

## Equation of state of iron and nickel to 370 gigapascals

The Earth's inner core is the deepest region and at 3.30–3.65 million atmospheres of pressure (330–365 gigapascals, GPa). It is mainly made of solid iron (Fe), and according to cosmochemical and geochemical studies, it contains a substantial (5 to 15%) amount of nickel (Ni) as the second component. Experimental measurements of the Earth's core material properties combined with seismic observations indicate that the inner core is a few percent less dense than pure iron. This implies that a light component is probably present in the inner core, such as sulfur, silicon, oxygen, carbon, and hydrogen. The description of the Earth's inner core, thus, highly depends on the compression property of Fe under high-pressure, high-temperature conditions determined experimentally.

Numerous works on Fe have continued for half a century through static and dynamic experiments and theoretical calculations, including those on the equation of state (EOS) and the phase relation in a high-pressure, high-temperature regime. Modeling the interior structure of the Earth's inner core requires an accurate determination of the EOS from the experimental data obtained at pressures corresponding to the inner core and then a direct comparison with the densities obtained from the seismological model. However, the maximum pressure achieved in static compression experiments has been limited to 300 GPa for iron [1-3] and below 160 GPa for nickel [4], and accurate experimental data of density that enable a direct comparison for the inner core region have remained elusive. The pressure–volume data collection through the inner core to the Earth's center has been one of the most significant challenges in deep Earth mineralogy.

We focused on the experimental investigation of the compression behavior of Fe and Ni at Earth's inner core pressures. High-pressure powder X-ray diffraction in diamond anvil cells was carried out at SPring-8 **BL10XU** and **BL04B2**. Using high-energy microfocused X-ray beams at 30 keV (or 28 and 37.8 keV), we succeeded in generating high pressures of up to 370 GPa corresponding to the central region of the Earth [5]. The compression data at 165 points for Fe and 103 for Ni were collected over the experimental pressure range. The isothermal EOSs of Fe and Ni were then determined at 298 K using quasi-absolute EOS pressure scale of platinum (Pt) proposed recently on the basis of high-precision measurements by a ramp (shockless) dynamic compression technique.

We observed that Fe underwent a phase transition from the body-centered cubic (bcc-Fe, or  $\alpha$ -Fe) phase to the hexagonal close-packed (hcp-Fe, or  $\epsilon$ -Fe) phase at  $\sim 15$  GPa, and then the hcp-Fe phase remained stable up to a maximum pressure of 354 GPa at 298 K, as shown in Fig. 1(a). Seven diffraction lines were identified for hcp-Fe, from which the lattice constants  $a$ ,  $c$ , and  $c/a$  were estimated to be 2.1294(17) Å, 3.390(5) Å, and 1.592(4), respectively. The volume at 354 GPa had shrunk to  $\sim 56.3\%$  of that at ambient pressure.

Ni has a face-centered cubic (fcc) structure at ambient pressure and does not show any structural phase transition up to 368 GPa, indicating that the fcc structure is stable up to the maximum pressure investigated in this study (Fig. 1(b)). At 368 GPa, six diffraction lines were observed for fcc-Ni, and eight diffraction lines were identified for Pt. The lattice constant  $a$  of fcc-Ni was estimated to be 2.9521(10) Å, and the volume compression ratio  $V/V_0$  was 0.5880. Our pressure–volume data of Fe and Ni, plotted in Fig. 2, were analyzed using a Vinet EOS, a universal formalism shown to be widely applicable to solids of different bonding types:

$$P = 3K_0(1 - x^{1/3})x^{-2/3} \exp\left[\frac{3}{2}(K_0' - 1)(1 - x^{1/3})\right],$$

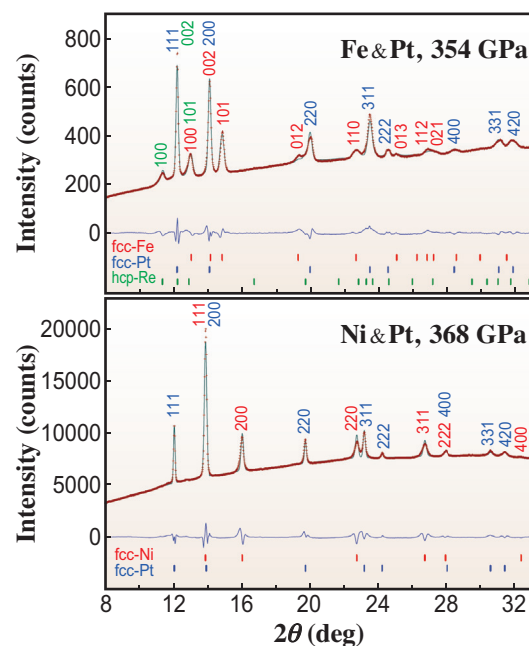


Fig. 1. Representative X-ray diffraction pattern (red crosses) and Rietveld simulation (green lines) for hcp-Fe at 354 GPa and Ni at 368 GPa. Blue lines show the difference between the observed and calculated patterns.

where  $x = V/V_0$ ,  $V_0$  is the ambient atomic volume, and  $K_0$  and  $K'_0$  are the bulk modulus at ambient pressure and its pressure derivative. The EOS parameters of  $K_0$  and  $K'_0$  were estimated to be 159.27(99) GPa and 5.86(4) for hcp-Fe, and 173.5(1.4) GPa and 5.55(5) for Ni, respectively.

