Angle-dispersive neutron diffraction under high pressure to 10 GPa

S. Klotz, Th. Strässle, G. Rousse, and G. Hamel
Physique des Milieux Denses, IMPMC, Université P&M Curie B77, 4 Place Jussieu, 75252 Paris, France

V. Pomjakushin
Laboratory for Neutron Scattering, ETH Zürich and PSI, 5232 Villigen PSI, Switzerland

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We present a method which allows high-quality powder neutron diffraction patterns to be obtained under pressure by angle-dispersive diffraction to at least 10 GPa. This technique uses a new type of Paris–Edinburgh press in conjunction with sintered boron nitride anvils. As an example, we show NiO diffraction patterns obtained under purely hydrostatic pressures up to 10 GPa. These data were collected within a few hours, and are free from any contaminating signal from the pressure cell. High-resolution nuclear and magnetic structural information can be readily extracted by Rietveld refinements, without additional data correction. This technique will allow powder neutron diffraction at elevated pressures to become a standard tool on continuous neutron facilities. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1855419]

There has been considerable progress in the last decade in structural studies of matter using powder neutron diffraction under pressure.[1] Neutrons are a key probe for solid-state research due to their sensitivity to light elements and magnetism, and the application of pressure has revealed a wealth of information on the behavior of matter under "extreme" conditions. A major impact in this domain was the advent of the "Paris–Edinburgh (PE) press,"[2,3] a compact high pressure device able to generate pressures up to 10 GPa on sample volumes of $\sim$100 mm^3, and pressures up to 30 GPa on sample volumes of $\sim$30 mm^3. A key feature of this method is that it enabled to collect powder patterns free of contaminant signal from the environment (anvils, pressure cell), and which can be readily treated by Rietveld refinement techniques. This has become possible by restricting the diffraction angle to $\sim$90°, which allows a very efficient elimination of stray signal by tightening the collimation of the incoming and diffracted beams. Consequently, in this method the data are collected in the energy-dispersive mode by time-of-flight (TOF) spectroscopy. The technique is hence ideally suited to pulsed sources, such as the neutron facilities ISIS in the United Kingdom or LANSCE in the United States. This explains the enormous success of the PE press for high-pressure structural studies at these facilities. Continuous neutron sources, such as reactor based facilities, where powder diffraction patterns are usually collected in the angle-dispersive mode, have, on the contrary, not been able to benefit from the recent progress in high-pressure techniques. The principal reason being that (a) no compact high-pressure devices with sufficiently large angular apertures were available, and (b) the strong contamination of the pattern by signal from the anvils (unavoidable in such a geometry) prevents a reliable data analysis by Rietveld methods. Consequently, accurate high-pressure powder diffraction studies in the 10 GPa range are inexistent at most of the present neutron facilities, i.e., reactor sources.

We present a method which overcomes these restrictions, opening the possibility of detailed structural studies by powder diffraction on most continuous neutron facilities. The method makes use of a newly developed PE cell providing two large openings of 140° (Fig. 1). The press has a capacity of 200 tn and a mass of 60 kg; its principal mechanical characteristics were described previously.[4] Pressure in the sample is generated by two toroidal anvils[5] deforming a metallic gasket which contains a sample volume of 30–100 mm^3, depending on the maximum sought pressure. Unlike the standard PE setup, the scattering plane is in the equatorial plane of the anvils, i.e., both the incident and diffracted neutrons pass through the gasket. An essential element is the use of cubic boron nitride anvils. Due to the strong absorption of natural boron (σ_a=767 barn), the anvils act as a beam stop for neutrons which hit parts made of BN. Since we use zero-scattering TiZr alloy as gasket material, the only illuminated material which gives rise to diffraction peaks is the sample. This is demonstrated in Fig. 2, which shows raw diffraction data of NiO collected at 9.5 GPa at the HRPT diffractometer[6] of the Swiss spallation neutron source SINQ at the Paul Scherrer Institute, Villigen, Switzerland. NiO is type II antiferromagnetic (T_N=523 K) with a slightly rhombohedrally distorted NaCl structure (at ambient conditions: $\sim$60.06° in $R\bar{3}m$ space group instead of 60° for the ideal cubic NaCl structure).[7] All visible diffraction peaks in Fig. 2 are from the sample, the reflections at 18° and 34° are of pure magnetic origin, as indicated by the tickmarks underneath the data points. Hydrostatic pressure was assured by using a deuterated 4:1 methanol-ethanol mixture[8] in conjunction with special TiZr gaskets described elsewhere.[9] The line through the data is a result of a Rietveld refinement including both the nuclear and magnetic structure, eventually yielding the extremely weak pressure dependence of the rhombohedral distortion α and the magnetic moment μ to very high precision $[d\alpha/dP = +0.007(1)°/\mathrm{GPa}, d\mu/dP = 0.00(1)\mu_B/\mathrm{GPa}]$.

