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X-ray diffraction on solids under pressure

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Résumé. — On passe d'abord en revue les différentes techniques de diffraction des rayons X par des poudres soumises à haute pression ; plus particulièrement, on compare les méthodes d'analyse à angle variable et à longueur d'onde variable. Dans une deuxième partie, on présente les techniques de diffraction par des monocristaux sous pression et on met en évidence quelques applications.

Abstract. — In the first part, various techniques and examples for X-ray diffraction on polycrystalline samples under high pressure will be reviewed with special emphasis on a comparison between angular and energy dispersive techniques. The second part reviews X-ray diffraction techniques for single crystals under pressure and demonstrates on few examples typical applications.

1. Introduction.

Solids under high pressure have been studied by various X-ray diffraction techniques already for many years [1-3]. The present review intends, therefore, to summarize only very briefly the basic techniques that have been described in more detail in previous reviews [3-7] and to emphasize in more detail recent developments and directions of future progress.

It should be recalled from standard text books of X-ray diffraction that basic application of X-ray diffraction is related to structure determinations on polycrystalline and single crystalline solids. In both cases, the lattice parameters, say a , b , c and α , β , γ , are determined through measurements of lattice spacings d_{hkl} (with the Miller indices h , k , l) and the atom positions within the crystalline unit cell, say (x_i, y_i, z_i) , of the various atoms on inequivalent sites i are derived from the relative intensities I_{hkl} of the different reflections.

Since the various standard techniques of X-ray diffraction find also special applications for studies on solids under pressure, the advantages and disadvantages of these different techniques should be elucidated in the next section.

2. High pressure techniques.

The basic features of various high pressure techniques are shown in the figures 1-3. These figures indicate that various types of anvil devices have to be used for

the generation of pressures above 1 GPa. Figure 1 illustrates the typical components of classical Bridgman-anvil high pressure devices [1-6], where two sintered tungsten carbide anvils compress a gasket, which contains the sample. The X-rays pass through the gasket and the diffracted X-rays are recorded

Fig. 1. — Diffraction geometry with Bridgman anvils.

primarily in the (horizontal) plane of the gasket. Various materials have been used in the past as gaskets. Boron mixed with some LiH as binder is very favourable from point of view of its low absorption, low and flat scattering background and reasonable mechanical stability [2]. Boron mixed with epoxy appears to be more favourable due to its better mechanical and chemical stability [6]. More recently [9], beryllium gaskets have been used. These gaskets show even lower absorption and allow pressure transmitting fluids to be used, however, they introduce also additional diffraction lines from the polycrystalline Be itself. Typical sizes are 0.3 to 0.5 mm thickness and 2 to 3 mm outer diameter of these gaskets.

With solid samples, pressures up to about 16 GPa are obtained with these devices [1-6]. With liquids, the generation of microcracks in the sintered tungsten carbide anvils limits at present the pressure range to below 10 GPa. Sintered diamond anvils may lead to some extension of this pressure range. Similarly, some lateral support on the conical anvil faces led to the generation of pressures up to about 25 GPa with solid pressure transmitting media [2].

Figure 2 shows the sample area of a split-octahedron type pressure cell [10], where eight sintered tungsten carbide anvils compress the eight sides of this octahedron and the slits between these anvils allow for X-ray diffraction in the horizontal plane. The inner octahedron is usually made from cured boron-epoxy.

Fig. 2. — Diffraction geometry with octahedral anvils.

It allows for a large sample volume (up to about 1 mm^3) and also for the addition of an internal heater with thermocouples. With a more recent cubic anvil X-ray system, maximum pressures of 8 GPa at 1700°C and 13 GPa up to 600°C are generated [11].

