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Thermal equation of state of iron and $\text{Fe}_{0.91}\text{Si}_{0.09}$

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Abstract We have carried out an in situ synchrotron X-ray diffraction study on iron and an iron-silicon alloy $\text{Fe}_{0.91}\text{Si}_{0.09}$ at simultaneously high pressure and temperature. Unit-cell volumes, measured up to 8.9 GPa and 773 K on the bcc phases of iron and $\text{Fe}_{0.91}\text{Si}_{0.09}$, are analyzed using the Birch-Murnaghan equation of state and thermal pressure approach of Anderson. Equation of state parameters on iron are found to be in agreement with results of previous studies. For both iron and $\text{Fe}_{0.91}\text{Si}_{0.09}$, thermal pressures show strong dependence on volume; the $(\partial K_T/\partial T)_V$ values are considerably larger than those previously reported for other solids. The present results, in combination with our previous results on ϵ -FeSi, suggest a small dependency of the room-temperature bulk modulus upon the silicon content, less than 0.3 GPa for 1 wt.% silicon. We also find that substitution of silicon in iron would not appreciably change the thermoelastic properties of iron-rich Fe–Si alloys. If this behavior persists over large pressure and temperature ranges, the relative density contrast between iron and iron-rich Fe–Si alloys at conditions of the outer core of the Earth could be close to that measured at ambient conditions, i.e., 0.6% for 1 wt.% Si.

Key words Iron · Fe–Si alloy · X-ray diffraction · Equation of state · Thermoelasticity

Introduction

Seismic data indicate that the Earth's outer core is about 10 wt.% less dense than pure iron at relevant pressure and temperature conditions (e.g., Birch 1964; Dziewonski and

Anderson 1981). It is generally accepted that this density deficit is attributed to lighter elements, such as silicon, sulfur or oxygen, which alloy with iron (e.g., Birch 1964). Over the years, the nature and the amount of the light elements in the outer core have become standing problems of geophysical and geochemical importance and are still uncertain. The difficulty is largely due to the imperfect estimate of the temperature in the core and to the small number of data available for evaluating the effect of possible alloying elements on the equation of state (EOS) of iron.

Silicon has been traditionally proposed to be an important alloying element in the Earth's outer core (Birch 1952; Ringwood 1959, 1966) based on its cosmochemical abundance and its ubiquity in the Earth's mantle. An excellent account of arguments for and against this proposal is in a review paper by Poirier (1994). Among the most recent works, Knittle and Williams (1995) studied the compressibility of ϵ -FeSi at ambient temperature up to pressures of 50 GPa in a diamond-anvil cell and suggested that silicon is unlikely to be the major alloying element in the outer core. Their conclusion was primarily based on the findings of a relatively high bulk modulus ($K_0=209\pm 6$ GPa) and low pressure derivative of the bulk modulus ($K'_0=3.5\pm 0.4$ rGPa) for ϵ -FeSi. Significantly different results were, however, reported in subsequent studies of the same compound. Guyot et al. (1997) obtained a value of $K_0=172(3)$ GPa from powder X-ray diffraction in a DIA-type large-volume apparatus. In another investigation using neutron powder diffraction, Wood et al. (1995) obtained a value of $K_0=160(1)$ GPa. These conflicting experimental results make it difficult to determine the effect of silicon on the compressibility of iron-rich alloys.

The purpose of the present study is to bring new experimental constraints on the density difference, at high pressure and temperature, between iron and iron-rich Fe–Si alloy. We have carried out X-ray diffraction experiments at pressures and temperatures up to 8.9 GPa and 773 K on iron and $\text{Fe}_{0.91}\text{Si}_{0.09}$, using not only the same experimental technique for the two compounds, but studying them in the same experiment for direct precise comparison.

