DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

DESY SR-80/12
September 1980

ON THE USE OF WIDE-ANGLE ENERGY-SENSITIVE DETECTORS IN WHITE-BEAM X-RAY SINGLE-CRYSTAL DIFFRACTION

by

B. Buras and J. Staun Olsen
Physics Laboratory II, University of Copenhagen

and

L. Gerward
Laboratory of Applied Physics III, Technical University of Denmark

NOTKESTRASSE 85 · 2 HAMBURG 52

To be sure that your preprints are promptly included in the
HIGH ENERGY PHYSICS INDEX ,
send them to the following address (if possible by air mail) :

DESY
Bibliothek
Notkestrasse 85
2 Hamburg 52
Germany

ON THE USE OF WIDE-ANGLE ENERGY-SENSITIVE DETECTORS IN WHITE-BEAM X-RAY SINGLE-CRYSTAL DIFFRACTION[+]

B. BURAS[*] and J. STAUN OLSEN

Physics Laboratory II, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

and

L. GERWARD

Laboratory of Applied Physics III, Technical University of Denmark DK-2800 Lyngby, Denmark

Abstract

Possibilities of multiple-element or large-area semiconductor detectors in single-crystal x-ray diffraction are discussed on the basis of experimental results using Bremsstrahlung as well as synchrotron radiation.

[+]To be published in Nuclear Instruments and Methods.

[*]Also at the Risø National Laboratory, DK-4000 Roskilde, Denmark.

1. Introduction

X-ray energy-dispersive methods have to a large extent been applied to powder diffractometry, whereas single crystal work is more sparse. Two energy-dispersive methods for single crystals, namely the rotating-crystal method and the fixed-crystal method , were proposed by Buras[1] and later proved experimentally by Buras, Staun Olsen, Gerward, Selsmark and Lindegaard-Andersen[2]. These authors also derived the theoretical formulas for the integrated intensities in the kinematical approximation for the ideally imperfect crystal and in the framework of the dynamical theory for the large perfect crystal.

The energy-dispersive methods are based on the use of semiconductor detectors. The energy resolution and the counting rate is limited by both device parameters and the processing electronics. New techniques may enable the fabrication of compact arrays of detectors so that some of these limitations can be reduced. Moreover, the use of large-area or multiple-element detectors will increase the amount of information in a single diffraction experiment. With the high intensity available from synchrotron radiation sources and rotating-anode sources, many interesting applications may soon be possible. The purpose of the present work is to discuss some of these possibilities on the basis of new experimental results from energy-dispersive single-crystal diffractometry.

2. Rotating crystals

2.1. A small-area (point) detector

Suppose that a small-area (point) energy-sensitive detector is placed so as to receive the x-rays scattered by the sample through a fixed scattering angle, $2\theta_0$ (Fig. 1). The crystal is mounted with a well defined zone axis perpendicular to the incident beam and rotated during the course of the exposure. In this way, successive planes pass through the orientation necessary for Bragg reflection, each producing a diffracted x-ray of a wavelength contained in the white incident spectrum according to Bragg's law.

$$E_H \, d_H \sin \theta_0 = hc/2 = 6.199 \ (\text{keV}\cdot\text{Å}) \qquad (1)$$

where E is the photon energy and d the lattice plane spacing for a particular reflection, θ_0 the Bragg angle, which is the same for all reflections, h Planck's constant, c the velocity of light, and H stands for the reflection indices hkl.

The energy spectrum of the diffracted x-rays is recorded by a multichannel pulse-height analyser. The basic vectors of the unit cell and the indices of the reflections are readily determined from equation (1).

The rotation speed is important only when a pulsed radiation source is used, for example a synchrotron radiation source. Let ω denote the angular frequency of the rotating crystal and T the repetition time of the x-ray pulses. A necessary condition is then

$$\Delta\theta/\omega \gg T \qquad (2)$$

where $\Delta\theta$ is the divergence of the x-ray beam. Condition (2) secures that many x-ray pulses contribute to the reflection each time a particular set of lattice planes is in a reflection position. For a fine collimation, say $\Delta\theta = 10^{-4}$ rad, and synchrotron radiation in a single-bunch mode with $T = 10^{-6}$ s one finds $\omega \ll 100\ s^{-1}$. In general a rather slow rotation is required.

