Stability Field and Thermal Equation of State of ε-Iron

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Introduction

The Earth's core consists of a liquid outer core and a solid inner core,[1] which are believed to be made predominantly of iron (Fe).[2,3] The crystal structure, melting temperature, and equation of state (EOS) of Fe, therefore, provide important clues from which to infer the composition and the thermodynamic state of the core. In the present study, we use a "T-cup" multi-anvil apparatus combined with the synchrotron x-radiation at the Advanced Photon Source (APS) to establish the stability field and EOS of ε-Fe up to 20 GPa and 1500K. The stability field of Fe is characterized by the location of the α-ε-γ triple point and the ε-γ boundary. The *P-V-T* (pressure-volume-temperature) data set obtained for ε-Fe is fitted to several high-temperature EOSs. The accuracy of our data allows us to examine structural distortion (represented by the c/a ratio) as a function of *P* and *T*. The density of ε-Fe is then calculated from the EOS of pure ε-Fe at the Earth's core conditions. Comparison to the density from the preliminary reference Earth model (PREM) provides constraints on the possible presence of light element(s) in the Earth's core.

Methods and Materials

High *P* and *T in situ* x-ray diffraction experiments were performed using the 250-ton press installed at the GSECARS 13-BM-D beamline at the APS, with a double-stage split-cylinder T-cup apparatus. Diffraction patterns were collected based on the energy dispersive method with an energy range of 20-100 keV. The incident x-ray beam size was 100 x 300 μm and diffracted x-rays were detected by a Ge solid-state detector at a fixed diffraction angle of 6°.

Both polycrystalline Fe and the pressure calibrant Au were mixed with MgO to inhibit grain growth. Temperature was monitored by a $W_{0.94}Re_{0.06}$-$W_{0.75}Re_{0.25}$ thermocouple. Pressure was determined from the Au diffraction lines based on the high *P* and *T* EOS of Au.[4]

The experiment consisted of two runs: one clarified the phase relations and the other collected *P-V-T* data of e-Fe. Our criterion to determine the phase boundary is as follows. A diffraction profile was taken from the sample first, followed by the diffraction pattern of Au to determine the pressure. Then the sample x-ray pattern was collected again without changing *P* and *T*. This procedure tests the kinetics of the transition, so comparison of the two patterns from before and after pressure determination (typical time interval is 6 min) clarifies the stable phase, whose diffraction intensity should grow. To extract EOS parameters, *P-V-T* data were collected only in the ε phase stability field to avoid peak overlap. The maximum temperature was kept at 1000K. Diffraction lines of the *111*, *200*, *220*, *311*, and *222* peaks from Au were used to determine pressure[4] whereas the *100*, *002*, *101*, *110*, and *103* lines of the ε-Fe were used to obtain cell volumes throughout the experiment.

Results and Discussion

Transformation boundaries between the ε and γ phases determined by this method are shown in Fig. 1. Our data indicate that the triple point of the α, ε, and γ phases of Fe is located at 8.0(3) GPa and 680(50)K, which is close to that determined by a previous study using a cubic-anvil high pressure apparatus (8.3 GPa and 713K)5 after carefully taking into account the effects of time dependence due to transition kinetics by repeating heating and cooling cycles. The slope of the ε-γ boundary is 36(3) $KGPa^{-1}$, which is steeper than that in one diamond anvil cell (DAC) experiment (24 $KGPa^{-1}$),[6] but is in excellent agreement with the results obtained from a cubic-anvil press (34$KGPa^{-1}$; as estimated from their Fig. 2)[5] and another DAC result (35 $KGPa^{-1}$).[7]

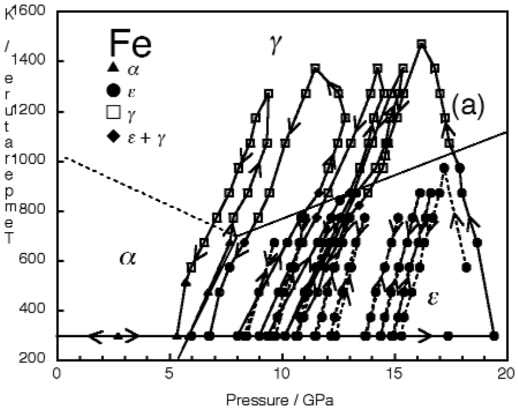

FIG. 1. Phase diagram of Fe determined by in situ *x-ray observation, together with experimental* P-T *paths. Triangles, circles, squares represent which phase of α, ε, and γ is dominant under corresponding* P *and* T *condition. Diamonds represent the data points where the dominant phase is inconclusive because of little time dependence of diffraction peaks. Thin solid and dashed lines indicate (a) first run (#T0105) to see the phase boundary and (b) second run (#T0134) for* P-V-T *measurement of ε-Fe, respectively. Arrows show directions of the P-T path. Temperature fluctuation was only about 5K at 1500K.*

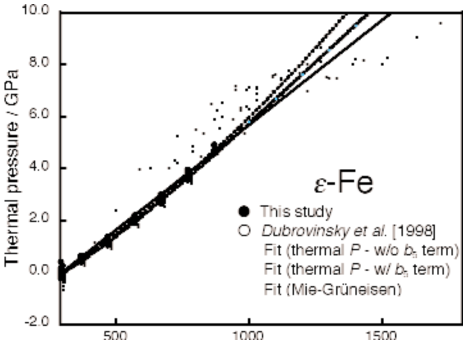

FIG. 2. Thermal pressure of ε-Fe up to 20 GPa and 1000 K, together with previous work.[8] The 55 cooling cycle data points are fitted to Anderson's thermal pressure approach with (dashed line) and without ($\partial^2P/\partial T^2$) term (solid line) and Mie-Grüneisen-Debye approach (dotted line). The best fit to our data is Mie-Grüneisen-Debye equations within this temperature range. Above the Debye temperature of 998K, the dotted line shows the extrapolation based on linear function.