Finally, figure 3 shows the arrangement of the sample, gasket, anvils and diffraction geometry for a typical diamond anvil device. This type of devices

Fig. 3. — Diffraction geometry with diamond anvils.

leads usually to a stronger absorption due to a total absorption length of 4 to 6 mm diamond, however, with a low scattering background from the diamonds, since these two single crystals result only in diffraction spots (or somewhat smeared out streaks). The total amount of sample in these devices is usually very small ($150 \mu\text{m}$ diameter and $20 \mu\text{m}$ thickness)

Fig. 4. — Mechanical press for Bridgman anvils [13].

and leads, therefore, to special provisions in the diffraction techniques, which will be discussed later. The Bridgman-anvil devices (Fig. 1) as well as the diamond-anvil devices (Fig. 3) are specially suited for use at low temperatures. Figure 4 illustrates one mechanical device [12, 13], which allows to generate pressures up to 15 GPa even at liquid helium temperature and which can be used with a liquid helium cryostat, (Fig. 5) [12-15], on a standard Debye-Scherrer powder

Fig. 5. — Cryostat with Bridgman anvil device [13].

diffractometer (Fig. 6) [12, 13]. More recently [16], also diamond anvil devices have been adapted for X-ray diffraction at low temperatures. Figure 7

Fig. 6. — Powder diffractometer with Bridgman anvil device [13].

shows the sample area of a diamond cell in more detail [6]. Usually, the sample is embedded in a pressure transmitting medium either methanol-ethanol or, more recently, solidified gases like nitrogen, argon and helium [7], and the pressure is determined from the shift of the red ruby fluorescence line [17-20].

Fig. 7. — Gasketed diamond anvil cell [6].

Figure 8 shows the diamond cell, which is used in our laboratory and which can be operated also by remote control using a gear box and a stepping motor to turn the threaded rods which pull the levers together for the application of force to the anvils.

Fig. 8. — Mechanical press for diamond anvils [6].

3. Powder X-ray diffraction.

X-ray diffraction on polycrystalline samples under pressure used initially the angular dispersive mode [1-4]. The energy dispersive mode was applied first for high pressure studies in 1969 [2]. However, it gained wide spread application only in combination with the diamond anvil high pressure technique [6].

In the angular dispersive mode, monochromatic X-rays (with a given wavelength λ) are diffracted by the sample, and the diffraction peaks are recorded at various angles θ_{hkl} according to the Bragg condition $\sin \theta_{hkl} = \frac{\lambda}{2 d_{hkl}}$. In the energy dispersive mode, white

X-rays are used and the diffraction peaks are analysed at a fixed angle θ at various energies

$$E_{hkl} = \frac{6.20 \text{ keV } \text{\AA}}{d_{hkl} \cdot \sin \theta}.$$

Both techniques have their advantages and disadvantages, and one has to compare these techniques in detail for each special application.

4. Angular dispersive powder X-ray diffraction.

The angular dispersive technique has been used with films [1-4], with standard powder diffractometers [6], and with linear detectors [22]. The highest resolution and accuracy has been obtained with diffractometers [13]. A typical diffraction pattern of this technique is reproduced in figure 9 [13]. By careful comparison

Fig. 9. — Angular dispersive powder pattern for NaCl [13].

of the two patterns for 1 bar and 103 kbar, one can notice not only the line shifts due to the changes in the lattice parameters, but also changes in relative intensities due to texture under high pressure. A quantitative evaluation of the line shifts in terms of $\Delta a/a_0 = (a_{hkl}(P) - a_0)/a_0$ in figure 10 with respect to the parameter $\Gamma(hkl) = (h^2 k^2 l^2 + k^2 l^2 + l^2 h^2)/(h^2 + k^2 + l^2)^2$ shows systematic effects of nonhydrostatic stresses [23] by the slope of the line in figure 10A. These effects limit the accuracy of the lattice parameter determination in non-hydrostatic environments to $\pm 1 \times 10^{-3}$ or ± 2 kbar already in the range below 10 GPa, if no special precautions are taken. Recently, we performed similar measurements on NaCl in Be-gaskets with a hydrostatic pressure transmitting medium, and a preliminary evaluation of these data [24] as shown in figure 10B and C indicate that these effects can be reduced indeed by a hydrostatic pressure transmitting fluid to a level, which allows for lattice parameter determinations with an accuracy of $\pm 2 \times 10^{-4}$.