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Experimental method

The powdered sample of iron from Johnson-Matthey Incorporated (purity 99.99%) and an iron-rich alloy $\text{Fe}_{0.91}\text{Si}_{0.09}$ from Goodfellow Corporation were used as the starting materials. For $\text{Fe}_{0.91}\text{Si}_{0.09}$, the electron microprobe analysis showed that the sample contained 8.87 wt.% silicon (averaged from 21 analyses), ranging from 8.33 to 9.26 wt.%. Experiments were performed using a DIA-type cubic anvil apparatus (SAM85) designed for in-situ X-ray diffraction studies at high pressure and temperature (Weidner et al. 1992). An energy dispersive method was employed using white radiation from the superconducting wiggler magnet at Brookhaven National Synchrotron Light Source. The incident X-ray beam was collimated to dimensions of $100 \times 200 \mu\text{m}$, and diffracted X-rays were collected by a solid state Ge detector at fixed angle of $2\theta = 7.5^\circ$. Energy discrimination used a multichannel analyzer (MCA) with 2048 channels.

The cell assembly used in this study was similar to the ones described by Weidner et al. (1992) and Wang et al. (1994). A mixture of amorphous boron and epoxy resin was used as pressure-transmitting medium, and amorphous carbon was used as heating material. Iron and $\text{Fe}_{0.91}\text{Si}_{0.09}$ were studied in a single experiment. The two samples were packed into a boron nitride container of 1 mm diameter and 2 mm length, separated by NaCl which also served as pressure standard.

Pressures were calculated from Decker's equation of state for NaCl (Decker 1971) using lattice parameters determined from X-ray diffraction profiles at each experimental condition. Five diffraction lines, (111), (200), (220), (222) and (420), were usually used for determination of pressure. The uncertainty in pressure measurements is mainly attributed to statistical variation in the positions of diffraction lines and is less than 0.2 GPa in the pressure range of the study. No appreciable pressure gradients existed in the sample, both at room and high temperatures, since the lattice parameters of NaCl were found identical at different locations in the sample container. Temperatures were measured by a W/Re24%-W/Re6% thermocouple that was at the center of the furnace. Temperature variations over the entire sample length were of the order of 20 K at 1500 K and the radial temperature gradient was less than 5 K at this condition (Weidner et al. 1992). X-ray diffraction patterns were obtained for both samples and NaCl pressure standard in close proximity to the thermocouple junction; errors in

temperature measurements were estimated to be less than 10 K. No correction for the effect of pressure on the thermocouple emf was made.

All the data reported here were obtained by the following procedures. We first compressed samples at room temperature to about 3 GPa, then heated to a maximum temperature of 773 K. Data were collected at 773 K and on cooling only, to minimize non-hydrostatic stress built up during the room-temperature compression. The same procedure was repeated several times at higher pressures within the stability field of the bcc phases of Fe and $\text{Fe}_{0.91}\text{Si}_{0.09}$.

Peak positions were determined by Gaussian peak fitting of the diffracted intensity. The unit-cell parameters for iron and $\text{Fe}_{0.91}\text{Si}_{0.09}$ were calculated by least-squares fitting using four diffractions of (110), (200), (211) and (220) based on bcc symmetry. The relative standard deviation in determinations of the unit-cell volume are less than 0.1% as shown in Table 1.

Results

The volume data were obtained for iron and $\text{Fe}_{0.91}\text{Si}_{0.09}$ at pressures up to 8.9 GPa along isotherms of 300, 573 and 773 K (Table 1 and Fig. 1). At ambient conditions, the lattice parameter and unit-cell volume in iron are $a = 2.8654(4) \text{ \AA}$ and $V = 23.526(11) \text{ \AA}^3$, which is in good agreement with values from the JCPDS card; for $\text{Fe}_{0.91}\text{Si}_{0.09}$, they are, respectively, $2.8429(8) \text{ \AA}$ and $22.976(20) \text{ \AA}^3$ (Table 1). Neither fcc nor hcp phase was observed at any experimental condition of this study. No wustite was detected in the present experiment, suggesting that oxygen fugacities in the experimental charge was below the Fe-wustite buffer. After the experiment, the two samples were recovered with the unit-cell parameters identical (within uncertainties of refinements) to those at the beginning (Table 1), indicating no changes in bulk composition or in system calibration over the entire experimental P - T range.

