

# Two-dimensional energy dispersive x-ray diffraction at high pressures and temperatures

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Diffraction studies at extreme pressure-temperature conditions encounter intrinsic difficulties due to the small access angle of the diamond anvil cell and the high background of the diffraction peaks. Energy-dispersive x-ray diffraction is ideal for overcoming these difficulties and allows the collection and display of diffracted signals on the order of seconds, but is limited to one-dimensional information. Materials at high pressures in diamond anvil cells, particularly during simultaneous laser heating to temperatures greater than 3000 K often form coarse crystals and develop preferred orientation, and thus require information in a second dimension for complete analysis. We have developed and applied a diamond cell rotation method for *in situ* energy-dispersive x-ray diffraction at high pressures and temperatures in solving this problem. With this method, we can record the x-ray diffraction as a function of  $\chi$  angle over  $360^\circ$ , and we can acquire sufficient information for the determination of high  $P$ - $T$  phase diagrams, structural properties, and equations of state. Technical details are presented along with experimental results for iron and boron. © 2001 American Institute of Physics. [DOI: 10.1063/1.1343865]

## I. INTRODUCTION

Recent technological developments have brought about major improvements in high pressure science and technology. In many ways, this began when the diamond anvil cell was utilized to generate high pressure in combination with the synchrotron x-ray diffraction techniques (see Refs. 1–5, for example). With further development and application of synchrotron light sources, the availability of high power lasers, sensitive and high-resolution charge coupled device (CCD) detectors, and advanced computer control techniques, we are now able to routinely perform *in situ* phase-related investigations at megabar pressures and temperatures greater than 1000 K. The long-awaited simulation of materials at the conditions of Earth's inner core is now only a matter of time. Among available techniques, *in situ* energy-dispersive x-ray diffraction with double-sided laser-heating in the diamond cell offers many technical advantages. The energy-dispersive method overcomes the limitation caused by the small seat opening of the cell, and it gives a lower diffraction background as a result of the limited detecting space. In an angle dispersive method, this narrow seat opening either (1) precludes acquisition of high-angle data with a lower x-ray energy, or (2) increases the background and lowers the resolution with a higher energy. The energy-dispersive method can employ a wide range of available energies, and one therefore obtains a much larger range of  $d$  spacings. Energy-

dispersive diffraction also greatly enhances the efficiency of the diffracted beam and provides a well-resolved diffraction pattern within seconds.

The double-sided laser heating system<sup>6,7</sup> consists of a focused, high-power laser beam entering both sides of the diamond cell and provides a homogenous temperature distribution within 20–50  $\mu\text{m}$  around the sample. This homogenous temperature region can be made larger than the diffracting spot, and the quality of experimental data has consequently been increased. We have designed a visual observation system that allows us to monitor the heating process during data collection. With these techniques, we can carry out the diffraction experiment *in situ* at high pressures and high temperatures, and can expect to identify a high  $P$ - $T$  phase within minutes. However, there are certain limitations inherent in the energy-dispersive x-ray diffraction system. Instead of detecting the diffracted x rays in a full circle as is done with an imaging plate, the energy-dispersive method allows us to detect a diffraction signal at only one point in the diffraction plane, so an ideal powder sample is required. With increasing temperature, however, the powder grain size grows and coarse crystals form; crystals also tend intrinsically to orient along certain directions in the diamond cell. In such circumstances, the diffraction signal may be partially or even completely lost. In particular, the problem becomes much more serious when using synchrotron radiation with the laser-heated diamond anvil cell to study solid-liquid phase transitions. In this article we discuss a sample rotation technique that improves the energy-dispersive synchrotron

