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3 **Composition-dependent thermal equation of state of B2 Fe-Si alloys at high pressure**

4

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22 **ABSTRACT**

23 Solid iron-silicon alloys play an important role in planetary cores, especially for
24 planets that formed under reducing conditions, such as Mercury. The CsCl (B2) structure
25 occupies a considerable portion of the Fe-Si binary phase diagram at pressure and
26 temperature conditions relevant for the core of Mercury, yet its thermodynamic and
27 thermoelastic properties are poorly known. Here, we report in situ X-ray diffraction
28 measurements on iron-silicon alloys with 7–30 wt% Si performed in laser-heated
29 diamond anvil cells up to ~120 GPa and ~3000 K. Unit-cell volumes of the B2 phase at
30 high pressures and high temperatures have been used to obtain a composition-dependent
31 thermal equation of state of this phase. In turn, the thermal equation of state is exploited
32 to determine the composition of the B2 phase in hcp+B2 mixtures at 30–100 GPa and to
33 place constraints on the hcp+B2/B2 phase boundary, determined to vary between ~13–18
34 wt% Si in the considered pressure and temperature range. The hcp+B2/B2 boundary of
35 Fe-Si alloys is observed to be dependent on pressure but weakly dependent on
36 temperature. Our results, coupled with literature data on liquid equations of state, yield

37 an estimation of the density contrast between B2 solid and liquid under Mercury's core
38 conditions, which directly relates to the buoyancy of the crystallizing material. While the
39 density contrast may be large enough to form a solid inner core by gravitational sinking
40 of B2 alloys in an Si-rich core, the density of the B2 solid is close to that of the liquid at
41 solidus conditions for Si concentration approaching ~10 wt% Si.

42

43 **Keywords:** Fe-FeSi system, equation of state, phase diagram, high pressure experiment,
44 planetary interiors, Mercury, inner core

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INTRODUCTION

48 The abundance of metallic iron and silicate minerals in telluric planets leads to the
49 expectation that iron-silicon alloys play a large role in planetary cores when formed under
50 reducing conditions (Kilburn and Wood 1997; Ricolleau et al. 2011). Varying quantities
51 of silicon alloyed with iron have been invoked to explain seismological observations of
52 Earth's core (e.g. Fischer et al. 2012; Badro et al. 2015; Antonangeli et al. 2018) and
53 geodetic observations of Mercury (e.g. Knibbe and van Westrenen 2018; Genova et al.
54 2019; Terasaki et al. 2019). In order to accurately model the interior structure and

55 dynamics of these planets, the phase diagram of Fe-Si alloys at high pressure (P) and high
56 temperature (T) and the thermal equations of state (EoS) of stable phases are crucial. In
57 particular, the high S/Si ratio and low FeO content of Mercury's surface indicate that its
58 interior is likely to be highly reduced (Nittler et al. 2011), leading to expected bulk core
59 Si concentrations in excess of 12 wt% Si (Chabot et al. 2014; Knibbe and van Westrenen
60 2018; Terasaki et al. 2019). Consequently, the chemical and elastic properties of Si-rich
61 Fe-Si alloys are key to understanding the present state and dynamics of Mercury's core.

62 Iron-silicon alloys at ambient pressure exhibit a complex phase diagram, with a
63 series of solid solutions over a wide compositional range, in addition to several
64 stoichiometric compounds such as FeSi, Fe₅Si₃, and Fe₂Si (Cui & Jung 2017).
65 Stoichiometric FeSi has a B20 structure at ambient conditions (FeSi is the B20 structure
66 prototype) and transforms into a B2 (CsCl type) structure at pressures above 30–40 GPa
67 at high T (Fischer et al. 2013; Geballe & Jeanloz 2014). On the other side, at these
68 pressures, the pure Fe end member exhibits fcc structure at high T and hcp structure at
69 lower T , and its stability field expands by the addition of silicon (Brosh et al. 2009;
70 Komabayashi et al. 2009; Komabayashi et al. 2019). Other stoichiometric compounds in
71 the Si-rich side of the Fe-Si system such as Fe₂Si and Fe₅Si₃ are reported to be unstable
72 with increasing P and T (Ponomareva et al. 2009; McGuire et al. 2017) although exact

73 phase boundaries are poorly constrained. The coexistence field of B2 and hcp phases is
74 also poorly constrained at high P - T (Kuwayama et al. 2009; Fischer et al. 2013).
75 Specifically, the boundary between the hcp and hcp+B2 regions has been constrained
76 experimentally by observing the decomposition of the hcp phase to an hcp+B2 mixture
77 with increasing T (Kuwayama et al. 2009; Lin et al. 2009; Fischer et al. 2013; Tateno et
78 al. 2015). In contrast, only a few experimental results were obtained for the transition
79 from an hcp+B2 mixture to a single B2 phase (Fischer et al. 2013). Kuwayama et al.
80 (2009) addressed the compositions of coexisting hcp and B2 phases at 45 GPa, but
81 electron microprobe measurements performed on samples with small grains are extremely
82 challenging, as the analysis of each individual grain is affected by spurious signals from
83 the surrounding grains, which leads to an underestimation of the compositional difference
84 between the two phases.

85 Densities of the Si-rich Fe-Si alloys are also not well known. Room- T and high- T
86 equations of state of stoichiometric B2 FeSi have been addressed by several high- P
87 studies (Sata et al. 2010; Ono 2013; Fischer et al. 2014). Conversely, with few exceptions
88 (Edmund et al. 2019b), thermoelastic properties of non-stoichiometric B2/DO₃ alloys are
89 largely limited to compositions which are commercially available, i.e. 8–9 wt% Si or 16–
90 18 wt% Si (Lin et al. 2003; Hirao et al. 2004; Fischer et al. 2012; Fischer et al. 2014).

91 While for the Si-poor hcp structure the thermal equation of state varies only marginally
92 with Si content compared to pure iron (Edmund et al. 2019a; Fei et al. 2016; Tateno et al.
93 2015), studies on the Si-rich B2 structure indicate that elastic and thermal parameters
94 strongly depend on Si content (Fischer et al. 2012, 2014; Edmund et al. 2019b). Since the
95 B2 stability field is expanded significantly at high pressures (Fischer et al. 2013), it is
96 important to place better constraints on the thermoelastic parameters of these alloys at
97 high P - T . Such EoS will provide an accurate formulation to model the structure and
98 composition of telluric planetary interiors.

99 Thus, we performed a systematic X-ray diffraction study of iron-silicon alloys in the
100 B2 and hcp+B2 stability fields over a large compositional (7–30 wt% Si), pressure (20–
101 120 GPa), and temperature (1100–3000 K) range. A composition-dependent
102 parameterized thermal equation of state for Fe-Si alloys in the B2 structure is constructed
103 using here-obtained experimental unit-cell volumes of single B2/DO₃ phases and
104 available literature reports. The thermal equation of state is applied to calculate the
105 composition and densities of B2 phases coexisting with hcp phases, which provides new
106 constraints on the Si-rich side of the Fe-FeSi phase diagram. Finally, implications of our
107 results concerning the buoyancy of solid Fe-Si alloys crystallizing in Mercury’s core are
108 discussed, as solid-liquid density contrast is crucial to constrain core structure and

109 dynamics.

110

111

METHODS

112 Foils of iron-silicon alloys with thicknesses ranging 2–5 μm were prepared by
113 physical vapor deposition (PVD) at the Institut de Minéralogie, de Physique des
114 Matériaux et de Cosmochimie (IMPMC). They were confirmed to be chemically
115 homogeneous Fe-7.1(3)wt%Si (Fe7Si), Fe-16.0(5)wt%Si (Fe16Si), Fe-22.0(5)wt%Si
116 (Fe22Si), and Fe-30(2)wt%Si (Fe30Si) alloys by scanning electron microscopy (SEM)
117 measurements. At ambient conditions, they are observed to be nano-grained bcc alloys
118 (Fe7Si), amorphous (Fe16Si and Fe22Si), or a mixture of amorphous and nano-grained
119 alloys (Fe30Si). High P - T conditions were generated by a laser heated, Le Toullec-type
120 membrane-driven diamond anvil cell (LH-DAC) equipped with diamond anvils of flat
121 350 μm , 250 μm , or beveled 150/300 μm culets, depending on target pressures. The
122 sample was loaded into the hole of a pre-indented rhenium gasket sandwiched between
123 two layers of 10–20 μm thick KCl that behave as thermal insulators and pressure media.
124 The whole DAC plus sample assembly was subsequently dried in a vacuum oven at ~ 393
125 K for several hours and then rapidly sealed in order to avoid sample oxidation or moisture
126 absorption by the KCl.