Table 1 Lattice parameters and unit-cell volumes

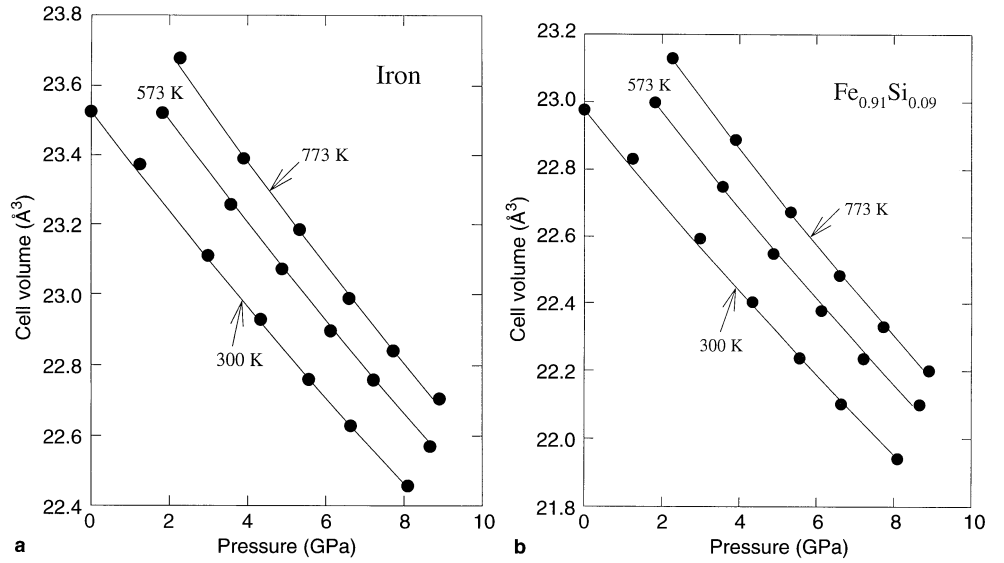
P (GPa)	T (K)	Iron		$\text{Fe}_{0.91}\text{Si}_{0.09}$	
		a (Å)	V (Å ³)	a (Å)	V (Å ³)
0.0 ^a	298	2.8654(4)	23.526(11)	2.8429(8)	22.976(20)
0.0 ^b	300	2.8658(7)	23.536(18)	2.8436(10)	22.994(26)
1.3	299	2.8591(6)	23.372(16)	2.8369(4)	22.831(10)
3.0	299	2.8484(8)	23.110(19)	2.8270(7)	22.593(17)
4.3	299	2.8409(7)	22.928(17)	2.8190(5)	22.402(13)
5.6	299	2.8339(8)	22.760(20)	2.8121(5)	22.237(12)
6.6	299	2.8285(7)	22.628(17)	2.8063(6)	22.102(13)
8.1	299	2.8213(8)	22.456(19)	2.7995(6)	21.941(14)
1.8	573	2.8652(8)	23.522(19)	2.8438(6)	22.998(13)
3.6	573	2.8544(7)	23.256(16)	2.8335(5)	22.749(12)
4.9	573	2.8468(6)	23.072(15)	2.8251(5)	22.548(12)
6.1	573	2.8396(8)	22.897(19)	2.8180(4)	22.377(10)
7.2	572	2.8339(6)	22.759(15)	2.8120(4)	22.235(9)
8.7	573	2.8260(8)	22.569(19)	2.8063(4)	22.100(10)
2.3	773	2.8716(6)	23.678(14)	2.8492(5)	23.130(12)
3.9	773	2.8599(6)	23.390(15)	2.8392(4)	22.888(10)
5.3	774	2.8515(5)	23.184(11)	2.8304(4)	22.674(9)
6.6	773	2.8434(6)	22.988(14)	2.8224(4)	22.482(10)
7.7	774	2.8373(5)	22.841(12)	2.8159(5)	22.329(12)
8.9	773	2.8317(6)	22.706(15)	2.8105(6)	22.200(14)