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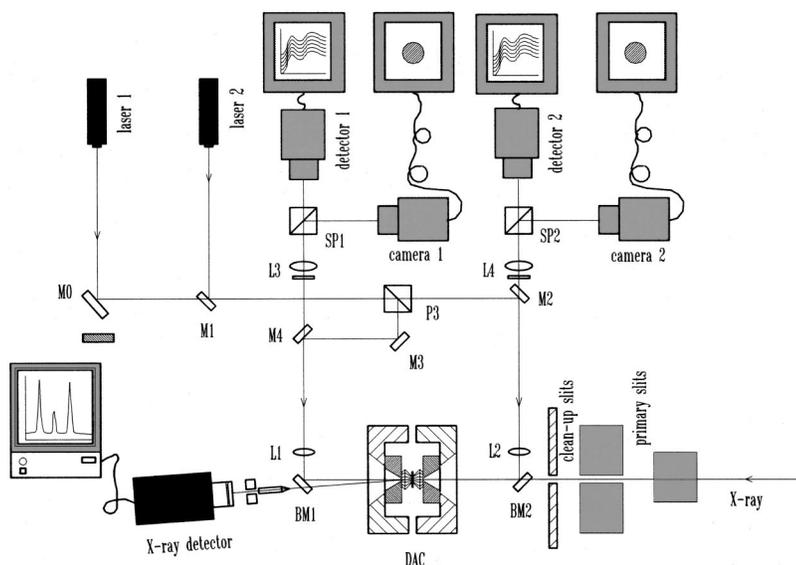


FIG. 1. Synchrotron x-ray diffraction system for double-sided laser heating with the diamond anvil cell. The system is installed at sector 13 of the advanced photon source (APS).

x-ray diffraction experiment by solving the coarse crystal and preferred orientation problems, and present some of our high  $P$ - $T$  experimental results.

## II. Experimental setup

### A. X-ray diffraction system

In Fig. 1 we show a schematic diagram of the experimental system for *in situ* synchrotron x-ray diffraction with the laser-heated diamond anvil cell. We introduce x rays (white beam) into the experimental hutch, the beam confined by the front end slits to  $100 \times 100 \mu\text{m}$  in size. This beam passes through a pair of perpendicular tungsten carbide slits, which further reduce the beam to a size determined by the configuration of the system. When using mirrors to focus the beam onto the sample, we select  $80 \mu\text{m}$  slits. When using the direct beam on the sample, the slit size is determined by diffraction from the sample; we determine the beam size by scanning the direct beam and then take the width at half height of the transmitted intensity. If necessary we can also introduce a pair of perpendicular mounted mirrors. With an  $80 \mu\text{m}$  incident beam, these mirrors can focus the x-ray beam to  $30 \mu\text{m}$  at the sample position. We apply a pair of clean-up slits in front of the sample to block the scattered wings on either side of the intense x-ray beam. The diffracted x rays pass through a narrow tip and a Huber slit, and are collected by a multichannel CCD detector.

### B. Laser heating setup

The double-sided laser heating setup we use is also shown in Fig. 1. A high-powered yttrium–aluminum–garnet laser was selected to generate a large, uniform heating spot ( $25$ – $50 \mu\text{m}$ ). The laser beam is split into two parts by a 50/50 high-energy laser prism, which is focused from both sides through the diamond onto the sample. We measure the thermal emission with a spectrometer/CCD detector system, from which we calculate the temperature of the diffracting sample. With this setup, we can also visually monitor the heating process with an optical microscope and camera.

### C. The sample rotation method

We have modified a high-precision rotation stage to mount a diamond anvil cell, which can then be laser-heated *in situ* to high temperatures. The high on-axis accuracy ( $0.023^\circ$ ) and low wobble (tilt angle,  $70 \mu\text{rad}$ ) makes the error in the sample position negligible. The high repeatability ( $\pm 0.003^\circ$ ) permits us to accurately relocate the sample position. The rotation speed can be preselected up to  $20^\circ/\text{s}$  with a resolution of  $0.001^\circ$ . Thus, we can precisely control and accurately locate the sample position during an *in situ* experiment. During the experiment, we mount the cell so that the back diamond surface is perpendicular to the normal axis of the cell rotation. This permits us to keep the focused lasers fixed on one spot of the sample during cell rotation. With systematic evaluations we have found that the main position error comes from the cell mount on the rotation stage, which causes a position error of  $2 \mu\text{m}$  within a  $360^\circ$  rotation. This error, however, is negligible when the sample, the laser heating spot and x-ray beam sizes are all well matched.