Fig. 2 shows an experimental diffraction spectrum of the zero layer reflections in the $[1\bar{1}0]$ zone from a silicon single crystal. The spectrum has been recorded using a conventional x-ray source. The irradiated sample volume is about 0.1 mm^3. With the high intensity available with synchrotron radiation sources it will be possible to obtain similar patterns from much smaller crystal volumes or in a much smaller time. This is especially important for the study of single crystals, which only can be grown to a very small size, for example some organic single crystals.

The number of reflections, which can be observed, depends on the scattering angle and the energy range of the incident x-ray spectrum. It

follows from equation (1) that the range of the modulae of the scattering vectors, $\vec{\kappa} = \frac{2\pi}{\lambda}(\vec{s} - \vec{s}_0)$, is given by the inequality

$$1.014\, E_{min}(\text{keV}) \sin\theta_0 < \kappa(\text{Å}^{-1}) < 1.014\, E_{max}(\text{keV}) \sin\theta_0 \quad (3)$$

where $\vec{s}$ and $\vec{s}_0$ are the unit vectors in the direction of the scattered and incident beam, respectively, and E_{min} and E_{max} are the minimum and maximum photon energies, respectively, of the incident spectrum.

Comparing with the standard method, in which one knows the wavelength of the used monochromatic x-rays, it is worthwhile to notice that in the energy-dispersive method one knows the Bragg angle. Moreover, the Bragg angle is the same for all the reflections in the case of a point detector.

2.2. A linear array of detectors

The point detector described in the previous section can be placed so as to record all the reflections in one layer of reflections, for example the zero layer. Reflections from several layers could be recorded simultaneously using a linear array of small detectors. The linear array should be arranged with its axis parallel to the axis of crystal rotation, that is perpendicular to the plane of drawing in Fig. 1. All reflections in each layer are then recorded for a well-defined Bragg angle.

3. Fixed single crystal and a large-area detector

The fixed-single crystal method ressembles the classical white-beam Laue method. However, the latter method is not accompanied by a wavelength analysis of the x-rays contributing to each Laue diffraction spot. The energy-dispersive method tried until now has used a detector with a small aperture, adjusted to receive the x-rays forming one particular Laue spot. In this case one will record the principal reflection and some of its harmonics. Buras et al.[2] have shown that structure factors can be determined with an R-factor of about 3% using this method and

Bremsstrahlung from a standard x-ray tube. Large synchrotron radiation sources for x-ray work generally have a spectrum which extends to higher photon energies than those available with Bremsstrahlung sources. As an example Buras, Staun Olsen, Gerward, Will and Hinze[3] have shown that silicon reflections up to the 16th order from the (111) planes can be recorded using synchrotron radiation. Thus it is possible to measure the scattered intensity for very large scattering vectors.

Suppose now that a large-area semiconductor detector is used. The detector may consist of a single large-area detector or an array of small detectors connected to an amplifying, analyzing and recording unit as shown in Fig. 3*). Such a system is at present expensive but some simplifications lowering the cost can already be envisaged, e.g. a joint cooling system and/or multi-chips detectors. For low count rates it is sufficient to connect the detector array in parallel to a single amplifying, analyzing and recording unit. However, the present-day detectors cannot make full use of the high intensity available with synchrotron radiation sources and rotating anode sources, In these cases it would be suitable to connect each detector in the array to a separate processing unit.

Fig. 4 shows a chart for the Ewald construction when using the fixed-crystal energy-dispersive method. Scattering will be observed in a region of reciprocal space determined by the spectral width of the incident white x-radiation and the angular acceptance of the detector. The diagram in Fig. 4 should be superposed on a reciprocal lattice in order to determine the photon energy and Bragg angle for each single-crystal reflection for a given direction of the incident beam ($\vec{k}_0$ in Fig. 4). Fig. 5 shows as an example the reciprocal lattice points corresponding to the $[1\bar{1}0]$ zone of silicon reflections.

Generally the orientation of the crystal and the directions of the scattered beams are unknown. The observed single-crystal reflections

---

*) In Fig. 3 we consider a one-dimensional array of small detectors along an arc of a circle. However, the analysis can easily be extended to a two-dimensional array.

can then be indexed by turning the crystal by a known angle, $\Delta\phi$, around the zone axis and measuring the shift, ΔE, in photon energy for each reflection (Buras[1]). By solving two Bragg equations

$$Ed \sin\theta = hc/2 \tag{3a}$$

$$(E+\Delta E)d \sin(\theta+\Delta\phi) = hc/2 \tag{3b}$$

where θ is the Bragg angle for a particular single-crystal reflection, one can show that θ can be calculated from the following relation:

$$\cot\theta = [E/(E+\Delta E) - \cos\Delta\phi]/\sin\Delta\phi \tag{4}$$

The d value is then obtained from (3) and the indexing can be performed in the usual way.

