Temperature of Earth's core constrained from melting of Fe and Fe_{0.9}Ni_{0.1} at high pressures

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Abstract

The melting points of *fcc*- and *hcp*-structured Fe_{0.9}Ni_{0.1} and Fe are measured up to 125 GPa using laser heated diamond anvil cells, synchrotron Mössbauer spectroscopy, and a recently developed fast temperature readout spectrometer. The onset of melting is detected by a characteristic drop in the time-integrated synchrotron Mössbauer signal which is sensitive to atomic motion. The thermal pressure experienced by the samples is constrained by X-ray diffraction measurements under high pressures and temperatures. The obtained best-fit melting curves of *fcc*-structured Fe and Fe_{0.9}Ni_{0.1} fall within the wide region bounded by previous studies. We are able to derive the γ - ϵ -I triple point of Fe and the quasi triple point of Fe_{0.9}Ni_{0.1} to be 110 ± 5 GPa, 3345 ± 120 K and 116 ± 5 GPa, 3260 ± 120 K, respectively. The measured melting temperatures of Fe at similar pressure are slightly higher than those of Fe_{0.9}Ni_{0.1} while their one sigma uncertainties overlap. Using previously measured phonon density of states of *hcp*-Fe, we calculate melting curves of *hcp*-structured Fe and Fe_{0.9}Ni_{0.1}

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using our (quasi) triple points as anchors. The extrapolated $\text{Fe}_{0.9}\text{Ni}_{0.1}$ melting curve provides an estimate for the upper bound of Earth’s inner core-outer core boundary temperature of 5500 ± 200 K. The temperature within the liquid outer core is then approximated with an adiabatic model, which constrains the upper bound of the temperature at the core side of the core-mantle boundary to be 4000 ± 200 K. We discuss a potential melting point depression caused by light elements and the implications of the presented core-mantle boundary temperature on phase relations in the lowermost part of the mantle.

Keywords: Fe, Fe-Ni, melting, core, high pressure

1. Introduction

Cosmochemical and seismological studies suggest that Earth’s core is primarily composed of iron with $\sim 5\text{-}10$ wt% nickel, plus ~ 10 wt% light elements, such as sulfur, oxygen, silicon and carbon (McDonough and Sun, 1995; Li and Fei, 2003; Deuss, 2014; Hirose et al., 2013). The core consists of a solid inner section surrounded by a convecting, liquid outer layer (Lehmann, 1936). Experiments show that the inclusion of light elements tends to lower the melting point of Fe-rich alloys (e.g., Boehler 1992; Fei and Bertka 2005; Stewart et al. 2007; Chen et al. 2008; Andraut et al. 2009; Asanuma et al. 2010; Terasaki et al. 2011, and references therein). The melting temperatures of pure iron and iron alloyed with a few percent nickel therefore provide the basis for understanding expected temperatures in the core. The temperature of the core at the core-mantle boundary (CMB) provides constraints on the heat flow across this boundary and thus affects the age determination of the inner core (Labrosse et al., 2001), influences the evolution of the geodynamo (Olson, 2013), and controls the temperature gradient within the thermal boundary layer above the CMB (Anderson, 1990; Lay et al., 2008).

Among the four crystalline forms of Fe, the high-pressure phases face-centered cubic (*fcc*) and hexagonal close packed (*hcp*) are the primary foci of this study. The melting curve of *fcc* Fe constrains the *fcc-hcp*-liquid (γ - ϵ -l) triple point, an

21 essential reference point for the melting curve of the *hcp* phase under large com-
 22 pression. However, the high pressure melting curves of *fcc*- and *hcp*-Fe are still
 23 controversial, leading to estimated temperatures at the inner core-outer core
 24 boundary ranging from 4850 K to 7800 K (Williams et al., 1987; Boehler et al.,
 25 1990; Shen et al., 1998; Jackson et al., 2013; Anzellini et al., 2013; Aquilanti et al.,
 26 2015). In particular, studies of the high pressure melting curve of *fcc*- and *hcp*-
 27 Fe-Ni alloys are not available.