The alignment of this system is one of the important factors in the acquisition of high-quality data. To make the

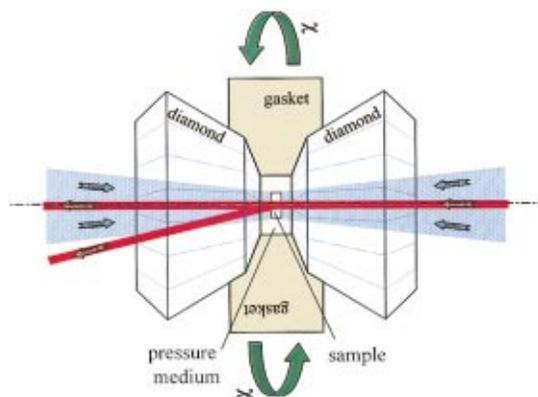


FIG. 2. (Color) Schematic diagram of *in situ* high  $P$ - $T$  x-ray diffraction in a rotating diamond anvil cell during heating, emphasizing that the x-ray beam, laser optical axis, visual observation optical axis, and the cell rotation normal are coaxial.

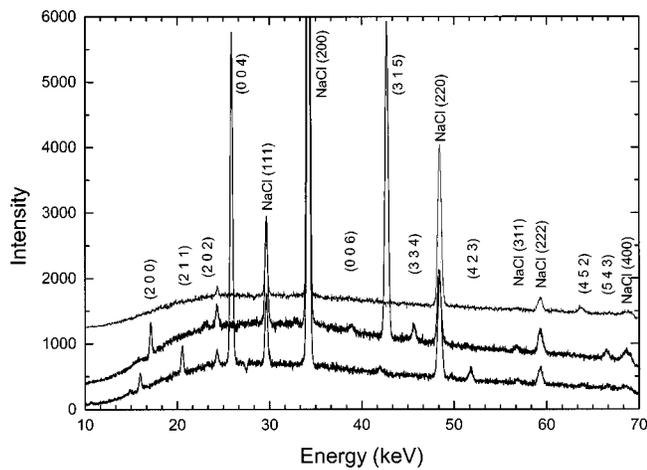


FIG. 3. X-ray diffraction of boron at different  $\chi$  angles at 11.7 GPa after heating. The unmarked peaks are from the x-ray diffraction system.

alignment process efficient, we also align each axis (the x-ray beam line, the heating laser lines, and the observation optical lines) through the rotation stage normal (Fig. 2). In this way, we essentially eliminate the interference of the diamond refraction at the sample location as well as the difficulty in matching the functioning part of the system through the same part of the sample. Some of the other possible alignment errors are discussed in detail elsewhere.<sup>8</sup>

There are two ways to utilize the cell rotation method: the continuous-rotation method and step-rotation method. With the continuous-rotation method, we keep the cell rotating on the stage at a given speed while collecting the diffraction signal. In this way, we can collect signals from the full circle of the diffracting ring and obtain an averaged diffraction spectrum within the covered angles. In the step-rotation method, we rotate the cell to a specific position at a predetermined step rate and collect diffraction data at each step. We need to determine the step of the rotation angle so that the two adjacent steps will permit the detector to completely cover the selected portion of the diffracting ring, but with minimal overlap. We can also determine the step by rotating the sample beforehand at a small enough step to determine the smallest step that can cause any change of the diffraction

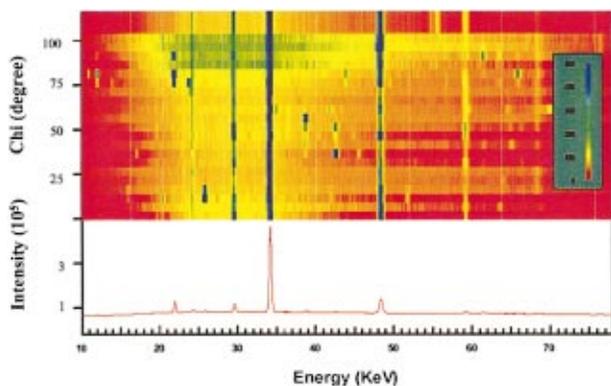


FIG. 4. (Color) Step-rotated x-ray diffraction image with the integrated pattern of boron at 11.7 GPa with NaCl as the pressure medium. Top, the image of the diffraction within  $100^\circ$  rotation in  $\chi$ ; bottom, the integrated pattern from all the patterns in the  $100^\circ$  range.