127 In situ angle dispersive X-ray diffraction (XRD) measurements were performed at
128 the beamline P02.2 at Petra III. Monochromatic X-rays with a wavelength of 0.2901 Å
129 were focused to a spot at the sample's position of $\sim 2 \mu\text{m} \times 2 \mu\text{m}$ full width at half
130 maximum. Diffraction patterns were collected using a Perkin Elmer flat panel detector.
131 Samples were heated from both sides with a single Nd:YAG laser split into two optical
132 paths. The heated area was $\sim 20 \mu\text{m} \times 20 \mu\text{m}$, significantly larger than the X-ray beam, so
133 as to minimize radial temperature gradients. Temperature was measured by a
134 spectroradiometric method. Errors in temperature are $\pm 5\%$.

135 Isothermal measurements with increasing pressure were conducted for Fe₂₂Si with
136 T kept at 1500–1600 K and P ranging between 40 and 100 GPa. Further quasi-isobaric
137 measurements with increasing laser power were performed for all samples for selected
138 pressures in the range spanning between 20 and 120 GPa. XRD patterns and temperature
139 measurements were collected in parallel for each investigated thermodynamic point.
140 Alignment of the X-ray beam and the laser-heated spot was confirmed before and after
141 successive heating cycles.

142 Sample to detector distance and detector orientation were calibrated with a CeO₂
143 standard. Collected diffraction images were azimuthally integrated using the software
144 Dioptas (Prescher and Prakapenka 2015) and analyzed with the Le Bail method using the

145 software JANA2006 (Petříček et al. 2014) (Figure 1). Integrated diffraction patterns
146 where sample peak positions strongly deviated from the refined Le Bail fit have been
147 omitted from the present dataset as these typically indicate the presence of strong non-
148 hydrostatic effects.

149 Pressure was determined from the volume of KCl at high temperature (Dewaele et
150 al. 2012). Temperature of KCl was corrected from the measured temperature following
151 Campbell et al. (2009):

$$152 \quad T_{KCl} = \frac{3T_{meas}+300}{4} \quad (1)$$

153 Total errors in pressure were estimated as the sum of 2% of the pressure at 300 K, to
154 account for intrinsic uncertainties in the calibration used, and 50% of thermal pressure
155 due to uncertainties in KCl temperature and thermal parameters (Dewaele et al. 2012;
156 Tateno et al. 2019).

157

158 **VOLUME AND THERMAL EoS OF B2 Fe-Si ALLOYS**

159 Fe₂₂Si exhibited a single B2 phase throughout the measured experimental
160 conditions (~20–120 GPa and 2500–3000 K), while a single B2/DO₃ phase was observed
161 at only <42 GPa in Fe₁₆Si, and >27 GPa in Fe₃₀Si. Data were collected for hcp+B2
162 mixtures at 86–93 GPa in the case of Fe₁₆Si starting material and at 33–99 GPa in the

163 case of Fe₇Si starting material. The DO₃ phase, observed in Fe₁₆Si only at ~25–35 GPa,
 164 is an fcc superlattice of B2 FeSi and bcc Fe, where off-stoichiometric alloys exhibit
 165 disorder on the Si sites of the lattice (Randl et al. 1995). Volume differences between the
 166 B2 and DO₃ phases were not resolvable at the P - T conditions where both phases were
 167 observed. The obtained B2/DO₃ P - V - T datasets (Supporting Table 1) along with the
 168 ambient and high-temperature volumes of Fe-16wt%Si alloys and stoichiometric FeSi
 169 reported in previous experimental studies (Fischer et al. 2012; Fischer et al. 2014) were
 170 fitted to a model based on the Mie-Grüneisen-Debye equation of state. As constraints for
 171 room- T volume, we included room- T data of the B2 or DO₃ phase measured in alloys
 172 containing 9–17wt%Si (Fischer et al. 2012; Fischer et al. 2014; Edmund et al. 2019b) as
 173 B2 and DO₃ alloys have been reported to have similar elastic properties (Fischer et al.
 174 2014; Karel et al. 2015; Edmund et al. 2019b). P - V relations at room temperature are
 175 described by the third-order Birch-Murnaghan equation of state:

$$176 \quad P_{300K} = \frac{3}{2}K_0 \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left[1 + \frac{3}{4}(K' - 4) \left\{ \left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right\} \right], \quad (2)$$

177 where V_0 is the volume at ambient pressure, K_0 is the bulk modulus, and K' is its pressure
 178 derivative. Thermal pressure P_{th} is expressed by the Mie-Grüneisen equation of state:

$$179 \quad P_{th} = \frac{\gamma}{V} [E(T, \theta_D) - E(300K, \theta_D)], \quad (3)$$

180 with the Grüneisen parameter given by

181
$$\gamma = \gamma_0 \left(\frac{V}{V_0} \right)^q, \quad (4)$$

182 where γ_0 is the ambient pressure Grüneisen parameter and q accounts for its volume
 183 dependence. The quasi-harmonic internal energy $E(T, \theta_D)$ is calculated according to the
 184 Debye model:

185
$$E(T, \theta_D) = 9nRT \left(\frac{T}{\theta_D} \right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^3}{e^x - 1} dx, \quad (5)$$

186 where n is the number of atoms and R is the gas constant. The Debye temperature θ_D is
 187 calculated by

188
$$\theta_D = \theta_0 \exp \left(\frac{\gamma_0 - \gamma}{q} \right), \quad (6)$$

189 where θ_0 is the Debye temperature at V_0 . The value of θ_0 is set to that of iron (Dewaele et
 190 al. 2006) as commonly done for B2 Fe-Si alloys (Fischer et al. 2012; Fischer et al. 2014).

191 To account for the composition dependence observed in the experimental data, we
 192 assumed a second-order dependence on X_{Si} (mole fraction of silicon) for K_0 and a linear
 193 dependence on X_{Si} for V_0 , K' , and γ_0 . EoS parameters of FeSi ($X_{Si}=0.5$) at room- T were
 194 fixed to the values obtained from a combined fit to available literature data (Sata et al.
 195 2010; Ono 2013; Fischer et al. 2014), with rescaled pressures consistent with the pressure
 196 scale employed in the present study (Dewaele et al. 2012). Also, X_{Si} dependence of V_0
 197 was fixed to the result of a linear fit to previous studies described in Edmund et al. (2019b).
 198 Fitting results are shown in Table 1 and Supporting Table 2 and compared to experimental

199 observations in Figure 2.

200 We observe that the volume of the alloys decreases with Si content over the measured
201 P - T - X_{Si} conditions. Likely related to this, the bulk modulus increases with Si content in
202 the 20–50 at% Si range (\sim 11–33.5 wt%). A K_0 value of \sim 165–170 GPa at 20–30 at% Si is
203 consistent with the adiabatic bulk modulus of single crystals of Fe-Si alloys obtained by
204 ultrasonic methods (Machová & Kadečková 1977). Some earlier experimental studies at
205 room- T argued that Fe-Si alloys in B2/DO₃ structure, namely Fe-17.0wt%Si and
206 17.8wt%Si, are less compressible than what is reported here (Lin et al. 2003; Hirao et al.
207 2004). This discrepancy is likely caused by non-hydrostatic compression of the sample in
208 those experiments. Indeed, no pressure medium was used in Hirao et al. (2004), and an
209 ethanol:methanol:water mixture was employed as pressure-transmitting medium in Lin
210 et al. (2003), which becomes strongly non-hydrostatic at pressures above 12 GPa (Klotz
211 et al. 2009). In the present study, stress is effectively released by laser heating, ensuring
212 quasi-hydrostatic conditions.

213 Thermal EoS obtained in the present study indicates that thermal expansion is larger
214 in alloys with low Si content. Although our thermal EoS was obtained from high-pressure
215 data, the fitting result well reproduces the thermal expansion measured at ambient
216 pressure on alloys with \sim 25 at% Si (Farquhar 1945; Lihl & Ebel 1961).