28 Several experimental methods have been used to explore the high pressure
 29 melting curves of metals, among which the laser heated diamond anvil cel-
 30 l (LH-DAC) is the most common (e.g., Boehler 1993; Errandonea et al. 2001;
 31 Shen et al. 2004; Dewaele et al. 2007, 2010; Jackson et al. 2013; Anzellini et al.
 32 2013; Zhang et al. 2015). In LH-DAC experiments, the temperature determina-
 33 tion is usually less accurate and precise than the pressure determination. One
 34 major contribution to the temperature uncertainty in LH-DAC experiments are
 35 rapid temporal fluctuations (10-100 Hz) of the sample temperature during the
 36 experiment (Jeanloz and Heinz, 1984; Zhang et al., 2015). These fluctuations
 37 are likely a result of the coupling between laser light and sample surface, and
 38 at temperatures close to a sample’s melting point $\sim 0.3\%$ of laser power fluctu-
 39 ation can lead to temperature fluctuations of up to 200 K (Jeanloz and Heinz,
 40 1984; Jeanloz and Kavner, 1996). Also slower (1 Hz) temperature fluctuations
 41 of several hundreds of Kelvin have been reported for samples near their melting
 42 points (Dewaele et al., 2007, 2010; Anzellini et al., 2013; Zhang et al., 2015).
 43 This magnitude of temperature fluctuation presents a challenge for accurately
 44 and precisely determining the melting temperature of a sample.

45 Melting experiments in a LH-DAC typically ramp up the laser power quickly
 46 (seconds to minutes) to convert the sample from solid to liquid. Therefore, a
 47 fast temperature readout system whose sampling frequency exceeds that of the
 48 melting diagnostic is necessary to obtain reliable sample temperatures with high
 49 precision. We have developed a multi-wavelength temperature readout spec-
 50 trometer named FasTeR to address this issue (Zhang et al., 2015). The FasTeR
 51 system features a well-calibrated sampling rate of 100 Hz (and up to at least 400

Hz) with large dynamic range, high sensitivity, and a well-constrained optical aperture. This new system is located at beamline 3-ID-B of the Advanced Photon Source (APS) at Argonne National Laboratory, IL and described in detail elsewhere (Zhang et al., 2015).

In this study, we combine the LH-DAC, the FasTeR spectrometer, and synchrotron Mössbauer spectroscopy to constrain the high pressure melting curves of *fcc*- and *hcp*-structured $^{57}\text{Fe}_{0.9}\text{Ni}_{0.1}$ and ^{57}Fe up to pressures of 125 GPa. The Mössbauer signal that scatters from the sample prior to melting is sensitive to the movement of the iron nuclei (Singwi and Sjölander, 1960; Boyle et al., 1961), and thus provides a unique diagnostic for the solid-liquid transition of Fe-rich materials (Jackson et al., 2013).

2. Experiments

2.1. Sample preparation

The Fe-Ni sample used in this study was synthesized at Caltech. Individual pieces of Ni and 95%-enriched ^{57}Fe are selected with an accuracy of 1.0 mg to produce 50 mg of $\text{Fe}_{0.9}\text{Ni}_{0.1}$. The Fe and Ni pieces are arc-melted in an argon atmosphere, then cold rolled to a physical thickness of about 13 μm . The elemental composition of the Fe-Ni sample is determined by a JEOL JXA-8200 electron probe micro-analyzer (EPMA) at Caltech’s Microanalysis Center. Quantitative data are acquired in focused mode, using wavelength-dispersive spectrometry, operating at 15 kV accelerating voltage and 20 nA beam current. Pure Fe, Ni and Re metal standards are used for the analysis. No elements other than Fe and Ni are detected within the uncertainty. EPMA analysis of 25 sampled regions gives an average composition of $\text{Fe}_{0.91(1)}\text{Ni}_{0.09(1)}$ for the ^{57}Fe -Ni alloy, where the numbers in parentheses indicate the uncertainties in the last digit, hereafter referred to as $\text{Fe}_{0.9}\text{Ni}_{0.1}$ for simplicity. The 95% isotopically enriched ^{57}Fe and $\text{Fe}_{0.9}\text{Ni}_{0.1}$ foils with thicknesses ranging from 9 to 15 μm are cut into rectangular sections with an EDM and cleaned. The sizes of the sections range from about $55 \times 55 \mu\text{m}^2$ to $80 \times 80 \mu\text{m}^2$. The ^{57}Fe samples used

81 in this study are cut from the same larger foils used in a previous melting study
82 (Jackson et al., 2013).

