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In situ determination of Fe–Fe_3S phase diagram and liquid structural properties up to 65 GPa

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ABSTRACT

Lighter elements than iron such as sulphur are required in the Earth's core to account of the core density deficit. Accurate determination of the evolution of the Fe–FeS phase diagram at high pressure is essential to determine sulphur amount in the Earth's core. *Ab initio* calculations predict extensive solubility of S in solid Fe at core pressures of 330 GPa, whereas multi anvil quench analysis exhibits deep eutectic system at moderate pressure of 21 GPa.

In this study, we investigated the Fe-rich part of Fe–FeS phase diagram up to 65 GPa and 2200 K using *in situ* angle dispersive X-ray diffraction. We report a uniform increase with pressure of the eutectic temperatures (T_{Eut}), of about 15 K/GPa. Above 50 GPa, we evidence a decrease of S content in eutectic liquid with increasing pressure. Extrapolating this trend to inner core boundary pressures suggests that S cannot account for the 10 wt.% outer core density deficit and that other light elements, such as Si and O, are needed.

Diffraction pattern recorded at 42 GPa and 2150 K was selected for structural investigations of the Fe–S liquid. By applying liquid structure simulation based on Gaussian distribution of atoms around crystalline positions, a good agreement has been found with hcp Fe model-structure, rather than with Fe_3S structure. It suggests that S acts as an interstitial impurity in the liquid state. Therefore, S could have a relatively minor effect on sound velocities in liquid outer core.

1. Introduction

Iron is generally accepted as the main constituent of the terrestrial planetary cores, but alloyed with Ni and other lighter elements. For the Earth, the outer and inner cores are estimated to be 6–10% and 2–3% less dense than pure iron, respectively (Birch, 1964; Badro et al., 2007). Influence of light elements on the Earth's core dynamics is largely dependent on their solubility in the inner core, because their rejection to the outer core promotes solutal convection (Kutzner and Christensen, 2000). Formation of a Fe-alloy solid solution with a small melting loop like in Fe–FeSi system at 21 GPa (Kuwayama and Hirose, 2004) or a large eutectic depression with extended melting loop like in Fe–FeS system at 21 GPa (Fei et al., 2000) lead to drastically different core properties, such as fractional crystallisation with small or large difference of density between liquid and solid.

Melting temperature in Fe–FeS system is an essential information concerning planetary cores (Boehler, 1996; Campbell et al., 2007; Chudinovskikh and Boehler, 2007; Stewart et al., 2007). Sulphur is believed to be present in small amount in Earth's core due to its high volatility (around 2 wt.% (Allègre et al., 1995)). Its content may be even higher if sulphur was trapped in the metallic phase at relatively low temperatures during an homogeneous accretion process during the Earth's formation (Righter et al., 1997). In this sense, sulphur is even more relevant for the Martian core. Indeed, it could contain a significant larger amount of volatile light elements, potentially up to more than 14 wt.% S (Sohl and Spohn, 1997) because lower temperature is expected for planetary orbital further from the Sun.

Liquid properties are intimately linked with their local structure. For example, Si does not modify largely the local structure of Fe-alloys up to 40 at.% Si (Kita et al., 1982), leading to high bulk modulus close to values of liquid pure Fe (Sanloup et al., 2004), whereas Fe–S alloys poorly ordered structures under low pressure (Urakawa et al., 1998; Sanloup et al., 2002) is linked with a low bulk modulus (Sanloup et al., 2000). Recently, we showed that the evolution toward compact atomic packing of the local structure in Fe–S eutectic liquid could lead

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to change in bulk modulus (Morard et al., 2007). It must be noted that a small percentage of S added to a Fe–Si, Fe–O or Fe–C liquid provoke the formation of two immiscible phases for $P<15$ GPa (Raghavan, 1988), which may have peculiar implication for planetary core's formation.

In this study, we will first discuss evolution of the eutectic temperature in the Fe–S system up to 65 GPa determined by *in situ* detection of melting, using X-ray diffraction in laser-heated diamond anvil cell (LH-DAC). Then, information about evolution of S contents in eutectic liquid and solid will be estimated from phase identification at high pressure and temperature. Finally, liquid structure properties will be discussed through partial distribution function $g(r)$ derived from analysis of the X-ray diffusion scattering recorded at high pressure and temperature for liquid Fe–S alloys.

2. Experimental techniques

The starting material was composed of a mixture between Fe (GoodFellow, 99.99% purity) and FeS (Sigma Aldrich, 99.9% purity) powders finely grinded ground in an agate mortar in order to obtain a homogeneous material with micron grain size. We used starting materials with two different compositions: 12.5 wt.% S (20 at.% S) and 6 wt.% S (10 at.% S). High pressures were generated with a Le Toullec type diamond anvil cell using diamonds with 250 and 300 µm diameter culets. Samples were pre-pressed between two diamonds to a thickness of ~10 µm, from which a 50 µm diameter flake was taken. Sample flakes were loaded between two dry NaCl layers in 70 to 100 µm diameter holes drilled in a preindented rhenium gasket. NaCl is soft pressure medium insuring good hydrostatic conditions and it is chemically inert in contact with iron alloys.