Combined with data from the DAC, room-temperature volume data yield a third-order Birch-Murnaghan EOS with K_0 =

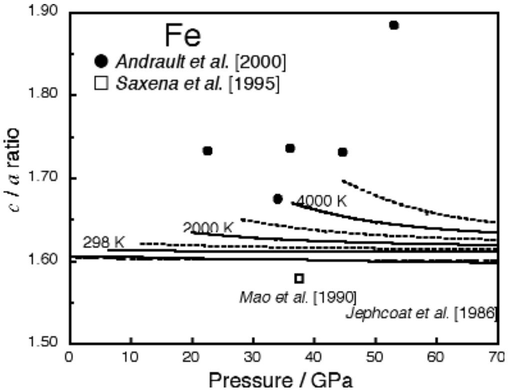

FIG. 3. Comparison of c/a ratio as a function of P *and* T. *Solid circle and open square shows the pseudo c/a of the orthorhombic phase*[12] *and the* c/a *of the dhcp phase,*[13] *respectively. Solid lines (298, 2000, and 4000K) and dashed lines (1000, 3000, and 5000K) show extrapolations of the present study. Room-temperature* c/a *variations as a function of pressure*[9,10] *are also plotted.*

135(19) GPa, $K'_0 = 6.0(4)$, and $V_0 = 22.7(3)$ Å^3. A total of 55 data points collected during cooling cycles are fit to several high-T EOSs. The fit to the Mie-Grüneisen-Debye EOS yields the Debye temperature, the Grüneisen parameter, and the parameter q to be 998(85)K, 1.36(8), and 0.91(7), respectively. The Mie-Grüneisen-Debye EOS, high-temperature Birch-Murnaghan EOS, and thermal pressure approach based on Mie-Grüneisen theory are all consistent in the current P and T range, but the Mie-Grüneisen-Debye EOS yields the best fit (Fig. 2).

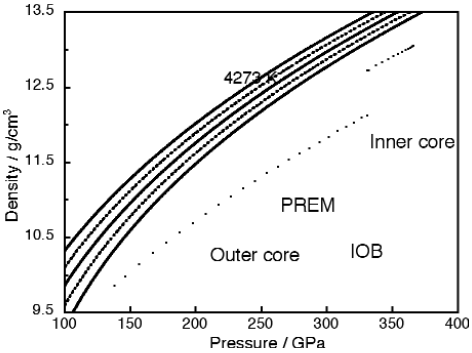

FIG. 4. Density of ε-Fe at the Earth's core condition. Solid and dashed lines are obtained by extrapolation of Mie-Grüneisen-Debye EOS. Solid lines indicate 4273, 6273, and 8273K and dotted lines 5273 and 7273K respectively. Open circles are PREM densities. The ε-Fe densities are significantly higher than those for PREM, supporting the existence of light element(s) in both the inner and outer core.

The c/a ratio increases with T and decreases slightly with P (Fig. 3). The room-temperature c/a ratio of ε-Fe is reported to decrease as a function of pressure [c/a = 1.606(1)-1.2(3) x $10^{-4}P$ (GPa)[9]; c/a = 1.604(2)-0.49(14) x 10^{-4}P (GPa).[10] Our room temperature c/a is represented by c/a=1.613-1.6 x $10^{-6}P$ (GPa) as a linear function, which is 0.4-0.8% larger than that at the pressure up to 200 GPa.[9] Pressure dependence of c/a is still smaller than that reported by Mao et al. [1990][10] by one order of magnitude. From the scatter of the data in these studies, however, a 0.4-0.8 % difference in c/a should be regarded as experimental error. The c/a ratio does not support the possibility of phase transition up to the Earth's core condition.

On the assumption that the inner core is composed of pure ε-Fe, extrapolation of Mie-Grüneisen-Debye EOS allows us to estimate the density under the Earth's core condition. Figure 4 shows density of e-Fe as a function of pressure along several isotherms, together with the density of PREM.[1] For the density of pure ε-Fe to match that of PREM, core temperatures must be exceedingly high. Even when the highest available estimate of inner-core boundary (ICB) temperature of 7600 K[11] is employed, ε-Fe still has about 4% excess density compared to PREM. This result supports the notion that light element(s) must be present in the inner core, as well as in the outer core.[14]

Acknowledgments

We thank N. Lazarz, F. Sopron, M. Jagger, G. Shen, M. Newville, P. Eng, J. Pluth, P. Murray, C. Pullins, L. Gubenko, P. Dell, and D. Weidner for their valuable contributions. Work was performed at GSECARS, APS at Argonne National Laboratory. GSECARS is supported by the National Science Foundation-Earth Sciences, Department of Energy-Geosciences, W. M. Keck Foundation, and the United States Department of Agriculture. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

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