83 In each melting run, a symmetric DAC is used to provide the high pressure
84 environment. Two quarter-carat Type-I diamonds with culet sizes ranging from
85 beveled 250 to 300 μm in diameter are mounted on backing plates (WC or
86 cBN) and aligned to form the anvils. A Re gasket is pre-indented to $\sim 45 \mu\text{m}$
87 thickness, and to form the sample chamber, a hole is drilled in the center of the
88 pre-indentation using an EDM or a laser drilling system. The sample chamber's
89 size ranges from 80 to 115 μm in diameter, depending on the diamond culet size.
90 Dehydrated KCl is pressed into transparent flakes and loaded together with an
91 individual pre-cut $^{57}\text{Fe}_{0.9}\text{Ni}_{0.1}$ or ^{57}Fe foil in a sandwich configuration into the
92 sample chamber. The KCl serves as both a pressure-transmitting medium and
93 thermal insulation. A few ruby spheres ($\sim 10 \mu\text{m}$ in diameter) are placed away
94 from the sample and used as pressure markers (Mao et al., 1986). The DAC is
95 first purged in a chamber filled with purified Ar gas and then heated in a vacuum
96 furnace before closing to remove oxygen and moisture. After the DAC is sealed,
97 pressure is increased to the approximate desired range and laser annealed to
98 about 1500 K before the X-ray experiments. The laser annealing is essential to
99 determine sample coupling behavior with the IR laser and to relax any stresses
100 induced by cold compression. When possible, X-ray diffraction is collected *in-*
101 *situ* to constrain the pressure of the sample.

102 2.2. Synchrotron Mössbauer spectroscopy measurements

103 The dynamics of the iron atoms are used as a diagnostic to detect melting
104 and are probed using nuclear resonant forward scattering, also known as syn-
105 chrotron Mössbauer spectroscopy (SMS) (Jackson et al., 2013). As explained
106 previously, the observed time-delayed signal is caused by coherent elastic s-
107 cattering of synchrotron X-rays while traversing a sample containing ^{57}Fe or
108 another accessible nuclear resonant isotope (Jackson et al., 2013). The emis-
109 sion of the SMS signal occurs into the direction of the incident X-rays and is
110 independent of the spatial positions of atoms. The strength of the SMS signal

Figure 1: X-ray diffraction patterns collected before (300 K, blue), during (green) and after (300 K, red) typical melting runs. Panels a,c and b show results for $\text{Fe}_{0.9}\text{Ni}_{0.1}$ and Fe, respectively. Diffraction patterns in panels a and b are collected at APS 3-ID-B with an X-ray wavelength of 0.086026 nm corresponding to an energy of 14.4125 keV (1 meV bandwidth). Panel c shows data collected at APS 13-ID-D with an X-ray wavelength of 0.0344 nm corresponding to an energy of 36.0 keV (1 eV bandwidth). The X-ray focal spots are aligned to the melted areas on the sample.

Figure 2: Comparison of the pressure determination at 300 K using XRD of pre-heated samples (horizontal axis) and post-melted samples (vertical axis). The black dashed line is the identity line. Circles: $\text{Fe}_{0.9}\text{Ni}_{0.1}$. Diamonds: Fe. Pressures are calculated from *fcc*- and *hcp*-iron's equation of state (Dewaele et al., 2006; Komabayashi, 2014).

111 is primarily determined by the effective thickness of the sample traversed by
 112 the X-rays. The effective thickness, η , is a dimensionless number given as the
 113 product of the numerical density of the ^{57}Fe nuclei, ρ , the physical thickness of
 114 the sample, d , the nuclear resonant cross section, $\sigma = 2.56 \times 10^{-22}\text{m}^2$ for ^{57}Fe ,
 115 and the dimensionless temperature-dependent Lamb-Mössbauer factor, f