217

218

Fe-FeSi PHASE DIAGRAM

219

Coexistence of B2 and hcp phases was observed at 33–99 GPa in measurements on

220

Fe₇Si starting material, and 86–93 GPa in measurements on Fe₁₆Si starting material

221

(Supporting Table 3). The DO₃ phase was never found in coexistence with the hcp

222

structure over the experimental conditions of this study. Kuwayama et al. (2009) and

223

Fischer et al. (2013) reported a single hcp phase stable at low temperature for starting

224

materials with ~10 wt% Si (<~1700 K at 50 GPa) and ~9 wt% Si (<~1300 K at 50 GPa),

225

respectively. However, here we never observed a single hcp phase, not even for the Fe₇Si

226

alloy at low temperature (1100–1300 K). The wide hcp stability field at low temperature

227

reported in previous studies is likely a consequence of the slow kinetics of phase

228

transformation from hcp to hcp+B2 (Nakajima et al. 2020). As the PVD samples used in

229

the present study were synthesized into out-of-equilibrium states, they rapidly equilibrate

230

upon heating to the most thermodynamically favorable assemblage at the investigated *P*-

231

T conditions, effectively overcoming kinetic barriers. Grain growth of the B2 phase was

232

observed right away upon heating, even at the lowest measured temperature (Supporting

233

Figure 1). In contrast, cold compression does not necessarily promote thermodynamic

234

stabilization, and XRD patterns here collected on starting materials at room *T* and high *P*

235 highlight structures different from phase stability expected according to previous room
236 temperature studies (Lin et al. 2003; Hirao et al. 2004; Kuwayama et al. 2009) with the
237 bcc structure here observed till higher pressures and a larger domain of coexistence of
238 bcc and hcp phases (Supporting Figure 2).

239 Compositions of coexisting hcp and B2 phases provide boundaries for the hcp+B2
240 coexistence region. While, in the hcp phase, Si alloying does not strongly influence the
241 volume (e.g. Morrison et al. 2018; Kamada et al. 2018; Edmund 2019a; Edmund et al.
242 2020), B2/DO₃ volumes vary significantly with composition (Edmund et al. 2019b).
243 Provided that the volume of the B2 phase and experimental conditions (P and T) are
244 known, Si content can be estimated using the parameterized P - V - T - X_{Si} equation of state
245 previously presented. The so-calculated compositions of the B2 phase in coexistence with
246 the hcp phase are shown in Figure 3a. They range from 13wt% Si at ~30 GPa to 18 wt%
247 Si at ~100 GPa. Observation of a single B2 phase in Fe₂₂Si throughout the measured P -
248 T range is well reproduced within the calculated boundary. The present experiments and
249 a previous study (Fischer et al. 2012) observed a single B2/DO₃ phase in Fe₁₆Si at
250 pressures below ~40 GPa and 60–80 GPa, respectively. These observations are also
251 consistent with the calculated phase boundary (~15–16 wt% Si at 80 GPa).

252 Over the pressure range of interest of the present study, the temperature dependence

253 of the slope of the hcp+B2/B2 boundary was below the detection limit of the applied
254 method (Figure 3a), compatible with a value of ~ 2 wt% Si per 1000 K as proposed in a
255 previous study (Fischer et al. 2013). On the basis of our data, positive temperature
256 dependence in Si content below 42 GPa cannot be excluded, but this becomes negligible
257 at higher pressure.

258 The hcp+B2/B2 boundary moves towards the Si-rich side with increasing pressure,
259 consistent with previous studies (Kuwayama et al. 2009; Fischer et al. 2013) (Figure 3b).
260 Kuwayama et al. (2009) reported Si concentrations of coexisting hcp and B2 phases at 45
261 GPa, estimated by electron microprobe analysis on recovered samples, which are about 2
262 wt% smaller than the present study. This difference may be attributed to underestimation
263 of the compositional gap between coexisting phases in the electron microprobe
264 measurements arising from the small grain sizes. The hcp/hcp+B2 boundary located in
265 the Si-poor side of the phase diagram and estimated at 7–10 wt% Si at 50 GPa also moves
266 toward the Si-rich side with increasing pressure at constant temperature (Kuwayama et
267 al. 2009; Fischer et al. 2013). The expansion of the hcp+B2 coexistence region towards
268 the Si-rich side could be used as an argument in favor of an increase of eutectic Si content
269 in an Fe-FeSi system with increasing pressure. This supports a small change in the
270 eutectic Si content with increasing pressure as recently reported (Hasegawa et al. 2021)

271 rather than a steep decrease of eutectic Si content argued on the basis of earlier
272 determinations (Ozawa et al. 2016).

273

274

IMPLICATIONS

275 Silicon is thought to be a dominant light element in Mercury's core along with sulfur
276 (e.g. Malavergne et al. 2010; Malavergne et al. 2014; Chabot et al. 2014). Estimations of
277 bulk core Si abundances can reach 25 wt% (Chabot et al. 2014). Knowledge of the Fe-
278 FeSi phase diagram and of the thermo-elastic properties of stable phases at relevant P - T
279 conditions is thus essential to accurately determine the structure and dynamics of
280 Mercury's core, and in particular to model dynamo mechanisms within the core capable
281 of explaining Mercury's exotic magnetic field (e.g. Anderson et al. 2011; Johnson et al.
282 2016). Compositional convection driven by core solidification is one of the main power
283 sources for a long-standing dynamo (Stevenson 2003), and the density contrast between
284 the crystallizing material and the coexisting liquid controls whether the solid sinks down
285 to form an inner core, or rises up to form a layer at the core-mantle boundary. Clearly,
286 these two scenarios lead to profoundly different core structures and dynamics.

287 Si-rich core compositions exceeding the Fe-FeSi eutectic (~ 10 – 15 wt% at ~ 50 GPa
288 according to Hasegawa et al. 2021) would crystallize a B2 solid, which is more enriched

289 in Si than the liquid. Whether the solid B2 Fe-Si alloy sinks or floats depends on whether
290 the effect of increased Si content on density is sufficient to overcome the density
291 difference due to solidification. Figure 4a illustrates the density of solid B2 Fe-Si alloys
292 calculated using the parameters of the present study and liquid Fe-Si alloys based on
293 Terasaki et al. (2019) over the 30–40 GPa pressure range, corresponding to the central
294 pressure of Mercury’s Fe-Si core (Knibbe & van Westrenen 2015). Densities have been
295 evaluated at the melting temperature of Fe₁₆Si (Asanuma et al. 2010; Morard et al. 2011;
296 Fischer et al. 2012). It is observed that liquid and solid densities are similar for Si
297 concentrations approaching 10 wt%, while a solid is significantly denser for
298 stoichiometric FeSi. In the case of Fe₁₆Si alloy, which has been investigated by both the
299 present study and Terasaki et al. (2019), the solid-liquid density contrast is equivalent to
300 a difference of ~7–8 wt% in Si content.

301 Figure 4b illustrates the density contrast between solid and liquid Fe-Si alloys for Si
302 concentrations 10–33.5 wt%, under the assumption of a narrow melting loop,
303 corresponding to Si solid-liquid partitioning close to 1. Differences in Si content of solid
304 and coexisting liquid are estimated at ~1 wt% at 2 GPa (Morard et al. 2014) and below 2
305 wt% at 50 GPa (Fischer et al. 2013; Ozawa et al. 2016), supporting the overall validity of
306 this first-order approximation. The solid-liquid density contrast increases with increasing

307 Si content of the bulk core. Crystallizing B2 alloys (with possible exception of those with
308 Si content approaching 10 wt%) are suggested to be sufficiently dense to gravitationally
309 segregate to form a solid inner core. On the other hand, a liquid with 22 wt% Si or more,
310 although unlikely for Mercury (c.f. Genova et al. 2019; Terasaki et al. 2019), is light
311 enough to have a B2 inner core regardless of the solid composition (Figure 4).

312 Ultimately, given the large stability field of the B2 phase in Fe-Si alloys, this
313 structure is a primary candidate for solid inner cores of Si-rich telluric planets having
314 formed under reducing conditions. Future determinations of the eutectic point and the
315 melting loop of Fe-Si alloys over an extended P - T range are however required to confirm
316 the possibility of a B2 inner core in Mercury.

317

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TABLE 1. Parameters for the thermal equation of state established in the present study in comparison to those of Fe-Si alloys.

