

Equation of state of liquid iron under extreme conditions

Iron is the sixth most abundant element in the universe and the main component of metallic cores of planets including Earth, Mars, Mercury, and likely some terrestrial planets outside of our solar system (so-called super-Earths). The Earth's core is considered to be composed mainly of iron but includes substantial amounts of lighter elements, particularly in its liquid outer part. The identification of core light elements is of great importance because it has wide implications, for example, for the Earth's building blocks, core formation process, thermal structure, and mechanism of core convection and geodynamo that generates the Earth's magnetic field. Since the properties of the liquid outer core that can be directly determined are the density ρ and longitudinal sound velocity V_P (equivalent to the bulk sound velocity V_ϕ in a liquid), which are derived from seismic observations, laboratory measurements of these properties at high pressures are necessary to understand Earth's and other planets' core composition and behavior.

Although the density of crystalline materials under high pressure and temperature (P - T) conditions has been extensively studied experimentally by *in situ* X-ray diffraction (XRD), such study is still challenging for disordered materials. Although XRD can potentially be applied up to 100 GPa and high temperature, analytical methods for extracting ρ from a diffuse XRD signal, which is characteristic of a disordered material, have not been well established. In particular, no density measurement for liquid pure iron under static compression has been performed because of experimental difficulties arising from its high melting temperature at high pressures. V_P is also a key property in understanding the liquid behavior at high pressures as it is related to properties such as compressibility, thermal expansivity, and the Grüneisen parameter γ . Although V_P of liquid iron was previously determined up to 5.8 GPa by ultrasonic measurements in a Kawai-type multi-anvil apparatus, this is much lower than the pressure conditions of the Earth's core. Furthermore, the structure of liquid iron may possibly be different above 6 GPa. Thus, measurements at higher pressures are required to understand the nature of the core. Although only shock-wave compression experiments previously yielded measurements of ρ and V_P of liquid iron at high pressures between 278 and 397 GPa [1,2], it is impossible to conduct experiments on liquid iron at lower pressures via shock experiments, since the shock compression can generate high P - T only along

the Hugoniot path which crosses the melting curve of iron at 270 GPa.

In this study, we measured ρ of liquid pure iron at high pressures for the first time via static compression using laser-heated diamond-anvil cell (LH-DAC) techniques [3]. The measurements were performed up to 116 GPa and 4350 K. This is close to conditions in the top region of the Earth's core. We measured angle-dispersive X-ray diffraction (XRD) spectra using a highly focused, brilliant X-ray beam at SPing-8 BL10XU. Strong diffuse scattering signals from liquid iron were found in the XRD spectra obtained at about 100–400 K above its melting point. After background subtraction, the result was converted into the structure factor $S(Q)$, where Q is the momentum transfer. Fourier transform of $S(Q)$ yielded the reduced pair distribution function $F(r)$ and the pair distribution function $g(r)$ (r , radial distance) (Fig. 1). The density of the liquid can, in principle, be determined from the slope of $F(r)$ for r smaller than the interatomic spacing. However, it has been considered that the conventional technique of analyzing the diffuse signals gives a liquid density with uncertainty exceeding 10%. To overcome this problem, we developed a new analytical method for deriving ρ from the diffuse X-ray scattering signal, in which the observed $S(Q)$ is extended beyond Q_{\max} (the maximum Q in experimental data) so that the corresponding $g(r)$ is physically reasonable; no atom exists within the distance between the nearest-neighbor atoms. This is the key to the precise determination of liquid density under pressure. We

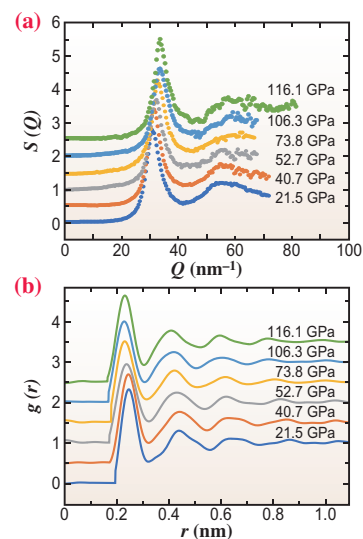


Fig. 1. (a) Structure factor $S(Q)$ of liquid iron up to 116.1 GPa. (b) Corresponding radial distribution function $g(r)$ determined in this study.

