Phase transitions and melting above100 GPa (1Mbar) using laser-heated diamond cells

Beam line development for laser-heating.

Detector and motion controls. During previous attempts to measure melting at very high pressure by X-ray diffraction, it became clear that these measurements require rapid data acquisition due to instabilities of the molten sample and optical drifting due to the high required high laser power. This required several improvements of the laser-heating setup and the X-ray accumulation. The flux at ID 27 was significantly increased resulting in an X-ray beam of about 5 μm^2. A new Mar345 CCD detector allowed to collect diffraction images every two seconds from very small samples (about 10 μm) while the laser power was gradually increased.

This fast data accumulation required very rapid alignment of the diamond cell and the optics to measure the X-ray diffraction and the temperature from the hottest portion of the often unstable sample area. There are 20 degrees of freedom in this optical setup to control laser-heating and temperature measurement. This requires "analog" control units because the adjustments via computer are far too slow. We tested a variety of custom made motion controls such a miniature DC-motor drives, "direct-drive " stepper motor electronics, and piezo-driven mirror mounts. As piezos have only a limited range, and DC-motors only limited resolution we are now building a single control unit for "direct-drive " stepper motors which can be controlled as easily as piezos but with much larger travel range. All the optics can then be aligned within seconds. This control unit will be build in Mainz.

For the rapid temperature collection of the "downstream" side of the diamond cell towards the X-ray detector, we installed a high precision pneumatic flip mirror, which is inserted during temperature measurement and removed during X-ray exposure in intervals of 1-2 seconds.

Optics. A significant improvement was the installation of an aperture mirror at the entrance of the temperature spectrometer. This mirror allows the simultaneous observation of entrance pinhole and sample with a single video camera, thus a very rapid alignment of the hot-spot with the spectrometer. Additionally, this video camera was equipped with a long-distance Zoom objective, allowing rapid alignment of the heating lasers.

One of the most important part of the optics are the objectives for collecting the incandescent light from the heated sample. We tested new achromatic lenses with adjustable aperture to reduce chromatic aberration. The alignment of these objectives, however, proved to be too complicated resulting in significant chromatic errors in the temperature measurement. Therefore, we will use the existing reflecting objectives, which will be equipped with new mirrors with higher than previous surface quality and resolution. These will be installed in spring 2008.

Heating lasers. For the last six months we are using new type lasers in our laboratory in Mainz. The new features are direct pumping of a single-mode fiber resulting in superior beam quality and power. These laser have some significant advantages over the lasers used at present at ID 27 with regards to power, power control, beam quality, and space requirement. We hope that such laser will also be installed at ID 27 in the near future.

X-ray markers. One of the most severe problems in combining laser-heating and X-ray diffraction is the perfect alignment of hot-spot and X-ray beam. We made several attempts to improve the X-ray beam alignment using suitable fluorescing "markers" and installed a highly sensitive, cooled CCD camera. However, with few exceptions the luminescence of most materials such as ruby or Gd_2O_2S:Tb became very week when approaching the megabar pressure region. Only pressure media such as LiF and KCl showed weak fluorescence at these pressures. We therefore propose to use a new technique to align the X-ray beam: we recently purchased a pulsed UV laser with a wavelength of 213 nm. A very small, micron-size hole will be "drilled" into the culet by laser ablation. We then will sputter the culet with platinum and repolish it with the platinum remaining in the hole. This platinum "bead" will be easily detected by the X-ray beam thus allowing micron alignment.

Preliminary results of the LTP on melting at megabar pressures.

Iron. Due to lack of time we could only collect few melting data, but for the first time we documented melting by X-ray diffraction above one megabar up to 130 G as a result of 20 different runs. A short paper has just been accepted in the Journal of Physics. Above 70 GPa only the ε (hcp)-Fe phase was found over the entire P-T range. We also obtained accurate and valuable data of the c/a ratio of iron. We used a large variety of pressure media such as Ar, Xe, KCl, Al_2O_3, SiO_2 and $MgSiO_3$. From the equations of state of iron and these pressure media we obtained pressures that are far more accurate than those measured by the ruby method in previous optical experiment. The melting results indicate that in the previous experiments the pressures were overestimated.

For the measurement of melting by X-ray diffraction, the pressure medium plays a key role. At very high pressure many materials have similar melting temperatures, which makes the sample-pressure medium assemblage unstable when the melting temperature is appraoched. This results in a dispersion of the sample during melting and the X-ray signal becomes very weak or is lost. We know from our previous work that Mg or Ca-Si perovskites have by far the highest melting temperatures. Initially amorphous $MgSiO_3$ dry gel proved to be the best choice. This material also proved to be chemically inert to both iron and molybdenum. This knowledge was obtained during the last beamtime and we hope to continue our research in this direction and also test other perovskites.

Melting is ideally determined by the disappearance of the X-ray diffraction peaks and their reappearance upon freezing. Melting is also ideally accompanied by the appearance of a diffusive ring in the diffraction pattern (see figure 1). These observations, however, are not very reproducible due to a) temperature gradients in the sample, b) dispersion of the molten sample into the pressure medium, and c) misalignment of X-ray beam and hot-spot. Figure 1 shows an original and integrated X-ray pattern on iron.

