radius, F is the structure factor.

(2) Secondary extinction depends on the mosaicity of the crystal. As is well known, mosaicity is increased in the surface region. The ratio (surface region)/(volume) increases with decreasing crystal size. Therefore, it is conceivable that crystals below a certain diameter are composed only of the extinction-free surface region. There is no way to make a prediction on this diameter from the theory. This question can be answered only by experiments.

The crystals of the test substance, CaF_2, are known to be highly perfect and are therefore strongly affected by extinction. In previous experiments (Abrahams *et al.*, 1967; Zachariasen, 1968*b*; Cooper, 1970), nearly all reflections were attenuated by extinction, the strongest intensities being reduced to less than 20% of the intensity expected from kinematical theory (Cooper, 1970). The extinction length, calculated with (2), is $L \simeq 5$ μm for the strongest reflections of CaF_2 at $\lambda = 1$ Å.

CaF_2 is composed of fairly light elements. The smallest CaF_2 single crystal that can be used for X-ray diffraction with synchrotron radiation allows a realistic extrapolation to crystals composed of lighter elements, *e.g.* organic crystals.

Experimental

Crystal preparation and testing

All CaF_2 crystals were chipped off one large single crystal grown by the Korth Company, Kiel, Federal Republic of Germany. We prepared a series of single crystals with decreasing volume of 3×10^6, 4×10^5, 4×10^3, 2×10^3 and 2×10^2 μm^3. The largest crystal was ground to a sphere of 90 μm in diameter. The volume of the smallest crystal corresponds to a cube of 6 μm edge length. Scanning electron microscope photographs were used to determine the shape (irregular pyramid) and the volume of the crystal. All crystals were manually mounted on glass pins with glue. A photograph of the mounted 6 μm crystal is shown in Bachmann, Kohler, Schulz, Weber, Kupcik, Wendschuh-Josties, Wolf & Wulf (1983), hereafter BK^2SW^4.

Before carrying out the experiments with synchrotron radiation at HASYLAB we oriented the CaF_2 crystals in our laboratory. We used a Philips PW1100 automatic diffractometer with a 200 W Mo Kα fine-focus tube and a graphite monochromator. The crystal with a volume of 2×10^3 μm^3 was the smallest one that could be oriented in a way similar to the one described below for the 6 μm crystal.

All efforts to orient the 6 μm crystal failed. Its scattering power S calculated with (1) is equal to $S = 1{\cdot}3\times10^{14}$ for $\lambda = 0{\cdot}91$ Å (BK^2SW^4). As far as we know, it is the single crystal with the smallest scattering power S used up to now for an X-ray diffraction experiment.

Measurements with synchrotron radiation

The synchrotron radiation measurements were carried out at HASYLAB at DESY (Hamburg, Federal Replublic of Germany), with storage ring DORIS II operated at 3.5 GeV and 60–25 mA. The five-circle diffractometer was used (Kupcik, Wulf, Wendschuh, Wolf & Paehler, 1983). The distance between source and instrument was approximately 30 m. The X-ray beam was monochromatized by a flat Ge (111) double-crystal monochromator. For technical reasons the experiments had to be carried out at $\lambda = 0{\cdot}91$ Å and with a horizontal diffraction plane.

The fluctuation of the intensity of the X-ray beam was monitored by measuring the stray radiation in the housing of the monochromator. The counter faced the outgoing beam. The intensities of the stray radiation were used for an on-line correction of all intensity measurements.

First we collected a data set for the 90 μm CaF_2 sphere. The crystal orientation and the refinement of the orientation matrix was carried out with the standard software of the instrument. The final orientation matrix was calculated from the angular positions of 25 reflections {111} and {044}. For the data collection the scan width was set to $\omega = 0{\cdot}243°$. This small scan width requires a very accurate determination of the orientation matrix in order to get a good centering of the peaks within the scan. The reflections were scanned repeatedly until $I/\sigma(I) \geq 25$ or until the time limit of 1 s step^{-1} was reached. The average time/step ranged from 0.5 to 1 s. Three control reflections did not show any significant fluctuations. The half-width of the reflections was about 0.03° in ω. The whole measurement including the orientation of the crystal took 24 h. Further details are listed in Table 1.