	This study	B2 FeSi ^a	DO3 Fe-16Si ^b	hcp Fe-9Si ^a
V_0 (cm ³ /mol)	6.419-1.536(X_{Si} -0.5) (fixed)	6.414	6.799	7.203
K_0 (GPa)	223+(382±13)(X_{Si} -0.5) +(616±41)(X_{Si} -0.5) ²	230.6	193.4	129.1
K'	4.3-(4.9±0.6)(X_{Si} -0.5)	4.17	4.91	5.29
θ_0 (K)	417 (fixed)	417	417	417
γ_0	1.93±0.13-(2.59±0.45)(X_{Si} -0.5)	1.3	1.89	1.14
q	1.8±0.4	1.7	1	1

a: Fischer et al. (2014)

b: Fischer et al. (2012)

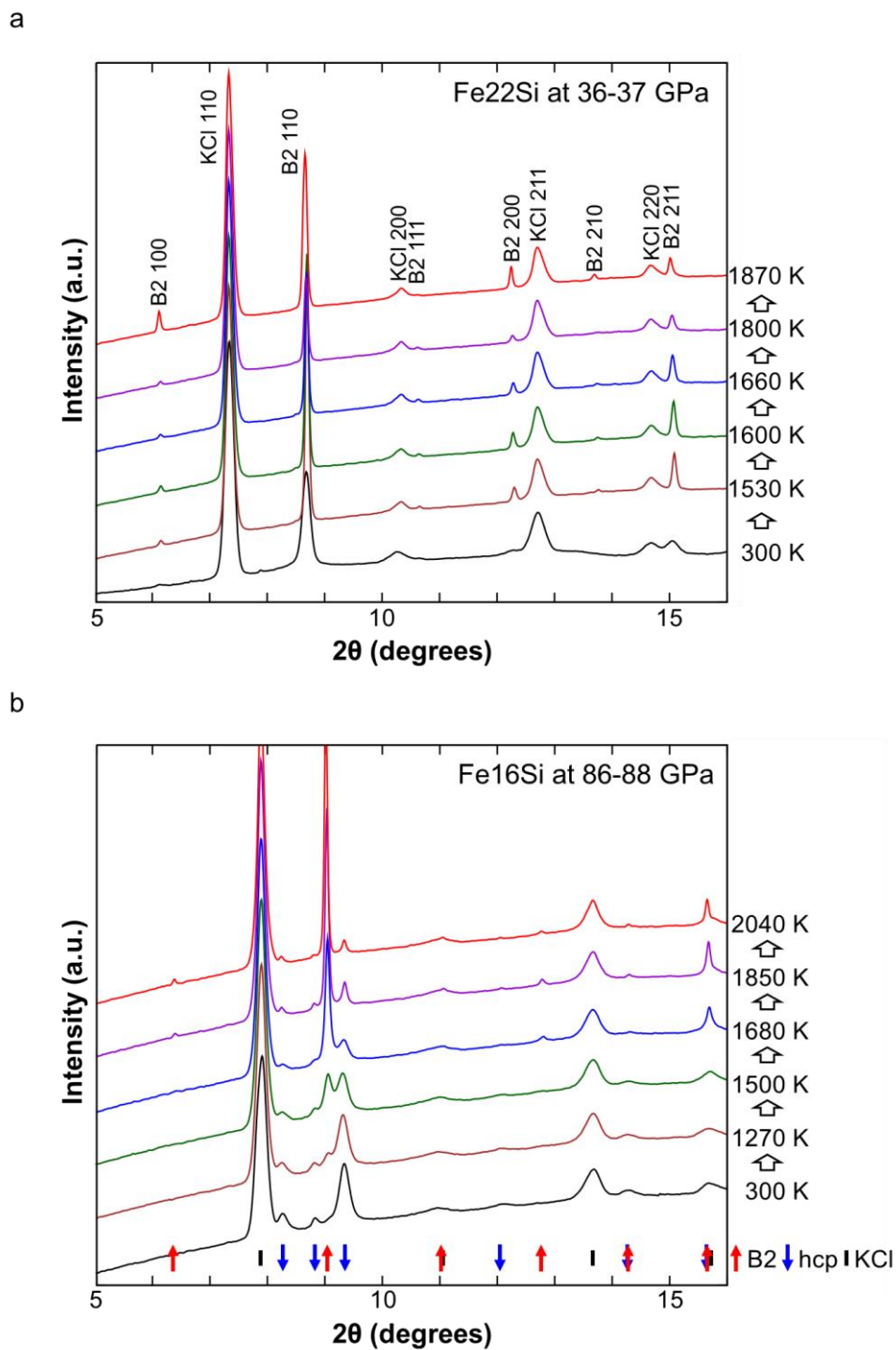


FIGURE 1. (a) X-ray diffraction patterns of Fe22Si at 36–37 GPa and 300–1870 K.

Fe22Si remained in the B2 phase over the P - T range studied. **(b)** X-ray diffraction patterns

of Fe16Si at 86–88 GPa and 300–2040 K. Red and blue arrows indicate the peak positions

of B2 and hcp phases, respectively. While the intensity of the KCl peaks remains nearly constant, significant changes in the B2 and hcp phase fractions occur at the lowest temperatures studied, above which the ratio of the two phases no longer changes. To minimize possible effects arising from kinetic barriers at low temperatures, only data obtained at sufficiently high temperatures to recrystallize the sample and relax non-hydrostatic stresses were used in the study.

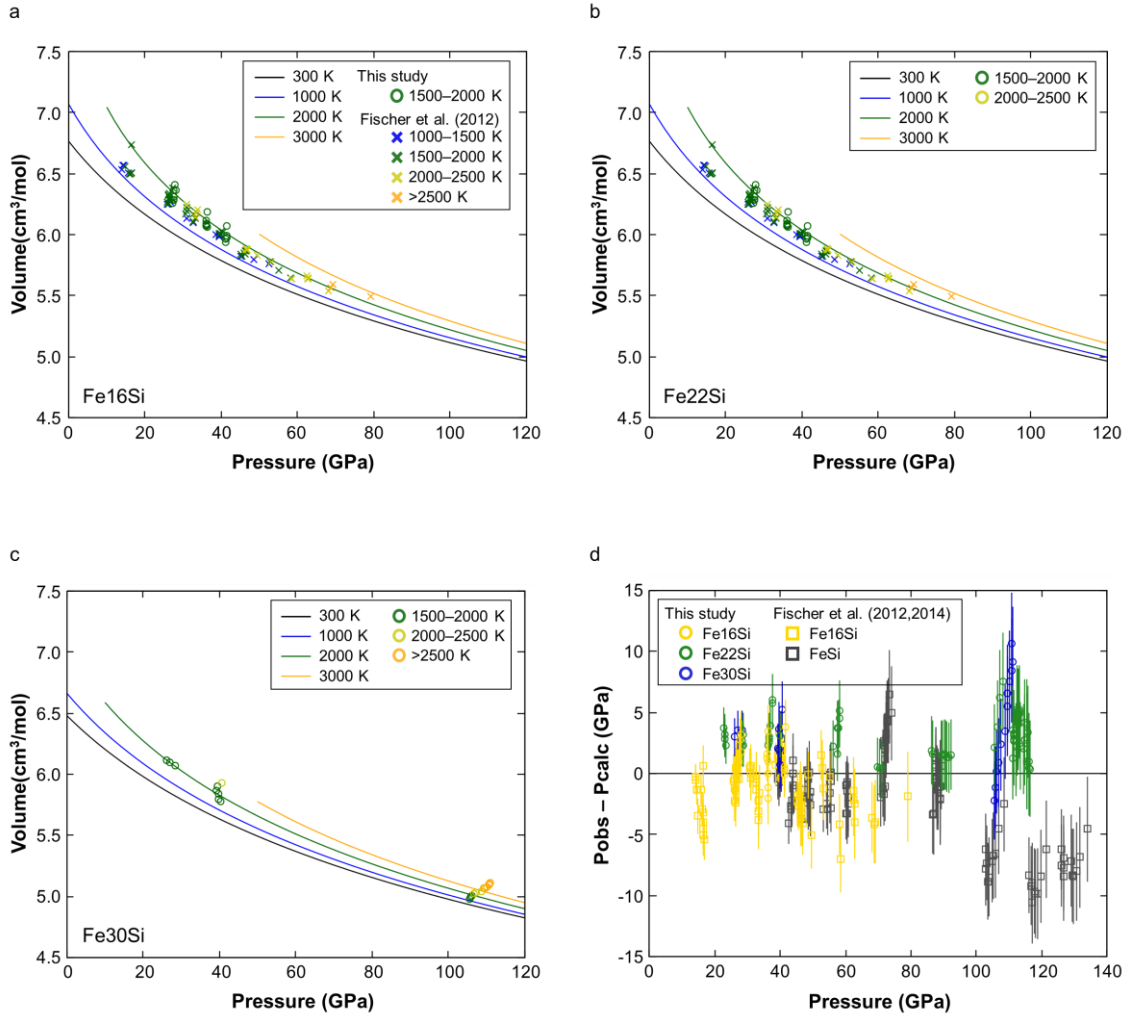


FIGURE 2. Compression curves of Fe16Si (a), Fe22Si (b), and Fe30Si (c) in the B2 structure at 300 K (black line), 1000 K (blue line), 2000 K (green line), and 3000 K (orange line) calculated according to the thermal equation of state established in the present study. Measured volumes are plotted as circles (green for 1500–2000 K, yellow for 2000–2500 K, and orange for >2500 K). Volumes of Fe16Si from Fischer et al. (2012) are also plotted as crosses in a. (d) Difference in pressure between the P - V - T - X_{Si} thermal equation of state from the present study, and P - V - T datapoints at high- T of the present

study and literature. Circles (yellow for Fe₁₆Si, green for Fe₂₂Si, and blue for Fe₃₀Si) are results obtained in the present study, while squares (yellow for Fe₁₆Si and black for FeSi) are from previous studies (Fischer et al. 2012, 2014).