$$\eta = \rho d \sigma f \quad . \quad (1)$$

116 The experiments are carried out at beamline 3-ID-B of the APS, which uniquely
 117 features nuclear resonant scattering techniques coupled with *in-situ* double-
 118 sided laser heating, a new FasTeR temperature measurements system, con-
 119 ventional CCD-based spectrometers, and X-ray diffraction (Zhao et al., 2004;
 120 Gao et al., 2009; Jackson et al., 2013; Zhang et al., 2015). The storage ring is
 121 operated in low-emittance top-up mode with 24 bunches that are separated by
 122 153 ns. The energy (14.4125 keV) and resolution (1 meV) of the X-rays are
 123 determined by a silicon high resolution monochromator (Toellner, 2000), and
 124 a focus area of $\sim 10 \times 11 \mu\text{m}^2$ (full width at half maximum) is achieved by a
 125 Kirkpatrick-Baez mirror system (Eng et al., 1998; Zhang et al., 2015). In-situ
 126 X-ray diffraction images are collected on the compressed samples at the same
 127 beamline to obtain the crystal symmetry and pressure of the sample (Figs. 1
 128 and 2). This is achieved by moving a high resolution MAR image plate (Mar-
 129 research GmbH), located 0.3 m downstream of the DAC, into the X-ray path.
 130 Some diffraction patterns are collected at APS beamline 13-ID-D using a MAR-
 131 CCD detector (Rayonix) (Fig. 1c), where 36.0 keV X-rays with 1 eV bandwidth
 132 are focused to $\sim 3 \times 3 \mu\text{m}^2$. CeO_2 and LaB_6 standards are used to calibrate
 133 the sample to image plate distance and correct for the tilt of the image plate at
 134 3-ID-B and 13-ID-D. The diffraction images are integrated into angular resolved
 135 files using the DIOPTAS software (Prescher and Prakapenka, 2015).

136 After a diffraction image is collected, the image plate is moved out of the
 137 X-ray path for the series of SMS measurements that constrain the melting point.
 138 The SMS signal is captured by an avalanche photodiode detector placed ~ 0.5

139 m downstream of the sample. For each melting run, a high-statistical quality
 140 reference SMS spectrum is collected for about 10 minutes at 300 K at the sample
 141 position where the melting measurement will be carried out. The sample is then
 142 scanned in both x and y directions to record sample topography with respect to
 143 alignment of the X-ray and IR laser focal areas. Then, we preheat the sample to
 144 about 1500 K, balancing the laser power upstream and downstream to achieve
 145 similar CCD readout temperatures, thus suggesting a uniformly heated sample.
 146 Another high-statistical quality SMS spectrum is collected at this elevated tem-
 147 perature (Fig. 3). This particular SMS spectrum provides the timing window
 148 and effective thickness of the sample at a reference elevated temperature imme-
 149 diately preceding the melting run, both necessary for later determination of the
 150 melting point.

151 Before discussing the next sequence of events for melting temperature deter-
 152 mination, we describe the profile, $S(t, \eta)$, of the time resolved delayed counts,
 153 the SMS spectrum. The SMS spectrum depends on the level splitting of the
 154 resonant nuclei, the effective thickness of the sample, η (as described above),
 155 and the time, t , relative to the excitation by the X-ray pulse. For *fcc* and
 156 *hcp* Fe and $\text{Fe}_{0.9}\text{Ni}_{0.1}$, it is known that the nuclear levels of ^{57}Fe are un-split
 157 (Macedo and Keune, 1988). Therefore S reduces to

$$S(t, \eta) = \eta^2 e^{-t/\tau} \frac{J_1^2(\sqrt{\eta t/\tau})}{\eta t/\tau}, \quad (2)$$

158 where J_1 is the first order Bessel function of the first kind, and τ is the life time of
 159 the excited nuclear state (141 ns for ^{57}Fe) (e.g., Sturhahn 2000; Jackson et al.
 160 2013). The sample's effective thickness at 1500 K, which is also the initial
 161 effective thickness for the melting run, is then obtained by fitting the measured
 162 SMS spectrum to the profile given by equation (2).

163 Melt detection using SMS aims at measuring the effective thickness as de-
 164 fined by equation (1) as a function of temperature. In the liquid state, the
 165 Lamb-Mössbauer factor and thus the effective thickness vanishes. In an experi-
 166 ment, the measurement of the time-integrated SMS signal is therefore sufficient if

Figure 3: SMS spectra of $^{57}\text{Fe}_{0.9}\text{Ni}_{0.1}$ and ^{57}Fe at high pressures and high temperatures. Each spectrum is collected for about 10 minutes. The SMS spectra provide the time window and are fitted to the profile given by equation (2) to determine the effective thickness. The red curves show the best-fits. The temperature shown here is determined from an average of the upstream and downstream CCD and FasTeR spectrometers over the data collection time. Pressures and their errors at 300 K are shown. a): $^{57}\text{Fe}_{0.9}\text{Ni}_{0.1}$ at $P_{300K}=74\pm3$ GPa and 1500 ± 120 K. The best-fit effective thickness is 72 ± 18 . b): ^{57}Fe at $P_{300K}=43\pm1$ GPa and 1500 ± 120 K. The best-fit effective thickness is 45 ± 20 . c): $^{57}\text{Fe}_{0.9}\text{Ni}_{0.1}$ at $P_{300K}=109\pm3$ GPa and 1500 ± 120 K. The best-fit effective thickness is 61 ± 12 .