^a Prior to the experiment

^b Recovered after the high P - T experiment

The values in parentheses are standard deviations and refer to the uncertainty of the last digit(s)

Fig. 1 **a** Pressure-volume-temperature data for iron; **b** pressure-volume-temperature data for $\text{Fe}_{0.91}\text{Si}_{0.09}$. In both diagrams, errors in volume measurements (see Table 1) are smaller than the size of *symbols*, and the *curves* represent results of the least-squares fit using the HTBM EOS



Room temperature compression

The cell volumes for Fe and $\text{Fe}_{0.91}\text{Si}_{0.09}$ at 300 K are shown in Fig. 1 as a function of pressure. These data are fitted with the Birch-Murnaghan EOS:

$$P = \frac{3}{2}K_0 \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \cdot \left\{ 1 + \frac{3}{4}(K'_0 - 4) \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right\} \quad (1)$$

where V_0 is the molar volume at ambient conditions, fixed in our data analysis, and K_0 and K'_0 the isothermal bulk modulus and its pressure derivative at 300 K, respectively. For bcc iron, K'_0 cannot be accurately determined using the finite strain method because of the relatively high incompressibility of iron and the occurrence of the bcc-hcp phase transformation around 10 GPa. When attempting to fit the parameter K'_0 from our pressure-volume data with Eq. (1), we obtained $K_0=164(5)$ GPa and $K'_0=2.4 (\pm 1.4)$. This K'_0 value is obviously too small compared with results of previous studies (see discussion later). We have therefore performed the data analyses with the K'_0 values fixed at 4 and 5.3; the value of $K'_0=5.3$ was obtained from ultrasonic measurements up to 1 GPa by Guinan and Beshers (1968) and that of $K'_0=4$ was used to examine the trade-off between K_0 and K'_0 . As summarized in Table 2, differences in the resultant values for K_0 from the two analyses on both iron and $\text{Fe}_{0.91}\text{Si}_{0.09}$ are very small. As also shown in Table 2, for iron, the K_0 values of this study are in agreement with previous measurements. For $\text{Fe}_{0.91}\text{Si}_{0.09}$, the K_0 values are nearly identical to those of iron within errors of the fitting, indicating that substitution of silicon in iron has little effect upon the room-temperature compressibility of iron-rich alloys.

Thermal equation of state

To take into account simultaneous effect of pressure and temperature on volumes, two approaches are commonly used in the literature. In one approach, the temperature effect is incorporated in terms of thermal pressure, which can be evaluated either by thermodynamic identities or from lattice dynamics consideration (see Jackson and Rigden 1996 for a comprehensive review on this issue). Alternatively, one can directly use the Birch-Murnaghan EOS at high temperature (HTBM) by modifying Eq. (1) in the following aspects (Saxena and Zhang 1990): (a) the temperature dependence of the bulk modulus is included, given by:

$$K_T = K_0 + (\partial K_T / \partial T)_P (T - 300) \quad (2)$$

and (b) V_0/V is replaced by V_T/V , where V_T is the molar volume at high temperature and ambient pressure and is calculated by

$$V_T = V_0 \exp \left[\int \alpha(0, T) dT \right]. \quad (3)$$

In this study, the HTBM EOS is used to analyze the entire P - V - T data set shown in Fig. 1, with the K'_0 values fixed at 4 and 5.3. $\alpha(0, T)$ in Eq. (3) is treated as a constant, representing average thermal expansivity over the experimental temperature range.