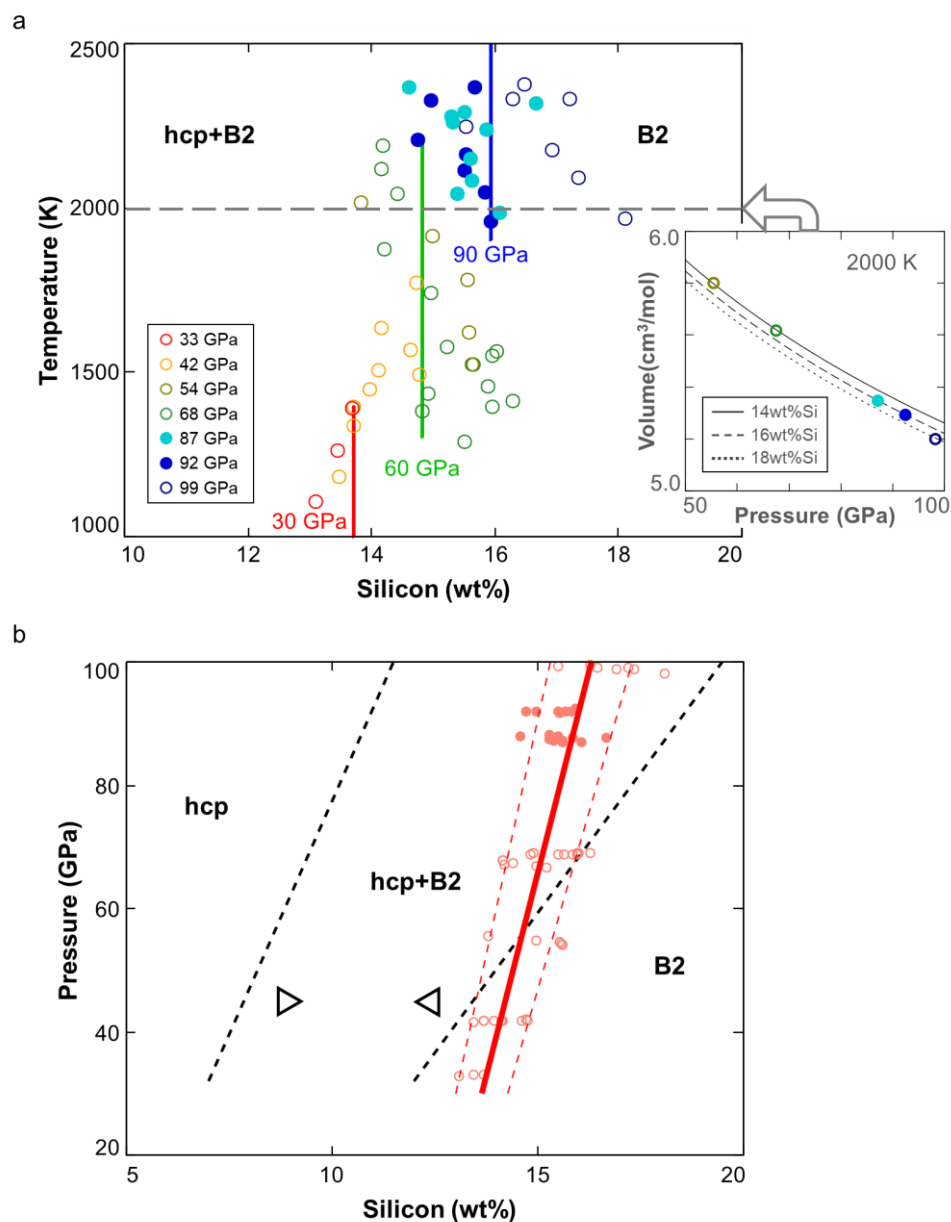


FIGURE 3. (a) Calculated Si content of B2 Fe-Si alloys within the hcp+B2 mixed phase region at 33–99 GPa. Open and filled circles indicate runs from Fe7Si and Fe16Si starting materials, respectively. Uncertainties in Si content are on the order of 1–1.5 wt%. Colored vertical bars indicate the hcp+B2/B2 phase boundary at 30, 60 and 90 GPa under the assumption of linear dependence on pressure, and negligible dependence on temperature.

The inset panel compares the compression curves of alloys with 14–18 wt% Si and the evolution of measured B2 volume with increasing pressure at ~2000 K. **(b)** Composition-pressure phase diagram from the present study and previous literature. The solid red line indicates the hcp+B2/B2 boundary from the present study, with uncertainties indicated by the red dashed lines. Datapoints from the present study are presented as red circles. Black dashed lines represent hcp/hcp+B2 and hcp+B2/B2 boundaries at 1500 K from Fischer et al. (2013). Triangles show the silicon contents of coexisting hcp and B2 phases at 45 GPa and 1650 K from Kuwayama et al. (2009).

