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A Camera Attachment for X-ray Diffractometry of Minute Mineral Samples

By *W. B. Stern* (Basel)*)

Abstract

With a simple attachment to a conventional X-ray diffractometry small mineral samples such as powder or single crystals may benefit from the advantages, high resolution and fast data output, characteristic of this apparatus. Two different methods for cell parameter determination of monoclinic minerals are described and the accuracy of the results briefly discussed.

Method 1 uses basal reflexes of the three main crystallographic directions, plus one generally indexed reflexion and an internal standard for peak shift corrections. The weight of the powdered sample can be in the order of 1 to 3 mg.

Method 2 is based upon difference measurements of two basal reflexes for each crystallographic direction. An internal standard is not needed if the corresponding basal reflexes are near each other. The measurements are made on a single crystal of 0.05 to 1 mg.

Zusammenfassung

Die hier vorgestellte apparative Anordnung erlaubt es, einige Vorteile der konventionellen Röntgendiffraktometrie – hohe geometrische Auflösung und Schnelligkeit des Datenzugriffs – für die Gittergrößenbestimmung kleiner und kleinster Probenmengen zu nutzen. Anhand monokliner Mineralien werden zwei Methoden der Gittergrößenbestimmung kurz diskutiert und Resultate sowie deren Fehlerabschätzung vorgeführt.

Das eine Verfahren beruht auf der Messung von drei verschiedenen Basisreflexen sowie eines allgemein indizierten Reflexes und eines Inneren Standards, dessen Wert für die Korrektur der einzelnen Messungen herangezogen wird. Das Untersuchungspräparat besteht aus 1 bis 3 mg Mineralpulver.

Das zweite Verfahren benützt für jede der drei kristallographischen Hauptrichtungen Differenzen zwischen je zwei benachbarten Basisreflexen; ein Innerer Standard wird nicht benötigt, wenn die zueinander gehörigen Linien nicht zu weit voneinander entfernt sind. Als Untersuchungsmaterial dient ein auf einer einfachen Eulerwiege montierter Einkristall von ca. 0,05 bis 1 mg Gewicht.

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X-ray counter diffractometry of small samples is usually limited to mineral powders, mounted or sedimentated on a flat surface. Sheet silicates – and other minerals – show orientation effects not always desired in case of cell parameter determinations. Moreover, peak/background ratios are normally poor, with broad peaks; the sample quantity needed generally exceeds several milligrams.

The attachment described here, fits on the goniometer of a conventional diffractometer (“camera”) and enables the determination especially of cell parameters for:

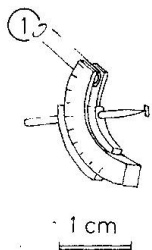
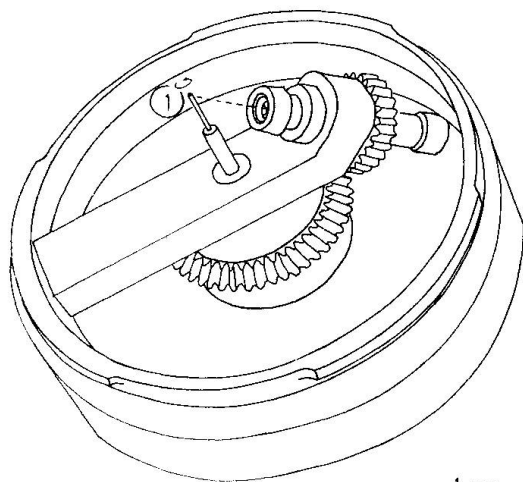
- Small powder/grain samples (1 to 5 mg) mounted on a pin either perpendicular to the primary X-ray beam (analogous to Debye-Scherrer exposures in case of film cameras), or diagonally (analogous to the Gandolfi technique);
- single crystals of minute minerals (few micro- to milligrams), especially in case of sheet silicates or fibrous minerals.

