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Neutron Diffraction of Large-Volume Samples at High Pressure Using Compact Opposed-Anvil Cells *

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Neutron diffraction techniques of large-volume samples at high pressure using compact opposed-anvil cells are developed at a reactor neutron source, China's Mianyang research reactor. We achieve a high-pressure condition of in situ neutron diffraction by means of a newly designed large-volume opposed-anvil cell. This pressure calibration is based on resistance measurements of bismuth and the neutron diffraction of iron. Pressure calibration experiments are performed at room temperature for a new cell using the tungsten carbide anvils with a tapered angle of 30°, Φ4.5 mm culet diameter and the metal-nonmetal composite gasket with a thickness of 2 mm. Transitions in Bi (I–II 2.55 GPa, III–V 7.7 GPa) are observed at 100 and 300 kN, respectively, by resistance measurements. The pressure measurement results of neutron diffraction are consistent with resistance measurements of bismuth. As a result, pressures up to about 7.7 GPa can routinely and stably be achieved using this apparatus, with the sample volume of 9 mm^3.

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The pressure is similar to the temperature and chemical component, which is one of the basic elements in thermodynamics to determine the existing form, changing the internal structure and property of materials. Nowadays, high-pressure science is being applied in significant scientific research areas more and more extensively, such as new materials, new energy sources, chemistry, geoscience, physics and planetary science.[1–4] However, the progress in high-pressure technology largely depends on *in situ* characterized methods, which are mainly represented by the synchrotron radiation x-ray technology and the neutron diffraction technology. Neutrons play a complementary role to x-rays in solid state physics and chemistry, geophysics, and material science at high pressure, because they are the unique probe for structural analysis of hydrogen bearing materials which work effectively even at high pressures. In recent years, the combination of the neutron diffraction technology with high-pressure apparatus has been an important high-pressure *in situ* characterization technique and has exhibited more effects especially on aqueous minerals, magnetic, superconducting, energetic materials and so on.[5–10]

The Paris-Edinburgh press (P-E press)[10,11] has been widely used as a simple and large volume high-pressure apparatus, which was mainly developed for neutron diffraction experiments. When diamond is used as the anvil material, the neutron diffraction experiment can be carried out under high pressure about 25 GPa. To obtain a higher pressure, the Carnegie institution in Washington developed a moissanite anvil cell (MAC), with silicon-carbide monocrystal as the anvil material, producing a pressure of 50 GPa.[12–14] However, the sample volume is very small (less than 1 mm^3), which limits the further promotion and applications of the apparatus. In 2013, Boehler *et al.*[15] designed a strong-support cone-angle diamond anvil, in which the neutron diffraction pattern of D_2O was obtained under 94 GPa, with a sample volume less than 0.02 mm^3. How to obtain high-pressure neutron diffraction data of high-quality on large-volume samples is a problem urgently needing to be solved.

The purpose of the present study is to increase the sample volume to 9 mm^3 or more and to establish experimental techniques for the easy generation of stable high pressures using an opposed-type high pressure apparatus utilizing tungsten carbide (WC) as the anvil material. The detail of this experimental technique and some examples of high-pressure *in situ* neutron diffraction measurements are presented. Results of some pressure calibration experiments and the obtained load versus pressure curves are presented.

The high-pressure neutron diffraction experiment is performed on the high-pressure neutron diffraction spectrometer in China's Mianyang Research Reactor (Fig. 1(a)). The monochromator of the diffractometer is made of 13 Ge (511) crystals, which generate the neutron wavelength of $\lambda = 1.59$ Å. The detector consists of 70 ^{3}He counting tubes, scanning the diffraction angle from 8° to 172°. The minimum resolution of the diffractometer is $\Delta d/d = 0.35\%$. The load is applied by the hydraulic oil loading system (Fig. 1(b)), which ensures the load pressures are continuously adjustable

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and maintains the pressures for a long time (>48 h). The loading system is capable of producing forces up to 1 MN. The mobile platform can make 3D translation and rotation (x, y, z, ω) operations. A detailed description of the high pressure press can be found elsewhere.[16,17]

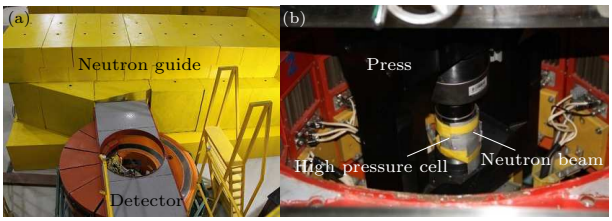

Fig. 1. (a) High-pressure neutron diffraction spectrometer, and (b) high-pressure loading system.

