ESRF	**Experiment title:** Structural changes associated with insulator to metal transitions in fluid halogens	**Experiment number**: HS 1877
Beamline:	**Date of experiment**: from: 5 February 2003 to:8 February 2003 8 November 2003 to: 11 November 2003	**Date of report**: 26 February 2004
Shifts:	**Local contact(s)**: Dr. Mohamed MEZOUAR, Dr. Wilson CRICHTON	*Received at ESRF:*

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Report:

The aim of this experiment was to develop experimental and analytical techniques for simultaneous laser heating and x-ray diffraction of fluids in the diamond anvil cell (DAC). We are developing these techniques with halogen (bromine) samples because bromine is expected to undergo an insulator to metal transition in the fluid: this transition is in a pressure and temperature range well-suited to the laser-heated DAC (6 GPa with temperature expected to be above 1000 K) and is also expected to be first-order, involving a density change as the fluid goes from molecular Br_2 to atomic Br. We expect that the local fluid structure will change significantly across the transition, making it potentially easier to observe than smooth density variations. Therefore bromine is a good material for these exploratory/ technique development experiments: even qualitative data may be scientifically useful.

During the two experimental runs in February and November, 2003, we brought seven samples of bromine and two of iodine at high pressure in a diamond-anvil cell to the ESRF, and were able to laser-heat four. Of those four, only two exhibited the diffuse diffraction of a fluid when heated, in each case along with significant persistance of crystalline diffraction. In only one case could we extract enough of the fluid data to achieve even qualitative results (Fig. 1 -3). Although this is a lower rate of success than we might desire, because this experiment is about technique development as well as science, we are learning nearly as much

from our failures as from our successes. Furthermore, we lost one full day of data from the experimental run in November, 2003, due to the simultaneous crash of the network hard disk and its backup.

The main obstacles to obtaining fluid diffraction data are sample preparation (preparing pure samples, finding a sample geometry that maximizes fluid signal) and alignment (both lasers into diamond cell; x-ray, lasers, and spectroradiometry to the same point). In our first experiments we tried to prepare thicker samples with no calibrating or thermally insulating material, in order to maximize the diffraction signal from the fluid material, which we expected to be weak. While this approach had merit, the presence of persistent crystalline material, as well as the error due to temperature gradients, have proven to be too great, and we conclude that a sample geometry that more tightly confines a thin sample will be more successful.

Specifically, in, February, 2003, we took data of single and double-sided laser heating with the same bromine sample. Though the single-sided heating clearly made the sample hotter than the melting temperature at the surface as evidenced by visible black-body glow, visible evidence of motion, and high temperatures measured by spectroradiometry, solid crystalline x-ray diffraction was always observed, and there was no diffraction evidence of coexisting fluid. We interpret this as evidence that not enough of the sample thickness was melted, and proceeded by double sided heating, which did yield x-ray diffraction evidence of fluid bromine (Fig. 1 – 3). In contrast, experiments intended to improve upon the data of February, 2003, removing persistent crystalline data by surrounding the bromine with non-reactive, thermally insulating NaCl, failed to obtain evidence of the fluid, despite reaching temperatures of 6000 K. (Fig. 4). While we do not entirely understand why this is the case, we can address the possibility that the melting of the NaCl made the bromine sample move during heating by using a more refractory thermal insulator in our next experiment.

Though we have not yet obtained quantitatively satisfactory x-ray diffraction of liquids in the laser-heated diamond cell, we have obtained qualitatively correct data. More importantly, we have made great progress in determining the sample preparation and experimental procedure that will be necessary to yield quantitative information about warm, dense fluids.

Figure Captions

Fig. 1. X-ray diffraction of bromine, laser heated at 6 GPa in February, 2003, plotted as diffraction intensity vs scattering momemtum, $Q=4\pi \sin\theta/\lambda$. Although some amorphous material is present in the cold (300 K) data, upon laser heating the amorphous material crystallizes, upon further heating Br_2 melts, and we observe the broad diffraction signature of the fluid near 20 nm^{-1}. (This peak is different in position and shape from the amorphous material.) As laser power and temperature increase, the relative amount of crystalline material decreases, but never disappears, despite the fact that the melting temperature of bromine at 6 GPa is ~1000 K. The persistence of crystalline material at the highest temperature is most likely a result of the large temperature gradients through the thickness of the sample. (T=300 K at the diamond surfaces.) It may also indicate a minor instability or inaccuracy in the alignment of the two heating lasers and the x-rays: a small motion of either the sample or just one of the lasers by a few microns is enough. We plan to improve sample preparation to minimize temperature gradients and to monitor sample alignment in future experiments.

Fig. 2. Structure Factor, S(Q) and **Fig. 3**. Radial distribution, g(r) of bromine, laser heated at 6 GPa. (Same data as figure 1.) S(Q) and g(r) were determined by subtracting the empty-cell reference from the raw diffraction data (Bragg diffraction peaks removed). The reference data was multiplied by a scaling factor that had been determined by interatively subtracting the reference and then computing the radial distribution function by Fourier Transform until the radial distribution function at low-radii agreed with known data (e.g. Br-Br bond length, 0.228 nm). This analysis technique is dependent on the quality of the known data, in this case constant bond length is assumed, as well as the quality of the actual data. Because the data extends only to Q ~ 50 nm-1, the integral in the fourier transform between 0 and infinity is not well-approximated, and quantitative densities cannot be determined. Therefore, a constant density (that of 6 GPa, 300 K) is also assumed. We need more data, especially data to higher Q, to confirm that this analytical technique, which works well for fluids in the resistively heated DAC *[Eggert, 2002]*, is quantitatively adequate for data from the laser-heated DAC.

