LASER HEATING UNDER PRESSURE: A BRILLIANT JOURNEY TOWARDS THE CENTRE OF THE EARTH

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INTRODUCTION

The study of the deep Earth has been motivating generations of scientists who have to take up the challenge given by the extreme conditions existing at the centre of the Earth: over 300 GPa (3 million bar) and 5000 Kelvin. As the study of the propagation of elastic waves created by earthquakes only allow the determination of the density profile of our planet, there remains the all important problem of the determination of the chemical composition and crystalline structures existing in the deep Earth, as these govern the Earth global exchanges (thermal regimes, convection drifts, plate tectonics...). Thus relationships have to be established between chemical composition, crystalline structure and specific volume over the whole range of pressures and temperatures existing within our planet, and x-ray diffraction is by far the best technique to obtain reliable structural and molar volume data on the compounds and materials of interest. Consequently, as very high pressures can only be generated in extremely small samples, the high brilliance of the ESRF, coupled with advances in detector, optics and high pressure technologies, has stimulated the rapid development of techniques for collecting structural data on geophysical samples in extreme conditions of P and T. We report here some recent results from a project concerned with in-situ x-ray diffraction studies of laser-heated samples under pressure [1], and the examples selected are studies devoted to the two major constituents of the deep Earth: iron and $MgSiO_3$ perovskite.

EXPERIMENTAL DEVELOPMENTS

Before this project, structural data on materials in laser-heated diamond-anvil cells (DACs) were obtained using white-beam energy-dispersive diffraction, a technique which suffers from an intrinsic low resolution and poor crystallite statistics (hence unreliable intensity data) due to the small window of diffraction space sampled, but thanks to the high brilliance of the ESRF, it is now possible to combine monochromatic angle-dispersive diffraction and image-plate detectors to collect quality data up to pressures and temperatures in excess of 90 GPa and 3000 K. This is achieved by focusing the high brilliance beam produced by two phased 40 mm period undulators [2] using single-electrode bimorph mirrors [3] on the High Pressure beamline (ID30). The resulting focal spot of about 8 μm x 15 μm (FWHM) is compatible with the size of the laser-heated hot spot, and the wavelength of the monochromatic beam, selected by a water-cooled channel-cut Si(111) monochromator in the 0.4 to 0.5 Å range, is well matched to the aperture of custom-built DACs. Combining these beam characteristics with an experimental set-up especially designed for the project, and consisting of TEM00 CO_2 and multimode YAG lasers, optical set-ups for on-line P,T measurements and alignment of the sample and beam, large aperture DACs allowing in-situ P,T measurements and full 4θ data collection, for the first time it has been possible to collect angle-dispersive diffraction data on image-plates during the laser-heating of samples only a few micron thick.

A NEW-PHASE OF IRON

Iron being the dominant constituent of the Earth's core, information on its behavior at high P and T is fundamental in Earth sciences, but despite numerous studies on this subject [4] there is still much uncertainty about its structure in the P,T conditions relevant to the core. The accurate determination of the phase diagram of this element is indeed an experimental challenge because of the extreme conditions involved, and even below 100 GPa, recent x-ray diffraction experiments have led to conflicting results on the structure of its β-phase. Thus that region of the phase diagram, which was previously regarded as simple, is in fact complicated and clearly in need of new experimental data. Indeed, as mentioned by Anderson [4], the final choice between the ε and γ phases for the core depends on the outcome of future studies aiming at proving the existence of the β-phase and identifying its crystallographic structure.

The iron phase diagram up to 100 GPa and 2700 K has thus been studied using the best diffraction technique