The standard software for crystal orientation failed for the 6 μm crystal. It was replaced by the following manual procedure. First the counter was set to the 2θ position of the {220} reflections and φ scans were carried out at different χ values with a scan speed of 0.3° s^{-1}. Each profile was plotted. If an event seemed to lie above background, this was checked by driving to the peak manually and then using the automatic centering procedure. In this way two reflection positions were found and they were used together with the lattice constants for the calculation of the initial orientation matrix. It was refined from 25 reflections

Table 1. *Experimental conditions*

	6 μm crystal			90 μm sphere	
	Data set 1		Data set 2		
Type of radiation	Synchrotron			Synchrotron	X-ray tube
Wavelength (Å)	0·91			0·91	0·71
Scan mode	ω			$\omega/2\theta$	$\omega(\theta<30°)$ $\omega/2\theta$
Number of steps	81		101	81	60
Scan width (°)	0·243		0·303	0·243	1·80
Steps/peak		35		51–67	26–44
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0·58 (1×0·73)		0·78	0·90	1·06
Reference reflections	220	202	022	335 044 22$\bar{4}$	642 264 0$\bar{2}$2
Detector aperture					
horizontal (mm)		1		1	2
vertical (mm)		1		1	1
Crystal-to-detector distance (mm)		235		235	225
Number of measured reflections	93		38	212	969
Number of unique reflections	16		18	41	65
Number of observed reflections $(I>3\sigma(I))$	15		18	41	65
Internal agreement R_I	0·041		0·042	0·040	0·028
μ(cm^{-1})		63·9		63·9	32·7

{111} and {440} whose angular positions were found by the standard procedure. The reflections had a half-width of approximately 0.02° in ω. A typical profile is shown in BK^{2}SW^4. The orientation procedure alone lasted 24 h.

The subsequent data collection was carried out in the same way as for the 90 μm crystal with the following exceptions: the time/step varied between 0.5 and 9 s; only two control reflections were used, which did not show any significant fluctuations. The data collection took 36 h. For further details, see Table 1.

Measurement with a conventional X-ray tube

The 90 μm sphere also underwent standard data collection with the diffractometer mentioned above. Three control reflections showed no significant changes in intensity or orientation. All reflections with $l \geq 0$ were measured up to $\sin\theta/\lambda = 1{\cdot}06$ Å^{-1}. Further experimental conditions are summarized in Table 1.

Data reduction

The data reduction was carried out with *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann, Schulz, 1983). The standard deviation was calculated from

$$\sigma(I)^2 = \alpha_c(I)^2 + (0.01I)^2,$$

where I = net intensity and σ_c = standard deviation from the counting statistics.

The data obtained with the 90 μm sphere were corrected for absorption (*International Tables for X-ray Crystallography*, 1968, 1974). The path lengths of X-rays in the sphere were calculated from the absorption correction factor. In the 6 μm crystal, the X-ray path lengths were estimated to be 4.5 μm.

In the averaging process standard deviations of the mean $\bar{I}$ were calculated from $\sigma(I)$ of the individual measurements [$\sigma_c(\bar{I})$] and from the deviations of the individual measurements from their mean [$\sigma_m(\bar{I})$]. The larger of the two values was taken as $\sigma(\bar{I})$.

Further details are listed in Table 1.*

Structure refinements

All structure refinements were carried out with *PROMETHEUS* (Zucker *et al.*, 1983).

The polarization correction plays a very important role in the diffraction geometry used (horizontal diffraction plane). The Lorentz-polarization correction was carried out with (3) for the experimental set-up of the five-circle diffractometer:

$$\mathrm{Lp} = \frac{P_H \cos^2 2\theta + P_V \cos^4 2\theta_m}{\sin 2\theta}, \qquad (3)$$

θ is the diffraction angle, θ_m the monochromator angle ($\theta_m = 8°$) and P_H, P_V are the percentages of X-ray intensity with horizontal or vertical electrical vector. This expression relates to an ideally imperfect monochromator crystal. If the Lp correction is carried out for an ideally perfect crystal the results are only unessentially changed [see also (5) below].

Equation (3) depends strongly on the degree of polarization of the synchrotron radiation

$$K = \frac{P_H - P_V}{P_H + P_V}. \qquad (4)$$

With the degree of polarization of 90% at the center of the beam measured by Materlik & Suortti (1984)

* Lists of observed and calculated structure factors, standard deviations and extinction corrections for the 90 μm and 6 μm crystals have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39665 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

we could not refine the data from the 90 μm crystal. Therefore, a series of Lp corrections was applied to the synchrotron data of both crystals, where K was varied in steps.

