Journal of
Synchrotron
Radiation

ISSN 0909-0495

Received 14 April 2005
Accepted 4 July 2005

A new paradigm to extend diffraction measurements beyond the megabar regime

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The possibility of using X-ray diffraction to precisely monitor crystal structure at the extremes of pressure and temperature produced by shock-wave loading is explored. A summary of the advantages of using various X-ray sources for this work and an outline of the necessary experimental layout is given.

Keywords: high pressure; shock waves; time-resolved X-ray diffraction; X-ray free-electron lasers.

1. Introduction

Understanding the effects of pressure and temperature upon crystal structure is an essential prerequisite to our being able to validate and improve predictions of the thermodynamic and mechanical behavior of solids from first principles. This requires a body of data, relating atomic position to pressure and temperature, to be produced.

Diffraction measurements are essential for the determination of accurate crystal structures. Determining crystal structures from diffraction data is a mature technique applied in the laboratory and also at synchrotron and neutron sources. Light-weight diamond anvil high-pressure cells, sometimes equipped with resistive heaters, provide a convenient method of applying well known diffraction techniques to samples held at high pressures and temperatures (Hazen & Finger, 1982). This has been established as a relatively routine procedure both in the laboratory and at synchrotron sources using both polychromatic and monochromatic radiation.

The main limitations of this method lie in the small sample size and potentially large pressure and temperature gradients inside the diamond anvil cell. Diamond cells are limited to relatively modest temperatures and pressures, have a very small sample volume, have restricted X-ray access, provide poor sample containment at high pressure and temperature, and X-ray absorption by diamonds limits the minimum wavelength that we can use and hence limits the available absorption edges for, say, anomalous scattering. Also, any uncertainties in temperature, owing to the remote positioning of thermocouples or temperature gradients and optical aberrations with pyrometry, lead to uncertainties in the pressure since it is usually determined by use of an internal diffraction pressure standard and the previously determined thermal equation of state for that material.

What is needed is the use of a complementary approach to pressure–temperature generation that overcomes these limitations. An alternative technology does exist: shock waves can be used to generate high pressures and temperatures, and might provide an alternative route to determining crystal structures under extreme conditions.

Here we explore the conditions necessary to determine high-quality crystal structures from materials held at shock-generated high pressures and temperatures. The ability of a crystal to withstand shock loading is an immediate concern. Fractures, twins *etc.* needed to break up a single crystal can only propagate at the shear-wave velocity, which is of the order of about 1–10 km s^{-1} (= 1–10 nm ps^{-1}). Therefore, any newly formed grain boundaries can only propagate about 1 nm during the course of the $\sim$100 fs experiments we describe below. This distance is small compared with the 1–10 μm dimension of our diffracting region, so our samples may remain quasi-single crystalline.

2. Pressure–temperature generation

The traditional method used to generate high pressure and temperatures for diffraction measurements involves using a diamond anvil cell and resistive heater. The diamond anvil cell comprises two opposed diamonds of about 2.5 mm height and 200 μm culet with a thin metal gasket between them. A hole drilled in the gasket and centered on the culet faces provides a sample chamber of about 50 nl volume. By pressing the diamonds together the sample volume can be decreased and the pressure increased to over 500 GPa. By heating the whole assembly using a resistive heater, combined high pressures and temperatures can be achieved. Single-crystal data have been collected using these devices up to combined temperatures and pressures of about 10–20 GPa and 1273 K. The maximum temperatures achievable using a diamond cell can be extended to a few thousand Kelvin by using laser heating. This is routinely carried out using polycrystalline samples but has not yet been successfully applied to single-crystal samples. One reason for this might be the very large temperature gradients that are present using laser heating causing strain in the single-

crystal sample and low-quality single-crystal diffraction patterns.

An alternative method of pressure and temperature generation involves using shock waves. Two methods of shock-wave generation are commonly used. In the first a metal plate or flyer is propelled into the sample using either an electromagnetic field or rapid expansion of a gas (Gupta, 1992). This commonly involves a large sample (∼cm diameter and ∼mm thick) but the impellor mechanism may take many hours to re-arm ready for the next measurement. In the second a laser is used to ablate a small portion of the sample or a material coated on the surface of the sample (Swift *et al.*, 2004). The force generated in opposition to the force of ablation passes through the sample and generates a shock wave. This method typically uses a sample size of about 1 mm diameter and 10 μm thick and has a repetition rate, that varies greatly with the laser system, of about 10^{-3} to 10 Hz.