As indicated by the results in figure 9, the intensity

Fig. 10. — Effect of nonhydrostatic stress on various d -spacings of NaCl : A) under nonhydrostatic stress [13], B) and C) under hydrostatic stress [24].

data from polycrystalline samples in nonhydrostatic environments are normally effected by these stresses and by texture, and only very special cases may allow for a quantitative evaluation of these intensities with respect to a determination of atom position parameters [25].

Diffraction patterns like the one in figure 9 can be recorded with a conventional MoK_α -fine focus tube and a total counting time of typically 12 h with Bridgman-type anvils. The use of a rotating anode X-ray generator can reduce the counting time by a factor of about 8 if one keeps all other parameters fixed.

The use of diamond anvil devices reduces the counting rate at least by a factor of 10 and requires therefore either film techniques [1-4] or the application of linear detectors [22] and favourably also the use of a rotating anode generator.

Another alternative is the application of the energy dispersive technique.

5. Energy dispersive powder X-ray diffraction.

Energy dispersive X-ray diffraction uses a multiplexer advantage similar to the use of a linear detector in the angular dispersive method to increase the total count rate. Since spectral brightness in the white spectrum even of a tungsten X-ray tube is at least two orders of magnitude weaker than the spectral brightness in the K_α -lines of a molybdenum X-ray tube, typical spectra (Fig. 11), in the standard small slit geometry [26] are quite comparable to the angular dispersive pattern (Fig. 9), also from point of view of total

Fig. 11. — Energy dispersive powder pattern for NaCl [26, 6].

counting time. A real advantage of the energy dispersive method is obtained only by either a special scattering geometry or by the use of white X-ray radiation from an X-ray synchrotron source.

The geometrical advantage can be obtained by a conical slit system together with a large area solid state detector [6, 16, 27-29], which can be optimized for high counting rate at a slightly reduced resolution and gives then count rates which are typically two orders of magnitude higher than in the simple slit geometry [15, 26] of the energy dispersive technique.

The present arrangement of our laboratory for the use of energy dispersive diffraction with a tungsten fine focus tube and a conical slit is illustrated in figures 12 and 13, which show the various degrees of freedom for the adjustment of the collimator, sample and conical slit, and indicate also the recent [30] addition of a lense and mirror in the conical slit for simultaneous pressure measurements by the ruby fluorescence technique. Typical energy dispersive X-ray diffraction data for silver under pressure in a diamond cell are shown in figure 14 [28], which illustrates also the effect of various digital smoothing procedures. A detailed evaluation of these data shows [28], that the precision of the lattice parameter

Fig. 13. — Mechanical components for energy dispersive X-ray diffraction with conical slit [30].

Block Diagramme

Fig. 12. — Energy dispersive technique with conical slit [28].

Fig. 14. — Energy dispersive X-ray diffraction pattern from silver at 16 GPa and different recording times [28]. A) 1 min. counting no smoothing, B) 1 min. counting smoothing, C) 30 min. counting no smoothing.

determination in the 1 min spectrum is 0.2 %, which is only a factor 2 worse than for the 30 min spectrum. In less favourable cases than silver, counting times of two hours are more typical for an optimized lattice parameter determination with this equipment.

This conical slit has not yet been used with synchrotron radiation. However, the use of synchrotron radiation with small area detectors and small angular divergence gives already very short counting times, typically below 10 min, with very good resolution and an improved signal to background ratio as shown in figure 15 [31]. Even light elements, like chlorine, can be studied reasonably with this technique

Fig. 15. — Energy dispersive diffraction with synchrotron radiation on bromine under pressure [31].