The extinction correction (type I, Gaussian) of Becker & Coppens (1974*a*) was included in the refinement. The equations for the correction depend on K of (4). The degree of polarization was included in the following way:

$$I_{kin} = I/y$$

I_{kin} is the kinematical intensity, y is the correction for extinction, y_H, y_V are the components of y for correction of the horizontal and vertical components of the synchrotron beam:

$$y = \frac{P_V y_V \cos^4 2\theta_m + P_H y_H \cos^2 2\theta}{P_V \cos^4 2\theta_m + P_H \cos^2 2\theta}. \qquad (5)$$

Equation (5) holds for the correction of primary and secondary extinction.

The scattering factors for Ca^{2+} and F^- and the correction for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974).

The data sets corrected for different degrees of polarization were used for the structure refinements. In a first refinement step only the scale factor and the two isotropic temperature factors B(Ca) and B(F) were simultaneously varied. In a second step isotropic extinction was added. The data set, which resulted in the lowest residual values $R(F)$, $R_w(F)$ and lowest GOF was corrected for thermal diffuse scattering (Skelton & Katz, 1969) and the structure refinement was repeated with this data set. The elastic constants of CaF_2 were taken from Ho & Ruoff (1967).

Structure refinements with the 90 μm data

R_w, R and GOF show a minimum for $K = 0{\cdot}50$ (Fig. 1). B(Ca) and B(F) display an approximately linear dependence on K around $K = 0{\cdot}50$. From Fig. 2 it follows that $B(\text{Ca}) = 0{\cdot}66\,(2)$ and $B(\text{F}) = 0{\cdot}92\,(2)$ Å^2. The correction for extinction was highly significant. The structure refinements were carried out for isotropic primary and secondary extinction using the formalism of Becker & Coppens (1974*a*). The secondary extinction clearly dominated. The extinction correction did not show any correlation with the polarization ratio (Fig. 3). In the range $K = 0{\cdot}3$–$0{\cdot}7$, g varied only within the standard deviations. For $K = 0{\cdot}50$ it amounted to $4{\cdot}2\,(5) \times 10^{-3}$ rad^{-1}. This corresponds to a mosaic spread of 33″ of arc. The largest correction was $y = 0{\cdot}49$ for the 220 reflection. The $R_w(F)$ and B values of Figs. 1 and 2 were calculated with this correction. The largest correlation coefficient of 0·92 was observed between the scale factor and B(Ca). All other coefficients were lower than 0·8. Correction for thermal diffuse scattering did not increase the temperature factors.

The most surprising result of the above refinement is the low degree of polarization. At first we thought that this might be an artifact of the refinement, such as an incorrect extinction model. We repeated the refinements with modified data sets. In a first attempt we excluded seven reflections with $y \leq 0{\cdot}92$ from the refinement. In a second attempt we excluded all reflections with $40 \leq \theta \leq 50°$ because these reflections are most strongly influenced by the polarization correction. The refinements were completely stable against these variations of the data set. The minima in the R and GOF values were not shifted. The

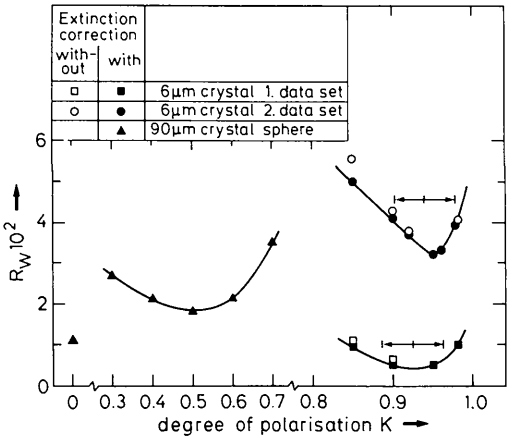

Fig. 1. Weighted $R_w(F)$ values as a function of the degree of polarization K for the 6 μm and 90 μm crystals.