These methods have been used to generate combined pressures and temperatures in the hundreds of GPa and thousands of Kelvin ranges and overcome the limitations of the diamond cell listed above, although they do have their own limitations; for example, lasers suffer from possible preheating effects and difficulty in ensuring constant pressure and the flyers are difficult to synchronize with diagnostics. An additional advantage of using shock waves to generate high pressures and temperatures is that the velocity of the shock can be measured using Doppler velocimetry; for example, visible interferometry system for any reflector (VISAR) (Barker & Hollenbach, 1972). This allows the pressure to be accurately determined and the temperature measured by spectroraidometry or calculated given adequate equations of state for internal standards. As such this method would seem to overcome the inherent limitations of the diamond cell technique but the shocked state is only transient with a stable temperature and pressure lasting for about 1 μs for a gas gun and ∼1–100 ns for a large laser. Also, the sample may be destroyed by the shock. We have to ask whether it is possible to collect data sufficient for accurate structure determination from samples on such short time scales and under these conditions.

3. X-ray diffraction from the shocked state

X-ray diffraction measurements from samples in the shocked state actually date back to the 1970s with a series of pioneering experiments performed at the Lawrence Livermore National Laboratory (Johnson *et al.*, 1970, 1972; Johnson & Mitchell, 1972). This capability has been developed over the years, and state-of-the-art systems now allow X-ray diffraction measurements with a temporal resolution of a few nanoseconds or less (Gupta *et al.*, 1999; Rigg & Gupta, 2003). Temporal resolution can be achieved by using a short X-ray pulse, and/or time-resolved diagnostics such as an X-ray streak camera. These devices typically have an aperture of only a few degrees, which allows only a limited volume of reciprocal space to be sampled during each shock event. Given the variations in pressure and temperature inherent when using shock waves to generate high pressures and temperatures, a much more satisfactory arrangement would be to collect all of the necessary reflections simultaneously or with the least number of measurements possible. Ideally one would want to achieve the necessary temporal resolution by using a single pulse of X-rays having a short time duration. That way, one could use a conventional area detector such as film, imaging plate or CCD detector, and sample a large volume of reciprocal space simultaneously. Before considering which X-ray source would be most appropriate for these measurements, we should ask ourselves how many X-rays are needed in a pulse in order to collect a powder or single-crystal diffraction pattern.

4. Number of X-rays required to collect a diffraction pattern

It is possible to calculate the number of X-ray photons needed to give an X-ray diffraction pattern of sufficient signal-to-noise ratio to allow a structure solution for a perfect crystal or aggregate of small perfect crystals in a powder (Warren, 1969). Under the extreme conditions of interest to us here, we find our samples to be far from perfect with stress, strain, dislocations and disorder, thereby reducing the quality of the data.

In order to get an idea of the number of incident X-ray photons that we will need to produce data of sufficient quality, we have made a simple estimate using real samples and a monochromatic X-ray source. Data were collected from three samples chosen to represent the range and quality of samples that one might encounter in future shock experiments: a 50 μm-thick aluminium foil, an amorphous carbon foil and a small kyanite single crystal. These were set up in a similar geometry to that which one would use for shock-wave measurements on beamline 12.2.2 at the Advanced Light Source (Kunz *et al.*, 2005). The X-ray beam was monochromated using a pair of silicon (111) crystals to give X-rays of 10 keV, which were focused to a 150 μm × 90 μm spot using a toroidal mirror. The incident-beam intensity was determined using an accurately calibrated ion chamber, and was varied by placing absorbing foils before the ion chamber. X-ray diffraction patterns were collected using a MAR 345 imaging-plate detector placed 300 mm behind the sample. A representative diffraction pattern from the amorphous carbon foil is shown in Fig. 1.

The series of diffraction patterns collected with varying incident-beam flux for the amorphous carbon and Al foils were radially integrated using the *fit2d* program (Hammersley *et al.*, 1996; Hammersley, 1997) to give two-dimensional diffraction patterns. The series of patterns for the amorphous carbon foil are shown in Fig. 2. Peak fitting of these patterns and the series of single-crystal diffraction patterns from the kyanite crystal were used to determine the minimum flux necessary to accurately determine peak intensities. This was found to be about 6×10^{11} photons for the amorphous carbon, 5×10^{10} photons for the aluminium foil and 6×10^{10} photons for the kyanite single crystal.

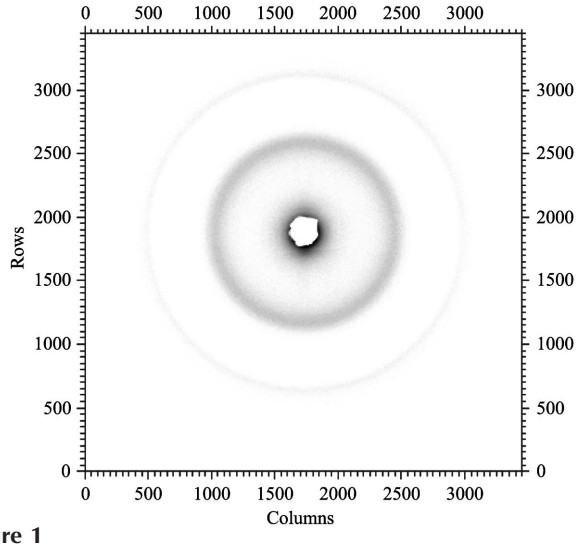

Figure 1
X-ray diffraction pattern collected from an amorphous carbon sample.