Pressure calibration experiments were conducted at room temperature. The phase transition of Bi (I–II transition at 2.55 GPa and III–V transition at 7.7 GPa) were used as fixed points to determine the generated pressures.[18] The resistance of the bismuth was measured using the four-wire method through the top and bottom anvils to detect phase transitions. A very thin Bi wire is placed on the center of the half-cut pyrophyllite gasket. Copper foils (0.01 mm thickness) are used as electrodes for the electrical connection with WC anvils. The resistance data were continuously recorded by a digital multimeter (Fluke, 8846A). The load was increased at a rate of approximately 2 kN/min.

An iron cylinder (Alfa, 99.99%) with the size of $\Phi 2 \times 3$ mm (volume of 9 mm^3) is used as a sample and simultaneously as an internal pressure marker. Cadmium foil was used to surround the cell, which stops scattered neutrons from entering the cell body. The neutron beam was directed horizontally at the sample through a hole in the cell, and then transmitted through the gasket and sample.

Figure 2 shows the major parts of the apparatus: opposed anvils, a cylindrical guide, a gasket-sample assembly and a pyrophyllite cap for lateral support. After assembly, these parts have an outer diameter, height and inner diameter of Φ about 40 mm, 25 mm and 21 mm, respectively. The two opposing anvils are contained in a cylinder, which contains windows for *in situ* neutron beam access. Unlike the piston-cylinder apparatus, this cylinder works only as a guide for the two anvils and no supporting force is applied to the anvils. Between the cylinder and the anvils, there is a bakelite insulation layer with a thickness of 0.5 mm, which will facilitate the pressure calibration experiment and future heating experiment.

To increase the sample volume, we used a cupped-type anvil. Anvils with a tapered angle of 30° and Φ4.5 mm culet diameter are made of cemented tungsten carbide (WC). The metal-nonmetal composite gasket has been used previously, as reported in Ref. [19]. The outer metal gasket (Φ20 mm × 2 mm thickness with a Φ7 mm hole) is made of the null-scattering Ti/Zr alloy (67.7 mol% Ti, 32.2 mol% Zr) while the inner nonmetal gasket (Φ7 mm × 2 mm thick with a Φ2 mm × 3 mm height hole) is made of sintered pyrophyllite. The culet size of the anvils is smaller than the inside diameter of the metal gasket, thus the anvils and metal gasket do not touch during compression. The metal-nonmetal composite gasket was quite effective for high-pressure generation and for preventing sample blowouts during high-pressure experiments. The main role of two pyrophyllite caps is to fill the spaces between the anvil and the gasket.

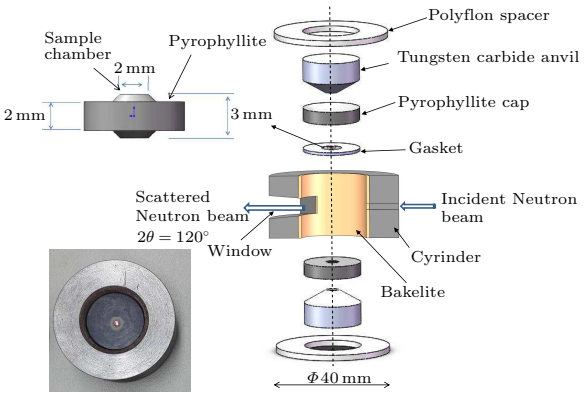

Fig. 2. Schematic illustration of the components of the high-pressure apparatus and a photograph of the new apparatus (bottom left). The inner nonmetal gasket (Φ7 mm×2 mm thick with a Φ2 mm×3 mm height hole) is made of sintered pyrophyllite (top left). Only 'cylinder' is drawn by cross section view and the 'window' is a hole for neutron access.