Fig. 6a and b show some experimental diffraction spectra simulating the results for a large-area detector. They have been recorded using a small-aperture detector and scanning over the angular ranges indicated in the figures. The spectra have been obtained using Bremsstrahlung from a standard copper-anode tube and synchrotron radiation from the storage ring DORIS (Hamburg, Germany). The indexing of the spectra has been performed using the procedure described above.

4. Discussion, mainly concerning fixed single crystals and large-area detectors

It follows from the preceding section that the reflected x-rays are in general separated in both space and photon energy when using a white incident beam. The energy analysis can be performed by a energy-sensitive semiconductor detector system. The scattering angles of the reflected x-rays can be found from two successive measurements as shown in equation (4) for the case of a one-dimensional detector. In the case of a two-

dimensional detector three measurements would be necessary. A structural analysis can then be performed provided, of course, that the necessary corrections for absorption, extinction etc. can be properly taken into account.

There has been increased interest for the last few years in electronic area detectors for use in x-ray crystallography[4,5]. Detectors based either on image intensifiers coupled to TV systems or on gas-filled multiwire proportional counters have been developed to display and record x-ray diffraction patterns. Recently, Bilderback[6] has developed a system that can display a back-reflection Laue pattern in real time on an x-ray display scope using a position-sensitive multiwire proportional counter. This system records the spatial distribution of the reflected x-rays but not the corresponding photon energies. On the other hand, a large-area semiconductor detector, as discussed in the present work, records the photon energies of the reflected x-rays but not their spatial distribution. In this case, however, the method of recording two (three) spectra, as discussed above, can be used. However, it would be useful to have a detector system for the simultaneous recording of the energy and space coordinates of the reflected x-rays.

In this context it is interesting to mention the area detectors being developed for neutron diffraction. The first observations of time and space resolved Laue patterns appear to be those obtained at the Argonne pulsed neutron time-of-flight single-crystal diffraction system[7]. The design of the system is based on the use of a multiwire, position-sensitive, area detector and time-of-flight techniques to permit data collection in the Laue mode. The system shown in Fig. 3 could be used for corresponding energy and space resolved Laue patterns in the x-ray case, provided each detector element has its own processing unit[4]. Multi-element detectors using one slab of a Si(Li) crystal and several electrodes are in the stage of development[8].

It follows that one can choose between two approaches for structural work:

1. A system that records only the photon energies (neutron wavelengths).

2. A system that records both the spatial distribution of the re-

flected x-rays (neutrons) and the corresponding photon energies (neutron wavelengths).

In the first case it is necessary to make two or three successive measurements in order to perform a structural analysis. In the second case it is possible to base a structural analysis on one single measurement. However, the electronic system is much more complicated (and expensive) and still not fully developed.

The financial support of the Danish Natural Sciences Research Council is gratefully acknowledged. The authors are grateful to Deutsches Elektronen-Synchrotron, Hamburg, for permission to use the facility and to European Molecular Laboratory for the temporary site.

References

1) B. Buras, Monograph 71-08, H.C. Ørsted Institute, University of Copenhagen (1971).

2) B. Buras, J. Staun Olsen, L. Gerward, B. Selsmark and A. Lindegaard-Andersen, Acta Cryst. A31 (1975) 372.

3) B. Buras, J. Staun Olsen, L. Gerward, G. Will and E. Hinze, J. Appl. Cryst. 10 (1977) 431.

4) Workshop on X-ray Instrumentation for Synchrotron Radiation Research, Stanford Synchrotron Radiation Laboratory Report SSRL 78/04 May 1978.

5) 25th Nuclear Science Symposium, IEEE Transactions on Nuclear Science, Vol. NS-26, No. 1, February 1979.

6) D.H. Bilderback, J. Appl. Cryst. 12 (1979) 95.

7) A.H. Reis,Jr., S.W. Peterson, J.M. Overhage, A.J. Schultz, J. Kolenko, P. Day and R.A. Jacobson, American Crystallographic Association Symposium: Crystallographic Studies Using Energy-Dispersive Diffraction, Boston, August 13-14, 1979.

