Thermal expansion of iron-rich alloys and implications for the Earth’s core

Bin Chen*,†, Lili Gao*, Ken-ichi Funakoshi‡, and Jie Li*

*Department of Geology, University of Illinois at Urbana–Champaign, 1301 West Green Street, Urbana, IL 61801; and ‡Japan Synchrotron Radiation Research Institute, SPring-8, Hyogo 679-5198, Japan

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The Earth’s core makes up nearly one third of the planet’s mass. Its composition, property, and dynamics are fundamental issues in the study of the Earth’s interior. Deeply buried in the center of the planet, the core has kept its chemical composition a long-standing mystery. Cosmochemical studies of meteorites and geochemical analysis of samples from shallower portions of the Earth suggest that the core is made of iron (Fe)-rich alloys containing nickel (Ni) and one or more lighter elements (1). A critical test for any candidate core composition model is that it must be able to reproduce the physical properties of the core. On the basis of observing seismic rays penetrating the deep interior of the Earth and the orbital dynamics of the Earth as a planet in the solar system, models have been constructed to describe the physical state, density profile, and velocity profiles of the Earth’s interior. One of the most widely used models is PREM (2). To perform the test of consistency between a composition model and the PREM model, we must know the thermal state of the core and the equation-of-state (EOS) of various Fe-rich alloys at the pressure and temperature conditions of the core. The thermal state of the core can be deduced from the freezing point of core composition at the pressure of inner–outer core boundary and the adiabatic temperature gradient of the core composition under core pressures through laboratory measurements. Uncertainties in the core composition directly lead to uncertainties in the thermal state. By iteration, a self-consistent model of the thermal–chemical state of the core may be found. To complement this approach, we need accurate and precise phase relation and EOS data of various Fe-rich alloys at megabar pressures and high temperatures. In this paper, we review existing data on the thermal expansion of Fe-rich alloys and report experimental data on thermal expansion of Fe3S, Fe, and Fe–Si alloys.

Fe3S | Fe–Si alloy | light element

The thermal expansion of iron-rich alloys at megabar pressures and high temperatures. Our survey of literature revealed a significant lack of such data. We have determined the unit-cell parameters of the iron–sulfur compound Fe3S by using synchrotron x-ray diffraction techniques and externally heated diamond–anvil cells at pressures up to 42.5 GPa and temperatures up to 900 K. The zero-pressure thermal expansivity of Fe3S is determined in the form $a = a_1 + a_2T$, where $a_1 = 3.0 \pm 1.3 \times 10^{-5}$ K$^{-1}$ and $a_2 = 2.8 \pm 1.5 \times 10^{-8}$ K$^{-2}$. The temperature dependence of isothermal bulk modulus ($\partial K_{T0}/\partial T$) is estimated at $-3.75 \pm 1.80 \times 10^{-13}$ GPa K$^{-1}$. Our data at 42.5 GPa and 900 K suggest that $a = 2.1$ at. % (1.2 wt. %) sulfur produces 1% density deficit in iron. We have also carried out energy-dispersive x-ray diffraction measurements on pure iron and Fe$_9$xSi$_{0.136}$ alloy samples that were placed symmetrically in the same multianvil cell assemblies, using the SPring-8 synchrotron facility in Japan. Based on direct comparison of unit cell volumes under presumably identical pressures and temperatures, our data suggest that at most 3.2 at. % (1.6 wt. %) silicon is needed to produce 1% density deficit with respect to pure iron.

Thermal Expansion of Fe-Rich Alloys Under Static High Pressure: A Survey

Thermal expansion is a fundamental aspect of EOS. Various parameters have been introduced to characterize thermal expansion under elevated pressures. They fall into two general categories, one focusing on macroscopic thermodynamic quantities and derivatives, and the other based on lattice vibration theories and microscopic view of solids. In the first category, $P–V–T$ data are grouped into isothermal, isobaric, or isochoric sets. A basic approach is to calculate the thermal expansion coefficient from isobaric data according to its definition $\alpha = (\partial ln V/\partial T)_p$. The temperature dependence of thermal expansion coefficient is normally expressed in the form of $\alpha = a_1 + a_2T$ or $\alpha = a_1 + a_2T + a_3T^{-2}$ (e.g., ref. 3). One can also calculate temperature-dependent bulk modulus ($\partial K_{T0}/\partial T$) by fitting isothermal data for the high-temperature Birch–Murnaghan EOS. Isochoric data allow the calculation of thermal pressure at constant volume, which is related to thermal expansion coefficient and isothermal bulk modulus: $\Delta P_{thermal} = aK_T\Delta T$, where $aK_T$ is commonly assumed to be constant at temperatures above the Debye temperature. In the second category, the Mie–Grüneisen–Debye EOS is widely used to extract a number of thermoelastic parameters from $P–V–T$ data, including the isothermal bulk modulus at ambient pressure ($K_{T0}$), its pressure derivative ($K_{T0}$), the Debye temperature at ambient pressure and temperature $\theta_D$, the Grüneisen parameter $\gamma$ (which describes the volume dependence of the Debye temperature), and $q$ (which is a parameter describing the volume dependence of the Grüneisen parameter). Jackson and Rigden (4) carried out a systematic analysis of $P–V–T$ data of mantle minerals and found excellent agreements between different methods.

