Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.


Short-time X-ray diffraction for the investigation of chemical reactions and phase transitions.* By K. KOSTEN and H. ARNOLD, Institut für Kristallographie der RWTH Aachen, Templergraben 55, D 5100 Aachen, Federal Republic of Germany

(Received 23 November 1983; accepted 31 January 1984)

Abstract

The usual powder diffraction technique needs about one hour for the registration of a pattern with either a Guinier camera or a powder diffractometer. This is a long time compared to the time of most chemical reactions and phase transitions. Quite recently the recording time has been reduced by using position-sensitive detectors and rotating-anode X-ray sources, but the registration time is still about one minute. With a Guinier diffractometer in front of a synchrotron-radiation source a time resolution of 300 μs can be achieved.

Experimental

The synchrotron-radiation source used was the storage ring DORIS II at HASYLAB, Hamburg, operating at 3.7 GeV and 60 mA. The experimental set up is shown in Fig. 1. The white beam from the storage ring A was monochromatized by a Si(111) single crystal F bent according to de Wolff (1948) in the form of a logarithmic spiral. The distance between source and monochromator was about 40 m. The design of the monochromator was as follows. A Si plate F of 75 × 25 × 0.5 mm was positioned on two polished steel rods D having a separation of 60 mm. These rods were the pivots of two 1:1 levers which had on the inner side another set of two rods E. Their separation was 40 mm. On the outer sides torques were applied in order to bend the crystal. The torque was controlled by motors acting on micrometer screws C. With this device the wavelength was easily changed in the region of 1 to 1.5 Å and the distance to the focus L was varied from 0.7 to 1.5 m. The bending device was mounted on a 'goniometer head' which allowed the variation of the angle θ of the monochromator and the alignment of the Si crystal to the beam.

The camera and, in particular, the computer control of the experiment has already been published by Arnold & Kosten (1983). Here only a short review is given in order to describe the whole experiment. The Guinier camera (Guinier, 1939) has the usual film radius of 57.3 mm. The film K is positioned at the focus L of the monochromator and the sample I on the focal circle. The angle γ between the monochromatized beam and film radius can be varied from −45 to 45° in steps of 15°. Also, back-reflection photographs can be taken. The camera can be equipped by a furnace from 300 to 1500 K and a cooling device from about 100 to 500 K. The temperature control is performed at high temperatures by an optical pyrometer, at low temperatures by thermocouples. In front of the film is a slit J of 1 mm width. The film is shifted behind this slit with a programmed speed so that time-dependent photographs can be taken. Before the entrance slit H an ionization chamber is positioned to monitor the film speed according to the flux of the monochromatic beam. The focus was not observed directly since the intensity was too high and the radiation contains harmonic multiples of the wavelength with n = 3, 4, .... However, from the line widths of the diffraction pattern a focus width of about 0.2 mm is concluded. The aperture of the monochromator was 3 × 6 mm. With a wavelength of 1.3 Å a diffraction pattern of fluorite CaF₂ with an exposure time of 10 s was obtained. Several chemical reactions and phase transitions have been observed with a resolution of 1 min/1 mm film. The synchrotron radiation is advantageous for the registration of powder patterns. The radi-

*The experimental results were presented at the Eighth European Crystallographic Meeting, 8–12 August 1983, Liège, Belgium.

0021–8898/84/030206–02$5.00 © 1984 International Union of Crystallography
The minimum scan range and detector aperture as a function of specimen size in X-ray diffractometry.

By A. MCL. Mathiesen, Division of Chemical Physics, CSIRO, PO Box 160, Clayton, Victoria, Australia 3168

(Received 13 July 1983; accepted 8 February 1984)

Abstract

The theoretical functional relationship of scan range and detector aperture to (spherical) crystal size in respect of scattering angle \( \theta \) in X-ray diffractometry for different scan modes is not clearly defined in the literature. It is shown that it is necessary to examine separately the factors determining the angular apertures of the beam incident on the crystal and of the beam diffracted from the crystal, and then the appropriate relationship is derived for a point source and a small spherical crystal for the \( \omega \)-scan mode. The required aperture is shown to be \( 2a\cos^2 \theta \), where \( a \) is the diameter of the crystal. Using \( (\Delta \omega, \Delta 2\theta) \) component diagrams (Mathieson, 1983). Aust. J. Phys. 36, 79–83), the corresponding results are derived for the \( \omega/\theta \)- and \( \omega/2\theta \)-scan modes and the three results are shown to be consistent with the earlier deductions which yielded \( \cos^2 \theta \) for the \( \omega \)-scan mode but not with those which yielded \( \cos \theta \).

Introduction

In single-crystal diffractometry, the specimen-crystal dimension is one of the various components whose multiple convolution determines the diffracted intensity of Bragg reflections. When the crystal specimen is small, as is the case quantitatively. Also, intermediate compounds can be observed if they exceed the amount of a few weight \% during the reaction. The heating or cooling rate of the diffraction experiment can now be chosen to be the same as that of thermal analysis.

The authors thank Professor Bonse, Dortmund, and the collaborators of HASYLAB for help and discussions, in particular Dr Graeff and Dr Materlik. They thank the men in the workshop of the institute for their enthusiasm in helping to build the equipment. The authors are grateful to the Bundesminister für Forschung und Technologie for financial support and a scholarship.

References


© 1984 International Union of Crystallography