# Precise stress measurements with white synchrotron x rays

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In situ measurement of stress in polycrystalline samples forms the basis for studies of the mechanical properties of materials with very broad earth science and materials science applications. Synchrotron x rays have been used to define the local elastic strain in these samples, which in turn define stress. Experimental work to date has been carried out on a prototype detection system that provided a strain measurement precision  $>10^{-4}$ , which corresponds to a stress resolution >50 MPa for silicate minerals. Here we report operation of a new, permanent, energy dispersive detection system for white radiation, which has been developed at the National Synchrotron Light Source. The new system provides differential strain measurements with a precision of  $3 \times 10^{-5}$  for volumes that are  $50 \times 50 \times 500 \ \mu\text{m}^3$ . This gives a stress precision of about 10 MPa for silicate minerals. © 2010 American Institute of Physics. [doi:10.1063/1.3263760]

# I. BACKGROUND

### A. Experimental approach

Our experimental system is focused on measuring rheological properties at high pressure and temperature. We use a D-DIA to generate pressure up to 10 GPa and temperature up to 2000 K. Two differential rams, independent of the main ram that provides pressure at each end of a sample, allow the superposition of a uniaxial stress on the hydrostatic stress state. A series of breakthroughs have enabled this new technology. They include the following.

- Use of a DIA—a cubic multianvil high-pressure device—in conjunction with a synchrotron source that enables x-ray analysis of the sample.<sup>1</sup>
- Development of D-DIA for deformation experiments.<sup>2</sup>
- Analysis of stress using x-ray diffraction.<sup>3,</sup>
- Analysis of strain from x-ray images.<sup>5</sup>
- Use of x-ray transparent anvils in the multianvil system in order to obtain the necessary diffraction data for stress analysis.<sup>6,7</sup>
- The understanding of the effect of plasticity on x-ray stress measurements.<sup>7,8</sup>
- Implementation of conical slits for collimation to allow white energy-dispersive or two-dimensional (2D) detectors and to allow monochromatic angle-dispersive measurements.<sup>6,7,9</sup> This initial detector—slit combination was a prototype for the system described here. It was capable of defining stress with a precision of about 100 MPa. The system described here is an order of magnitude better.

### B. Analysis of stress from diffraction spectra

X-ray diffraction has been used over the past several years to define the stress field within the sample.<sup>4,7,10</sup> Here we provide a brief background that illustrates the process and

required data. The spacing between lattice planes is defined by pressure, temperature, and stress at the point in the specimen where the lattice spacing is sampled. For a cylindrically symmetric stress field, the change in lattice spacing parallel and perpendicular to the unique stress axis define the differential elastic strain, which when multiplied by the appropriate elastic moduli, yields the differential stress.

A Debye ring representing diffraction of a polycrystalline sample becomes distorted from a circle when the x rays pass along the radial direction of this cylindrical symmetry as illustrated in Fig. 1. It has been shown<sup>3</sup> that the shape of the lattice spacing sampled by the Debye ring for a uniaxially stressed sample is given by

$$d_{hkl}(\psi) = d_0 + \{1 - 3\cos^2(\psi)\}F,\tag{1}$$

where  $d_{hkl}$  is the lattice spacing for the *hkl* diffraction peak,  $d_0$  is the hydrostatically defined lattice spacing,  $\psi$  is the angle between the diffraction vector, and the unique stress axis, and *F* is a constant. The differential elastic strain  $\varepsilon_{hkl}$ (diff) is found from

$$\varepsilon_{hkl}(\text{diff}) = \varepsilon_{hkl}(\psi = 0) - \varepsilon_{hkl}(\psi = 90) = -3F, \qquad (2)$$

and the differential stress  $\sigma_{hkl}$  (diff) is given by

$$\sigma_{hkl}(\text{diff}) = \varepsilon_{hkl}(\text{diff})^* E_{hkl},\tag{3}$$

where  $E_{hkl}$  is the Young's modulus for the particular orientation that is defined by the orientation of the normal to the diffraction planes, *hkl*. References 11 and 12 give expressions for  $E_{hkl}$  for all crystal systems in terms of the single crystal elastic moduli. Each subpopulation of grains defined by the *hkl* diffraction peak may experience a different stress if the material has either elastic or plastic anisotropy.