At 365 GPa (the pressure of the center of the Earth), by comparing the present EOS to EOS extrapolated from the recent compression curve [3,4], the present volumes of Fe and Ni are found to be 2.3% and 1.5% larger than those estimated from the extrapolation, respectively. When the pressure values in the literature curve are corrected using the latest Pt-EOS pressure scale, the volume difference in Fe is within  $\pm 0.7\%$  at 365 GPa. Our compression curve for Ni also is in perfect agreement with the literature curve with corrected pressure values. We conclude that these discrepancies are due to the pressure scale.

Generally, a sample compressed between two anvils without any pressure-transmitting medium is under non-hydrostatic stress conditions. We examined the non-hydrostatic pressure effect in the diffraction data by analyzing the  $d$ -spacing using the lattice strain equations. The difference between the axial and radial stress components in the diamond anvil sample, referred to as the differential or uniaxial stress component, is a measure of non-hydrostaticity. The uniaxial stress component was estimated under the isostrain (Voigt) condition, giving the lower bound. The obtained values for fcc-Pt at 354 GPa and 368 GPa and fcc-Ni at 368 GPa were all below 0.9 GPa and within the uncertainty of pressure, suggesting that the uniaxial stress effect is negligible.

Figure 3 shows the room-temperature densities of hcp-Fe and fcc-Ni as functions of pressure in

the Earth's core, along with the seismic Preliminary Reference Earth Model (PREM) density profile. The new static compression data allow the density to be constrained directly at inner core pressures without the extrapolation of the data. As both Fe and Ni have a close-packed structure under high compression, we also expect that the density of the Fe–Ni alloy can be estimated from our EOSs of Fe and Ni using the mass fraction of Ni in Fe. The present data covering the entire pressure range of the Earth's inner core will provide a better understanding of the solid inner core's interior structure and composition, including light element(s).

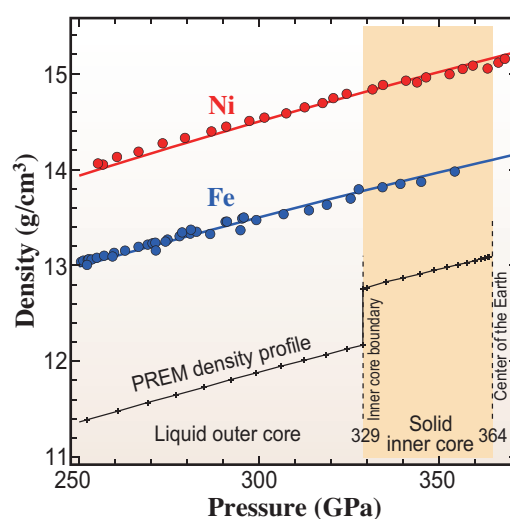


Fig. 3. Densities of Fe and Ni at 298 K as functions of pressure. Circles, experimental data points. Circles, experimental data points; curves, calculated profiles using isothermal EOSs. The seismic Preliminary Reference Earth Model (PREM) is also shown for comparison.

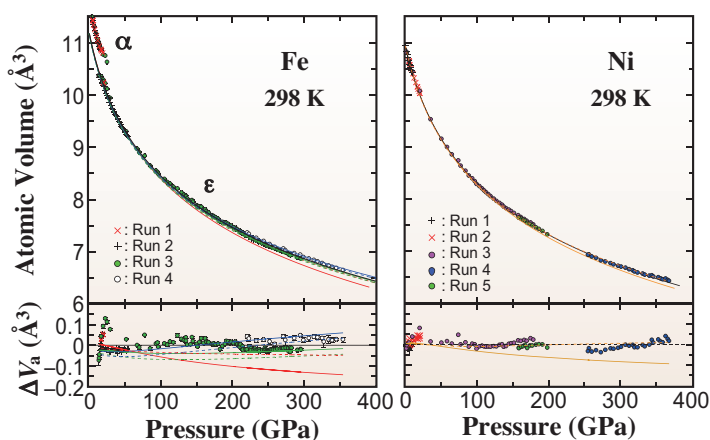


Fig. 2. Pressure–volume curves for Fe and Ni, along with literature data. Black (this work), green [1], blue [2], red [3], and orange [4]. Dashed curves show pressure-corrected EOSs based on the latest Pt scale.  $\Delta V_a$  denotes the deviations of the atomic volume between the measured and fitted volumes.

Naohisa Hirao<sup>a,\*,\dagger</sup> and Yuichi Akahama<sup>b</sup>

<sup>a</sup> Japan Synchrotron Radiation Research Institute (JASRI)

<sup>b</sup> Graduate School of Science, University of Hyogo

\*Email: naohisa.hirao@j-tec.co.jp

<sup>†</sup> Present address: JTEC Corporation

### References

- [1] H. K. Mao *et al.*: J. Geophys. Res. **95** (1990) 21737.
- [2] L. S. Dubrovinsky *et al.*: Phys. Rev. Lett. **84** (2000) 1720.
- [3] A. Dewaele *et al.*: Phys. Rev. Lett. **97** (2006) 215504.
- [4] A. Dewaele *et al.*: Phys. Rev. B **78** (2008) 104102.
- [5] N. Hirao, Y. Akahama, Y. Ohishi: Matter Radiat. Extremes **7** (2022) 038403.