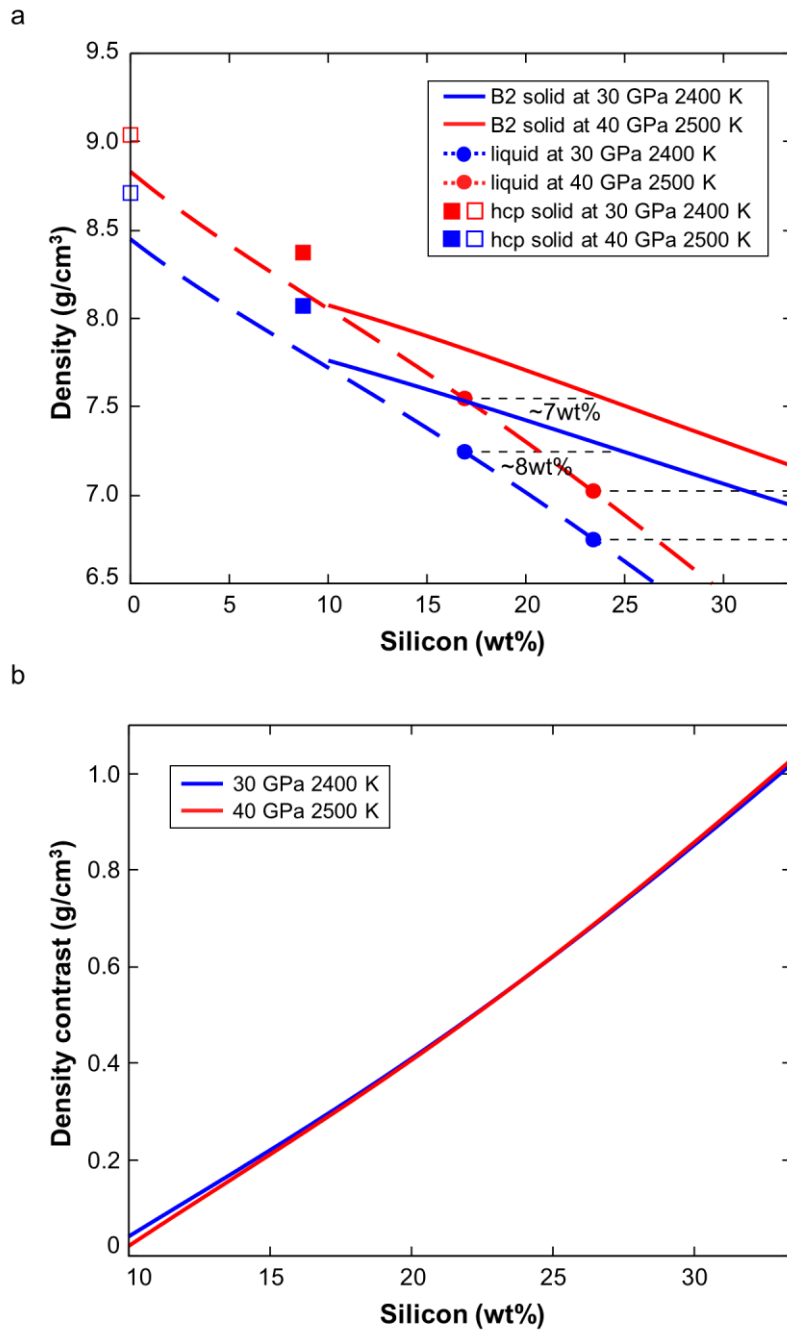
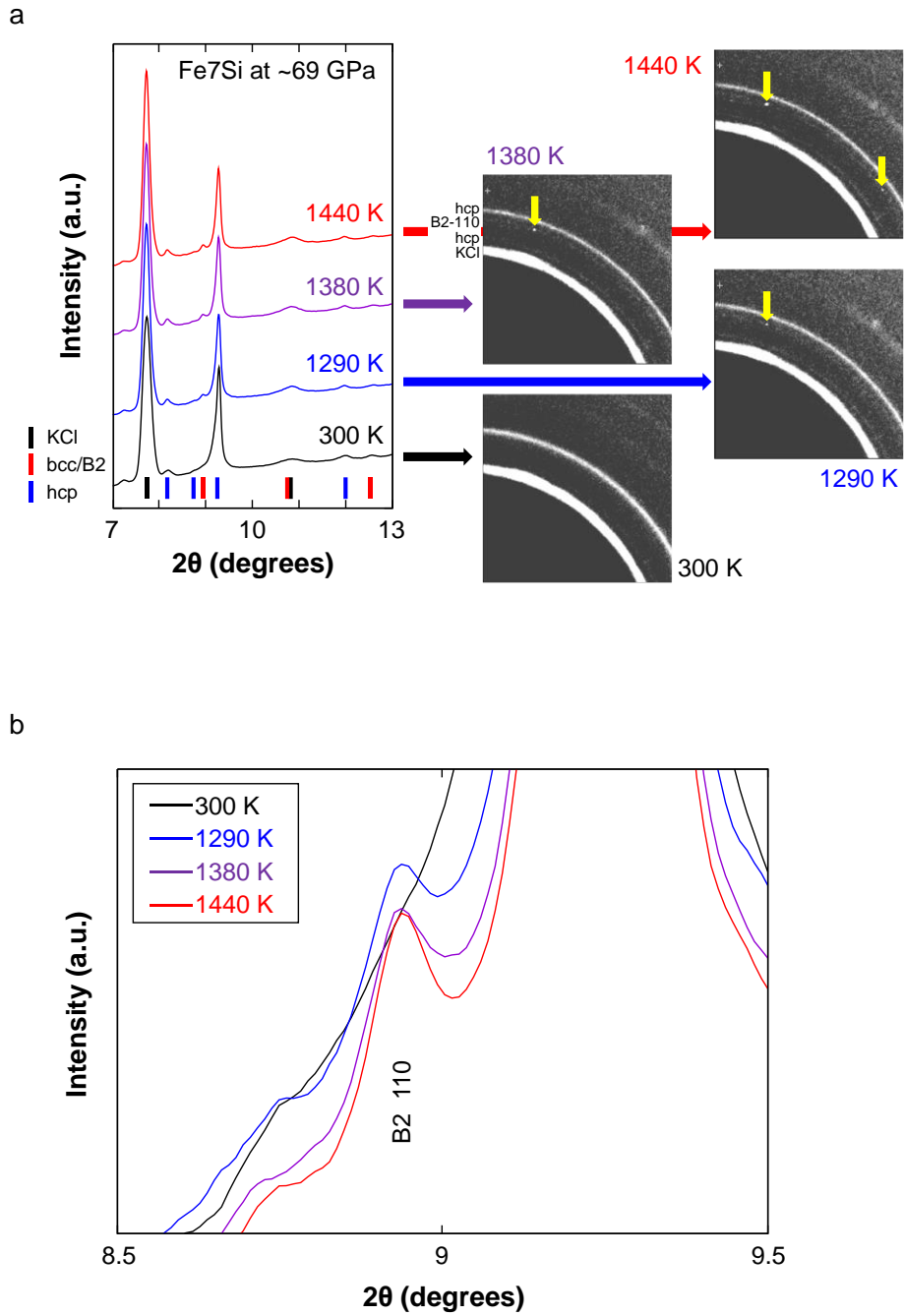
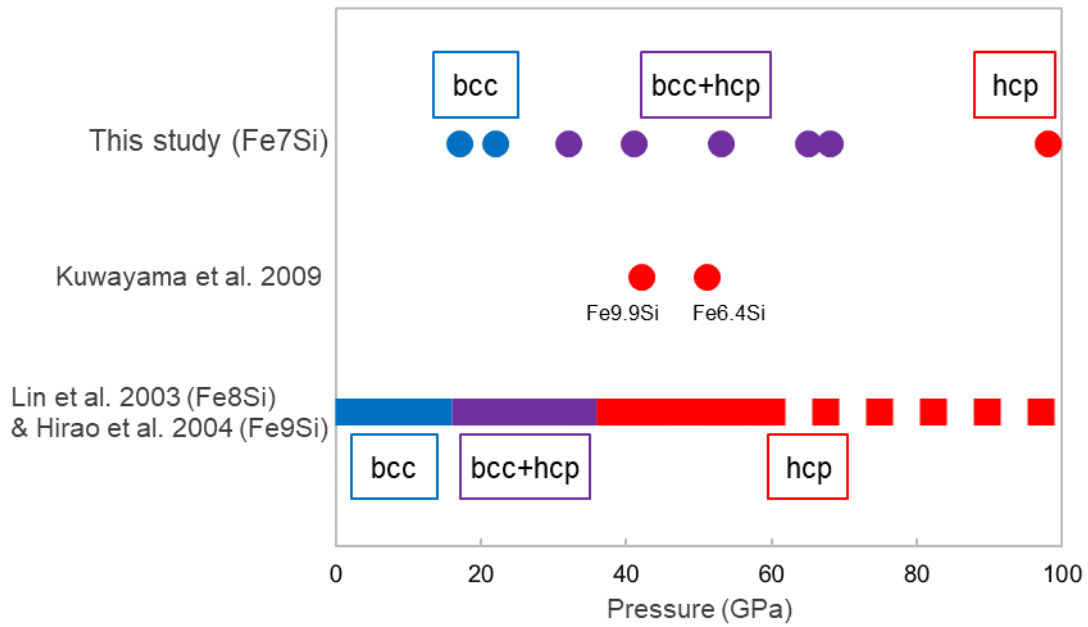


FIGURE 4. (a) Density of B2-structured solid and liquid Fe-Si alloys at 30 GPa and 2400 K (blue) and at 40 GPa and 2500 K (red). Solid lines indicate the densities of solid B2 alloys calculated in the present study, and dashed lines indicate liquid densities from Terasaki et al. (2019). Circles on the dashed lines indicate the sample compositions

studied in Terasaki et al. (2019). Densities of hcp-structured solid Fe and Fe-9Si are shown as open and filled squares, respectively (Fei et al. 2016; Fischer et al. 2014). **(b)** Density contrast between solid and liquid alloys at 30 GPa and 2400 K (blue), and at 40 GPa and 2500 K (red) assuming Si solid-liquid partitioning of 1.



SUPPORTING FIGURE 1. (a) X-ray diffraction patterns of Fe₇Si at ~69 GPa for increasing temperature (left) and enlarged images of 2D patterns around a 110 peak of B2 phase (right). Yellow arrows indicate bright spots formed by the grain growth. **(b)** Zoomed profiles of a 110 peak of B2 phase in XRD patterns in **a**.



SUPPORTING FIGURE 2. Comparison of observed phases in cold compression of starting material in this study and phases reported in literature studies at room-*T* and high pressure. Blue circles/line indicate bcc phase, purple indicate bcc+hcp, and red indicate hcp phase. The dotted red line shows the pressure range investigated only by Hirao et al. (2004).

SUPPORTING TABLE 2. Correlation coefficients between each parameter.