A survey of literature revealed a significant lack of thermal expansion data on Fe-rich alloys under static high pressure (Table 1). Extensive efforts have been focused on pure Fe. With the recent development in high-pressure and high-temperature experimental techniques and concurrent advance in synchrotron radiation facilities, this simplified core composition model has become amenable to investigations under increasingly higher pressures and temperatures. Using diamond–anvil cells and internal heating technique, Dubrovinsky et al. (5, 6) determined the thermal expansion of Fe to a maximum pressure of 300 GPa and a maximum temperature of 1,500 K. Two multianvil studies covered similar range of temperature at moderate pressures (7, 8). An independent estimate of the Debye temperature has been

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Abbreviations: EOS, equation-of-state; hcp, hexagonal close-packed.

†To whom correspondence should be addressed: Department of Geology, University of Illinois at Urbana–Champaign, 1301 West Green Street, Urbana, IL 61801. E-mail: binchen2@uiuc.edu.

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obtained from nuclear resonant inelastic scattering measurements, which determined the phonon density of states of Fe up to 153 GPa and at ambient temperature (9). The Debye temperature at 1 bar derived from the phonon density of states data agrees well with that from a x-ray diffraction study in a diamond–anvil cell (420–430 K) (10), but they are in stark disagreement with the result of multianvil experiments (>1,000 K) (8). All of the reported thermal expansion coefficients at ambient conditions agree within uncertainties. Although laser-heated diamond anvil cells have been used extensively to determine the structural phase transition of Fe, no thermal expansion data have been reported. Due to limited temperature coverage by the existing static experiments, current discussions concerning the effect of thermal expansion on the density deficit in the Earth’s core have largely relied upon shock wave data (11, 12).

The leading candidates for alloying elements in the Earth’s core include Ni, sulfur (S), silicon (Si), carbon (C), oxygen (O), and hydrogen (H) (see reviews in refs. 13–16). The phase relations and thermoelastic properties of a number of binary systems including Fe and one of the alloying elements have been studied under high pressures and temperatures. We found that thermal expansion data for Fe-rich alloys are extremely limited. With laser-heated diamond–anvil cells, thermal EOS of Fe3S has been measured to 80 GPa and 2,500 K (17). High-pressure data on Fe–Si alloys were collected in multianvil apparatus at pressures below 10 GPa (18, 19). Two studies were conducted at ambient pressure using neutron diffraction method, one on Fe3C and the other on FeSi (20, 21). In general, the thermal expansion coefficients at ambient conditions are lower than that of pure Fe by ≳20%, with that of Fe3C being the lowest. It is clear that more thermal expansion data are needed to evaluate the effects of alloying elements on the thermoelastic properties of Fe.

**Experimental Results and Discussion**

**Thermal Expansion of Fe3S.** In Fe-S binary system, Fe3S with 16.1 wt.% S is the most Fe-rich sulfide known to date. Fe3S belongs to the tetragonal crystal system with space group I4 and is isostuctural with Cr,P (22). The unit-cell parameters of Fe3S at ambient condition are a = 9.144(2) Å and c = 4.509(2) Å, with a zero-pressure density of 7.033 g/cm3. Our x-ray diffraction patterns are consistent with this structure model, indicating no structural phase transition up to 42.5 GPa and 900 K. The volume-pressure data of Fe3S at temperatures of 300, 600, and 900 K have been determined under pressures up to 42.5 GPa [see Fig. 1a and supporting information (SI) Table 2]. The high-temperature Birch–Murnaghan EOS (ref. 23 and references therein) is used to fit the isothermal compressional data

\[
P(V) = \frac{3}{2} K_{T0} \left[ \left( \frac{V_0}{V} \right)^{2} - \left( \frac{V_0}{V} \right)^{7} \right] \\
\times \left\{ 1 - \frac{3}{4} (4 - K_{T0}) \right\} \left[ \left( \frac{V_0}{V} \right)^{3} - 1 \right],
\]

