16. APPARATUS AND TECHNIQUES

16.6-1 ESTIMATION OF UNIAXIAL STRESS COMPONENT IN DIAMOND ANVIL HIGH PRESSURE CELL. By S. Danu Devi and A.K. Singh, Materials Science Division, National Aeronautical Laboratory, Bangalore 560017, India.

The stress distribution in a solid specimen pressurized in a diamond anvil cell can be approximated to a superposition of hydrostatic component and an uniaxial stress component (USB). The USB vanishes only when a fluid pressure transmitting medium is used. The USB of detectable magnitude can be present if no pressure transmitting medium is used or the solid specimen comes directly in contact with the anvils. The estimation of USB is important, because the presence of USB introduces systematic errors in x-ray diffraction data. In this paper a method has been suggested for analyzing the high pressure x-ray diffraction data to detect the presence of USB. In the present method, the theoretical expression for the lattice strains derived for the diamond-anvil geometry (A.K. Singh and C. Balasingh, J. Appl. Phys. 1977, 45, 641). In this paper a method has been suggested for analyzing the high pressure x-ray diffraction data to detect the presence of USB. In the present method, the theoretical expression for the lattice strains derived for the diamond-anvil geometry (A.K. Singh and C. Balasingh, J. Appl. Phys. 1977, 45, 641) is fitted to the measured lattice strains, and the magnitude of USB obtained. The method has been used to analyze the high pressure x-ray diffraction data on sodium chloride.

16.6-2 NEW CONSTRUCTED DIAMOND-ANVIL CELL FOR HIGH-PRESSURE SINGLE CRYSTAL X-RAY DIFFRACTION. By M. Malinowski, Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, Poland.

A new diamond-anvil high-pressure cell has been developed for use on several types of commercial automatic four-circle diffractometers and precession cameras. This cell has repeatedly attained pressure of up to 100 kbar. The diffraction geometry of this cell is presented in the figure. It is a combination of the geometry presented by Schifferi (Schifferi, Rev. Sci. Instrum. 1977, 8, 24-30) and the geometry used in the majority of high-pressure cells (Merrill, Rev. Sci. Instrum. 1974, 45, 290-294). For this construction a very large area of the Ewald sphere is available and a continuous range of 2θ value is available from low to very high angles. This allows very accurate lattice constant determinations and facilitates more accurate determinations of atom positions from intensity measurements as well. Pressure calibration is done by NaCl as the internal standard to calibrate. The pressure or can also be determined by using the fluorescence technique. High-pressure is generated by a bracket system, similar to suggested by Keller (Keller, Rev. Sci. Instrum. 1975, 46, 973-979).

16.6-3 HIGH-PRESSURE STRUCTURAL STUDIES OF CERIUM METAL UP TO 30 GPa USING SYNCHROTRON RADIATION. By U. Benedict, L. Gerward and J. Staun Olsen. a) Commission of the European Communities, Joint Research Centre, European Institute for Transuranium Elements, Karlsruhe, FRG, b) Lab. of Applied Physics III, Technical Univ. of Denmark, Lyngby, c) Physical Lab. II, H.C. Orsted Institute, Univ. of Copenhagen, Denmark.

At 0.8 GPa there is an isosymmetric change from γ-Ce to α-Ce, both with the fcc structure. At 5 GPa we find a transition from γ-Ce to monoclinic α'-Ce and at 12 GPa another transition from α'-Ce to tetragonal Ce. The high-pressure phases can be described as distorted fcc structures as shown by the following examples:

\[ P(\text{GPa}) \quad a : b : c \quad a^0 \quad \text{Structure} \]

- 0 - 1 \quad 1 : 1 : \sqrt{2} \quad 90.0 \quad \gamma: \text{fcc}
- 6.9 \quad 1.001 : 1 : 1.52 \quad 92.0 \quad \alpha': \text{monoclinic b.c.}
- 17.1 \quad 1 : 1 : 1.67 \quad 90.0 \quad \text{tetragonal b.c.}

α'-Ce has previously been observed by Zachariasen et al. (1) for 5 < P < 10 GPa, and tetragonal Ce by Endo et al. (2) for 12 < P < 17.5 GPa. We have compared our data with the equation of state calculated by Skriver (3) and found a good agreement between 5 and 20 GPa. At higher pressures deviations occur, probably because the theory works with a frozen core.