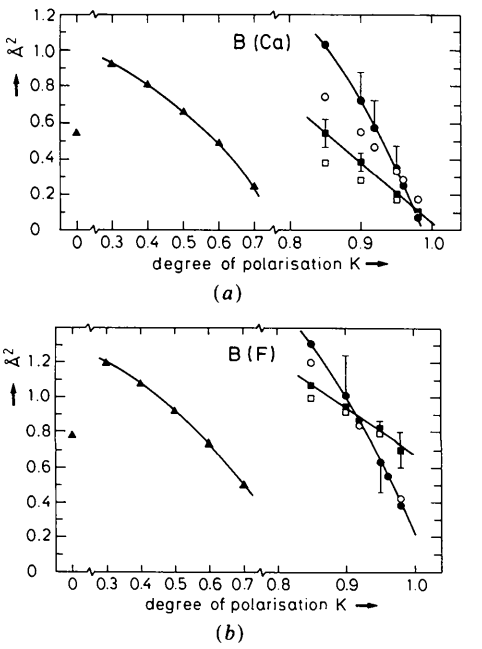

Fig. 2. Isotropic temperature factors B(Ca) and B(F) as a function of the degree of polarization for the 6 μm and 90 μm crystals. The standard deviations of the B values of the 90 μm crystal are equal to or less than the size of the symbols. (*a*) B(Ca); (*b*) B(F).

structure parameters varied only within their standard deviations.

The data measured with a conventional X-ray tube were corrected with the normal Lp correction, *i.e.* with $K = 0$. The structure refinements were carried out in the same way as described above, but with a third-order term in the temperature factor of the F atoms. The corresponding temperature-factor formalism is based on the Gram–Charlier expansion (Zucker & Schulz, 1982). This parameter varied only within its standard deviation and did not significantly influence structure parameters and R values.

The secondary extinction parameter g amounted to $2{\cdot}9\,(1)\times10^3$ rad^{-1}. This corresponds to a mosaic spread of 47″ of arc. The largest correction was $y = 0{\cdot}65$ for the 220 reflection. $R_w(F)$, the temperature factors B and extinction coefficient g are shown in Figs. 1–3 for $K = 0$. The correction for thermal diffuse scattering increased the B values significantly. The difference can be read from data points 3*a* and 3*b* in Fig. 4. This is in sharp contrast to the synchrotron data: here the temperature factors were not influenced by the TDS correction. This was expected because the TDS correction is a function of the peak width. The largest intensity correction was only about 2%.

Structure refinements with the 6 μm *data*

The structure refinements were carried out as described for the 90 μm data. The minimum R_w values were $R_w = 0{\cdot}005$ and 0·031 for the data sets 1 and 2 (Fig. 1). However, these minima are not as significant as for the 90 μm crystal because only 18 reflections were used for the refinement of five parameters (scale factor, two temperature factors, secondary extinction correction, degree of polarization). The arrows in Fig. 1 show the range of insignificant R_w values based on the Hamilton test for $\alpha = 0{\cdot}25$ (Hamilton, 1965). We have used the center of these intervals to read the polarization ratio K from Fig. 1. It follows from Fig. 1 that $K = 0{\cdot}93$ and 0·94 for the first and second data sets.

Fig. 1 shows, furthermore, that there is only an insignificant decrease in R_w when applying an extinction correction. The lowest extinction factor is now $y = 0{\cdot}96$ and only the two strongest reflections (111 and 220) are attenuated. In contrast to the 90 μm data the extinction coefficients g show a strong dependence on the degree of polarization K (Fig. 3). The standard deviations, however, are so high that this has to be considered as insignificant. Also, the B values show a strong variation with the degree of polarization K. They increase insignificantly when corrected for extinction (Fig. 2). The B values from the best fit are displayed in Fig. 4 as data points 1 and 2. Their weighted averages give $B(\mathrm{Ca}) = 0{\cdot}34\,(5)$ and $B(\mathrm{F}) = 0{\cdot}87\,(5)$ Å^2. As expected, the B values were not influenced by a TDS correction. The highest correlations, 0.95 and 0.89, were obtained for scale factor/extinction and scale factor/B(Ca), respectively.

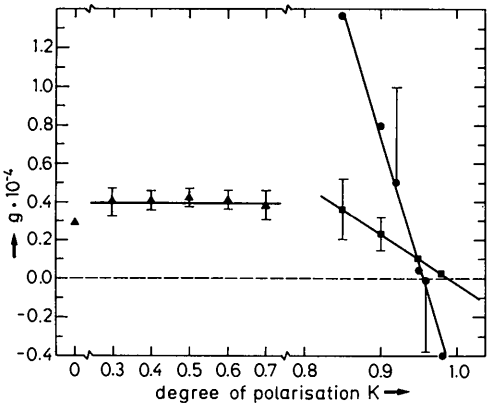

Fig. 3. Parameter g of the secondary extinction correction as a function of the degree of polarization for the 6 μm and 90 μm crystals.