Results of analysis using the HTBM EOS are summarized in Table 2 and compared with thermoelastic parameters obtained from previous measurements. For iron, the thermal expansivity of this study at ambient pressure is consistent with that of Skinner (1966) in the temperature range studied. The measured bulk modulus of Dever (1972) in the temperature range 300–973 K suggested a value of $(\partial K_T / \partial T)_P = -0.049(1)$ GPa K^{-1} [$(\partial K_T / \partial T)_P = -0.045(2)$ GPa K^{-1} between 300 and 773 K], and is thus in excellent agreement with the present study. In a recent work by Isaak and Masuda (1995), the bulk modulus has been determined between 300 and 900 K, and the result-

Table 2 Equation of state parameters of Fe, Fe_{0.91}Si_{0.09} and ε-FeSi

Phases	K_0 GPa	K'_0	$(\partial K_T/\partial T)_P$ GPa K ⁻¹	$(\partial K_T/\partial T)_V$ GPa K ⁻¹	$\alpha_T \times 10^5$	Source of study
Fe	159(2)	4	-0.043(6)	-0.024(4)	4.51(14)	This work
	155(2)	5.3	-0.049(6)	-0.022(4)	4.67(15)	This work
	164(7)	4	–	–	–	Wilburn and Bassett (1978)
	162(5)	5.5(8)	–	–	–	Takahashi et al. (1968)
	163(1)	–	-0.053(2) ^a	–	–	Isaak and Masuda (1995)
	164	–	-0.045(2) ^b	–	–	Dever (1972)
Fe _{0.91} Si _{0.09}	–	–	–	–	4.40(2) ^c	Skinner (1966)
	161(2)	4	-0.046(7)	-0.022(6)	4.74(17)	This work
	157(2)	5.3	-0.052(7)	-0.020(6)	4.90(18)	This work
ε-FeSi	172(3)	4	-0.043(8)	–	5.10(40) ^d	Guyot et al. (1997)
	209(6)	3.5(4)	–	–	–	Knittle and Williams (1995)
	160(1)	4	–	–	–	Wood et al. (1995)

Temperature ranges:

^a 300–750 K;

^b 300–773 K; see text for detail discussion of the data of Dever (1972) and Isaak and Masuda (1995);

^c 300–873 K;

^d 300–1273 K. The values of $(\partial K_T/\partial T)_P$ of the present study were obtained from the HTBM EOS, and those of $(\partial K_T/\partial T)_V$ were obtained from thermal pressure approach (see text for detail)

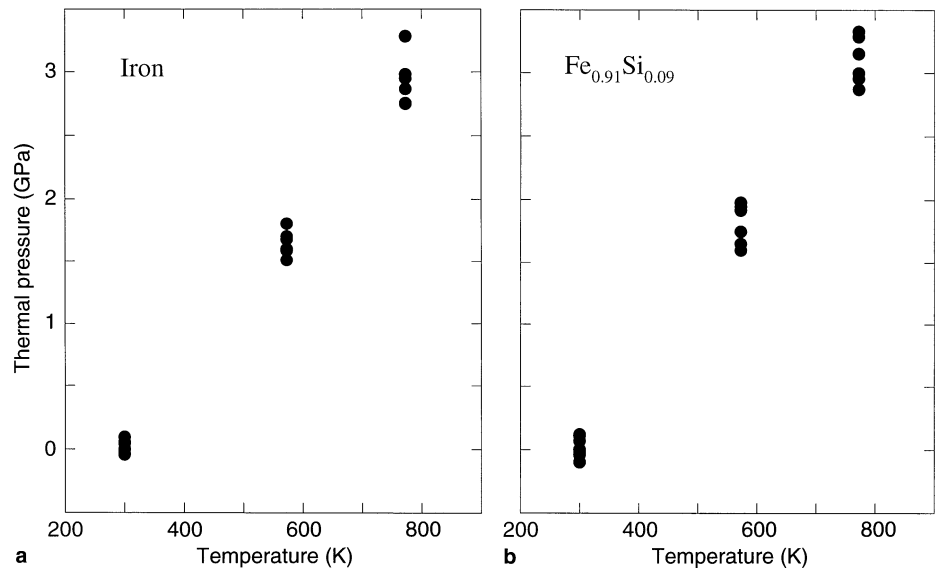
tant value of $(\partial K_T/\partial T)_P$ was $-0.060(3)$ GPa K⁻¹. Using their data below 800 K, however, a value of $(\partial K_T/\partial T)_P = -0.053(2)$ GPa K⁻¹ was found. The three studies are thus in good agreement in the temperature range of the present study. Isaak and Masuda (1995) explained that the discrepancy between results of Dever (1972) and their own at the highest temperatures was probably due to differences in the estimation of magnetic contributions to the compressional moduli. For Fe_{0.91}Si_{0.09}, both the $(\partial K_T/\partial T)_P$ value and thermal expansion are almost identical to those of pure iron within errors of the fitting (Table 2). It is interesting to note that a similar trend has also been found between iron and other Fe–Si alloys that have higher silicon content, as is the case between iron and ε-FeSi shown in Table 2. In addition, the measured thermal expansivity for Fe₃Si over a temperature range of 300–

