Applications of a Two-Circle SSD Diffractometer in the Angle-Dispersive Mode

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A standard two-circle diffractometer with a Ge(Li) solid-state detector controlled by a microcomputer has been constructed. Its characteristics [good signal-to-noise (s/n) ratio, simple optical collimation, without any monochromator or filter] are described. A single angle-dispersive scan with this system can give diffraction patterns with Kα, Kβ and fluorescence radiation simultaneously: diffractometry with the present system can be carried out in a shorter time than with a conventional diffractometer and a proportional or scintillation counter and will give a better s/n ratio. Powder or amorphous samples of small volume can be more easily studied with the present system; typical examples reported include crystalline InSb and amorphous GaSb, both in a diamond-anvil high-pressure cell.

Introduction

As is already known, an energy-dispersive diffractometer with an SSD (solid-state detector) can be very conveniently used for investigating samples under various extreme conditions, partly because its optical system is simple and partly because the diffraction pattern can usually be obtained through fixed paths for incident and diffracted X-rays. In fact, in situ measurements with this system have been carried out in the energy-dispersive mode at liquid-He temperature (Nakajima, Fukamachi, Terasaki & Hosoya, 1976, 1977), and at high pressure and high temperature (e.g. Akimoto, Yagi & Inoue, 1977) for measuring a small difference in lattice constant and determining the phase boundary of pressure-temperature diagrams respectively. However, there have been published only a few papers on the angle-dispersive use of the diffractometer with an SSD instead of with a conventional scintillation or proportional counter. In a few papers (Lauriat & Péro, 1972; Laine, Lähde, Lähde & Hämäläinen, 1974), the use of this mode has been only partially reported.

In the present work, the merits of the angle-dispersive use are described with reference to its applications, particularly to high-pressure work, although it can be applied to other extreme conditions as well.

Description of the system

The present system consists of a two-circle goniometer (Fig. 1) and data-processing system (Fig. 2). The former is more or less similar to the conventional powder goniometer except that it has neither a monochromator nor a filter. Several reports have been published on SSD diffractometers in which the tube is rotated and others in which the detector is rotated. In the present case, the former type was adopted, because Ge(Li), the SSD used, has a heavy 30-litre liquid-N₂ Dewar. If a pure-Ge detector with a small Dewar is used, the latter type of diffractometer may be preferred.

Fig. 1. The goniometer system used in the present work.

Fig. 2. Block-diagram of the complete present two-circle SSD diffractometer system.
The present system includes a multichannel analyser (MCA) with 2 kilowords memory. The amount of data accumulated in this MCA is usually substantial. The data processing to be carried out depends upon the aim of each measurement, and both the programming for measurements and the data processing often require flexibility and promptness. Because of these reasons, a simple microcomputer is equipped with 32 kilobyte memory and 256 kilobyte floppy disks. Therefore all procedures can quickly be programmed in Fortran according to the object of each measurement.

**Main characteristics**

In order to test the capabilities of the present system in the angle-dispersive mode, an Fe powder sample was measured with Cu Kα and Kβ lines separately but at the same time. The two results are shown together in Fig. 3: The peaks shown are those due to the Fe fluorescence, analysed by an SSD and a MCA, and those due to Cu Kα and Kβ lines diffracted by a glass sample at an arbitrary fixed angle. The glass was used only because it causes diffraction for the characteristic X-rays at any incident angles. These diffraction peaks were used for determining the position and width of each channel window to select the relevant X-ray lines.

Figs. 4 to 7 show the five different curves measured in the angle-dispersive mode during one angle-scan through the five channel windows a–e shown in Fig. 3. The lines due to Cu Kα and Kβ are shown in Figs. 3 and 5, respectively. The curves in Fig. 6 show the angular dependence of Fe Kα and Kβ fluorescence X-rays. For comparison, the curve in Fig. 7 is the result of integrating the X-rays over an energy range corresponding to the poor energy resolution of a typical scintillation counter.

Fig. 3. The peaks marked as F are due to fluorescence X-rays from an Fe powder sample, and peaks D are diffraction peaks of a glass sample with Cu K used as the incident beam. The range shown by a bar e is the simulated typical value of the energy window for a typical scintillation counter. The letters a, b, c and d show the energy windows of the MCA actually used for adding respective counts. The windows a–e correspond to the five patterns in Figs. 4 to 7 respectively.

Fig. 4. Diffraction pattern from an Fe powder sample due to Cu Kα.

Fig. 5. Diffraction pattern from an Fe powder sample due to Cu Kβ.