X-ray angle dispersive diffraction measurements have been performed on ID27 High Pressure beamline at ESRF (Grenoble, France). The monochromatic X-ray beam was focused to 5*5 µm size for energy of 47 keV (Sm K edge: 0.26472 Å). More details are reported elsewhere (Mezouar et al., 2005). Sample pressure has been evaluated using the equation of state of (a) NaCl pressure medium at 300 K and (b) hcp Fe at high temperature during the YAG laser heating (Dewaele et al., 2006). The quenched hcp Fe indicates pressure 10% lower than the NaCl pressure medium, possibly due to S incorporation. Similar effect was also observed in previous study (Seagle et al., 2006). Thus, we use positive error bars of 10% of the nominal pressure at all temperatures. Negative error bars are evaluated at 2 GPa, from the maximal uncertainty in determining the unit-cell volume of hcp Fe with this experimental set set-up (Guignot et al., 2007). When melting of Fe-alloys is completed, we assume that pressure is similar to the lower temperature spectra, when crystalline Fe was still visible. Therefore, pressure uncertainty is estimated to ±5 GPa at the highest temperatures.

3. High temperatures

To generate high temperatures, we used two 40 W single-mode (TEM 00) continuous YAG lasers with excellent power stability focused on each side of the sample. Temperature was equilibrated by tuning the lasers power while measuring on both sides of the sample by the spectroradiometric method using reflective collecting optics (Schultz et al., 2005). We achieved laser spots of more than ~20 µm diameter. Therefore, the X-ray spot is significantly smaller than the laser spot. The very high X-ray flux available on ID27 makes it very precise the alignment between X-ray spot and laser spot (Schultz et al., 2005), because diamond fluorescence (in the visible and UV range) is clearly visible on the CCD camera used for the optical alignments. During acquisition of the X-ray pattern, temperatures stability was checked by measurements on one sample side only. Time exposure of 30 s was required for diffraction pattern acquisition. Such short exposure time is necessary to avoid liquid migration in the sample.

Despite our precautions, temperature gradients may remain in the laser-heated samples. The small size of the X-ray spot (5*5 µm) is the

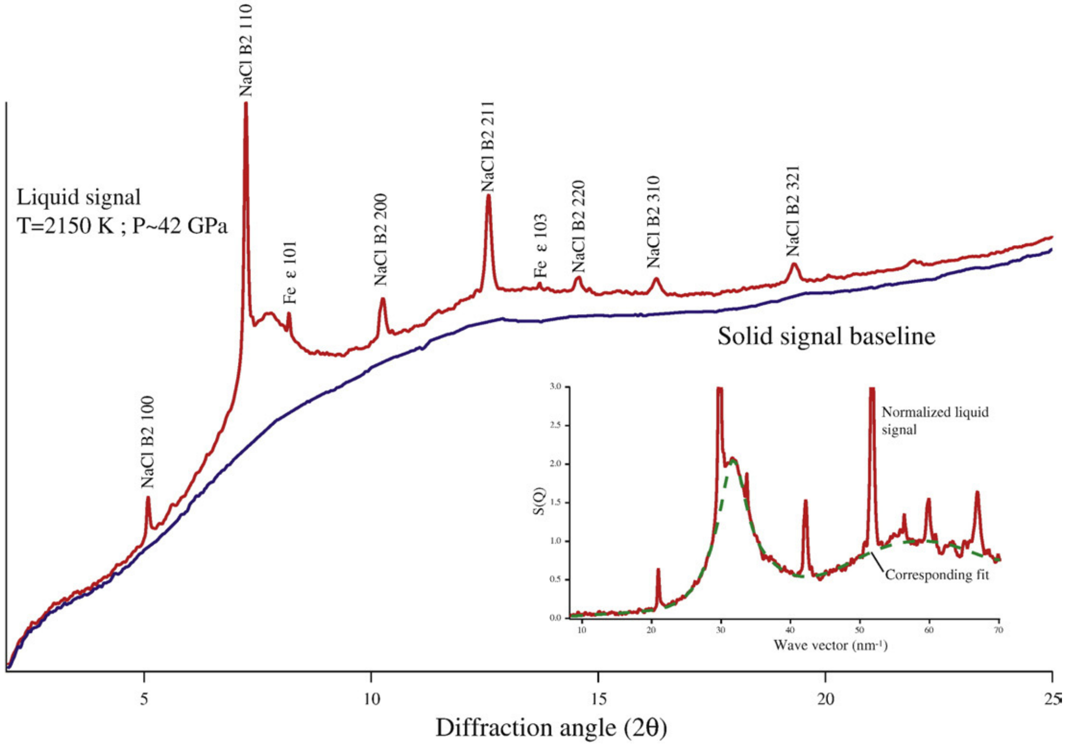

Fig. 1. Diffraction patterns recorded with increasing temperature at a nominal pressure of 52 GPa and initial composition of Fe–20 at.% S. Dashed lines indicate the position of solid phases diffraction peaks (Fe ε, Fe_3S and NaCl B2) at 1813 K. Progressive increase in intensity of diffuse scattering in the 7° to 9° 2θ region is related to the sample partial melting (Andrault et al., 2006).