Instead of the conventional goniometer cover, a sample holder (fig. 1 a, 1 b), with a motor device for sample rotation is mounted on a PW 1361/01 Philips counter diffractometer. The main axis (no. 1) moves with θ , but is externally adjustable by means of either a cog- or a screw-wheel.

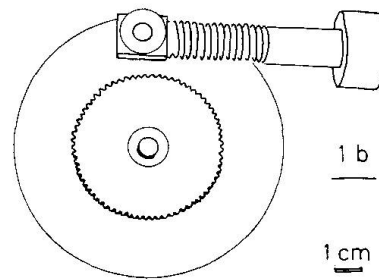
Thus, it becomes possible to bring into reflexion either one grain of a mineral powder or a single crystal mounted on an Eulerian cradle (Fig. 1 a). A 2θ scan shows the preselected (h00), (0k0), (00l) peaks (Fig. 2 a–c). The peaks show a high peak to background ratio and good resolution already below $30^\circ 2\theta$: $K\alpha_1$, and $K\alpha_2$ are resolved (Fig. 2 d). For comparison, two line scans of conventional sample mountings (300 mg powder) are shown on Fig. 2 e, f.

Sample geometry is a crucial point: an eventual internal standard (IS) has to be located at virtually the same spot as the source of X-ray information. For these reasons a finely powdered IS like Ag or Si is fixed with hair spray directly at the surface of the sample as soon as the mineral reflexes have been checked.

The location of a single crystal peak is generally possible within a read-off error of $\pm 0.01^\circ 2\theta$, whereas the IS – with its randomly oriented grains – generally presents more difficulty (error ± 0.01 to $0.05^\circ \theta$). This implies that in a 2θ range of 40° to 50° e.g. the 0 0 10 peak of mica enables a c-determination with an accuracy of one digit in the second decimal at its best, and of one digit in the third decimal in case of a 0 0 22 reflex at $2\theta = 118.7^\circ$. As a consequence, cell parameter determinations are preferably made at high angles – a rather difficult task using conventional powder cameras, but often feasible working with reflexions of single crystals.



1 a



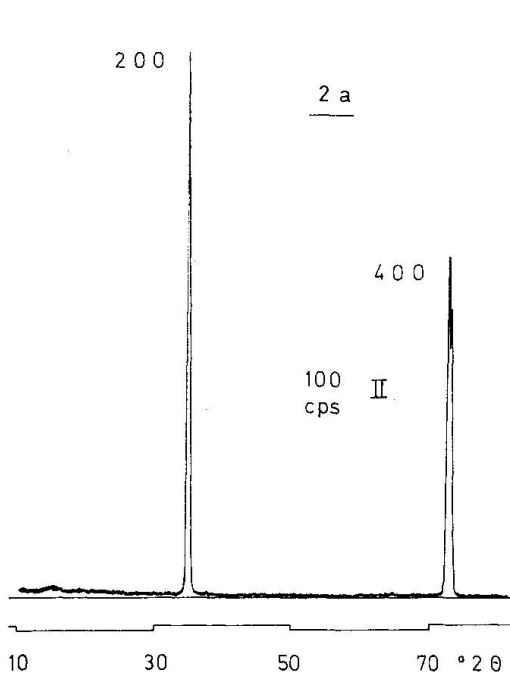
1 b

1 cm

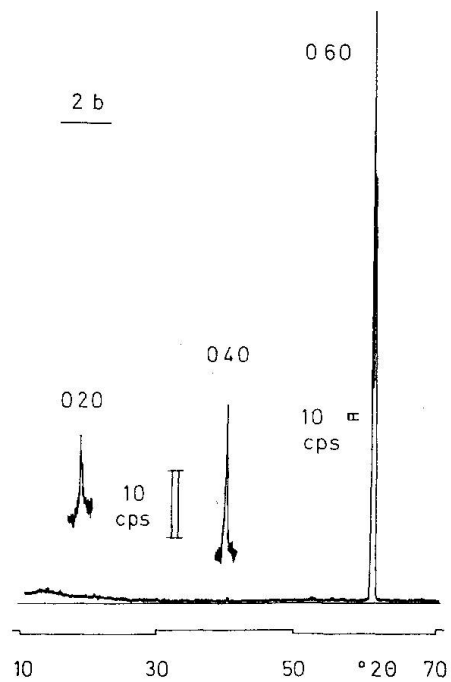
Fig. 1b. Outside of sample holder showing the cog-wheel for fine adjustment of main axis 1 (or Eulerian cradle). Motor device for sample rotation removed.