8) T. Fukamachi (private communication).

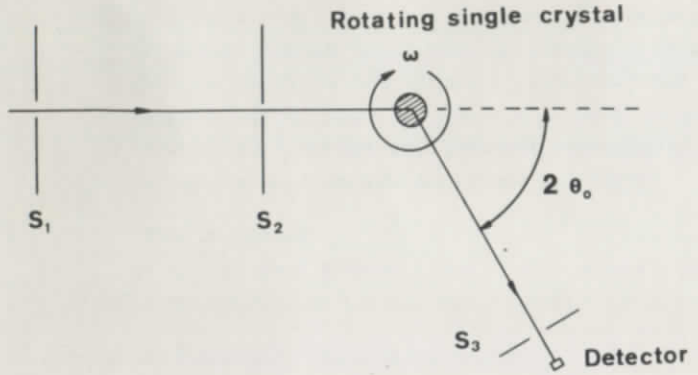

Fig. 1. Experimental arrangement for the rotating-crystal energy-dispersive method. S_1, S_2, S_3 slits, ω crystal rotation and $2\theta_0$ fixed scattering angle.

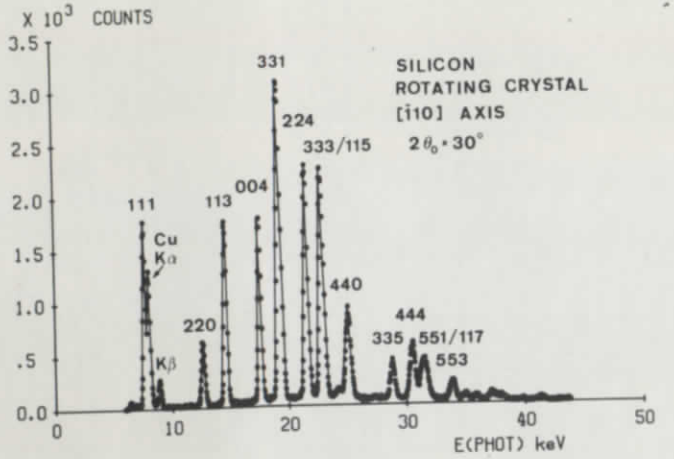

Fig. 2. Energy-dispersive diffraction spectrum for a rotating silicon single crystal, $[1\bar{1}0]$ zone, scattering angle $2\theta_0 = 30^\circ$. Bremsstrahlung from a copper tube (50 kV, 20 mA) and a Si(Li) detector have been used. Exposure time 1000 s.

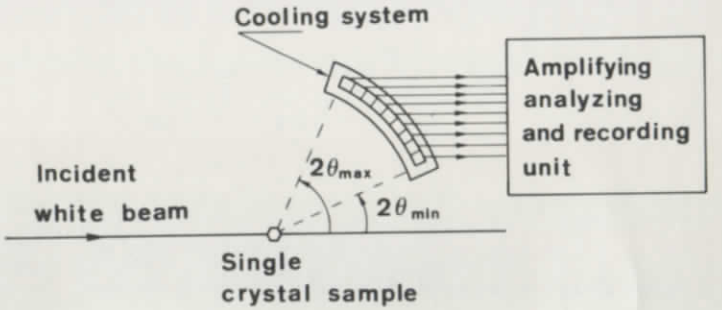

Fig. 3. Principle of the energy-dispersive method for a fixed crystal and a large-area detector.