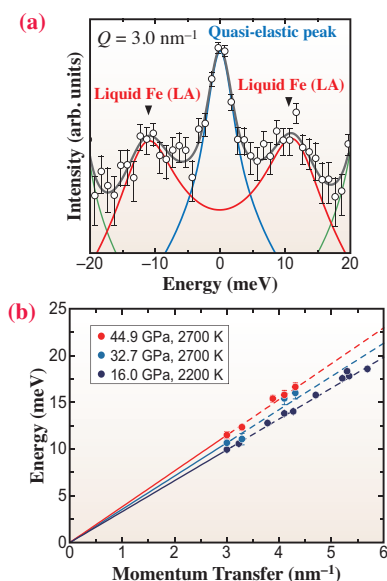


Fig. 2. (a) Typical IXS spectrum of liquid iron collected at 44.9 GPa and 2700 K at momentum transfer $Q = 3.0 \text{ nm}^{-1}$. (b) Longitudinal acoustic phonon dispersion of liquid iron at pressures from 16.0 to 44.9 GPa.

verified the new method by analyzing 1) the XRD data previously collected for a Ce-based metallic glass ($\text{Ce}_{70}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{10}$) and 2) a synthetic XRD pattern, and found that the new analytical method is universally applicable to density determinations of amorphous materials.

We also determined V_P of liquid iron up to 45 GPa by inelastic X-ray scattering (IXS) measurements in the LH-DAC at SPring-8 BL43LXU. The experimental temperature was determined from the thermal radiation from the sample, as in the XRD experiments. The IXS spectra of liquid iron included three peaks in the present scanned energy range: Stokes and anti-Stokes components of the longitudinal acoustic phonon mode from the sample, and a quasi-elastic contribution near zero energy transfer (Fig. 2). V_P of liquid iron was determined using dispersion relations.

Now we have both P - T - ρ and P - T - V_P data for liquid iron from the present experiments, in addition to the P - ρ - V_P - γ relation (γ , Grüneisen parameter) from previous shock experiments [1,2]. From these data, we obtain the P - T - ρ - V_P - γ relation for the Earth's entire outer core conditions (136–330 GPa and 4000–5400 K) using the Mie-Grüneisen equation of state (EoS). To compare the liquid iron properties with seismological observations [4], we calculated the isentropic T profiles considering three different model temperatures at the liquid/solid core boundary (inner core boundary, ICB) ($T_{\text{ICB}} = 5000 \text{ K}$, 5400 K, and 5800 K) (Fig. 3). Compared with ρ and V_P of liquid iron calculated along the isentrope with $T_{\text{ICB}} = 5400 \text{ K}$, the Earth's liquid outer core exhibits ρ lower by 0.99–0.81 g/cm^3 (7.5–7.6%) and V_P higher by

0.43–0.29 km/s (4.3–3.7%). Our results also show that liquid iron is less dense than solid hexagonal-close-packed (hcp) iron by $\Delta\rho_{\text{melting}} = 0.32 \text{ g/cm}^3$ at 330 GPa and its melting point of 6230 K [5]. This is only half of the seismologically observed density difference between the liquid outer and solid inner cores at the ICB, indicating a compositional difference between the outer and inner cores. With the knowledge of the phase diagrams of iron alloys, our results show that the oxygen concentration in the outer core is limited to 1.6–3.8 wt%, although it has been repeatedly suggested to be the main core light element, indicating that the core should include other impurity elements.

We determined the EoS of liquid iron that is applicable to all core conditions. This will serve as an important baseline for understanding the composition and behavior of the Earth's core.

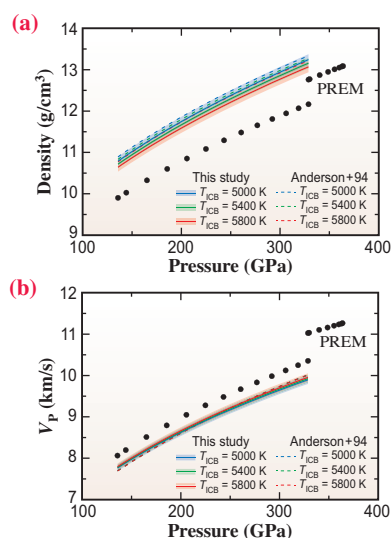


Fig. 3. Seismic observations (black circles, PREM [4]) and ρ , V_P , and K_S of liquid Fe under core pressures along the isentropic temperature profiles with $T_{\text{ICB}} = 5800 \text{ K}$ (red), 5400 K (green), and 5000 K (blue).

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