Fig. 1a. Attachment (sample holder) replacing conventional cover of goniometer. Main axis of rotation = 1. On the left side sketch of the Eulerian cradle for single crystal examinations.

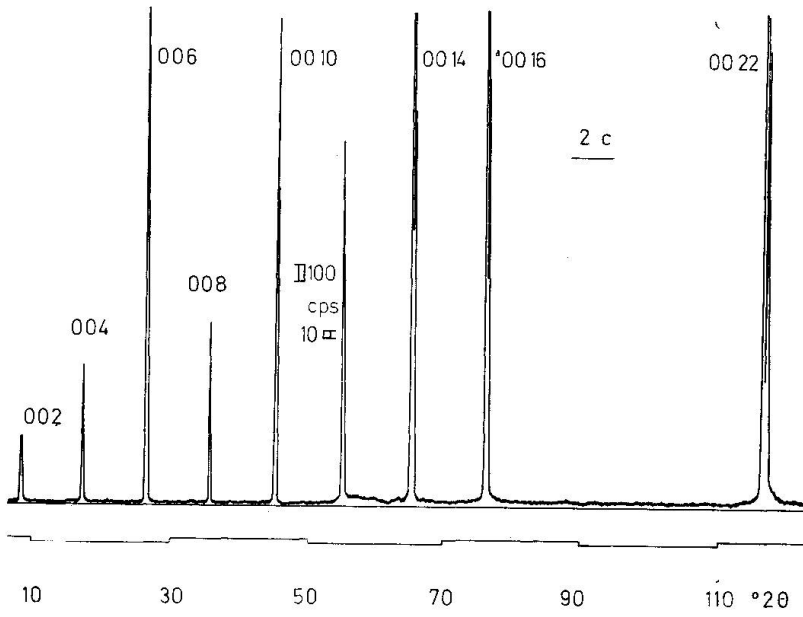
Fig. 2. Line scans of white K-mica single crystals (1 mg). For technical details see Table 1.



