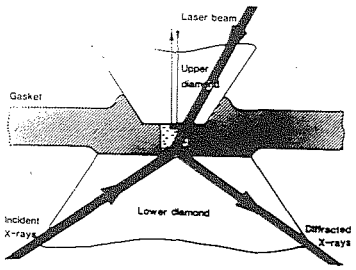
16.6–1 ESTIMATION OF UNIAXIAL STRESS COMPONENT IN DIAMOND ANVIL HIGH PRESSURE CELL. By S.Usha Devi and A.K.Singh, Materials Science Division, National Aeronautical Laboratory, Bangalore 560017, India.

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 (USC). The USC vanishes only when fluid pressure transmitting medium is used. The USC 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 USC is important, because the presence of USC introduces systematic errors in x-ray diffraction data (A.K.Singh, High Temp-High Pressures, (1978), 10, 641). In this paper a method has been suggested of analysing the high pressure x-ray diffraction data to detect the presence of USC. 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) 48, 5338) is fitted to the measured lattice strains, and the magnitude of USC obtained. The method has been used to analyse the high pressure x-ray diffraction data on sodium chloride.

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

A new diamond-anvil high-ressure 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 Schiferl (Schiferl,Rev.Sci.Instrum. (1977)48,24-30) 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 continous 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 calibratation 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 presented 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[a], L. Gerward[b] and J. Staun Olsen[c].
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. Ørsted 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 α-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 (GPa)	a : b : c	β(°)	Structure
0 - 1	1 : 1 : $\sqrt{2}$	90.0	γ,α: fcc
6.9	1.001 : 1 : 1.52	92.0	α": monoclinic b.c.
17.1	1 : 1 : 1.67	90.0	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.

(1) W.H. Zachariasen and F.H. Ellinger, Acta Cryst. A33 (1977), 155-160.
(2) S. Endo, N. Fujioka and H. Sasaki, in High-Pressure Science and Technology, Vol. 1 (ed. by K.D. Timmerhaus and M.S. Barber), Plenum 1979, pp. 217-222.
(3) H.L. Skriver, in Systematics and Properties of the Lanthanides (ed. by F.P. Finka), Reidel 1982, pp. 213-254.

16.6–4 AN IMPROVED DIAMOND-ANVIL HIGH-PRESSURE CELL FOR SINGLE CRYSTAL WORK. By W. Dieterich, J. Glinnemann, J. Koepke, 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), 159 (1-4), 93). The primary and secondary beams penetrate only one anvil (Fig. 2). This diffraction geometry has been used among others also by Schiferl et. al. (Rev. Sci. Instr., (1978), 49 (3), 359).

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

(1) The proportion of measurable non-Friedel reflections for $2\theta < 90^{\circ}$ increases from about 40% in usual cells to over 90% in our construction.

(2) No counterbearing is needed due to the weight of about 700g. Therefore the cell will work on diffractometers without full χ-circles.

(3) Size and diffraction geometry allow the use of Weißenberg cameras with double-radius film cylinders and adequately enlarged layer line screens.

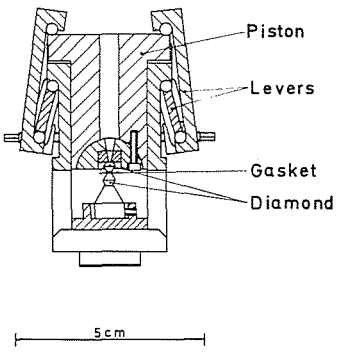


Fig. 1

(4) The cell is mounted on a particularly stable STOE XYZ goniometer head with a height adjustment of 1omm and fits on a Philips single crystal diffractometer, which has a rather small χ-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.

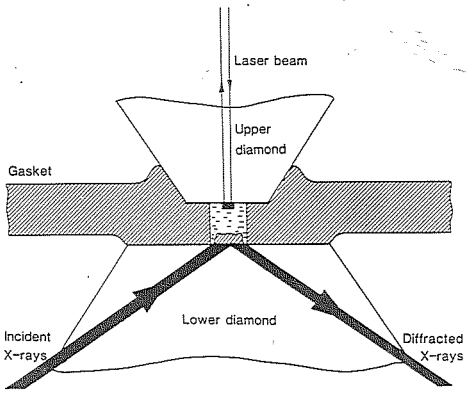


Fig. 2

16.6–5 HIGH PRESSURE PHASES OF SOME ORGANIC COMPOUNDS. By H. Ahsbahs and U. Ohms, Institute for Mineralogy, University of Marburg, Lahnberge, 3550 Marburg, FRG

We investigated the behaviour under pressure of a number of organic compounds whose electron densities have been determined in the Sonderforschungsbereich "Kristallstruktur und chemische Bindung" in Marburg.

A single crystal of the UREA high pressure phase (transition 4.6kbar) 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 $P2_12_12_1$, Z=4. Asymetric unit: one molecule in general position. R-value 0.087. In the normal pressure phase the molecules are connected by four hydrogen bonds of about 300pm length. In the high pressure phase there are only three hydrogen bonds, two of them shortend by ≈10pm, one is extended a little.

At ambient conditions HEXACYANOBENZENE is cubic, space group Pa3. At 4kbar a high pressure modification is formed. The X-ray powder diffraction lines can be indexed hexagonal with a=870 and c=2460pm.

4-METHYLPYRIDINE is liquid at room temperature and freezes under pressure (1.3kbar) in the same structure as at low temperature. With increasing pressure the structure deforms.

TETRACYANOETHYLENE is dimorph at ambient conditions. The cubic form changes to a high pressure modification with only slightly increased density in the order of 20kbar, the monoclinic one has two high pressure phases at 3kbar and at 20kbar. On release both return to their original cubic and monoclinic phase respectively.

16.6–6 IN SITU HETEROGENEOUS CATALYSIS STUDIES AT VARIABLE TEMPERATURES BY AUTOMATED X-RAY DIFFRACTION SPECTROMETRY. By Glover A. Jones, Central Research & Development Department, E. I. du Pont de Nemours & Company, Experimental Station, Wilmington, Delaware 19898, U.S.A.

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) to γ-butyrolactone over a V_2O_5-SiO_2 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 H_2 at temperatures above 443° Kelvin gives rise to V_4O_9, which is similar to the effect when the reduction is induced by THF.

16.6–7 HIGH-PRESSURE CELL FOR GUINIER X-RAY DIFFRACTION. By K. Knorr, Institut für Kristallographie der Universität Tübingen, West-Germany.

Diamond anvil cells for x-ray diffraction are available up to very high pressures. 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 conditions and with large sample areas suitable for Guinier diffraction geometrie. We have designed and tested such a cell for applications in the temperature range from 100 to 400 K and for pressures up to 4.1 Kbar at all temperatures. This pressure cell with a diameter of 26 mm and a hight of 20 mm is machined from CuBe alloy, the windows from 2 mm thick Be plates. The slits for the diffracted and the primary beam, respectively, allow diffraction angles from $2\theta = 60°$ to - 30° and oscillation of the sample of ± 10° relative to the primary beam. As the experiments have shown this movement is necessary because many powder samples develop texture effects as a result of recrystallisation during pressure and temperature treatment. He gas is used as the pressure medium. The pressure of 4 kbar is generated by a small transportable (weight 35 kp) supply unit which is operated manually. The pressure cell has been tested successfully in a reinvestigation of the ammonium nitrate p-T-diagram.