Static Pressure of 255 GPa (2.55 Mbar) by X-Ray Diffraction: Comparison with Extrapolation of the Ruby Pressure Scale

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X-ray-diffraction studies have been carried out to 255 GPa on various sample and gasket configurations in the diamond-anvil cell. Intense fluorescence emission bands were observed at 793 and 830 nm in some cases which correspond to 360 and 550 GPa on the extrapolated ruby pressure scale. The x-ray measured pressures were only 185 and 201 GPa, respectively. Reasons for this discrepancy between x-ray methods and optical methods at ultrahigh pressures are proposed.

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Static pressures attainable by diamond-anvil cells have shown a steady increase over the past few years dramatically extending the range of experimentation, some of which has been reviewed by Jayaraman.[1,2] The ruby fluorescence manometer[3] has been calibrated with use of x-ray-diffraction techniques against the isothermal equation of state (derived from shock data) of Cu, Mo, Pd, and Ag to 100 GPa (1 Mbar)[4] and later to 180 GPa[5] against Au and Cu. Recently two groups[6,7] reported static pressures of 460 and 550 GPa based on fluorescence emission in the 800-nm range from ruby grains in the diamond-anvil cell. These claims were based on the characterization of the emission as the R_1 band of ruby and the extrapolation of the 180-GPa calibration to 550 GPa. However, x-ray-diffraction studies coupled with the isothermal equation of state from shock-wave measurements are needed to verify these claims.

We have extended x-ray-diffraction studies above 200 GPa in the diamond-anvil cell[8] using energy dispersive x-ray-diffraction techniques[9] at the Cornell High Energy Synchrotron Source. Recently a collimated x-ray beam of 5-μm diam was used to record pressure distributions above 200 GPa in a rhenium (Re) gasket.[10] These studies showed that it is possible to record high-quality x-ray-diffraction patterns above 200 GPa and obtain pressure distributions with 5-μm resolution on the diamond face as has been done with optical ruby-fluorescence techniques.[11]

The motivation for the present series of experiments was twofold; to compare x-ray–measured pressures with the pressures based on the extrapolation of the ruby fluorescence scale and to find the limit of static pressures attainable in the diamond-anvil cell. Five experiments were carried out above 200 GPa as listed in Table I where the gasket and sample configuration, diamond geometry, and the maximum pressure achieved as measured by x-ray diffraction are shown. Experiments 1 and 2 were carried out with use of a Re gasket with no hole

TABLE I. Gasket and sample configuration, diamond geometry, and the maximum x-ray–measured pressure in the five experiments.

Experiment	Gasket	Sample configuration	Diamond Geometry: Central flat diameter (μm)	Bevel angle	Culet diameter (μm)	Maximum pressure, x ray (GPa)
1	Rhenium	1 ruby (no hole)	50	10°	300	216[a]
2	Rhenium	1 ruby (no hole)	50	7°	200	212[a]
3	Spring steel	ruby+W powder in 50-μm hole	50	5°	300	201
4	Spring steel	ruby layer on gasket	50	7°	300	255[b]
5	Rhenium	thick ruby layer both gasket sides (double bevel)	50	7° 3°	175 300	245[b]

[a]One diamond fractured during laser irradiation for ruby measurements.
[b]One diamond fractured during a subsequent increase of load.

and an isolated ruby chip (0.5-wt.% Cr^{3+}) of 5–10-μm diam at the center of the flat. In experiment 3 a 50-μm-diam hole in a spring-steel gasket was filled with ruby and 2.8-vol.% tungsten, as in the experiment of Ref. 6 where 550-GPa static pressure was claimed. In experiment 4 a layer of powdered ruby ($\cong 5$ μm thick) was deposited on one side of the spring-steel gasket. In experiment 5 10–20-μm ruby powder layers were deposited on both sides of the Re gasket. The last two experiments are similar to the one where 460 GPa was claimed.[7]

In experiment 1, the ruby R_1 emission could not be detected above 140 GPa because of diamond fluorescence. On further increase of pressure a new strong emission band was observed at 793 nm which was clearly visible in addition to the diamond fluorescence. Figure 1, curve A, shows the fluorescence emission due to 488-nm laser excitation with $\cong$15-mW power at the sample. The spectrum shown was recorded using a 0.25-m grating monochromator with a 512-diode array detector. All spectra shown are raw data corrected for the spectral and thermal response of the system; no background subtraction was applied. The x-ray–measured pressure was only 185 GPa as determined from the isothermal equation of state of Re derived from shock data[12] available to 280 GPa (first-order Birch-Murnaghan equation of state with $B_0=372$ GPa and $B_0'=4.05$). The pressure profile across the diamond face at the peak pressure of 185 GPa is shown in Ref. 8 and shows quasihomogeneous pressure on the central flat. The peak at 793 nm, if interpreted as a ruby R_1 peak, would correspond to a pressure of 360 GPa, twice that of the x-ray determination. X-ray collimation was determined empirically by traversing either a sample-gasket interface or pressure discontinuity[8] and noting the range of collimator positions over which two different powder patterns are observed. For experiments 1 and 2 the latter method gave a 10-μm collimator diameter.