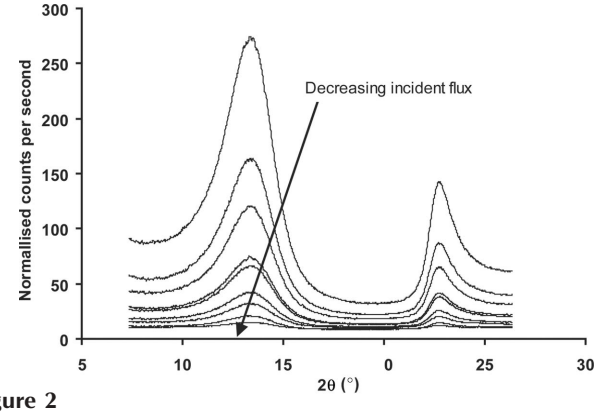

Figure 2
Radially integrated diffraction patterns from an amorphous carbon sample with decreasing incident X-ray flux.

5. Possible X-ray sources

Many technologies are being developed for producing intense pulses of X-rays with short time duration, including higher-harmonic generation, laser-generated plasmas, Thompson scattering sources, synchrotrons and free-electron lasers (FELs).

(i) Higher-harmonic sources. Higher harmonics of laser pulses can be produced in gases (L'Huillier & Balcou, 1993; Ditmire *et al.*, 1995) and at solid surfaces (Carman *et al.*, 1981; Bezzerides *et al.*, 1982). This radiation is coherent, but is limited to the soft X-ray region (Seres *et al.*, 2005) and this method will not be considered further here.

(ii) Laser-generated plasmas. Femtosecond to tens of nanosecond multi-terawatt lasers, when focused onto solid targets, generate high-density plasmas that emit short pulses of polychromatic X-rays (Kmetec *et al.*, 1992; Rousse *et al.*, 1994) with a similar distribution to those produced from a traditional X-ray tube. For example, a laser-driven plasma source developed in San Diego using a copper wire target produced 5×10^{10} photons in the Cu $K\alpha$ fluorescence line, and was used for a diffraction study of melting in semiconductors (Rose-Petruck *et al.*, 1999). A disadvantage of this technique is that the radiation is emitted over 4π steradians, so the number of photons that can usefully be used in a high-resolution X-ray diffraction measurement is probably limited to a fraction of a percent of those produced. Also, the X-ray energies that can be produced are limited by the materials that make useful emitters.

Table 1
Comparison of key parameters for various X-ray sources.

Source	X-ray energy (keV)	Photons per pulse	Pulse repetition rate	Pulse length
San Diego Plasma Source	8.05	10^5	20 Hz	300 fs
Pleiades	40–140	10^7–10^8	10 Hz	5 ps
Advanced Light Source Bend Magnet	8–12	2×10^4	0.5 GHz	70 ps
Advanced Light Source Slicing Source	8–12	2	20 kHz	200 fs
Advanced Photon Source	20–100	10^7	6.3 kHz	100 ps
Linac Coherent Light Source	8	10^{12}	120 Hz	200 fs

(iii) Thompson scattering sources, for example the Pleiades source (Anderson *et al.*, 2004). These produce short pulses of X-rays by colliding an ultra-relativistic picosecond-duration electron beam with a sub-picosecond high-intensity laser pulse. These sources are capable of producing very high energy X-rays (10–200 keV) in short coherent pulses.

(iv) Synchrotron sources. These produce intense pulses of X-rays. They tend to have a pulse length of about 100 ps, in order to have a reasonably long lifetime, with reasonably high intensity. A difficulty with synchrotron sources is that their repetition rate is not well matched to the duty cycle of the lasers suitable for producing shock waves in our samples. Selecting single X-ray pulses requires the use of a fast X-ray shutter. The fastest available X-ray shutters still require the synchrotron to operate in a special operation mode, with a reduced number of bunches in order to be able to select single bunches. An alternative method of single-pulse selection is to use a slicing source (Zholents & Zolotorev, 1996). Here, a laser beam is used to perturb the electron bunch in a synchrotron, and produce a very short pulse of X-rays on a different trajectory to those normally produced by the synchrotron. The disadvantage of this technique is that the X-ray pulses tend to have very low intensity.

(v) X-ray free-electron lasers, *e.g.* the Linac Coherent Light Source (LCLS) at the Stanford Linear Accelerator Center. These use a beam of relativistic electrons passing through a periodic transverse magnetic field to produce coherent radiation. Most scientific use of FELs has been in the infrared, but new sources such as LCLS are extending the energy range into the hard X-ray region of the electromagnetic spectrum.