873 K (Skinner 1966), which was $4.70(11) \times 10^{-5}$ K⁻¹, is similar to that of pure iron.

Thermal pressure and $(\partial K_T/\partial T)_V$

Thermal pressures (P_{th}) have been calculated for the present P – V – T data set as the difference between the measured pressure at a temperature for a given volume (Fig. 1) and the calculated pressure from Eq. (1) at room temperature at the same volume. For both iron and Fe_{0.91}Si_{0.09}, an inspection of Fig. 2 reveals that thermal pressures vary linearly with temperature, a trend that has been found for many classes of solids (see Ch. 10 in Anderson 1995).

Fig. 2 a Thermal pressure of iron and b Fe_{0.91}Si_{0.09} as a function of temperature. Different data points at a given temperature represent thermal pressures at different volumes (or pressures) from Fig. 1 (see Fig. 3 for more detail on iron). Scattering of data points at room temperature can be taken as uncertainties in thermal pressure calculations from the present P – V – T measurements



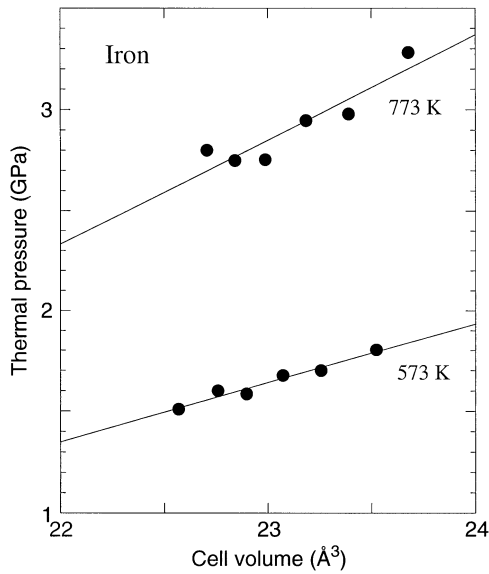


Fig. 3 Variation of thermal pressure as a function of volume at 573 and 773 K for iron

Thermal pressure at any temperature above 300 K for a given volume can also be analyzed from thermodynamic relations, and following the method of Anderson (1984) and his subsequent studies, is calculated by

$$\Delta P_{\text{th}} = P_{\text{th}}(V, T) - P_{\text{th}}(V, 300) \\ = [\alpha K_T(V_{300}, T) + (\partial K_T / \partial T)_V \ln(V_{300}/V)](T - 300). \quad (4)$$