where \(K_{T0}\), \(K_{T0}^*\), and \(V_0\) are the bulk modulus, its pressure derivative, and the unit cell volume at zero pressure and temperature \(T\), respectively. The room-pressure unit cell volume \(V_0\) is given by the following expression: \(V_0(T) = V_0 (300 K) \exp(f_{V0}(T, dT))\), where \(V_0\) and \(\alpha_{T0}\) are the unit cell volume at room pressure and 300 K and the thermal expansion coefficient.
at room pressure and temperature $T$, respectively. Results of the least-squares fit of the third-order Birch–Murnaghan EOS to the compression data are plotted in Fig. 1a (see SI Table 3). The $F − F$ plot (Fig. 1b) confirmed that the compression data of Fe$_3$S are adequately described by a third-order truncation of EOS (ref. 23 and references therein). The temperature dependence of isothermal bulk modulus $(\kappa T o / \partial T)$ is estimated at $-3.75 \pm 1.80 \times 10^{-2}$ GPa K$^{-1}$. We calculated the thermal expansion coefficients of Fe$_3$S at 1 bar. Assuming a linear temperature dependence in the form of $\alpha T = \alpha o + \alpha T T$, we found $\alpha o = 3.0 \pm 1.3 \times 10^{-5}$ K$^{-1}$ and $\alpha T = 2.8 \pm 1.5 \times 10^{-8}$ K$^{-2}$.

Fei et al. (22) determined the compression curve of Fe$_3$S at 300 K. They reported isothermal bulk modulus $K_{T=0} = 170(8)$ GPa with a corresponding pressure derivative $K_{T=0}' = 2.6(5)$ or $K_{T=0} = 150(2)$ GPa with fixed $K_{T=0} = 4$. Seagle et al. (17) extended the thermal EOS of Fe$_3$S to 80 GPa and 2,500 K and determined the bulk modulus of Fe$_3$S at room temperature $K_{T=0} = 156(7)$ GPa with pressure derivative $K_{T=0}' = 3.8(3)$ by fitting a third-order Birch–Murnaghan EOS to room temperature compression data by using NaCl in B2 structure as a pressure scale. They also reported $\kappa o = 0.011 (2)$ GPa K$^{-1}$ for Fe$_3$S, by expressing the thermal contribution of Fe$_3$S in the form of $\Delta \nu / \nu |_{\text{thermal}} = \kappa o \Delta T$. The $\kappa o$ calculated from $\alpha K o / \partial T = 0.011 (2)$ GPa K$^{-1}$ and $K_{T=0} = 113(9)$ given in Seagle et al. (17) is significantly higher than our results. The discrepancy may result from the temperature dependence of thermal expansion coefficient. Extrapolating our calculated thermal pressures at 600 and 900 K to higher temperatures, our trend agrees with that in Seagle et al. (17) within experimental uncertainties, but falls within the negative side of their error bars.

**Thermal Expansion of Fe and Fe–Si Alloys.** Pairs of x-ray diffraction measurements were taken on both pure Fe and an Fe$_{0.864}$Si$_{0.136}$ sample in the same cell assembly, within the pressure range of 21–27 GPa and the temperature range of 300 to $>2,000$ K. Within this pressure range and between 300 and 1,273 K, Fe adopts the hexagonal close-packed (hcp) structure, whereas Fe$_{0.864}$Si$_{0.136}$ breaks down to a mixture of a Si-enriched body-centered cubic phase and a Si-depleted hcp phase (24). These are proposed to be the stable forms of Fe and Fe–Si alloy in the Earth’s inner core. At higher temperatures, the hcp–Fe phase disappears; thus, data collected at temperatures above 1,273 K are not reported here. Calculated minimum density deficit of hcp–Fe$_{0.864}$Si$_{0.136}$ relative to hcp–Fe from the paired data are shown in Fig. 2. Because the hcp phase of Fe–Si alloy contains less Si than the starting material, these values represent lower limits of density deficits caused by 13.6 at. % Si. The variations in density deficit reflect varying Si content in the Fe–Si alloys as a function of pressure and temperature and the differences in compressibility and thermal expansion between the Fe–Si alloys and pure Fe.