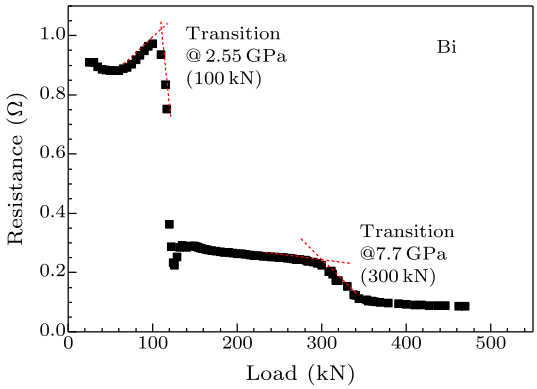

Fig. 3. Resistance variation of bismuth with load at ambient temperature.

Resistance measurement with applied load in bismuth is shown in Fig. 3. Resistance increased gradually from ~0.89 Ω to ~0.97 Ω between 50 and 100 kN. We observed a large decrease of resistance from ~0.97 Ω to ~0.3 Ω, from ~0.3 Ω to ~0.2 Ω and from ~0.2 Ω to ~0.09 Ω at 100 kN, 125 kN and 300 kN, respectively. This behavior is similar to that observed by Bean *et al.*[20] Using this observation, we judged that pressures of 2.55 GPa and 7.7 GPa were generated at 100 kN and 300 kN, respectively.

Figure 4 shows the neutron diffraction patterns collected at different loads using the new assembly.

Curve a in Fig. 4 is the pattern of the original iron sample (with size of $\Phi 2 \times 3$ mm). Curve b in Fig. 4 is the pattern of iron collected at 150 kN. Apart from several peaks derived from the WC anvil, the peaks of 110, 200 and 211 reflection of iron were detected. The peak positions of 110, 200 and 211 are slightly shifted toward the high-angle side and their intensities are reduced as compared with the starting sample. The diffraction peaks such as 211 suggest that the diffraction signal of iron changes obviously. Curves c and d in Fig. 4 are the patterns of iron collected at 200 kN and 290 kN, respectively. The peaks of 110, 200 and 211 reflection of iron were further shifted toward the high-angle side. It should be mentioned that the three strongest peaks of iron 110, 200 and 211 all exist in the pattern.

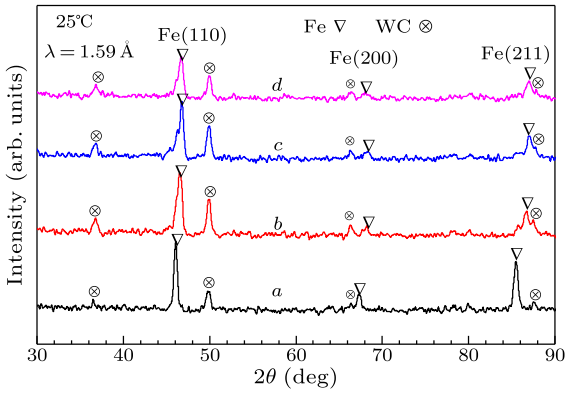

Fig. 4. The neutron diffraction patterns of iron collected under the ambient condition (a), 150 kN (b), 200 kN (c), and 290 kN (d), respectively. All of the peaks of Fe coming from the sample are indexed in the figure. The peaks of WC are obtained from the WC anvils.

The pressure was determined from the d-spacing of the (211) diffraction peak (d_{110}) of iron. The relationship of the lattice parameter of iron (bcc), which is calculated from peak d-spacing at room temperature as a function of pressure, was calibrated previously,[21] and can be written as

$$\alpha = 0.2866\left(1 + \frac{10P}{275}\right)^{-0.056}, \qquad (1)$$

where α is the lattice constant of the bcc phase iron in nanometer, and P is the pressure in GPa. The PDIdexer software is used to fit the neutron diffraction data, and the lattice constant of the bcc phase iron is obtained. Table 1 lists the lattice constants (α, V) and pressure under different loading forces.

Table 1. Lattice constants (α, V) and pressure under different loading forces.