Figure 1, curve B, shows the fluorescence emission recorded in experiment 3. A strong emission band at 830 nm corresponds to a pressure of 550 GPa based on the extrapolation of the ruby pressure scale.[5] The x-ray–measured pressure is only 201 GPa with use of a 5-μm-diam collimated beam and the 300-K isothermal equation of state of bcc W (Ref. 12) available to 270 GPa (first-order Birch-Murnaghan with $B_0=312$ GPa and $B_0'=3.826$). The factor of 2.7 between these two pressure measurements cannot be attributed to pressure averaging since the sampling area of a 5-μm-diam x-ray beam is comparable to the focused laser spot in the optical experiments. The ruby x-ray-diffraction pattern indicates that the structure of ruby remains hexagonal to 201 GPa based on the tungsten pressure scale. Although our four ruby diffraction peaks are consistent with the hexagonal cell, they are relatively weak; when used with the ultrasonic equation of state of ruby,[13] the corresponding pressure found is 177 GPa. (The first-order Birch-Murnaghan parameters are $B_0=254$ GPa and $B_0'=4.3$.[13]) If we consider the extensive extrapolation involved in the ultrasonic data, this difference is not surprising. A pressure distribution at a slightly lower

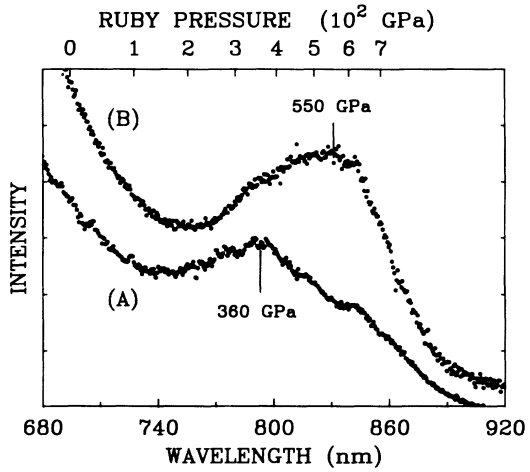

FIG. 1. The fluorescence emission (488-nm laser excitation) in the spectral range 680 to 920 nm, corrected only for the spectral and thermal response of the system. Curve A, Re and ruby chip (experiment 1) with fluorescence band at 793 nm corresponding to 360 GPa on the extended ruby scale (Ref. 5). Maximum x-ray–measured pressure, 185 GPa. Curve B, ruby and 2.8 vol% tungsten (experiment 3) with band at 830 nm corresponding to 550 GPa on the ruby scale. Maximum x-ray–measured pressure, 201 GPa.

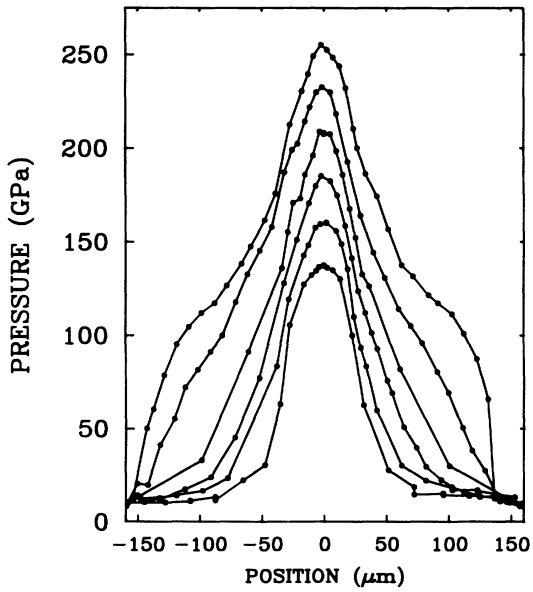

FIG. 2. The pressure profile across the diamond face as measured by x-ray diffraction (experiment 4), a ruby layer on a spring-steel gasket. The maximum pressure for this set of profiles is 255 GPa. All of the pressure profiles were taken with a 5-μm-diam collimator, except the profile at a peak pressure of 135 GPa which was taken with a 15–20-μm-diam collimator.

load of this experiment showed continuous pressure variation across the sample-gasket interface.

Figure 2 shows x-ray pressure distributions at various loads on increasing pressure in the case of a spring-steel gasket and a layer of ruby (experiment 4). This cell reached the highest pressure of 255 GPa. Pressures are based on the isothermal equation of state of iron[14] obtained from shock data available to a Hugoniot pressure of 400 GPa (first-order Birch-Murnaghan equation with $B_0=163$ GPa, $B_0'=5.34$, and the volume of the zero-pressure hcp phase being 0.95 of the volume of bcc iron). At small loads the pressure is concentrated more on the central flat, but at pressures above 200 GPa the bevel appears to flatten out and the pressure starts going up on the beveled region. At the peak pressure of 255 GPa the outer edge pressure is in the range of 80–100 GPa. A subsequent increase of load beyond this point caused one of the diamonds to fracture. Figure 3 shows that in experiment 4, as well as in experiment 2, no strong emission bands such as the ones shown in Fig. 1 were observed, even though the x-ray pressures were higher than in the previously discussed experiments.