	$\frac{1}{2} \frac{d^2 K_0}{dX_{Si}^2}$	$\frac{dK'}{dX_{Si}}$	$\gamma_0 \Big _{X_{Si}=0.5}$	$\frac{d\gamma_0}{dX_{Si}}$	q
$\frac{dK_0}{dX_{Si}} \Big _{X_{Si}=0.5}$	0.9405	-0.6111	0.0647	-0.0374	0.0606
$\frac{1}{2} \frac{d^2 K_0}{dX_{Si}^2}$		-0.3705	-0.0327	-0.0719	-0.0700
$\frac{dK'}{dX_{Si}}$			-0.3857	-0.1917	-0.4947
$\gamma_0 \Big _{X_{Si}=0.5}$				0.6817	0.8504
$\frac{d\gamma_0}{dX_{Si}}$					0.3566

SUPPORTING TABLE 1. Experimental *P-T* conditions and measured volumes of samples for which a single B2/DO3 phase was observed.

Composition	Pressure (GPa)	Error (GPa)	Temperature (K)	Error (K)	Volume (cm ³ /mol)	Error (cm ³ /mol)
Fe16Si (DO3)	27.4	1.6	1520	60	6.25989	0.00066
Fe16Si (DO3)	27.5	1.6	1590	60	6.28725	0.00086
Fe16Si	27.5	1.7	1650	70	6.28588	0.00100
Fe16Si	27.5	1.7	1730	70	6.30919	0.00278
Fe16Si	27.6	1.8	1790	70	6.36842	0.00175
Fe16Si	27.9	1.9	1910	80	6.40511	0.00155
Fe16Si	28.1	1.9	1950	80	6.36566	0.00156
Fe16Si (DO3)	36.0	1.7	1510	60	6.06993	0.00056
Fe16Si	36.0	1.9	1660	70	6.09049	0.00139
Fe16Si	36.1	2.0	1780	70	6.08151	0.00617
Fe16Si	36.2	2.0	1870	80	6.11872	0.00834
Fe16Si	36.3	2.1	1940	80	6.19120	0.00317
Fe16Si	36.2	2.0	1890	80	6.07488	0.00096
Fe16Si	36.4	2.1	1980	80	6.06711	0.00803
Fe16Si	41.3	1.9	1580	60	5.94171	0.00027
Fe16Si	41.3	2.0	1680	70	5.96813	0.00038
Fe16Si	41.4	2.0	1770	70	5.97806	0.00117
Fe16Si	41.4	2.1	1850	80	5.98933	0.00109
Fe16Si	41.6	2.2	1930	80	6.07394	0.00098
Fe22Si	39.9	1.8	1550	60	5.92655	0.00035
Fe22Si	56.2	2.1	1530	60	5.62997	0.00013
Fe22Si	57.6	2.2	1500	60	5.59685	0.00011
Fe22Si	69.8	2.4	1540	60	5.42492	0.00014
Fe22Si	70.5	2.4	1520	60	5.41257	0.00014
Fe22Si	71.1	2.4	1510	60	5.40505	0.00015
Fe22Si	86.2	2.8	1540	60	5.25600	0.00013
Fe22Si	86.8	2.7	1510	60	5.24456	0.00013
Fe22Si	89.4	2.9	1580	60	5.22258	0.00012
Fe22Si	89.8	2.9	1600	60	5.21927	0.00012
Fe22Si	90.1	2.9	1580	60	5.21565	0.00012
Fe22Si	90.5	2.9	1570	60	5.21054	0.00012
Fe22Si	91.1	2.9	1570	60	5.20331	0.00012
Fe22Si	91.6	2.9	1580	60	5.19879	0.00012
Fe22Si	92.2	2.9	1530	60	5.19157	0.00012
Fe22Si	105.4	3.6	2050	90	5.10726	0.00010
Fe22Si	106.4	3.8	2300	100	5.12984	0.00009
Fe22Si	107.2	3.8	2350	100	5.14761	0.00009
Fe22Si	108.3	4.0	2450	110	5.15694	0.00007
Fe22Si	114.8	3.5	1770	70	5.02837	0.00012
Fe22Si	113.7	3.6	1870	80	5.02717	0.00010
Fe22Si	114.4	3.7	1950	80	5.02355	0.00012
Fe22Si	114.9	3.7	2000	90	5.02897	0.00012
Fe22Si	115.6	3.8	2030	90	5.02536	0.00010
Fe22Si	115.8	3.8	2070	90	5.02988	0.00014
Fe22Si	115.4	3.7	1970	80	5.03319	0.00009
Fe22Si	116.0	3.9	2250	100	5.01934	0.00008
Fe22Si	115.5	3.9	2200	100	5.02024	0.00007
Fe22Si	115.6	3.9	2170	90	5.01753	0.00007
Fe22Si	116.1	4.0	2270	100	5.01512	0.00007
Fe22Si	116.4	3.9	2240	100	5.01030	0.00006
Fe22Si	111.3	3.4	1740	70	5.03108	0.00012
Fe22Si	112.1	3.5	1850	80	5.03349	0.00012
Fe22Si	112.1	3.4	1750	70	5.03379	0.00013
Fe22Si	112.6	3.4	1740	70	5.03770	0.00011
Fe22Si	112.8	3.5	1840	80	5.04674	0.00011
Fe22Si	112.9	3.5	1810	80	5.04764	0.00011
Fe22Si	112.8	3.5	1780	70	5.05005	0.00011
Fe22Si	112.8	3.5	1770	70	5.04734	0.00011
Fe22Si	112.7	3.4	1730	70	5.04794	0.00011
Fe22Si	112.8	3.5	1780	70	5.04644	0.00011
Fe22Si	113.0	3.7	2070	90	5.05968	0.00010
Fe22Si	112.8	3.7	2000	90	5.06179	0.00010
Fe22Si	112.8	3.6	1970	80	5.06330	0.00010
Fe22Si	112.6	3.6	1960	80	5.06631	0.00010
Fe22Si	112.7	3.6	1960	80	5.06179	0.00011
Fe22Si	112.8	3.6	1950	80	5.05938	0.00011
Fe22Si	112.6	3.6	1940	80	5.06270	0.00012
Fe22Si	112.7	3.6	1970	80	5.06119	0.00008
Fe22Si	112.6	3.6	1940	80	5.06360	0.00007
Fe22Si	112.6	3.6	1930	80	5.05818	0.00007

Fe22Si	112.5	3.6	1910	80	5.06149	0.00008
Fe22Si	111.3	3.6	1950	80	5.06239	0.00009
Fe22Si	113.2	3.6	1930	80	5.05908	0.00008
Fe22Si	113.2	3.6	1930	80	5.05788	0.00008
Fe22Si	112.6	3.6	1930	80	5.05637	0.00007
Fe22Si	113.2	3.6	1940	80	5.05667	0.00007
Fe22Si	111.7	3.6	1950	80	5.05607	0.00008
Fe22Si	111.5	3.6	1920	80	5.05667	0.00008
Fe22Si	111.6	3.6	1960	80	5.05637	0.00008
Fe22Si	111.5	3.6	1920	80	5.05246	0.00007
Fe22Si	111.6	3.6	1930	80	5.05125	0.00007
Fe22Si	23.3	1.5	1510	60	6.28576	0.00013
Fe22Si	23.2	1.5	1580	60	6.32159	0.00014
Fe22Si	23.2	1.6	1670	70	6.35441	0.00031
Fe22Si	22.8	1.7	1810	80	6.41554	0.00082
Fe22Si	28.5	1.6	1560	60	6.15900	0.00018
Fe22Si	28.5	1.7	1640	70	6.18610	0.00017
Fe22Si	28.6	1.8	1740	70	6.19453	0.00022
Fe22Si	28.6	1.8	1810	80	6.23307	0.00065
Fe22Si	36.6	1.8	1530	60	5.97924	0.00019
Fe22Si	36.3	1.8	1600	60	5.99189	0.00033
Fe22Si	36.6	1.9	1660	70	6.00454	0.00050
Fe22Si	36.7	2.0	1800	80	6.03073	0.00071
Fe22Si	36.9	2.0	1870	80	6.05934	0.00050
Fe22Si	37.7	2.1	1950	80	6.10360	0.00017
Fe22Si	37.8	2.2	2010	90	6.10902	0.00021
Fe22Si	57.7	2.2	1520	60	5.62937	0.00012
Fe22Si	57.9	2.3	1670	70	5.64231	0.00012
Fe22Si	58.1	2.4	1780	70	5.66399	0.00013
Fe22Si	58.3	2.5	1870	80	5.68085	0.00014
Fe30Si	40.3	1.9	1570	60	5.77540	0.00027
Fe30Si	39.8	1.9	1650	70	5.80039	0.00022
Fe30Si	39.8	2.0	1770	70	5.83983	0.00023
Fe30Si	39.3	2.1	1880	80	5.86332	0.00035
Fe30Si	39.5	2.2	1980	80	5.90367	0.00030
Fe30Si	40.6	2.3	2100	90	5.93257	0.00090
Fe30Si	28.3	1.6	1540	60	6.07138	0.00012
Fe30Si	27.0	1.6	1550	60	6.10239	0.00018
Fe30Si	26.2	1.6	1570	60	6.11293	0.00032
Fe30Si	105.6	3.2	1620	70	4.98050	0.00012
Fe30Si	105.8	3.4	1830	80	4.99796	0.00009
Fe30Si	106.2	3.4	1890	80	5.00880	0.00010
Fe30Si	106.8	3.6	2080	90	5.02114	0.00010
Fe30Si	107.4	3.8	2260	100	5.03801	0.00012
Fe30Si	108.8	3.9	2380	100	5.04222	0.00013
Fe30Si	109.4	4.0	2430	110	5.06781	0.00013
Fe30Si	109.6	4.1	2590	110	5.06541	0.00020
Fe30Si	110.3	4.1	2610	120	5.07895	0.00009
Fe30Si	110.7	4.2	2680	120	5.10846	0.00013
Fe30Si	110.8	4.3	2760	120	5.09130	0.00032
Fe30Si	111.0	4.5	3060	140	5.11388	0.00010