Several conclusions can be drawn from these experiments. First, the fact that it is possible to obtain accurate diffraction data in the 10 GPa range in a reasonable amount of time (hours) clearly demonstrates the suitability of this technique for most existing continuous neutron facilities, provided full advantage of modern instrumentation is taken. The multidetector neutron powder diffractometer HRPT at SINQ allows simultaneous data acquisition within a scattering angle range of 160° and stepsize of 0.1°. This instrument

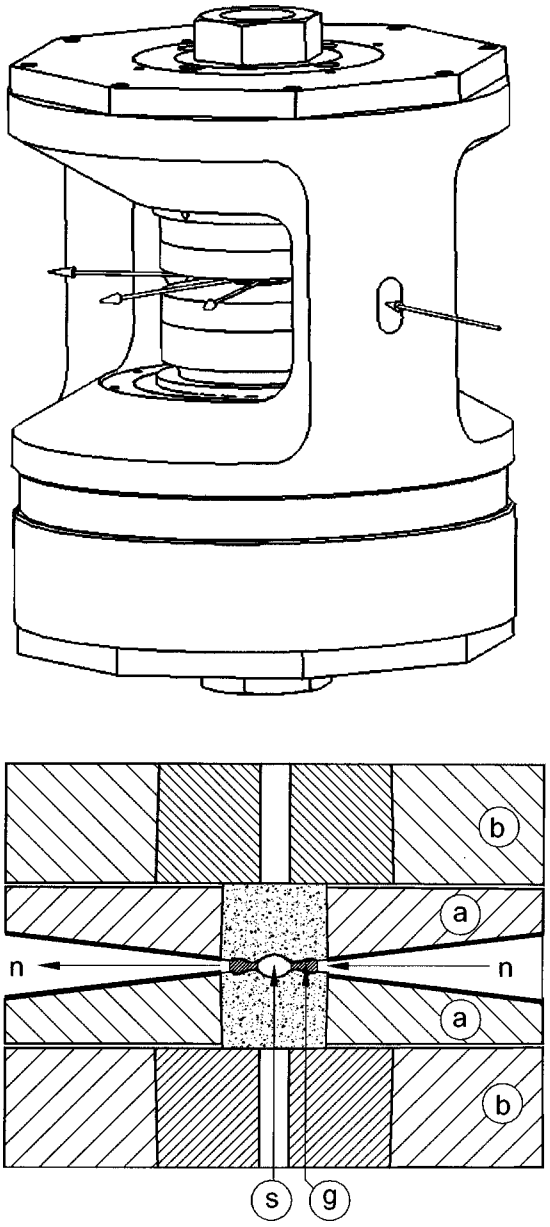

FIG. 1. Upper: VX Paris–Edinburgh press indicating the scattering geometry with the incident and diffracted neutron beams. The diameter of the press is 250 mm, its mass 60 kg. Lower: enlarged cross section of the anvil assembly: (a) anvils (speckle: cubic boron nitride, wide hatch: steel binding ring); (b) backing seats (narrow hatch: tungsten carbide, wide hatch: steel binding ring); (s) sample chamber; (g) gasket made of zero-scattering TiZr alloy. Bold lines on the anvil faces indicate 0.2 mm cadmium shielding. The diameter of the assembly is 90 mm.