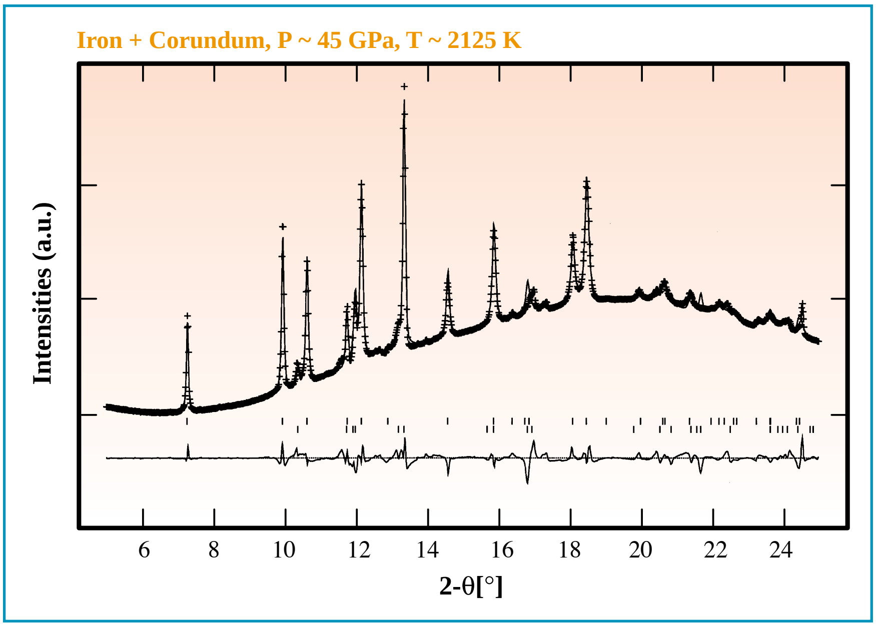

Fig. 1: Full structure refinement of a spectrum recorded at 2125 K, 44.6 GPa. The cell is orthorhombic with space group Pbcm and iron location {0.239, 0.472, 0.25}. Observed, calculated and difference spectra are shown, with lower ticks for iron and upper ticks for Al_2O_3.

currently available, and these results introduce strong constraints on its structures at high P and T. Having significantly improved both the resolution and the reliability of the data, it has been possible for the first time to perform full structural Rietveld-refinement in these extreme conditions of P and T (Figure 1). The space group determined is Pbcm, and the atomic topology is close to that of the ε-hcp phase. The structure is also closely related to the lower pressure, high-T polymorph, γ-fcc. The high-T polymorph appears unquenchable at moderate pressures, but the spectra of the back-transformed γ-phase show some anomalies which can explain ambiguities reported in previous structure determinations [5].

To eliminate possible artifacts introduced by the pressure transmitting medium (corundum, which is also used as thermal insulator), the occurrence of the orthorhombic lattice in a SiO$_2$ medium was also checked. This is illustrated in Figure 2 which shows results obtained up to about 100 GPa. Unfortunately at this pressure the sample was not sufficiently insulated from the diamonds, and it was too difficult to obtain *in-situ* spectra during stable laser heating. However, spectra quenched from about 2500 K clearly show the doubling of the 100 and 101 lines of the hcp-lattice, here again an evidence of a transformation at high P and T. All the experimental lines are explained by an orthorhombic lattice similar to that previously observed, and in contrast with results obtained at moderate pressures, the structure of the high-T polymorph is now preserved after the quench. At this pressure, the orthorhombic lattice is found to be about 1% denser than ε-iron.

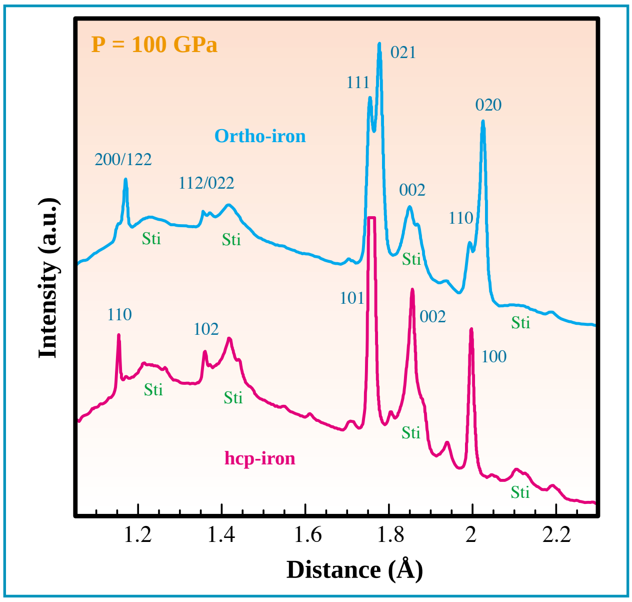

Fig. 2: Diffraction spectra of hcp and orthorhombic iron recorded at 100 GPa in a SiO$_2$ medium (labeled Sti). The 101 reflection of ε-iron is truncated for better clarity. The top spectrum, quenched from about 2500 K, clearly shows the doubling of the 100 and 101 ε-iron lines, evidence of the phase transition toward the orthorhombic phase.