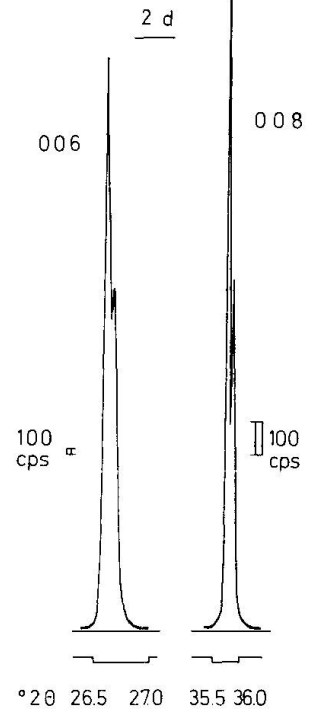
a) (h 0 0) reflexes



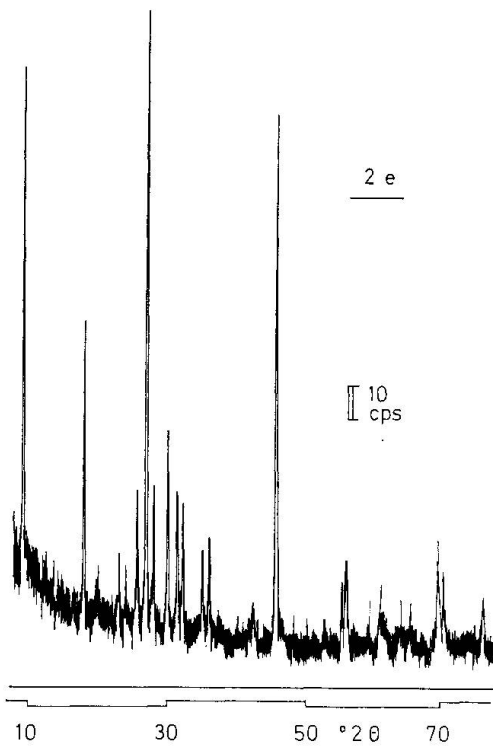
b) (0 k 0) reflexes



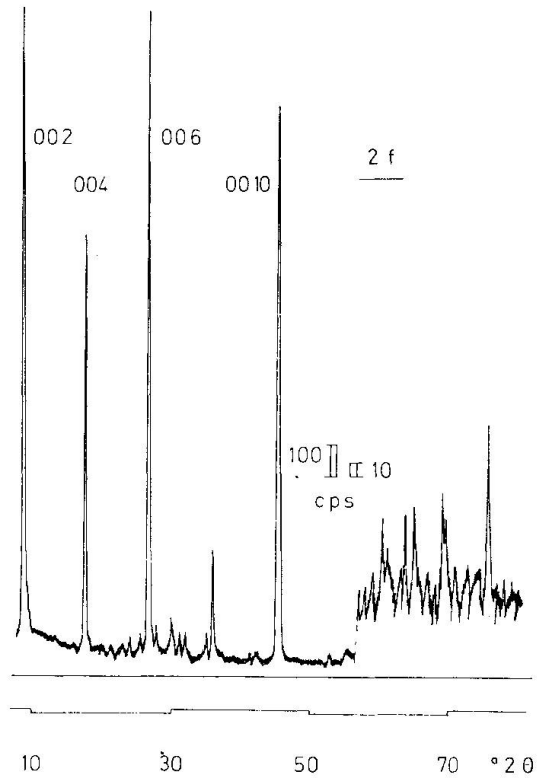
c) (0 0 1) reflexes



d) Resolution of $K\alpha_1$ and $K\alpha_2$ in the lower 2θ range.



e) Conventional powder diffractogram for comparison (400 mg, rough surface, spinner).



f) Conventional powder diffractogram for comparison (300 mg, smooth surface, no sample rotation).

But not only read-off errors have smaller effects at higher angles, peak shift due to inexact positioning of the sample in relation to the camera axis is also smaller (Fig. 3), and even becomes zero at $2\theta = 180^\circ$.

It might be of interest to discuss a cell parameter determination of monoclinic mineral in some detail: from a white mica (sample HuSt 915, see SCHWANDER et al., 1968) two different preparations were made and checked.

1. Approximately 2 mg powder (grain size 0.1 to 0.2 mm \varnothing) was fixed with a highly viscous lubricant on a pin at the main central axis (no. 1) of the attachment. Four reflexes, namely h00, 0k0, 00l and HKL¹⁾, plus Ag as internal standard were checked. By means of graph Fig. 3, the deviation of the four mineral reflexes was corrected.
2. One grain of 0.3 mg was mounted on an Eulerian cradle. For each crystallographic direction at least two basal reflexes were measured. From the differences between two corresponding peaks the desired cell parameters were calculated without using an internal standard. This method gives fair results if either the sample displacement, and therefore H (see Fig. 3), is low, or if

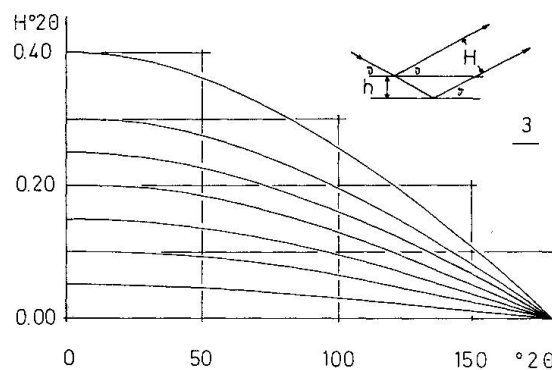


Fig. 3. Correction nomogram for peak shift. Displacement of sample according to $H = h \frac{\sin 2\theta}{\sin \theta}$, where h = vertical displacement of the sample in relation to goniometer main axis, H = observed deviation of an internal standard from literature value.