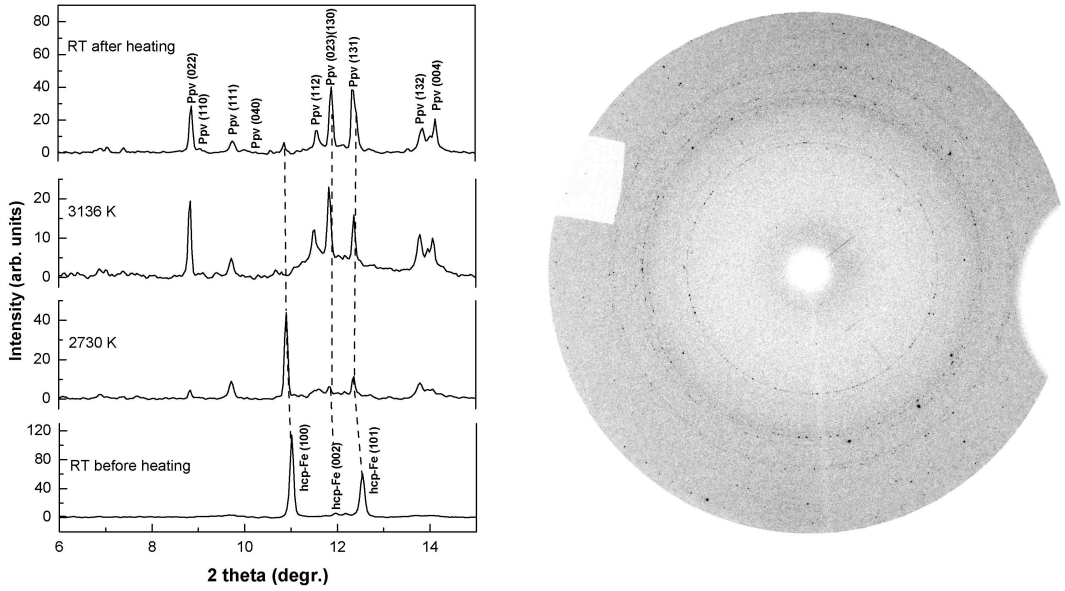

Figure 1 – (left) Diffraction patterns of a 10 micron iron sample. Before heating at 148 GPa, after heating at 130 GPa. The pressure medium was $MgSiO_3$ dry gel. At 3136 K all hcp iron peaks disappear and a diffuse ring associated to liquid iron appears also visible in the original spectrum (right). At this temperature only peaks belonging to the post-perovskite phase are present. After heating hcp iron peaks reappear.

The onset of melting was always accompanied by rapid changes in the position and intensity of the spots in the diffraction patterns of the highly recrystallized sample. Figure 2 shows a plot of the total sum of all area changes of the iron peaks in consecutive diffractograms ($|I_{(100)} - I'_{(100)}| + |I_{(002)} - I'_{(002)}| + \ldots$) versus time. Large fluctuations are observed when the melting point is reached. The melting temperature is then taken at the onset of these strong fluctuations assuming that the fast reorientation of crystallites is only possible in a partially molten sample. These melting temperatures are in agreement with those obtained from the disappearance of diffraction peaks.

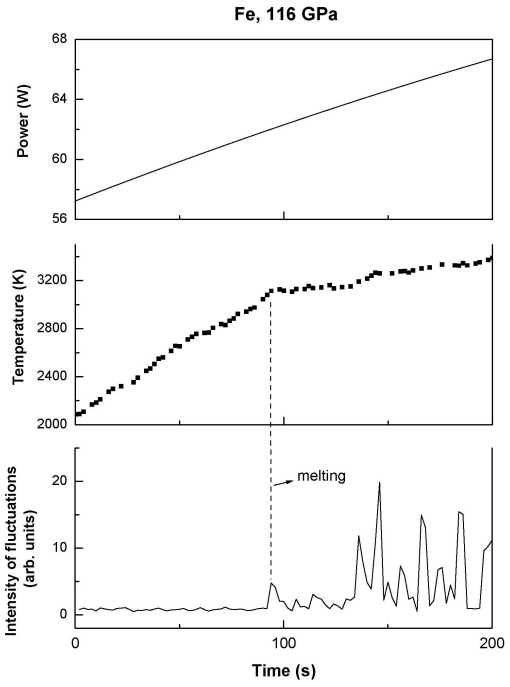

Figure 2. Effect of recrystallization during melting of iron at 116 GPa. Top: Laser power, middle: maximum sample temperature, bottom: peak intensity fluctuation versus time. When the melting point (3160 K) is reached, large fluctuations are observed and the temperatures remain nearly constant with increasing laser power

Molybdenum. The melting temperatures of molybdenum we measured a few years ago using optical methods are in very serious disagreement with theoretical calculations and common interpretations of shock data. We observe a nearly flat melting curve above 50 GPa, whereas the melting curve in other studies is very steep. This is presently a subject of intense debate.