Most existing EOS measurements are performed on individual phases for the sake of minimizing interference in x-ray diffraction spectra and possible chemical reactions. Any discrepancies in pressure and temperature between separate experiments would introduce uncertainties to the calculated density deficit. Direct comparison of densities between an Fe-rich alloy and pure Fe under identical conditions has the advantage of eliminating or reducing such uncertainties. The technique of measuring symmetrically placed samples in a multianvil apparatus was pioneered by Zhang and Guoyt (19). That of measuring well mixed samples in a laser-heated diamond–anvil cell was first applied by Seagle et al. (17). In this study, we have extended the pressure range of such multianvil investigation from <10 GPa to nearly 30 GPa. Our data place a lower limit on the capability of Si to reduce the density of solid Fe. Further constraints can be obtained by carrying out chemical analysis of run products quenched from each temperature and pressure conditions.
in Mars, Fe3S is a possible component of the Martian inner core. The deficit decreases a function of pressure and temperature. The deficit decreases of Fe3S with respect to Fe at 1 bar and 300 K. The filled circle denotes density deficit versus S content in an Fe–S alloy. The open circle denotes the density deficit (1.2 wt. %) S is needed to produce the same amount of density deficit (Fig. 3). Extrapolating our data based on Birch–Murnaghan EOS to the core conditions leads to unreasonable results. Probably due to uncertainties in the fitted KT values. Given 6–10% deficit between the outer core and solid Fe, and 1–3% deficit between the inner core and solid Fe (ref. 16 and references therein), we estimated 12.5–20.7 at. % (7.6–13.0 wt. %) S in the outer core and 2.2–6.2 at. % (1.3–3.7 wt. %) S in the inner core based on our data at the highest experimental pressure and temperature. Implicit in the estimated S content in the outer core is the assumption that S has a negligible effect on the volume change across the liquid–solid boundary.

Si is among the top three most abundant elements in the Earth’s crust and mantle. A considerable amount of Si may be incorporated into the core through chemical reactions, especially under reducing conditions (31, 32). Geochemical data suggest that, depending on the accretion history and the distribution of Si in various layers inside the Earth, the Si content of the core may vary between virtually zero to 14 wt. % (31, 33, 34). Existing estimates of the amount of Si needed to account for 1% density deficit in the core range from 2.9 at. % (1.5 wt. %) to ~5.8 at. % (3 wt. %) (18, 19, 24, 35). Assuming a linear relationship between density deficit and Si content, we estimated that, between 22.1 and 26.8 GPa, no more than 3.2 at. % (1.6 wt. %) Si is needed to produce 1% density deficit in hcp–Fe. This estimate agrees well with the lower estimate in the literature (19). Given 6–10% deficit between the outer core and solid Fe, and 1–3% deficit between the inner core and solid Fe (ref. 16 and references therein), our experimental data suggest an upper limit of 19–32 at. % (11–19 wt. %) Si in the outer core, and an upper limit of 3.2–9.6 at. % (1.6–5.1 wt. %) Si in the inner core.

**K** and Velocity Gradient in the Outer Core. The fitting of our thermal EOS data to Fe3S third-order Birch-Murnaghan EOS gives pressure derivative of bulk modulus K < 4 (see SI Table 3), similar to the results of Fei et al. (22). Williams and Knittle (36) proposed that K can place an effective constraint on the primary alloying element in the outer core. They concluded that a K value that is <4 cannot reproduce the large gradient of bulk sound velocity in the outer core. Although their application of this constraint to Si was invalidated by later studies (e.g. refs. 18, 19, and 37), it is still a useful criterion for testing core composition models. If the small K of Fe3S persists to higher pressures and temperatures, the model of a S-rich core would be challenged. The K from our study and Fei et al. (22) are much smaller than that given in Seagle et al. (17). Independent studies are needed to resolve the discrepancy.
Effect of Spin Transition. Fe-rich alloys may undergo pressure-induced high-spin to low-spin transitions. Magnetic transitions in pure Fe and troilite (FeS) are accompanied by structural phase transformation (38, 39), whereas those in Fe$_3$C and cementite (Fe$_3$C) do not seem to involve major structural changes (40, 41). 

About $ab$ initio calculations of Fe$_3$C predicted abrupt volume reduction at the transition, which has not been observed in experiments (42). Nevertheless, such transition has been shown to affect the elastic and thermodynamic properties of Fe$_3$C and Fe$_3$S (40, 41). Without prior knowledge of the magnetic transition, fitted EOS may be erroneous.