167 the nuclear level splitting is known as in our case. The measured time-integrated
 168 SMS signal is then given by

$$I(\eta) = A e^{-\mu d} \sum_{n=0}^{\infty} \int_{t_1+nt_B}^{t_2+nt_B} S(t', \eta) dt' \quad . \quad (3)$$

169 Here t_1 and t_2 are the beginning and end of the accessible time window, t_B is
 170 the time interval between subsequent X-ray pulses (given by the synchrotron
 171 operation mode, here $t_B=153$ ns), n is indexing X-ray pulses into the past, A is
 172 a scaling factor that depends on experimental conditions such as spectral X-ray
 173 flux incident on the sample, d is the physical thickness of the sample, μ is the
 174 electronic absorption coefficient of the sample material, S is the profile of the
 175 SMS spectrum specified in equation (2), and η is the temperature-dependend
 176 effective thickness of the sample (Jackson et al., 2013).

177 After collecting a high temperature SMS spectrum, we immediately proceed
 178 to a computer-controlled acquisition sequence, which constitutes the melting
 179 run. In this sequence, the laser power is ramped up every 3 seconds while
 180 recording salient parameters, such as laser power, time-integrated SMS spec-
 181 trum (delayed counts), X-ray intensities upstream and downstream of the sam-

182 ple via ionization chambers, and temperature readouts from FasTeR and the
 183 CCD spectrometer. The downstream X-ray intensity is used to normalize the
 184 time-integrated SMS spectrum which accounts for the electronic absorption ter-
 185 m in equation (3) and for potential upstream X-ray intensity fluctuations. As
 186 described in Zhang et al. (2015), the temperature of the sample is recorded si-
 187 multaneously by the FasTeR system and by upstream/downstream CCD spec-
 188 trometers. Since the FasTeR system has a high sampling frequency, the FasTeR
 189 temperature is reported as the average of about 300 samplings for each 3 s
 190 interval. The temperature obtained from the CCD-based spectrometer is mea-
 191 sured once for each 3 s interval using the SpecT code (Shen et al., 2001) and is
 192 reported as the average of upstream and downstream temperatures. The CCD-
 193 based spectrometer in this study tends to underestimate the sample temperature
 194 compared to the FasTeR measurement, because the CCD-based spectrometer
 195 has a slightly larger aperture (Zhang et al., 2015). Therefore, the temperatures
 196 determined from the FasTeR system are used in determination of the melting
 197 temperatures (Tables 1 & 2, Section 3.2). Sample temperature and normalized
 198 time-integrated delayed counts are shown as a function of laser power for three
 199 typical melting runs in Figure 4. One can see that the duration of a melting
 200 run typically ranges from about two to four minutes.

201 Immediately after a melting run is completed on a localized region of the
 202 sample, the laser power is shut off, and a SMS spectrum is acquired. The
 203 sample is then scanned in both x and y directions to assess whether sample
 204 topography has changed with respect to scans before the melting run (i.e., to
 205 re-confirm that the sample area is relatively flat). Finally, we determine the
 206 sample pressure using in situ XRD (or ex situ ruby fluorescence) to document
 207 a potential pressure drift during the experiment. The pressure of the sample at
 208 300 K is reported as the average of the pressures determined before and after
 209 heating. We also examine the Ni/Fe atomic ratios of the melted and unmelted
 210 regions on one $\text{Fe}_{0.9}\text{Ni}_{0.1}$ sample (recovered from D1R9, Tab. 1) using the
 211 EPMA facility at Caltech. The average Ni/Fe atomic ratio for the unmelted
 212 regions is $9.91 \times 10^{-2} \pm 6.5 \times 10^{-3}$ (25 data points), and the average Ni/Fe atomic

Figure 4: Temperatures and time-integrated normalized delayed counts as a function of laser power. Sample composition, pressure and pressure error at 300 K are indicated in each panel. Temperatures are determined by the FasTeR system. Both un-binned (light grey) and binned (blue) temperatures are shown in the top panels. Binned temperatures and their standard deviations are used in determining the melting temperatures (Figure 6). The melting run in panel a required insertion of a neutral density filter at ~ 100 W laser power to avoid saturation. Panels a and c display data corresponding to melting runs D1R9 and D4R3 in Table 1. Panel b display data corresponding to melting run D6R6 in Table 2. The duration of a melting run typically ranges from about two to four minutes.

ratio for the melted regions is $9.51 \times 10^{-2} \pm 1.19 \times 10^{-2}$ (18 data points). The Ni/Fe atomic ratios in the melted regions have more scatter because the melted regions have more relief at the surface. Within our experimental uncertainty, there is no clear evidence for nickel segregation in the melted regions.