SUPPORTING TABLE 3. Experimental *P-T* conditions, measured volumes, and Si content of samples for which hcp+B2 coexistence was observed.

Starting material	Pressure (GPa)	Error (GPa)	Temperature (K)	Error (K)	Volume of B2 (cm ³ /mol)	Error (cm ³ /mol)	Si in B2 (wt%)	Error (wt%)	Volume of hcp (cm ³ /mol)	Error (cm ³ /mol)
Fe7Si	32.8	1.3	1110	40	6.0934	0.0075	13.1	1.0	6.0752	0.0030
Fe7Si	33.0	1.5	1260	50	6.1095	0.0070	13.5	1.1	6.0918	0.0026
Fe7Si	33.1	1.6	1390	50	6.1250	0.0057	13.7	1.2	6.1202	0.0024
Fe7Si	41.8	1.8	1490	60	5.9437	0.0076	14.8	1.3	5.9310	0.0021
Fe7Si	41.8	1.8	1510	60	5.9602	0.0067	14.1	1.3	5.9543	0.0022
Fe7Si	41.6	1.6	1180	40	5.9285	0.0066	13.5	1.0	5.9069	0.0037
Fe7Si	41.7	1.7	1340	50	5.9450	0.0048	13.7	1.1	5.9098	0.0037
Fe7Si	41.7	1.7	1390	50	5.9536	0.0046	13.7	1.2	5.9329	0.0040
Fe7Si	41.8	1.8	1450	60	5.9543	0.0045	14.0	1.2	5.9249	0.0030
Fe7Si	41.8	1.9	1570	60	5.9602	0.0046	14.6	1.3	5.9438	0.0031
Fe7Si	41.8	1.9	1640	70	5.9801	0.0052	14.2	1.3	5.9631	0.0029
Fe7Si	41.9	2.1	1770	70	5.9868	0.0039	14.7	1.4	5.9795	0.0019
Fe7Si	54.0	2.1	1520	60	5.7254	0.0047	15.6	1.3	5.7172	0.0026
Fe7Si	54.3	2.2	1620	70	5.7351	0.0050	15.6	1.3	5.7244	0.0032
Fe7Si	54.6	2.3	1780	70	5.7505	0.0043	15.6	1.4	5.7452	0.0031
Fe7Si	54.9	2.4	1910	80	5.7738	0.0040	15.0	1.4	5.7815	0.0032
Fe7Si	55.5	2.5	2010	90	5.8024	0.0037	13.8	1.4	5.8060	0.0037
Fe7Si	66.6	2.4	1580	60	5.5629	0.0049	15.2	1.2	5.5675	0.0024
Fe7Si	66.9	2.5	1740	70	5.5818	0.0044	15.0	1.3	5.5704	0.0025
Fe7Si	67.0	2.6	1870	80	5.6097	0.0046	14.2	1.3	5.6021	0.0026
Fe7Si	67.4	2.8	2040	90	5.6180	0.0061	14.4	1.4	5.5896	0.0047
Fe7Si	67.7	2.9	2120	90	5.6269	0.0065	14.2	1.4	5.6117	0.0046
Fe7Si	67.9	2.9	2190	90	5.6326	0.0056	14.2	1.4	5.6364	0.0041
Fe7Si	68.8	2.2	1290	50	5.5031	0.0075	15.5	1.1	5.5063	0.0036
Fe7Si	68.7	2.3	1380	50	5.5257	0.0053	14.8	1.1	5.5115	0.0034
Fe7Si	68.9	2.3	1440	60	5.5263	0.0054	14.9	1.1	5.5013	0.0033
Fe7Si	68.8	2.3	1390	50	5.5044	0.0066	16.0	1.2	5.5165	0.0036
Fe7Si	69.0	2.3	1410	60	5.4975	0.0066	16.3	1.2	5.5009	0.0038
Fe7Si	68.9	2.3	1460	60	5.5106	0.0061	15.9	1.2	5.5118	0.0034
Fe7Si	69.0	2.4	1550	60	5.5163	0.0064	16.0	1.2	5.5240	0.0036
Fe7Si	68.9	2.4	1530	60	5.5219	0.0065	15.6	1.2	5.5351	0.0049
Fe7Si	69.0	2.4	1560	60	5.5163	0.0067	16.0	1.3	5.5097	0.0055
Fe16Si	87.1	3.1	1980	80	5.3460	0.0009	16.1	1.3	5.3753	0.0021
Fe16Si	87.3	3.2	2040	90	5.3612	0.0011	15.4	1.3	5.3776	0.0024
Fe16Si	87.3	3.2	2080	90	5.3601	0.0010	15.6	1.3	5.3900	0.0026
Fe16Si	87.0	3.3	2150	90	5.3691	0.0009	15.6	1.3	5.3987	0.0019
Fe16Si	87.6	3.4	2260	100	5.3778	0.0025	15.3	1.4	5.4088	0.0026
Fe16Si	87.8	3.4	2290	100	5.3736	0.0019	15.5	1.4	5.4104	0.0030
Fe16Si	87.8	3.4	2320	100	5.3548	0.0028	16.7	1.5	5.3855	0.0040
Fe16Si	87.7	3.4	2240	100	5.3634	0.0026	15.9	1.4	5.4421	0.0037
Fe16Si	88.1	3.4	2280	100	5.3741	0.0015	15.3	1.4	5.3924	0.0047
Fe16Si	88.0	3.5	2370	100	5.3960	0.0031	14.6	1.4	5.3678	0.0041
Fe16Si	92.4	3.2	1960	80	5.2919	0.0008	15.9	1.3	5.3280	0.0030
Fe16Si	91.9	3.3	2050	90	5.3059	0.0009	15.8	1.3	5.3514	0.0035
Fe16Si	91.8	3.3	2110	90	5.3174	0.0010	15.5	1.3	5.3515	0.0027
Fe16Si	91.6	3.4	2160	90	5.3226	0.0010	15.5	1.3	5.3601	0.0045
Fe16Si	91.9	3.4	2210	100	5.3394	0.0012	14.7	1.3	5.3416	0.0042
Fe16Si	92.0	3.5	2330	100	5.3432	0.0020	15.0	1.3	5.3262	0.0043
Fe16Si	91.9	3.6	2370	100	5.3333	0.0025	15.7	1.4	5.2945	0.0048
Fe7Si	98.2	3.4	1970	80	5.2005	0.0044	18.1	1.4	5.2363	0.0014
Fe7Si	98.9	3.5	2090	90	5.2144	0.0055	17.4	1.4	5.2535	0.0011
Fe7Si	98.9	3.5	2180	90	5.2271	0.004	16.9	1.4	5.2789	0.001
Fe7Si	99.3	3.6	2250	100	5.2544	0.0052	15.5	1.3	5.2884	0.0012
Fe7Si	99.5	3.7	2330	100	5.2434	0.0041	16.3	1.4	5.3018	0.0013
Fe7Si	99.0	3.7	2330	100	5.2325	0.0057	17.2	1.5	5.3034	0.0013
Fe7Si	99.1	3.7	2380	100	5.2471	0.0051	16.5	1.4	5.3211	0.0013