The strain is measured with both monochromatic x rays in angle dispersive mode with a 2D detector<sup>13</sup> and with white radiation using energy dispersive tools with multiple detectors with a conical slit system.<sup>7,14</sup> The energy dispersive sys-



FIG. 1. (Color online) Diffraction geometry for stress measurement. The sample under a cylindrical stress field has a synchrotron x-ray beam pass through, which is diffracted into a distorted Debye ring. The *d*-spacing is determined by the  $2\theta$  angle which is a function of  $\psi$  (the angle between the diffraction vector and  $\sigma_3$ ). The variation of *d* with  $\psi$  results because the lattice spacings depend on their orientation relative to the applied stress field.

tem with a conical slit provides a collimated signal that limits the extent of the sample volume that is recorded. This latter feature allows sample stress to be determined for samples in high pressure cells without diffraction interference from the pressure media. It also allows a three dimensional evaluation of the stress field within the sample. In addition, energy-dispersive diffraction data can be collected very rapidly (e.g., 15 s for a complete set of 10 patterns), allowing the strain to be monitored in dynamic experiments.

# II. NEW ENERGY DISPERSIVE DETECTOR SYSTEM

#### A. Conical slit system

A few years ago, we began using a conical slit prototype that was a machined cone constructed from brass with two rings defining the slits along with a four element detector.<sup>6,7,9</sup> Here we report the details of a new system that is designed to provide an order of magnitude improvement of the differential stress resolution (10 MPa). Two coaxial circular slits with different diameters define a cone, with the point of the virtual cone defining the scattering volume. An array of energy dispersive detectors placed in the path of the virtual cone, downstream of the larger circle, can analyze the diffraction signal as a function of the diffraction vector azimuth  $\psi$ . Note however that in uniaxial compression, although the maximum stress axis is normal to the x-ray beam, the diffraction vector differs by  $\theta$ , the diffraction angle from that normal. This angle is usually small, of the order of  $3^{\circ}$  or  $4^{\circ}$ . Figure 2 illustrates the geometry of the entire system. The point of the virtual cone must lie in the x-ray beam and in the sample. Figure 3 illustrates the geometry of the detector array that receives the diffracted x rays. Ten independent active elements are arrayed in a circle with diameter of 140 mm. Nine of the detectors subtend 180°, 22.5° apart, with one detector at 90° from the ends of the semicircle. The detector is an array of ten model GL0110S LEGe Detectors, custom made by Canberra Industries, Inc. They have an active area of 100 mm<sup>2</sup> per detector and are 10 mm thick.

Each of the two circular slits is the projected (from the point of diffraction in the sample) annulus defined by the



FIG. 2. (Color online) The conical slit shown with the T-cup device and a multielement energy dispersive detector. The diffracted x ray from the sample is collimated by a conical slit system, which allows diffraction at a fixed  $2\theta$  angle. The multiple-detector is placed behind the slit system to capture the diffracted beam for several values of  $\psi$ .

outer diameter of an inner ring and the nearly matching inner diameter of an outer ring. All four rings are cut from 1-mmthick tungsten plate with working edges ground to a circularity of about 2  $\mu$ m and cut at an angle of 6.5° from normal to the plate. Rigidity of the four rings is provided by mounting each on 12.5-mm cast iron plate. Each slit thus defined can be adjusted in width from >1 mm to <10  $\mu$ m by displacing its two rings axially with respect to one another. As machined, the slit width is zero when the two rings are coplanar (which turns out to be an important aid to alignment). Figure 4 also illustrates how the scattering volume is thereby limited by the slit width. The two-slit geometry is illustrated in Fig. 5. The geometry is set at a fixed  $2\theta$  of 6.5°, although this can be altered, within limits.

## **B. Alignment**

Remote control of most alignment parameters allows real-time adjustment and alignment. Each of the slits can be



FIG. 3. Array of energy dispersive detectors. The diameter of the array is 140 mm.