3. Results and Discussion

3.1. Thermal contribution to the pressure

In all of our experiments, *hcp*-structured Fe and $\text{Fe}_{0.9}\text{Ni}_{0.1}$ are observed at 300 K. The thermal equations of state from Komabayashi (2014) and Dewaele et al.

(2006) are used to calculate the pressures for *fcc*- and *hcp*-phases, respectively. The pressures determined from ruby fluorescence and XRD are consistent with their relatively large error bars. Pressure uncertainties determined from the rubies are large due to their spread in values around the sample chamber and/or changes during a melting run. The quoted uncertainty for pressure determined using XRD can be large due to the limited number of accessible diffraction peaks at 14.4125 keV, despite the use of cBN backing plates. The final pressure we report is that determined from XRD (when available), measured at the same location on the sample where it is melted. In some of the melting runs, we collect a series of diffraction images, first at 300 K before heating, then at high temperatures to constrain the trend of thermal contribution to pressure, and finally at 300 K after heating, to constrain potential pressure drifts (Fig. 1, Section 2.2).

In order to determine the thermal pressure contribution at the sample's melting point, we assume that: *fcc*-Fe and *fcc*-Fe_{0.9}Ni_{0.1} share the same thermoelastic parameters as *hcp*-Fe and *hcp*-Fe_{0.9}Ni_{0.1}; thermal pressure is only a function of temperature. The first assumption has been adopted by an XRD study using resistive heating (Komabayashi et al., 2009) and is observed in LH-DAC XRD experiments (Anzellini et al., 2013). The addition of ~10% Ni is suggested to have minor effect on the thermal pressure determination (Komabayashi et al., 2012). The second assumption is supported by nuclear resonant inelastic scattering experiments on *hcp*-Fe at high pressures which report a weak volume dependence of the vibrational thermal pressure up to 171 GPa (Murphy et al., 2011).

At the melting temperature T_m , the sample's pressure can be written as

$$P(T_m) = P(T_0) + P_{th}(T_m) \quad , \quad (4)$$

where $P(T_0)$ is the pressure at reference temperature $T_0 = 300$ K. The thermal pressure

Figure 5: Thermal pressure derived from XRD data at high pressure and temperature. Pressures of the data points at 300 K range from 10 GPa to 150 GPa. Solid circles (this study): XRD data taken at 13-ID-D. Empty circles (this study): XRD data taken at 3-ID-B. Black curve (this study): thermal contribution to pressure estimated from equation (5). Grey shaded region: estimated uncertainty of the thermal contribution to pressure. The dashed part of the curve is extrapolated. Resistive heating and optical spectroscopy temperature reading are used in Komabayashi et al. (2009, 2012). *fcc*- and *hcp*-Fe’s equations of state from Komabayashi (2014) and Dewaele et al. (2006) are used to determine the pressure.

$$P_{th}(T_m) = a(T_m - T_0) + c(T_m^2 - T_0^2) \quad (5)$$

has two contributions: a linear term arising from the harmonic component of the vibrational thermal pressure; a quadratic term originating from the anharmonic and electronic components (Anderson, 1980; Dewaele et al., 2006; Murphy et al., 2011). Values of $a = (4.6 \pm 0.5) \times 10^{-3} \text{GPa/K}$ and $c = (0.2 \pm 3.4) \times 10^{-6} \text{GPa}^2/\text{K}^2$ are obtained from a best fit to data from our high P-T diffraction measurements (Figs. 1 and 5).

For reference, we also show thermal pressures determined from recent high pressure and temperature XRD studies on Fe and Fe-Ni (Komabayashi et al., 2009, 2012; Anzellini et al., 2013). A subset of the data from Komabayashi et al. (2009, 2012) and Anzellini et al. (2013) shows signs of relaxation during heating as pressure changes significantly when temperature is increased. Because Anzellini et al. (2013) didn’t provide the volumes (pressures) of the Fe sample at 300 K, we cannot directly compare their thermal pressures with our results.