[31]. Typically, the accuracy in the lattice parameter determination with this technique was up to now of the order of 1×10^{-3} and this rather large value resulted most probably also from effects of non-hydrostatic stresses. Very recently, measurements on gold using energy dispersive diffraction with synchrotron radiation on samples in nearly hydrostatic environments in the sample space of a cubic press [32] showed that a precision in the lattice parameter determination of 1×10^{-4} can be obtained with this technique.

The major limitation of these powder diffraction techniques resulted from the fact that the intensities of the diffraction lines are usually effected by texture and do not allow, therefore, a quantitative evaluation of changes in the atom position parameters. To overcome this limitation, also single crystal X-ray diffraction techniques have been supplemented with high pressure devices.

6. Single crystal X-ray diffraction.

First X-ray diffraction studies on single crystals under pressure were published already in 1965 [33, 34]. Various improvements in the design of the high pressure cells and in the adaptation to commercial Buerger-precession-cameras [35-37] and to automatic four-circle-diffractometers [38-41] extended the application of this technique essentially. Special features of our diamond anvil cell [37] for single crystal X-ray diffraction are illustrated in figure 16, and a pre-

Fig. 16. — Gasketed diamond anvil cell for single crystal X-ray diffraction.

cession X-ray photograph of Se at 8.7 GPa with streaks from the diamonds and more than 20 small spots from the Se-(*hhl*)-planes [42] is shown in figure 17. The adaptation of our diamond anvil cell to a commercial automatic single crystal diffractometer [43] is shown in figure 18. Just one application of this device is illustrated by the results in figure 19 to figure 21. Figure 19 shows the changes in the lattice parameters of GaS as determined by this single crystal X-ray diffraction technique [44]. The disconti-

Fig. 17. — Precession X-ray photograph of selenium at 8.7 GPa [42].

Fig. 18. — Diamond anvil cell on an automatic X-ray diffractometer [43].

nuity of the curves at about 1.3 GPa results from a structural phase transition, which does not destroy the single crystal and corresponds to a rearrangement of all the Ga-layers [44] as shown in figure 20. The space group remains the same ($P6_3/mmc$) in this phase transition, but the Ga-atoms change their position

Fig. 19. — Changes in lattice parameters of GaAs under compression [44].

Fig. 20. — Change in atom positions for gallium in GaAs under pressure; (top : low pressure phase, bottom : high pressure phase) [44].

from the 4f sites ($1/3, 2/3, z(\text{Ga})$) to the 4e sites ($0, 0, z(\text{Ga})$), whereas the S-atoms remain in their positions 4f ($1/3, 2/3, z(\text{S})$) however, with some discontinuity in the variation of the atom position parameter $z(\text{S})$ at the phase transition as shown in figure 21 [44].

Fig. 21. — Effect of pressure on the atom position parameters $z(\text{Ga})$ and $z(\text{S})$ in GaAs before and after the structural transition at 1.3 GPa [43].

Besides such studies on single crystals under high hydrostatic pressures, in special cases, single crystals have been studied also under uniaxial stress by X-ray diffraction techniques [45] to learn more about the bond-bending parameters in the diamond lattice.

7. Conclusion.

Powder X-ray diffraction techniques have been adapted to various high pressure techniques which allow either for high precision in the lattice parameter determination ($\pm 0.01\%$) at pressures below 10 GPa and temperatures between 4.2 and 900 K or for an extended pressure range (up to 150 GPa) and lower precision ($\pm 0.1\%$) due to nonhydrostatic stresses. Progress in handling of solidified gases as pressure transmitting media may still improve the precision in this extended pressure range.

The application of synchrotron radiation with conical slit systems in energy dispersive diffraction may lead to very high counting rates which will allow for time resolution down to parts of a second in kinetic studies of phase transitions.

The use of solidified gases as pressure transmitting media in single crystal X-ray diffraction studies could also extend the present limit of 10 GPa in the pressure range to much higher values.

Small heaters around the diamonds are currently developed in various laboratories, and seem to work reliably up to 800 °C [46].

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