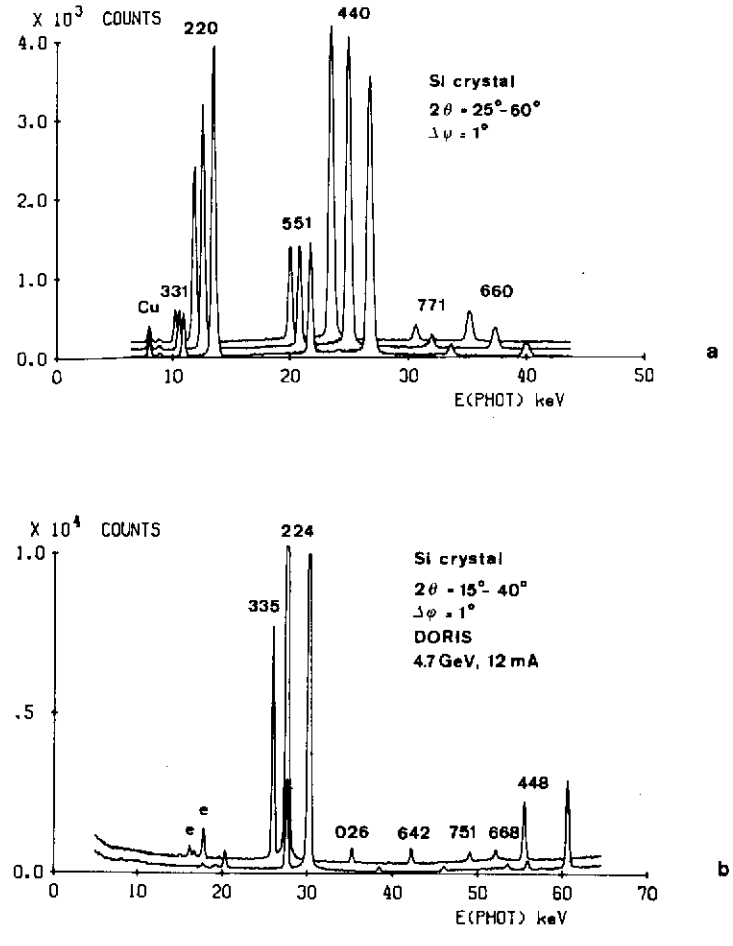

Fig. 6. Energy-dispersive diffraction spectra for a fixed silicon crystal simulating a large-area detector.

a) Bremsstrahlung from a copper tube operated at 50 kV and 20 mA. Continuous scanning 2°/min, Si(Li) detector. Zero layer reflections.

b) Synchrotron radiation from the storage ring DORIS, operated at 4.7 GeV and 12 mA. Step-wise scanning 0.5°/step, counting time 10 s/step, ultra-pure Ge detector. In this case the crystal has been slighly tilted so that some reflections from the second layer are recorded in addition to the zero layer reflections (the first-layer reflections are forbidden in the diamond structure). e = escape peaks.

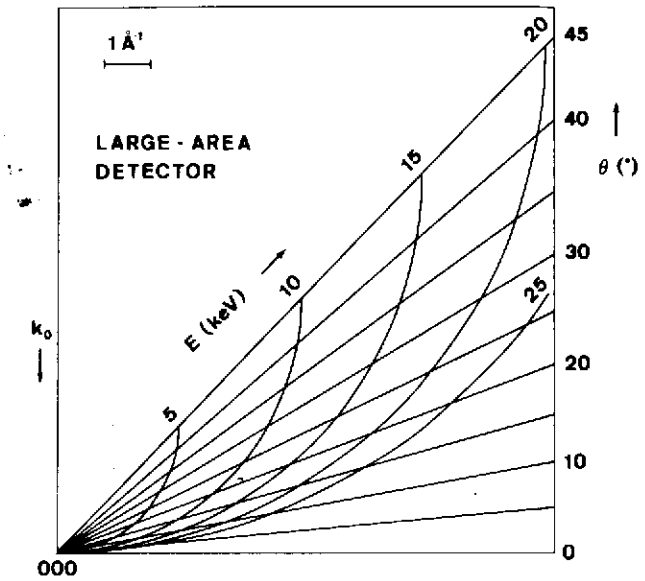

Fig. 4. Chart for the Ewald construction for a fixed crystal, a white incident beam and a large-area detector. The chart shows Ewald circles for photon energies up to 25 keV and Bragg angles up to 45°.

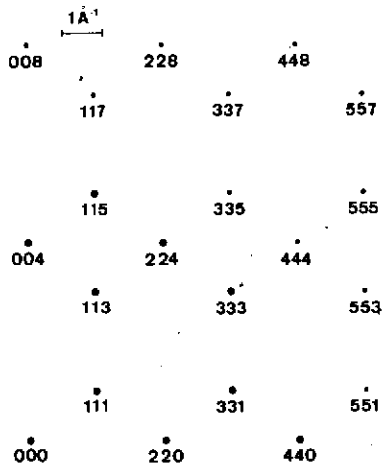

Fig. 5. Reciprocal lattice points corresponding to the $[1\bar{1}0]$ zone of silicon reflections.