the correction values of corresponding reflexes do not differ by much. In cases where the mentioned H values differ considerably, it is recommended to use the following equation

$$\frac{\lambda \cdot x_1}{2 \sin\left(\theta_1 - h \frac{\sin 2\theta_1}{\sin \theta_1}\right)} - \frac{\lambda \cdot x_2}{2 \sin\left(\theta_2 - h \frac{\sin 2\theta_2}{\sin \theta_2}\right)} = 0.$$

¹⁾ Upper case letters indicate general reflexes, lower case letters basal ones.

$2\theta_1$ and $2\theta_2$ are measured; x_1 and x_2 are known being the Miller indices of the two basal reflexes used. The only unknown value – h – can easily be determined, eg by means of an iteration program.

All lattice parameters were calculated with a Diehl- α microcomputer. Cell parameter determinations according to method 1 and 2: formulae used and results (sample HuSt 915 white K-mica)

Formulae

<i>Method 1</i>		<i>Method 2</i>	
formulae	used reflexes	formulae	used reflexes
$a_0 = \frac{d_{(h00)} \cdot h}{\sin \beta}$	(4 0 0)	$a = \frac{\left(\frac{4-2}{2}\right) \cdot \lambda}{\sin \theta_{(400)} - \sin \theta_{(200)}}$	(2 0 0), (4 0 0)
$b_0 = d_{(0k0)} \cdot k$	(0 6 0)	$b_0 = \frac{\left(\frac{6-4}{2}\right) \cdot \lambda}{\sin \theta_{(060)} - \sin \theta_{(040)}}$	(0 4 0), (0 6 0)
$c_0 = \frac{d_{(00l)} \cdot l}{\sin \beta}$	(0 0 10)	$c = \frac{\left(\frac{22-16}{2}\right) \cdot \lambda}{\sin \theta_{(0022)} - \sin \theta_{(0016)}}$	(0 0 16), (0 0 22)
$\cos \beta = \frac{a \cdot c}{2 HL} \left(\frac{1}{d^2_{(HKL)}} - \frac{H^2}{a^2} - \frac{K^2}{b_0^2} - \frac{L^2}{c^2} \right)$			
(HKL) = (1 3 5)		Cu $K\alpha_1 = 1.5405 \text{ \AA}$	

Results

a_0	5.19 \AA	5.19 \AA
b_0	9.024	9.00 ₈
c_0	20.1 ₃	20.0 ₈
β	95.10°	
V	941 \AA^3	935 \AA^3

The results of method 1 and 2 agree to within 0.2%, but an absolute error could still exist. To check this possibility, a monoclinic mineral of simple chemistry and well known lattice parameters, gypsum, was chosen and investigated according to method 1 using Ag and Si respectively as IS. For technical details see Table 1.

Table 1. *Technical data*

Apparatus	Philips counter diffractometer
Radiation	Cu tube, Ni filter
Excitation	40 kV, 40 mA
Slits	1 – 0.05 – 1/4 and 1 – 0.1 – 1
Pulse selector	Z = 3, threshold 050. Window open
Goniometer speed	Wide range line scans: 2° 2 θ p. minute, single reflexes: 1/2° 2 θ p. minute. Time constant 1
Sample rotation	Mostly for IS measurements; or for simulation of conventional diffractograms in case of unknown samples

Gypsum	Ag = internal standard	Si = internal standard	Literature ASTM 6-046
a_0	5.68 Å	5.69 Å	5.68 Å
b_0	15.20	15.20	15.18
c_0	6.54	6.56	6.51
β	118° 30'	118° 40'	118° 23'

The lattice parameters of gypsum found agree with the data from literature within 0.0–0.7%. For routine determinations, the reliability of the data found might generally be in the order of 0.2 to 0.5%. If better results are desired one could use reflexions of higher order, since for powder measurements a clear dependence of relative error and the two theta range taken exists – even when the read-off error remains the same, i.e. $\pm 0.01^\circ 2\theta$, see Fig. 4.