Fig. 6. Angle dependence of the intensity of fluorescence Fe Kα and Kβ X-rays from an Fe powder sample.
From these results, the following can be concluded:
(1) The diffraction patterns in Fig. 4 and 5 are very much improved in $s/n$ ratio in comparison with the curve in Fig. 7, which would be obtained with a scintillation counter. It is, therefore, possible to detect faint lines or peaks which cannot be detected by a diffractometer with a conventional counter.
(2) It is possible to collect the data with two or more kinds of characteristic X-rays at the same time if an X-ray tube is equipped with an anode made of a suitable alloy. This may be useful in particular for such a case as was reported by Hoppe & Jakubowski (1975).
(3) In relation to (2), measurements with several kinds of energies which are not necessarily characteristic X-rays can be carried out by this system.
(4) The contamination of the target in a tube, if any, does not matter much: even the notorious W L lines do not cause a serious effect in most cases, and therefore the effective life of a tube becomes longer.
(5) The fluorescence X-rays from a sample can be measured at the same time as the measurements are carried out. In a conventional system, they are noise which is difficult to remove. The curves in Fig. 6 gradually decrease in intensity in a low-angle region. This is due to the surface roughness. This surface effect obtained from Fig. 6 may be used for correcting for diffraction intensities (Weiss, 1966). In addition to or apart from such a correction, the simultaneous measurement of the fluorescence X-rays is useful for monitoring the variation of the incident X-ray intensity and/or the state of the sample.
(6) Generally speaking, neither a monochromator nor a filter is needed, and therefore the incident X-rays are efficiently used. The counting rate for a wide energy range usually does not need substantial correction for counting loss and pile-up phenomena when a conventional X-ray tube is used.

The precision in diffraction intensity was not considered in the present work, because it has already been published (Uno & Ishigaki, 1975).

Application to high-pressure diffractometry
The sample in a diamond-anvil cell is a few tens of a micron in both diameter and thickness. The diffraction from such a sample is too weak to be measured by a conventional diffractometer. However, if use is made of the present SSD diffractometer with a good $s/n$ ratio, it can be easily carried out, as shown here.

The diamond-anvil cell shown in Fig. 8 (Shimomura, Takemura, Fujii, Minomura, Mori, Noda & Yamada, 1978) is set at the position shown by the broken line in Fig. 1. The diffraction is measured by letting X-rays pass through a pair of diamond pieces and the sample with the maximum scattering angle of about 35° on both sides. The X-rays from the source, viewed as a point focus, are led into the anvil through a collimator 100 μm in diameter, so that the rays cannot irradiate the gasket made of Ni alloy (Takemura, Shimomura, Tsuji & Minomura, 1978). The receiving slit has an angular divergence of $±0.05^\circ$ and the measurements were carried with a step of $0.1^\circ$ in 2θ.

Before using the present apparatus, some of the present authors had tried to get the diffraction pattern [such as shown later in Fig. 9(a) and (b)] from the small sample in a diamond anvil with the use of a scintillation counter. In that case, the Kα radiation was separated by a monochromator, but the X-rays obtained were too weak and, besides, the $s/n$ ratio of the scintillation counter was not good enough and the system was not of practical use, because the measuring time was about ten times as long as that used in the present work.

Two examples of the results from the present system are shown in Fig. 9 for an InSb powder sample: Fig.

![Fig. 7. Diffraction pattern from an Fe powder sample accumulated in an energy window $e$. The pattern therefore includes fluorescence X-rays as well as diffraction lines.](image)

![Fig. 8. The diamond-anvil cell used for the present work. The ruby is for monitoring the pressure value.](image)
**Conclusion and discussion**

The use of an SSD diffractometer in the angle-dispersive mode allows us to carry out the following measurements in a reasonable duration of time:

1. A single angle scan enables us to obtain diffraction data at several energy values.
2. The peaks due to fluorescence X-rays are simultaneously recorded. These peaks are useful for monitoring the state of a sample, particularly when it is under extreme conditions.
3. A sample of small volume can be measured: this is useful in general and particularly so in studying samples under extreme conditions.
4. The present system can naturally be used also in an energy-dispersive mode when required. In this sense, this system can be called a universal two-circle diffractometer.

As the possible applications of the present system, the following studies will be considered:

(i) The merit described in (1) is helpful to get information necessary for making extinction corrections.
(ii) The data will be very helpful in carrying out the analysis of amorphous materials in order to obtain the partial interatomic radial distribution functions separately, making use of anomalous dispersion. The necessary data at several different energy values will be obtained more conveniently and with better accuracy than in the measurements already published (Waseda & Tamaki, 1975, 1976a, b).

References