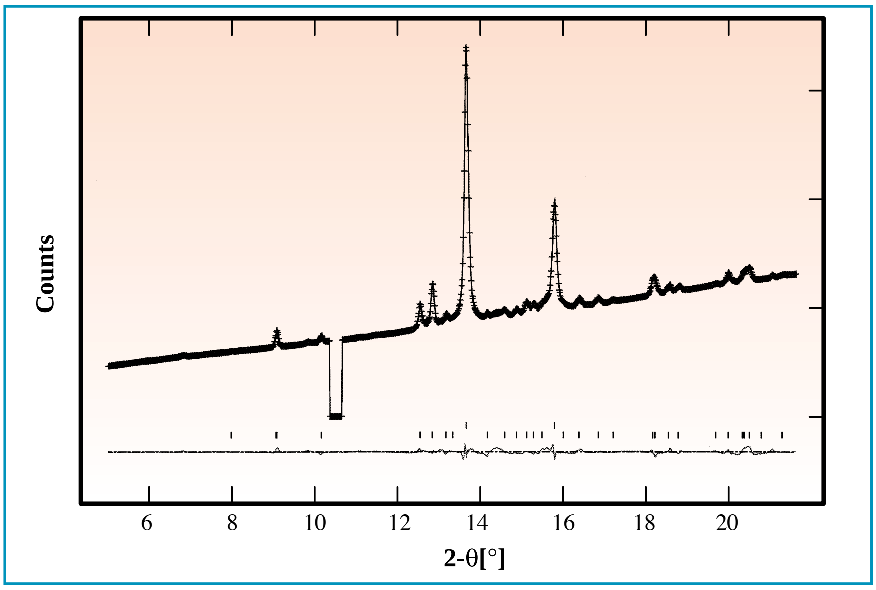

Fig. 3: Full Rietveld structure refinement of a diffraction spectrum of MgSiO$_3$ at 86 GPa and 2310 K integrated from an image plate exposed for 10 minutes using a monochromatic beam focused to 10 µm x 20 µm. Sample and platimum (the pressure calibrant) reflections are shown by lower and upper ticks respectively.

THE STRUCTURE OF MGSIO$_3$ PEROVSKITE

The perovskite form of (Mg,Fe)SiO$_3$ being currently accepted as the dominant phase of the Earth's lower mantle (700 to 2900 km deep), its equation of state (EOS) plays an important role in many fields of geophysics. It is however presently impossible to choose between the perovskite-pure and perovskite-magnesiowüstite (Mg, Fe)O models for the Earth's lower mantle on the basis of the existing data, and in-situ high P and T diffraction is certainly the only method available to measure correctly its EOS and solve the stuctural problem. Previous studies were conducted in the stability field of the perovskite, but energy-dispersive diffraction and large-volume presses limited the performance and P,T ranges to 30 GPa and 2000 K respectively. Using the technique described earlier, our measurements on MgSiO$_3$ perovskite were extended to 86 GPa and 2700 K. Here however the new on-line image-plate detector (the «Fastscan» [6]) now available on the ID30 beamline was used for the data collection.

Silicate perovskite MgSiO$_3$ samples were synthesized from synthetic MgSiO$_3$ enstatite crystals or synthetic MgSiO$_3$ glass mixed with platinum powder, and once loaded in a large aperture DAC, the starting materials were transformed at high P using either the CO$_2$ or the YAG infrared lasers, depending of the pressure transmitting medium. The temperature was determined by analyzing the thermal emission spectra recorded during the diffraction measurements and the pressure conditions were calculated from the EOS of platinum, used here as internal pressure calibrant [7].

Le Bail profile refinements were performed on the diffraction patterns to obtain reliable high P, high T cell parameters for the sample and the pressure calibrant up to 86 GPa and 2700 K, and the most remarkable result was that Rietveld structural refinements were successfully carried out on selected patterns in these extreme conditions [8] (Figure 3). This gave for the first time precious structural information on these compounds, as for instance the first observation of the increase of the internal distortion of the SiO_6 octahedra with increasing pressure in a powder sample. Furthermore, the data analysis allowed us to identify a set of thermoelastic parameters to constrain the compositional model of the Earth's lower mantle. Assuming that the thermoelastic parameters obtained from this study are applicable to perovskites with moderate iron content, then the comparison of the density and K_T profiles calculated for a mixture of perovskite and magnesiowüstite with those obtained from the PREM [9] model indicates that a pure perovskite lower mantle is very unlikely. On the other hand, a very good match between the PREM density and K_T profiles is obtained for a mixture of 83 vol% $(Mg_{0.93}, Fe_{0.07})SiO_3$ perovskite and 17 vol% $(Mg_{0.79}Fe_{0.21})O$ magnesiowüstite [8].

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DENSITY MEASUREMENTS OF LIQUID IRON ALLOYS AT HIGH PRESSURES: TOWARDS A BETTER UNDERSTANDING OF THE PLANETS

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Physical properties of iron-based liquids are of much interest to better understand both the current state of planetary cores and their formation during the differentiation of planets. Here we present the first experiments performed on metallic liquids in the Fe-Ni-S system, which might be relevant at least to the terrestrial outer-core and the martian core. Using a large-volume press apparatus (a Paris-Edinburgh press), the P-T range of 0-4 GPa and 20-1250 °C was explored by measuring the absorption profiles, hence density, of samples using high-energy x-rays. Equations of state of liquid iron alloys are therefore on the way to be determined, along with accurate melting-phase diagrams as a function of pressure and temperature relevant to geophysical conditions.

GEOPHYSICAL INTERESTS

Density measurements of Fe-based liquids at pressure and temperature relevant to planetary cores are essential to model accurately the core composition and convection. This should help resolve two important geophysical issues: the generation of the Earth's magnetic field and the thermal history of the planet.

Also relevant to these measurements is the differentiation of planets, i.e. at first order, the individualization of a metallic core towards the center of the planet. All these phenomena refer to the liquid state of core materials, which concerns at least the outer terrestrial core, but also probably Mars, Venus and some Galilean satellites such as Ganymede for example, as a substantial magnetic field (roughly a