Loading force (kN)	α (nm)	V (nm^3)	P (GPa)
0	0.2873	0.02372	0
150	0.2842	0.02297	4.35
200	0.2835	0.02278	5.48
290	0.2830	0.02268	7.23

The pressure calibration curves can be obtained based on the phase transition of bismuth and the neutron diffraction of iron, as shown in Fig. 5. The pressure measurement results of neutron diffraction are consistent with electrical resistance measurements of bismuth. This is partly a validation of bismuth pressure calibration results. The pressure increases almost linearly with the applied load, achieving a pressure of 7.7 GPa at about 300 kN. However, this does not mean that 7.7 GPa is the pressure limit of this apparatus because neither a sample blowout nor anvil failure has occurred at this pressure.

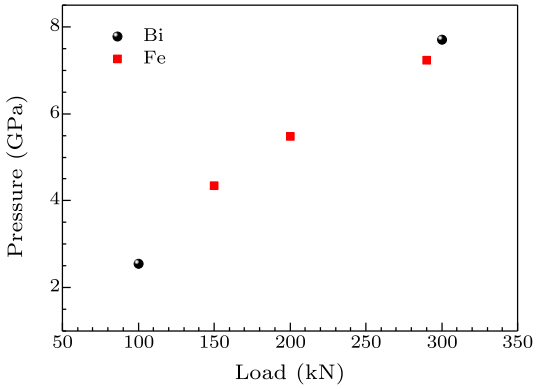

Fig. 5. Pressure generated as a function of applied load at room temperature. Symbols: the circles are determined for the phase transition of Bi by resistance measurement; and the squares are for the neutron diffraction of iron.

According to the definition of pressure $P = F/S$, for 4.5 mm diameter culet of anvil, the calculative pressure should be 12.5 GPa for 200 kN. However, the practical pressure at the load of 200 kN for assembly is 6 GPa. Thus the pressure generation efficiencies can be calculated to be about 48%. The pressure generation efficiency is related to the diameter culet of the anvil, the yield strength and the thickness of the gasket, and the size of the sample cavity. When the diameter culet of the anvil is constant, the pressure generation by the opposed-anvil apparatus can be calculated by[22,23]

$$\delta_n = nk + \frac{2k}{\sqrt{3}}\left(\frac{r_0}{d} - \frac{r_g}{d}\right), \qquad (2)$$

where δ_n is the normal stress on the gasket surface, k is the yield strength of the gasket material, r_0, r_g and d are the radius of the anvil surface, the radius of the sample cavity and the thickness of the gasket, respectively. Under the near-hydrostatic pressure, the stress on the gasket surface can be equivalent to the pressure generation on the sample. Therefore, when r_0/d and $r_0 - r_g$ increase, the pressure P also increases, that is, reducing the thickness of the gasket or reducing the diameter of the sample cavity can increase the pressure generation efficiency. If the pressure generation efficiency increases to 80%, the practical pressures at the load of 200 kN should be 10 GPa. On the other hand, for this high-pressure apparatus with an anvil culet diameter of 4.5 mm, it is necessary to use the stiffer material as the anvil[24] to further improve its pres-

sure generation efficiency. For this purpose, a nano-polycrystalline diamond anvil has been purchased by our laboratory that can withstand ultra-high pressure. The anvil has high hardness and strength, and relevant experiments are under way. According to the definition of pressure, if the pressure generation efficiency is calculated as 85%, the anvil with culet diameter 4.5 mm can produce the pressure of about 17 GPa when the load is 300 kN.

In summary, we have developed an opposed-anvil-type high-pressure apparatus for *in situ* neutron diffraction. The diffraction patterns of iron at high-pressure conditions in this apparatus are achieved. It is confirmed that this apparatus combined with the reactor neutron source is a useful experimental tool. Using WC anvils with a culet diameter of 4.5 mm and a tapering angle of 30°, pressure of 7.7 GPa is generated at 300 kN, with sample volume of 9 mm^3. The neutron diffraction patterns show that iron can be compressed to 7.23 GPa at 290 kN with the WC anvil. In the future, by applying a synthetic polycrystalline diamond anvil, the pressure could be extended much higher in the near future with the same sample volume.

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