261 Instead, we compare the relative pressure change between two different elevated
 262 temperatures. We assume that in each heating run from Anzellini et al. (2013)
 263 the thermal pressure of the first data point follows equation (5), and the ther-
 264 mal pressures of subsequent data points in the same heating run are calculated
 265 by integration of subsequent relative pressure changes. The thermal pressure
 266 trend as a function of temperature defined by equation (5) is slightly higher than
 267 that observed by Anzellini et al. (2013) (Fig. 5). In general, the thermal pres-
 268 sures observed in these studies are about half of the constant-volume values for
 269 *hcp*-Fe from an *ab initio* calculation (Dewaele et al., 2006) and nuclear resonant
 270 inelastic X-ray scattering measurements (Murphy et al., 2011). A similar effect
 271 was reported for laser-heated platinum in an argon medium (Goncharov et al.,
 272 2010). Based on the scatter in these independent measurements, we assess a
 273 reasonable error estimate on the thermal pressure (Tables 1 & 2).

274 3.2. Melting temperature determination

275 The melting temperatures of Fe and $\text{Fe}_{0.9}\text{Ni}_{0.1}$ are determined by fitting
 276 the measurable quantity, namely normalized delayed counts, as a function of
 277 sample temperature using the SIMX module of the MINUTI software package
 278 (Sturhahn, 2015) (Fig. 6). The effective thickness of the sample is determined
 279 immediately before the melting run begins, at around 1500 K (Fig. 3). The
 280 laser’s hotspot profile is estimated from optical observation, and the X-ray focus
 281 profile is determined by knife-edge scanning. Both profiles are provided as inputs
 282 to SIMX to determine the effective thickness distribution weighted by the X-ray
 283 intensity distribution. From equations (2) and (3) and the assumption of zero
 284 effective thickness of melted material, SIMX calculates the normalized delayed
 285 intensity as a function of sample temperature and provides a fit to the measured
 286 data. For the fitting procedure, uncertainties of temperature and of the time-
 287 integrated normalized delayed counts must be provided. The latter are simply
 288 given as the square root of accumulated counts in the collection span (3 s in our
 289 case), and the temperature uncertainties are the sum of the standard deviation of
 290 all FasTeR readings during the 3 s collection span (Fig. 4), the root-mean-square

Figure 6: Time-integrated normalized delayed counts (top panels) and calculated effective thicknesses (bottom panels) as a function of temperature for typical melting runs. Panels a and c display data corresponding to melting runs D1R9 and D4R3 in Table 1. Panel b displays data corresponding to melting run D6R6 in Table 2. Sample composition and pressure are indicated in each panel. Pressure values include the thermal contribution at the melting point, and temperatures are determined using the FasTeR spectrometer. The solid curves result from fits using the SIMX module of the MINUTI software package (Sturhahn, 2015). Best-fit melting temperatures are indicated as the red bands in the figure. Best-fit melting temperatures are: panel a, $T_m = 3059 \pm 106$ K, $\chi^2 = 1.4 \pm 0.1$; panel b, $T_m = 2835 \pm 114$ K, $\chi^2 = 1.5 \pm 0.2$; panel c, $T_m = 3317 \pm 104$ K, $\chi^2 = 1.1 \pm 0.1$.

value of the dark current fluctuation, and chromatic aberration, as described in detail previously (Zhang et al., 2015). These uncertainties are displayed in Figure 6. The fitting error of the melting point, along with its associated reduced χ^2 value from SIMX are reported in Tables 1 & 2. The uncertainty for a melting temperature is reported as the quadrature sum of the SIMX fitting error, the temperature difference of values given by the upstream and downstream CCD-based spectrometers, chromatic aberration of the CCD system (about 10 K), and the appropriate level of uncertainty assessed from the spectroradiometric method and detailed balance principle (100 K) (Sturhahn and Jackson, 2007; Zhang et al., 2015). The melting temperatures, pressures, and all associated parameters obtained in this study are summarized in Tables 1 & 2.