In a series of runs we observed a clear indication of melting above one megabar. The observations are very similar to those of iron: the disappearance and reappearance of diffraction peaks at and after melting, respectively, and the appearance of diffuse scattering during melting (see figure 3). The pressure medium was $MgSiO_3$.

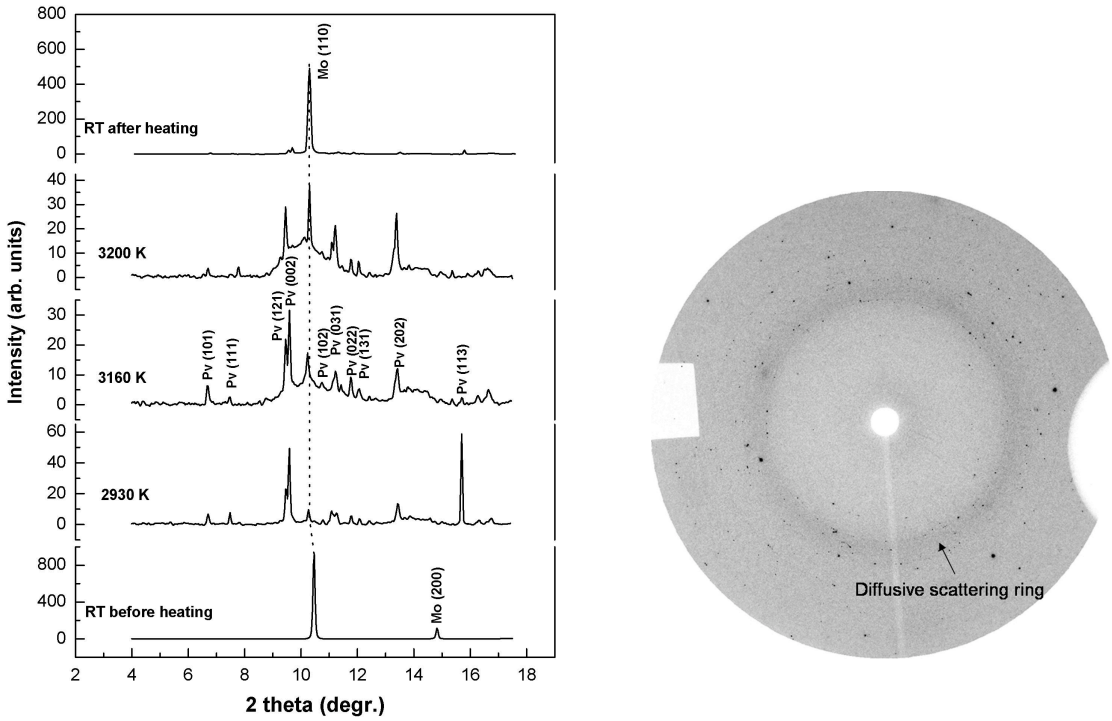

Figure 3.- (left) X-ray diffraction patterns of a 20 microns molybdenum sample. Before heating at 109 GPa, after heating at 81 GPa. The pressure medium was $MgSiO_3$ dry gel. At 3160 K all bcc-Mo peaks disappear and a diffuse ring associated to liquid molybdenum appears also visible in the original spectrum (right). At this temperature only peaks belonging to the perovskite phase are present. After heating bcc-Mo peaks reappear.

References

Boehler, R., and M. Ross: Properties of rocks and minerals – High-pressure melting. In: Treatise in Geophysics, Volume 2, Mineral Physics, (Eds.) G.D. Price, G. Schubert. Elsevier B.V., Amsterdam, 527-541 (2007)

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Boehler, R., D. Santamaria-Pérez, D. Errandonea, and R. Mezouar: Melting, density, and anisotropy of iron at core conditions: new X-ray measurements to 150 GPa. J. Physics: Conference Series. (2007) in press.

Errandonea, D., R. Boehler, S. Japel, M. Mezouar, and L.R. Benedetti: Structural transformation of compressed solid Ar: An x-ray diffraction study to 114 GPa. Physical Review B 73, 092106 (2006).

Ross, M., D. Errandonea, and R. Boehler: Melting of transition metals at high pressure and the influence of liquid frustration: The early metals Ta and Mo. Physical Review B 76, 184118 (2007).

Ross, M., R. Boehler, and D. Errandonea, Melting of transition metals at high pressure and the influence of liquid frustration: The late metals Cu, Ni, and Fe, Physical Review B 76, 184117 2007

Santamaría-Pérez, D, D. Errandonea, G. D. Mukherjee, M. Mezouar and R. Boehler, Evidence for a shallow melting curve of molybdenum from X-ray diffraction measurements (to be submitted)

Errandonea, D., R. Boehler, B. Schwager, and M. Mezouar: Structural studies of gadolinium at high pressure and temperature. Physical Review B 75, 014103 (2007).