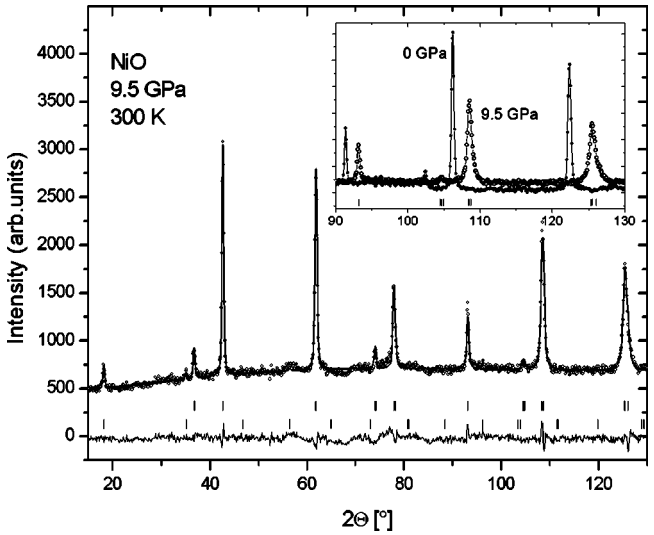

FIG. 2. Rietveld refinement pattern and difference plot of the neutron diffraction data of NiO obtained in the pressure cell at hydrostatic pressure of 9.5 GPa after 4 h of data collection at the HRPT/SINQ diffractometer ($\lambda = 1.494$ Å in high-intensity mode). The line through the data (dots) is a result of a Rietveld fit to the nuclear and magnetic structure. Upper and lower tick marks show the calculated nuclear and magnetic Bragg peak positions, respectively. Inset: high-angle part of the spectrum (open circles) compared to corresponding data at ambient pressure (closed circles). Note the broadening of the multiple reflection at ~126° (and ~108°) due to the increased rhombohedral splitting under pressure, compared to the single reflection at ~93° which remains sharp.

is equipped with a radial collimator, which efficiently lowers the background, a feature which may be critical at other instruments. Second, high resolution may be essential for various studies, such as the present one on NiO. Using HRPT's high-intensity mode (with primary collimation of 40′) the resolution in this experiment was as high as $\Delta d/d = 0.2\%$ (at $2\theta \approx 120°$), which is a factor 3–4 better than what could so far be achieved on TOF instruments in the standard $2\theta = 90°$ configuration. The possibility of obtaining data with such elevated resolution (while maintaining hydrostatic conditions) opens unexpected opportunities in structural research under pressure. The ability of constant-wavelength diffractometers to vary easily the resolution function versus intensity (by changing the primary and secondary beam collimations or by changing the takeoff monochromator angle, for example) adds additional flexibility to this method, which generally lacks on TOF diffractometers. Third, using a monochromatic neutron beam the patterns can be directly used for Rietveld analysis without any correction. In contrast, in methods using a polychromatic beam, the intensity of the incident beam is heavily distorted by the wavelength dependent absorption of the anvils, which needs sophisticated correction of the data prior to the Rietveld analysis.[10] This procedure is crucial to all TOF measurements and requires detailed knowledge of the absorption properties of the anvil material, including the presence of steep "Bragg edges," i.e., step changes in the attenuation occurring at wavelengths $\lambda = 2d_{hkl}$, where d_{hkl} is the d-spacing of reflection hkl.

We conclude that the method presented here may have a significant impact for research under high pressure since it can be readily implemented at most of the current continuous neutron sources. This will allow a wide community to benefit from new and important experimental conditions. We expect that the technique can be easily extended to pressures beyond 20 GPa by the use of double-toroidal boron–nitride anvils having a profile as described previously[2] (though the pressure in this domain can no longer be expected to be hydrostatic unless better pressure media are found). The use of the cell at low temperature down to ~20 K is currently under development.

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measurements using BN anvils (provided by W. Crichton) were carried out.

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