FIG. 4. (Color online) Geometry of new conical slit system. 10  $\mu$ m slit widths allow a 500  $\mu$ m length of the sample that contributes to the diffraction signal. This eliminates contributions from the cell assembly and reduces background. It also limits the 2 $\theta$  range of the signal to the detector.

moved in Y and Z, the coordinates are perpendicular to the direct beam (Fig. 5). This allows independent control and equalization of  $2\theta$  for the vertical and horizontal diffracted beams. Axial positioning control of the width of the larger slit is also motorized and remote. There is provision for remote control of the width of the smaller slit, but at the current time it appears that manual adjustment, rarely used so far, is sufficient. Despite the increased complexity and number of positional variables in the new system, alignment protocols developed for the prototype system are still generally applicable in the new system. Initial coaxiality of inner and outer rings was built into the system and has not drifted after several months of use. In principle the rings of the outer system can be realigned axially by loosening four large mounting bolts in the base of one, then moving the rings axially to the point of coplanarity-at which point they must return to coaxiality-then retighten the bolts. A slightly simpler remounting can be done for the rings of smaller slit.

The most significant issue regarding alignment for both the prototype and new systems is to place the x-ray beam so that it passes through the apex of the virtual cone that is defined by the two circular slits. If the x-ray beam is lower than the apex of the cone, then the top and bottom detectors



FIG. 5. (Color) Conical slit system. Dash-dotted lines represent the diffracted x rays (red, vertical, blue, and horizontal), pointing at the sample. Remotely controlled stages move each slit normal to the direct x-ray beam (green). Slit opening controlled by motion of inner and outer slit components relative to each other.



FIG. 6. (Color online) Energy dispersive diffraction pattern of the garnet sample. The diffraction peaks used in this analysis are identified. This is a typical diffraction pattern from one of the detectors.

in Fig. 4 will receive the diffracted x rays at different positions of the sample along X, the direction of the x-ray beam. Thus, taking spectra during a scan along X will reveal displacement of the x-ray beam from the apex of the cone. Adjustments of the beam (using slits) or the slits themselves can correct this misalignment issue. It is for that purpose that detectors in Fig. 3 are located at top, bottom, right, and left. Otherwise the detector array is distributed to optimize resolution of the *d* spacing with  $\psi$ .

A second alignment issue is to align the axis of the cone parallel to the x-ray beam, in which case the  $2\theta$  defined by the slits will not vary as a function of  $\psi$ . Slight nonparallelism is inevitable, and the effect can be simply accounted for by calibrating instrument  $2\theta(\psi)$  with a standard with known lattice spacing, and identifying the actual value of  $2\theta$  for each detector. Each detector is independently calibrated with reference materials and diffraction data for all detectors can be analyzed by identifying the peaks of interest in only one of the spectra. This allows a calculation of  $2\theta$  for each detector in near real time in order to adjust the position of the two-slit systems. Typically the nonparallelism after alignment is less than a few hundredths of a degree.

#### C. Strain resolution

Whereas the prototype conical slit had a fixed width of  $\sim 50 \ \mu$ m, a larger ring diameter of 50 mm, and an axial baseline between rings of 50 mm, the new slit operates with both rings having a 10–15  $\mu$ m width, and has a larger ring diameter of 140 mm and a distance between the slits of 475 mm (Fig. 5). The advance represented by the new system is thus the combination of three effects: (1) a more precise definition of  $2\theta$ ; (2) a smaller scattering volume (Fig. 5) of length 0.5 mm in the new system versus >1.5 mm in the old, that now excludes inference from diffraction sources outside the sample; and (3) an array of detectors that allows unique identification of the major and minor axes of the projected strain ellipse, which we find is not necessarily aligned with the principle axes of the externally applied stress.

Here we demonstrate the precision of the measurements using diffraction data from a pyrope-rich garnet and a magnesium-rich olivine. Both samples were prepared *ex situ*,



FIG. 7. (Color) Differential strain for the garnet sample as a function of time. The sample is being deformed at high temperature during this time.

compressed to a few gigapascals and annealed at around 1200 °C for 2 h. The samples were deformed with the D-DIA apparatus at elevated P and T. Our purpose here is to evaluate the precision of the results rather than report the rheological properties.