16.6-4 AN IMPROVED DIAMOND-ANVIL HIGH-PRESSURE CELL FOR SINGLE CRYSTAL X-RAY WORK. By W. Disterek, J. Glinsemann, J. Koppke, and H. Schulz, Max-Planck-Institut für Festkörperforschung, Stuttgart, FRG.

A high pressure cell has been developed especially for single crystal X-ray diffraction (Malinowski, et al., 1982). The primary and secondary beams penetrate only one anvil (Fig. 2). This diffraction geometry has been used among others also by Schifferi et al. (Rev. Sci. Instr., 1978, 49 (3), 393).

Work on quartz with this prototype cell (Glinsemann and Schulz, this meeting) led to a modified construction (Fig. 1). The main characteristics are:

(1) The proportion of measurable non-Friedel reflections for 2θ < 90° increases from about 40% in usual cells to over 90% in our construction.
(2) No counterboring is needed due to the weight of about 700g. Therefore the cell will work on diffractometers without full x-circles.
(3) Size and diffraction geometry allow the use of Weissenberg cameras with double-radius film cylinders and adequately enlarged layer line screens.

![Fig. 1](image-url)
The monoclinic one has cubic and monoclinic phase respectively. At ambient conditions two hydrogen bonds of about 300pm are connected by four kets. The cell is mounted on a particularly stable STOE XTA goniometer head with a height adjustment of 10mm and sits on a Philips single crystal diffractometer, which has a rather small x-circle. So the whole equipment can easily be used on different types of four-circle diffractometers.

In our construction the gasket is the only strong absorber left in the paths of the X-rays. The use of beryllium reduces this shortcomings dramatically. Recently pressures up to 80kbar have been reached with these beryllium gaskets.

For a great number of experiments e.g. investigations of plastic crystals or incommensurate structures pressures below 4 kbar are sufficient. For this range it is possible to construct small gas-pressure cells for hydrostatic pressure determination are well-known. The disadvantages as very small samples, nonuniformity of the pressure, and inaccuracy of the pressure determination are well-known. For a great number of experiments e.g. investigations of plastic crystals or incommensurate structures pressures below 4 kbar are sufficient. For this range it is possible to construct small gas-pressure cells for hydrostatic pressure determination are well-known. The disadvantages as very small samples, nonuniformity of the pressure, and inaccuracy of the pressure determination are well-known.

A single crystal of the UREA high pressure phase (transition 4.5kbar) could be grown. Using our pressure cell for four-circle diffractometers (Ahsbahs, Rev. Sci. Instr. (1984) 55, 99) the structure has been determined. The crystal was of poor quality. Another measurement with a better crystal will be performed. Crystal data determined so far: a=858, b=827, c=364pm, space group P212121, Z=4.

A fixed-bed microreactor, capable of operating with mixtures of reducing or oxidizing liquids or gases at pressures between 100 millitorr and one atmosphere, and at temperatures between 80° and 1000° Kelvin, has been constructed especially for x-ray diffraction applications. In a model system study, the crystalline phase catalyst transformations during the oxidation of tetrahydrofuran (THF) over a V₂O₅-SiO₂ catalyst have been examined. The fixed-Bed reactor, operated in isothermal mode and computer-controlled at temperatures between 443° and 488° Kelvin at atmospheric pressure, was used to collect x-ray diffraction data at each programmed setpoint. XRD measurements in situ show significant proportion of V(IV) on carrying out the oxidation of THF on the catalysts. Reduction in H₂ at temperatures above 443° Kelvin gives rise to V₃O₅, which is similar to the effect when the reduction is induced by THF.