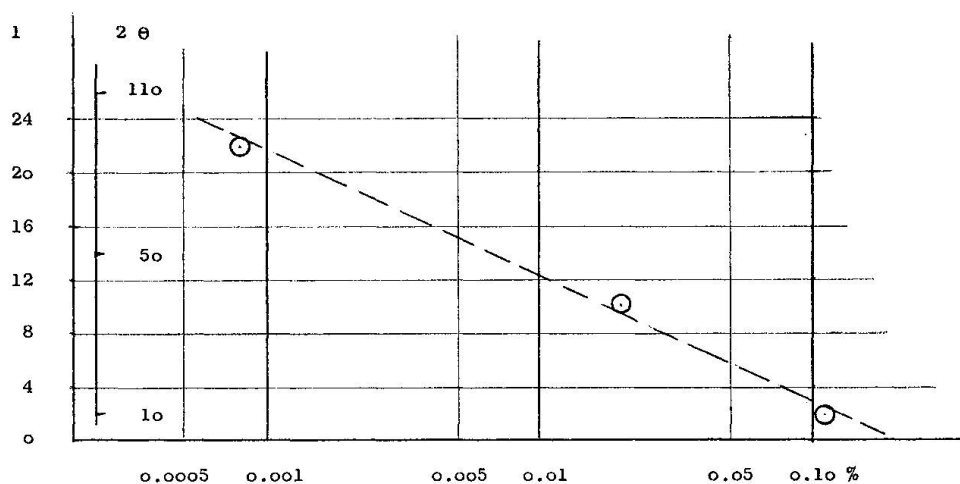


Fig. 4. Relation between error (%) and 2θ range, based upon a read-off error of $\pm 0.01^\circ 2\theta$. (001) reflexions of white K-mica, single crystal.

The addition of an internal standard for peak shift correction is advisable in case of powder exposures (method 1). Although geometrical effects become more and more negligible in the high 2θ range, experiments show better results when an IS is used (see Fig. 5).

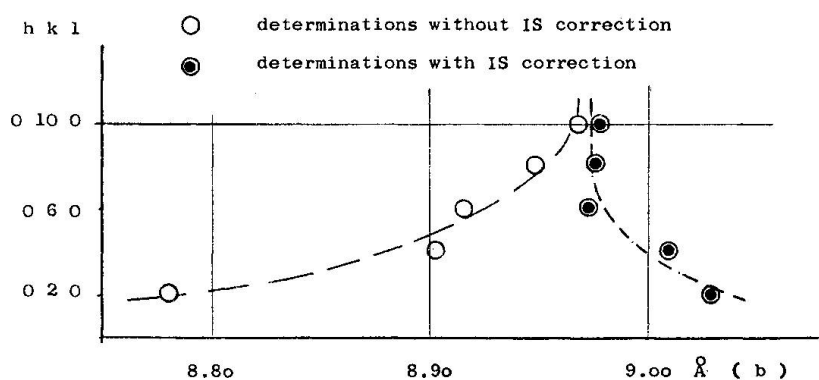


Fig. 5. Determination of b-parameter (white K-mica, powder exposure, 2 mg) with and without internal standard (Ag). For technical details see Table 1.

In case of difference measurements without IS (method 2), the error – calculated on the basis of a read-off error of $0.01^\circ 2\theta$ again – is in the order of $\pm 0.2\%$ for the entire 2θ -range. Thus, method 2 seems useful whenever several basal reflexes for each crystallographic direction are available.

Acknowledgment

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