Nonetheless, the computed S(Q) is qualitatively consistent with ambient (pink crosses) and low-pressure data (dark blue) *[Filabozzi, 1994 and Szornel, 1993 respectively]*. In particular, the position of the first peak of S(Q) shifts to slightly higher Q between 0 and 1 kbar and to even higher Q at the 6 GPa of our

data. Furthermore, according to Misawa [1989] the presence of a shoulder at higher Q on the first peak at ambient pressure indicates orientational correlation between neighboring Br_2 molecules. The absence of a shoulder in our high-pressure, high-temperature data may indicate that the Br_2 molecules are able to spin freely and are not orientationally constrained by their nearest-neighbors, which may be reasonable at 2500 – 5000 K.

Fig. 4. Temperature measurement by spectroradiometry. Raw data (red), calibration lamp (2500 K, peach), normalized data (black) and its fit to the Planck distribution (red, 6213 K) all vs. wavelength (bottom axis). Wien function (a linear approximation to the Planck distribution, blue) and its fit (pink, 6547 K) vs. 1/wavelength (top axis). Sliding two-color pyrometer temperature (gray) vs. 1/wavelength. **Upper left corner.** Histogram of two-color temperature. We used the width of the histogram, σ, to determine a consistent upper-limit uncertainty to our temperature measurements (997 K). One surprising result of this experiment was the measurement of extremely high temperatures, which may be the highest reported by heating with a YAG laser. We are now preparing a manuscript about the measurement of such high temperatures.

References

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Figure 1.

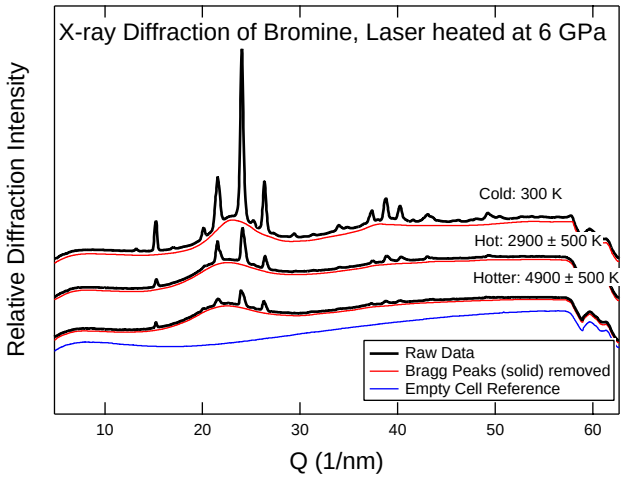

Figure 2.

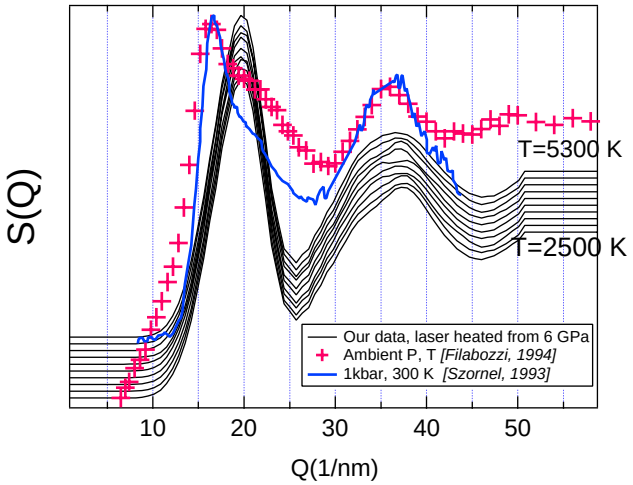

Figure 3.

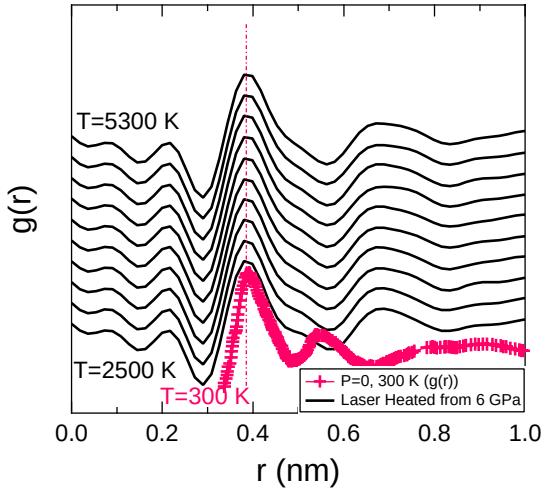
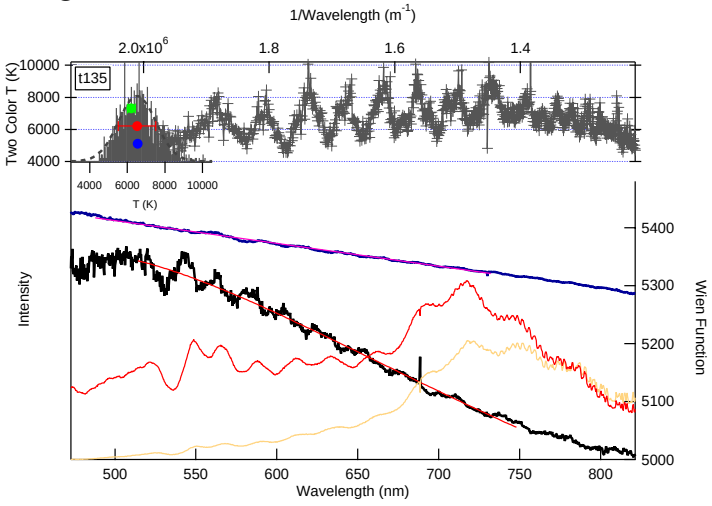
Figure 4.