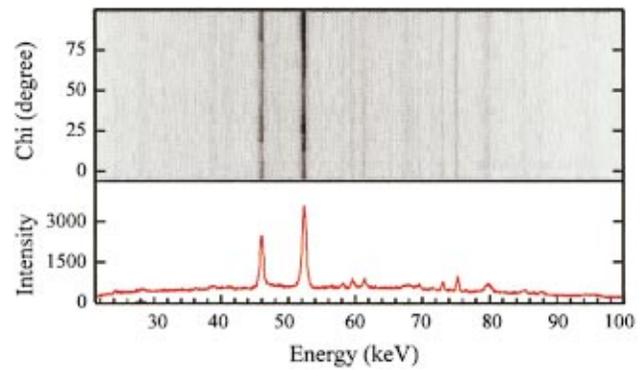


FIG. 5. (Color) X-ray diffraction images of iron at 161 GPa and 2450 K. Top, as a function of  $\chi$  angle; bottom, integrated pattern.

pattern. Ultimately, we obtain a set of diffraction patterns corresponding to the  $\chi$  angles covered. This method combines the advantage of a continuous-rotation method by adding the whole series of patterns together to form an averaged pattern. Most often, we apply the step-rotation method in our experiments.

### III. EXPERIMENTAL RESULTS

#### A. Boron quench experiment

Boron is a low-Z element that has a very low scattering cross section and causes difficulty for x-ray diffraction studies at high pressure. So far, the only available high-pressure diffraction data is the equation of state at  $\sim 10$  GPa from a neutron diffraction experiment.<sup>9</sup> The high pressure and high temperature studies are much more difficult because of the formation of preferred orientation and coarse crystals at these conditions. Figure 3 shows our comparison of the spectra of boron at 11.7 GPa after heating at 1800 K, taken at three different  $\chi$  angles. From a comparison of the individual patterns, it is clear that the diffraction position and intensity dramatically change at different  $\chi$  angles, and we can easily lose the diffraction completely at certain positions. Such experimental difficulties have kept the high  $P$ - $T$  phase of boron a mystery. This problem, however, has been solved by adopting the step-rotation method. Figure 4 shows the dif-

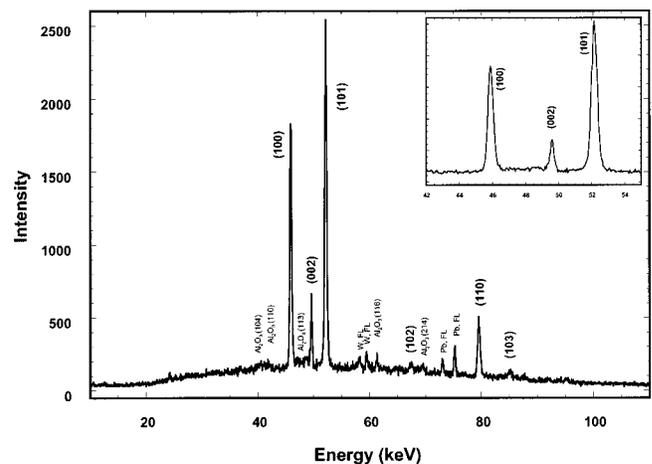


FIG. 6. X-ray diffraction pattern of iron at 161 GPa and 2450 K. Inset shows the intense peaks of iron on an expanded scale.

fraction image in comparison with the integrated pattern of a temperature-quenched sample at 11.7 GPa. The dark lines and spots represent the diffraction peaks of boron from this imaging technique. We can clearly resolve 37 diffraction peaks. With these results, we find that rhombohedral R-105 boron transforms to a tetragonal T-192 form, a stable high-pressure phase.<sup>10</sup>

### B. Fe at 161 GPa and 2450 K

Iron has been one of the most widely studied minerals and is of fundamental importance for understanding the behavior of Earth's inner core. There has been much debate on its phases at high pressure and high temperature (see Ref. 11, for example). We have carried out an *in situ* x-ray diffraction study of iron at conditions approaching those of Earth's outer core. Figure 5 shows the diffraction image of iron at 161 GPa and 2450 K. With the sample rotation technique, we can perform well-controlled experiments to determine its high  $P$ - $T$  phases. We can also simulate the possible error that may result from the experiments, such as the shoulders that appear on the peaks. We find that the only high-pressure solid phase of iron is hexagonal-close-packed (hcp) above the  $\epsilon$ (hcp)- $\gamma$ (face-centered-cubic) liquid triple point. The integrated diffraction pattern shown in Fig. 6 indicates that the peak width approaches the detector resolution, and no peaks except those from the hcp phase can be observed. The only

change identified is the intensity variation with increasing temperature associated with texture effect. This further clarifies the iron phase diagram, as discussed more fully elsewhere.<sup>8</sup>

### ACKNOWLEDGMENTS

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