At room temperature, the high- to low-spin transition in Fe$_3$S occurs between 20 and 25 GPa (40). Concurrent reduction in the unit-cell volume was not observed in our study. However, a plot of $c/a$ ratio as a function of pressure revealed an obvious change between 20 and 27 GPa, with a valley located at $\approx$18 GPa (see Fig. 4c). This pressure range matches that of magnetic transition in Fe$_3$S. The change in $c/a$ ratio results from an increased resistance along the $c$ axis accompanied by a softened $a$ axis, with little change in volume in Fig. 4). The data at 600 K suggest a similar but less obvious change in the $c/a$ ratio between 25 and 28 GPa. The existence and condition of this change is poorly constrained due to the sparse data coverage. The observed $c/a$ ratio change may be associated with the high- to low-spin transition of Fe$_3$S, unless it is fortuitously caused by redistribution of stress due to the B1–B2 transition in the NaCl pressure medium, which occurs within the same pressure range. To determine the spin state of Fe in a S-rich core, we need more measurements to cover a larger pressure range at high temperatures. Different pressure media should be used to avoid the interference from phase transition in NaCl.

Materials and Methods

Fe$_3$S. The starting material Fe$_3$S was synthesized stoichiometrically from metallic Fe and troilite (FeS) in a subsolidus experiment at 21 GPa and 1,000°C in a multianvil apparatus at Carnegie Institution of Washington. Electron microprobe and powder x-ray diffraction analysis indicate that the quenched run product is predominantly Fe$_3$S phase with $<2\%$ metallic Fe.

Energy-dispersive x-ray diffraction measurements were carried out by using polychromatic (white) wiggler synchrotron x-ray radiation at X17C beamline, the National Synchrotron Light Source, Brookhaven National Laboratory. The experimental procedure was similar to that described by Fei et al. (22). A germanium solid-state detector was used to collect the diffraction data at a fixed 20 angle of 12.01°, which was calibrated by the x-ray diffraction spectrum of gold at ambient conditions. Two diamond–anvil cell assemblies were used for the measurements, both containing Fe$_3$S sample sandwiched between NaCl pressure medium. A small amount of MgO, Au, and Pt was placed next to the sample in one assembly, whereas only Au was included in the other.

An externally heated diamond–anvil cell was used to generate high pressures and temperatures (43). X-ray diffraction data were collected in several compression–heating–quench cycles covering pressures up to 42.5 GPa at 300, 600, and 900 K. Temperatures were measured with a platinum-rhodium (Pt-Rh) thermo-couple. The tetragonal unit-cell parameters for Fe$_3$S were fitted by using the GSAS/EXPGUI program (44, 45), primarily from the diffraction lines 321, 330, and 112. Typical diffraction patterns collected in this study are shown in SI Fig. 5. Pressures were primarily determined from Au pressure scale (46). NaCl was also used as a secondary pressure scale (47). Above the B1–B2 transition in NaCl at $\approx$29 GPa, pressures were calculated only from the lattice parameters of Au.

Fe and Fe$_{0.864}$S$_{0.136}$. The experiments on Fe and Fe$_{0.864}$S$_{0.136}$ (7.3 wt.% of Si) were carried out by using a Kawai-type multianvil press at the BL04B1 high-pressure and high-temperature beam line at the SPring–S synchrotron facility in Japan. The experimental procedure was similar to that described by Fei et al. (48). In each run, we placed two samples symmetrically inside a cylindrical heater. One sample is a mixture of polycrystalline Fe (a few microns in average grain size, and >99.99% purity, from Goodfellow, Oakdale, PA) and MgO powder (99.99% purity, from Alfa Aesar, Ward Hill, MA) at a weight ratio of 1:4. MgO served as a pressure marker, and was also used to inhibit Fe crystal growth at high temperature. The other sample is a polycrystalline Fe$_{0.864}$S$_{0.136}$ alloy from Goodfellow. The two samples were separated by a layer of packed MgO powder. In the first run, samples were first compressed to a target pressure of 800 tons (~21 GPa). They were then annealed at 1,173 K to reduce nonhydrostatic stress, followed by a series of x-ray diffraction measurements along a heating ramp from room temperature to the peak temperature of 2,373 K. In the second run, a target pressure of 1,200 tons (~25 GPa) and a peak temperature of 2,273 K were reached. Samples were annealed at 973 K. For the energy dispersive x-ray diffraction measurements, the solid state detector was fixed at an angle of 5.814° relative to the incident x-ray beam. The acquisition time for each spectrum is 200 s. The position of x-ray beam was monitored through an x-ray absorption image. X-ray diffraction spectra were analyzed by using the XRAYANA software provided by the beamline, and using the GSAS/EXPGUI (44, 45). Typical diffraction patterns collected in this study are shown in SI Fig. 6.

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