Figure 4 shows the variation of the observed strong 830-nm emission (experiment 3) across the diamond flat. In this case the laser spot has a diameter of 5 μm which was obtained by a beam expander with a spatial filter. It shows the emission from the center and emission from half way to the outer bevel edge (radius $=75$ μm). It is remarkable that the 830-nm emission (equivalent to 550 GPa on the extrapolated ruby scale) is strong in the beveled region where no ruby grains are present (the ruby sample extends only to a 35-μm radius).

We can summarize our experimental observations as follows: (1) Strong fluorescence emission bands centered at 793 and 830 nm were observed in two sample configurations in experiments 1 and 3. These would correspond to pressures of 360 and 550 GPa if they were interpreted as R_1 lines of ruby and the extrapolation of the ruby pressure scale was used. The x-ray–measured pressures were only 185 and 201 GPa, respectively, which would imply a break in the ruby R_1 pressure calibration. It is unlikely that this strong emission in the 800-nm range is due to the R_1 line of ruby. Further, for a given excitation wavelength the R_1 peak intensity becomes progressively weaker as pressure increases and extrapolation to 500 GPa would give a peak of negligible intensity. This raises serious doubts about the attainment of 460- to 550-GPa static pressure in the diamond cell.[6,7]

(2) There are two explanations for this discrepancy between x-rays and optical methods for pressure measurements above 200 GPa. (a) The strong emission observed near 800 nm comes from impurity or defect levels in diamond. Type-Ia diamonds used in high-pressure experiments contain approximately 1% impurities, and emissions may be enhanced by shear stresses in the diamond. However, the type of impurity and possible shear-enhancement mechanisms are unknown at the present time. This might also explain the situations where this emission was weak. Subsequent to these pressure studies, fluorescence emission in the spectral range 770 to 880 nm from type-Ia diamonds was carefully studied at atmospheric pressure. Although a few of the diamonds tested did not show this emission at atmospheric pressure, most did. This demonstrates clearly that one must use extreme caution in identifying any peaks in this region with the ruby R_1 peak. (b) The strong emission observed in the present set of experiments and earlier experiments[6,7] is due to a different

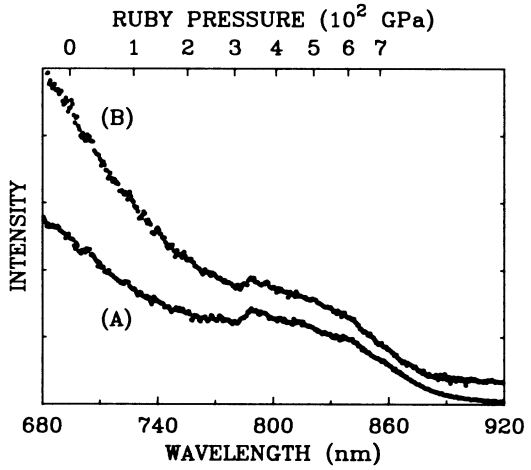

FIG. 3. Curve A, fluorescence emission spectra for Re and single ruby chip (experiment 2), and curve B, spring steel and ruby layer (experiment 4). The x-ray–measured peak pressures were 212 GPa for A and 255 GPa for B. In contrast to Fig. 1, only weak emission bands were observed in these cases, even though the x-ray peak pressures were higher.

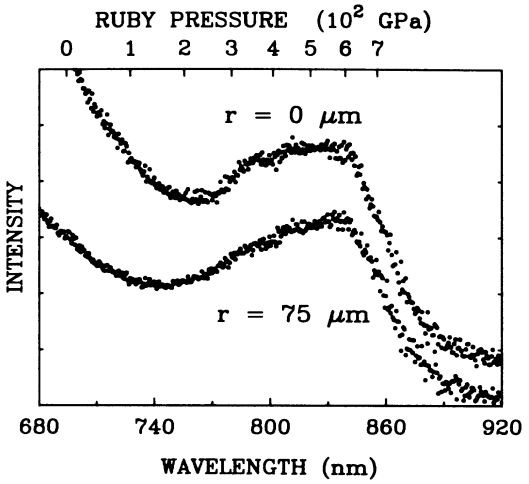

FIG. 4. Variation of the fluorescence shown in Fig. 1, curve B, across the diamond flat. The spectra shown are taken with identical data collection times. The $r=75$-μm spectrum is multiplied by 1.2 to account for differing laser powers and offset for clarity.

emission band of ruby (not R_1). This would also require an intensity-enhancement mechanism as other bands of ruby are weak at ambient pressure and this Cr^{3+} concentration.[15]

(3) The x-ray collimation used in these experiments is as good as the optical focusing in Refs. 6 and 7, and so the difference between the x-ray pressures and the previously reported ruby pressures cannot be attributed to a difference in the sampling size.

(4) The pressure of 255 GPa is the highest static pressure which has been measured without extrapolation in the diamond-anvil cell (with use of x-ray measurements and the equation of state of iron).

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