From the best fit of the thermal pressure data of Fig. 2, using Eq. (4) and the measured volume data (Table 1 and Fig. 1), we obtain average values of $\alpha K_T(V_{300}, T)$ and $(\partial K_T / \partial T)_V$ that are, respectively, $6.48(10) \times 10^{-3}$ and $-0.022(4)$ GPa K^{-1} for iron and $6.95(14) \times 10^{-3}$ and $-0.020(6)$ GPa K^{-1} for $\text{Fe}_{0.91}\text{Si}_{0.09}$ when $K'_0 = 5.3$ is used. From the thermodynamic identity

$$(\partial K_T / \partial T)_V = (\partial K_T / \partial T)_P + (\partial K_T / \partial P)_T \alpha K_T(V_{300}, T), \quad (5)$$

the values of $(\partial K_T / \partial T)_P$ can be calculated and are, respectively, $-0.056(6)$ and $-0.057(8)$ GPa K^{-1} for iron and $\text{Fe}_{0.91}\text{Si}_{0.09}$, which are compatible with results of the HTBM EOS within errors of the least-squares fitting (Table 2). As also shown in Table 2, similar values of $(\partial K_T / \partial T)_V$ are obtained when $K'_0 = 4$ is used in the data reduction.

The fact that the $(\partial K_T / \partial T)_V$ values for iron and $\text{Fe}_{0.91}\text{Si}_{0.09}$ are not zero within the uncertainties of the fits suggests that there is a volume dependence of thermal pressure, with an example shown in Fig. 3 from the experimental data for the bcc iron. Indeed, iron and $\text{Fe}_{0.91}\text{Si}_{0.09}$ are among the solids so far measured that have the largest negative numbers of $(\partial K_T / \partial T)_V$. In comparison with literature values, we find $(\partial K_T / \partial T)_V = 0$ for many solids such as alkali metals and alkali halides (see Ch. 10 in Anderson 1995), olivine (Guyot et al. 1996) and CaSiO_3 (Wang et al. 1996), -0.007 to $-0.008(1)$ GPa K^{-1} for MgCO_3 (Zhang et al. 1997), -0.006 to -0.008 GPa K^{-1} for MgO

and -0.013 GPa K^{-1} for gold (Anderson et al. 1989). The effect of volume on P_{th} is thus material-dependent.

Discussion

Results of the present work on iron and $\text{Fe}_{0.91}\text{Si}_{0.09}$ indicate that substitution of silicon has very little effect on the thermoelastic parameters of iron-rich alloys in the system Fe–Si. The present results, in combination with our previous results on ϵ -FeSi (Guyot et al. 1997), also suggest a small dependency of the room-temperature bulk modulus upon the silicon content; with the assumption that $\text{Fe}_x\text{Si}_{1-x}$ alloys ($0.5 < x < 1$) have the similar K'_0 , the $(\partial K_0 / \partial \text{Si})$ is less than 0.3 GPa for each wt.% silicon. The effect of the silicon content on the compressibility of iron-rich Fe–Si alloys is thus more than three times smaller than that suggested by Knittle and Williams (1995). This discrepancy is mainly due to the difference between the K_0 values measured for ϵ -FeSi in the two previous studies (see Guyot et al. 1997 for detailed discussion).

The similarity of thermoelastic parameters of pure iron and iron-rich Fe–Si alloys would be of geophysical importance if it remains true for different phases of iron, including melts, up to the conditions of the Earth's outer core. Further experimental studies at higher pressure and temperature in the system Fe–Si are, of course, needed to test this point. With our current knowledge, however, this similarity would imply that the relative density contrast between iron and iron-rich Fe–Si alloys at conditions of the outer core could be close to that measured at ambient conditions, i.e., 0.6% for 1 wt.% silicon. It is interesting that this simple estimation is actually consistent with the results of Balchan and Cowan (1966), who concluded, based on shock compression experiments, that the 10% density deficit in the outer core could be interpreted by the presence of 14–20 wt.% silicon in iron.

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