The garnet diffraction pattern is illustrated in Fig. 6. This is for one of the detectors from one of the data sets. Collection time was 600 s. We identify 10 diffraction peaks that we use in this study. Several data sets were collected as the sample experienced a deformation protocol. Each data set contains the diffraction data from 9 detectors; the tenth one was in the shadow of a high pressure anvil. Each diffraction peak for a data set was fitted to obtain a d spacing and the values of  $d_0$  and F were obtained by fitting d as a function of  $1-3\cos^2(\psi)$  as indicated in Eq. (1). Differential strain is derived from Eq. (3) and is illustrated in Fig. 7 as a function of time during the experiment. A differential displacement was applied to the sample from 5:00 until 9:30; the sample was then heated with no applied differential force, followed by a renewed differential displacement at about 10:00. We see an increase in differential strain - and hence stressduring the times of applied force. Each diffraction peak indicates a slightly different differential strain, which is to be expected as either elastic anisotropy or plastic anisotropy will generate such a difference.<sup>9</sup> The corresponding differential stress is given in Fig. 8. While the individual peaks may



FIG. 8. (Color) Differential stress for the garnet sample as a function of time. The sample is being deformed at high temperature during this time.



FIG. 9. (Color) Differential stress in olivine at elevated pressure and temperature during deformation. Data are illustrated as a function of deformation time.

reflect a different strain or stress due to anisotropies, their departure from the average value should remain fairly constant. We use the standard deviation of the value of the differential strain from the average as a measure of the precision of the measurement. For these data, the average (for the ten peaks) of the standard deviation is  $6 \times 10^{-5}$  for differential strain and 11 MPa for differential stress.

Α similar study of polycrystalline olivine. (Mg,Fe)<sub>2</sub>SiO<sub>4</sub>, provides the stress versus time curves illustrated in Fig. 9. This experiment was done with a detector configuration identical to the pyrope garnet tests (nine detectors, the tenth blocked by an opaque anvil). Collection time for diffraction spectra was 600 s and four diffraction peaks were used in the analysis. The noncoincidence of the four stress-time curves in Fig. 9 again reflects the plastic anisotropy of olivine. During this run stress climbed to roughly 400 MPa as the deforming pistons compressed the sample, after which deformation continues at nearly a constant rate. Precision as indicated by the scatter of the measured value appears to be approximately 10 MPa.

#### **D. Software**

Near real-time data analysis is now possible with the software PLOT85. In all cases diffraction data were analyzed with the program PLOT85 written and maintained by Ken Baldwin. The program is available and can be found on the website for software used at the NSLS for Multianvil Press experiments (http://www.mpi.stonybrook.edu/ NSLS/SAM85/Software/software.htm) along with instructions (http://www.mpi.stonybrook.edu/NSLS/SAM85/ Support/Plot85/plot85.htm). stress. It used to take 6 weeks to turn a diffraction pattern into a value of differential stress. Now it takes 6 min and is soon to be real-time. This allows the operator better control, particularly of confining pressure, during a dynamic experiment, and also provides a basis for intelligent decision making during an experiment. For example, it is an occasional experimental advantage to conduct a multistep deformation, wherein an environmental variable (say, temperature or strain rate) is changed once deformation in a current step has reached an apparent steady-state. Realtime data analysis now allows the operator to see when an apparent steady state is reached. The increased data reduc-

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tion capacity of the new software also allows measurementintensive studies, such as that of Ref. 15 on elastic modulus changes during phase transformation, to be carried out.

# **III. CONCLUSION**

A new x-ray detector and slit system designed for energy dispersive measurements of differential stress is now operational. We demonstrate that we can achieve measurements of differential strain with a precision of  $5 \times 10^{-5}$  which corresponds to 10 MPa for silicate minerals. Collection times of 600 s were used in these experiments for samples that are inside a pressure vessel at elevated pressure and temperature. The gauge volume is about 0.5 mm long with a two theta of 6.5°. This capability allows a new generation of high pressure high temperature measurements of mineral rheology.

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