Discussion

(1) *Degree of polarization*

The most serious error was introduced into our data by the unknown polarization of the synchrotron beam. In the diffraction geometry used this is the most important correction. We can correct only for a mean polarization, which does not take into account the fluctuations of the electron beam that occurred during the experiments. The largest beam instability was observed during the measurements with the 90 μm sphere. This may be the reason for the unexpectedly low $K = 0{\cdot}5$. The large difference from the K values of the 6 μm crystal ($K \simeq 0{\cdot}93$) demonstrates

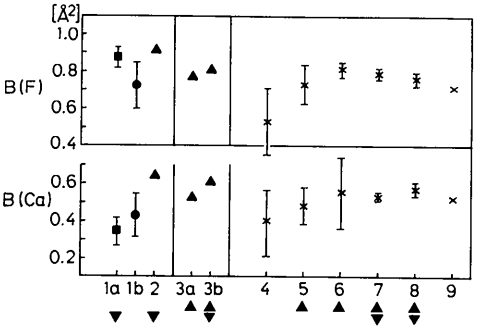

Fig. 4. Isotropic temperature factors for Ca and F from refinements with single-crystal data (nos. 1–8) and from lattice dynamics calculations (no. 9). 1: 6 μm crystal; 2 and 3: 90 μm crystal measured with synchrotron radiation and X-ray tube, respectively; 4: Willis (1965); 5 and 6: Cooper [(1970) with data sets from Abrahams *et al.* (1967)] and Zachariasen (1968*a*); 7: Strock & Batterman (1972); 8: Harvey & Prager (1975); 9: Elcombe & Pryor (1970). Data points without error bars have errors less than the size of the symbol. ▲: refinement of third-order parameter of F; ▼: TDS correction.

clearly that a correction for polarization of each step in an intensity scan is indispensable.

(2) *Intensity of the primary beam*

The intensity of the synchrotron beam continuously decreases during the life-time of the fill of the storage ring. Our results show that the intensity variation could be reasonably well corrected by measuring the stray intensity in the monochromator housing.

(3) *Extinction correction*

The 90 μm data are strongly affected by extinction ($y \simeq 0{\cdot}5$ for the strongest low-angle reflections). Such a large correction in the low-angle region is nearly independent of the degree of polarization K assumed (Fig. 3). This is in sharp contrast to the 6 μm crystal, where $y = 0{\cdot}96$ and where g is correlated with K (Fig. 3). g assumes now the character of an artificial fit parameter, which adjusts mainly the two reflections 111 and 220 to the calculated values. Owing to the uncertainty in the polarization correction we cannot conclude that the intensity data are free of extinction; however, its influence has nearly vanished. It seems that this behavior is not only caused by the small size of the crystal, but also by the reduction of the crystal perfection.

(4) *Temperature factors*

The insufficient correction for polarization and the limited resolution of our data sets are probably responsible for the only poor agreement of the temperature factors of the synchrotron measurements with the literature values. This is in contrast to the measurement with the X-ray tube (Fig. 4). However, we would like to stress that the synchrotron data are not affected by thermal diffuse scattering in contrast to the X-ray data, which changed significantly when corrected for TDS (data points 3*a* and 3*b* in Fig. 4).

(5) *Outlook*

We have demonstrated that it is possible to use a crystal with a scattering power of only $S \simeq 10^{14}$ for data collection. We had to carry out the investigations with a flat double-crystal monochromator, horizontal diffraction geometry and a given wavelength in only 36 h. With a slightly focused beam and with vertical diffraction geometry it should be possible to measure crystals with a scattering power of $S \simeq 10^{13}$. This corresponds to a CaF_2 crystal of 3 μm edge length. If it is possible to normalize each individual count rate to the incident-beam intensity and to correct it for polarization, these diffraction data could be considered as quasi free of absorption, extinction and thermal diffuse scattering. They will satisfy the kinematical diffraction theory and will allow the study of crystal structures on a level of accuracy unknown to date.

We carried out the measurements in cooperation with V. Kupcik, M. Wendschuh-Josties, A. Wolf and R. Wulf of the Institut für Kristallographie und Mineralogie of the Universität of Göttingen. Some experimental results have already been published (Bachmann *et al.*, 1983).

Note added in proof: A recent measurement (June 1984) of the beam polarization at the five-circle diffractometer yielded values ranging from 0·52 to 0·90. The cause is as yet unknown, but this supports our conclusion that the polarization should be measured on-line.

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