The key parameters of these sources are listed in Table 1. We see from this table that a source of considerable potential for these measurements from powder or amorphous samples would be the FEL, since it is the only source that appears capable of allowing the entire diffraction pattern to be collected in one shot. Single-shot single-crystal measurements require a polychromatic beam of X-rays. Thompson sources would appear to be more suited to this type of measurement,

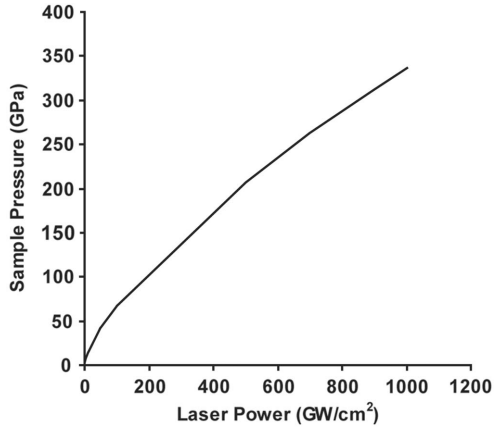

Figure 3
Variation of achievable sample pressure with laser power for a 530 nm-wavelength laser pulse of duration 100 fs.

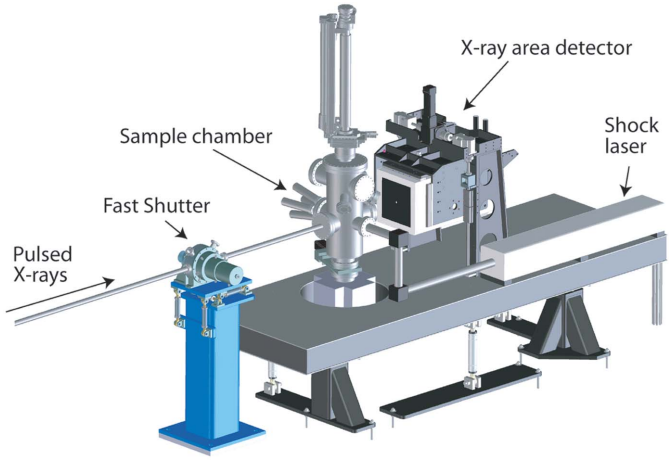

Figure 4
Schematic outline of the proposed experimental layout for diffraction measurements from samples under shock compression.

although they do not as yet produce sufficient X-ray flux per pulse to allow single-shot structure solutions.

6. Choice of laser system for shock generation

The pressure (P) generated by a shock wave produced using a laser of power I, wavelength λ and pulse length t can be approximated by the formula (Fabbro *et al.*, 1990)

$$P\ [\mathrm{GPa}] = 0.393\, I^{0.7}\ [\mathrm{GW\,cm^{-2}}]\ \lambda^{-0.3}\ [\mu\mathrm{m}]\ t^{-0.15}\ [\mathrm{ns}].$$

Fig. 3 shows a pressure–power curve for a laser of wavelength 800 nm with a pulse length of 0.5 ns. This suggests that a laser with a power of a few terawatts would be suitable for achieving pressures in excess of a few megabars.

7. Possible experimental layout

The basic components necessary for X-ray diffraction from shocked materials include a high-power laser to produce the shockwave, a suitable source of pulsed X-rays, possibly a fast X-ray shutter, possibly a sample manipulation device allowing the automatic selection of a fresh area of sample per shot, a VISAR system and a large-area X-ray detector. Previous experience using these high-power laser systems suggests that the sample will need to be contained in a vacuum enclosure. A schematic diagram of a possible experimental arrangement is given in Fig. 4. All of these components are commercially available.

8. Conclusions

It seems likely that X-ray diffraction measurements from shocked materials could be used for structure determination under extreme conditions of pressure and temperature from powder and amorphous materials. X-ray free-electron lasers appear to offer the only monochromatic sources with sufficient flux per pulse to allow single-pulse data collection. Alternatively, polychromatic sources with sufficient X-ray flux per shot need to be developed for single-shot structural studies using single crystals. This paradigm shift in the way we approach the determination of crystal structure under extreme conditions offers the only prospect available to extend measurements into the tens of megabars regime.

We would like to thank the many colleagues who have contributed to the generation of these ideas, in particular Bill Nellis, Howard Padmore, Gilbert Collins, Phil Heimann and Dick Lee. We would like to thank Martin Kunz for help with the diffraction measurements, Greg Morrison for producing Fig. 4, and Dave Walker for supplying the kyanite crystal. We would also like to thank an anonymous referee who's comments greatly improved this manuscript. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, of the US Department of Energy under Contract No. DE-AC03-76SF00098 at Lawrence Berkeley National Laboratory.

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