3.3. Melting curves of the fcc-phases and triple points

Melting temperatures and pressures obtained in this study (Tables 1 & 2) are now used to construct melting curves of *fcc*-structured Fe and $\text{Fe}_{0.9}\text{Ni}_{0.1}$ (Figure

Figure 7: Melting points of *fcc*-structured Fe and $\text{Fe}_{0.9}\text{Ni}_{0.1}$. Solid blue circles and red diamonds (this study): $\text{Fe}_{0.9}\text{Ni}_{0.1}$ and Fe. Blue and red solid curves (this study): best-fits for $\text{Fe}_{0.9}\text{Ni}_{0.1}$ and Fe using equation (6). The following studies include thermal contributions: empty squares (Jackson et al., 2013), dark green dash-dotted curve (Anzellini et al., 2013), orange dashed curve (Aquilanti et al., 2015), grey square: shock compression (Ahrens et al., 2002). Black solid circle: Strong et al. (1973), corrected with thermal contribution of pressure using Eq. (5). The following studies did not consider thermal pressure: black dashed curve (Boehler et al., 1990; Boehler, 1993), magenta dashed curve (Shen et al., 1998, 2004), cyan dashed curve (Liu and Bassett, 1975). All experiments except for Ahrens et al. (2002) were carried out with laser-heated diamond anvil cells.

7). The reported pressures include the 300 K value and the high temperature contribution. The 300 K pressures are determined before and after the melting runs on annealed samples by X-ray diffraction (or ruby fluorescence), and the high temperature contributions are calculated from equation (5) as outlined in Section 3.1. At ambient pressure, a very narrow two-phase field, reported to be less than 10 K wide (Cacciamani et al., 2010), exists for *fcc*- $\text{Fe}_{0.9}\text{Ni}_{0.1}$ and liquid. However, the precision of our high-pressure measurements is not sufficient to identify such a coexistence region.

The shape of the melting curve has been modeled previously using the empirical Simon-Glatzel equation (Murphy et al., 2011; Anzellini et al., 2013)

$$T_m = T_{m0} \left(\frac{P_m - P_{m0}}{x} + 1 \right)^y, \quad (6)$$

where melting points (P_m , T_m) are related to a reference melting point (P_{m0} ,

316 T_{m0}), and x, y are adjustable, material specific parameters. In our study, the
 317 best-fit parameters are: $T_{m0}=2194\pm100$ K, $P_{m0}=21.4\pm0.9$ GPa, $x=20\pm5$ GPa,
 318 and $y=0.25\pm0.04$ for Fe; $T_{m0}=2199\pm100$ K, $P_{m0}=21.5\pm0.7$ GPa, $x=18\pm3$ GPa,
 319 and $y=0.22\pm0.02$ for $\text{Fe}_{0.9}\text{Ni}_{0.1}$. The corresponding melting curves are shown
 320 in Figure 7. Considering uncertainties, these melting curves overlap in the tails
 321 of their one sigma confidence regions.

322 The γ - ϵ -l triple points of Fe and $\text{Fe}_{0.9}\text{Ni}_{0.1}$ are constrained by the γ - ϵ phase
 323 boundary reported in previous studies. Komabayashi et al. (2009) and Komabayashi et al.
 324 (2012) measured the γ - ϵ boundary of Fe and an Fe-9.7 wt% Ni alloy using
 325 resistively-heated DACs and X-ray diffraction. They reported the slope of the
 326 phase boundary dP/dT as 0.0394 GPa/K (at 88 GPa, 2800 K) for Fe and as
 327 0.0426 GPa/K (at 61.8 GPa, 1992 K) for Fe-9.7 wt% Ni alloy, respectively. In
 328 principle, a γ - ϵ -l triple point is not meaningful for an alloy such as $\text{Fe}_{0.9}\text{Ni}_{0.1}$, be-
 329 cause melting should be described by a solidus and liquidus. Within our experi-
 330 mental resolution however, the solidus and liquidus of $\text{Fe}_{0.9}\text{Ni}_{0.1}$ coincide and are
 331 addressed as the melting curve of $\text{Fe}_{0.9}\text{Ni}_{0.1}$. Accordingly we define a quasi γ - ϵ -l
 332 triple point for $\text{Fe}_{0.9}\text{Ni}_{0.1}$ as the intersection of γ - ϵ phase boundary and melting
 333 curve. By combining the *fcc-hcp* boundaries from Komabayashi et al. (2009,
 334 2012) and our *fcc* melting curves, the γ - ϵ -l triple points of Fe and $\text{Fe}_{0.9}\text{Ni}_{0.1}$ are
 335 calculated to be 110 ± 5 GPa, 3345 ± 120 K and 116 ± 5 GPa, 3260 ± 120 K, respec-
 336 tively (Fig. 8). The triple point of Fe is found at higher temperature and lower
 337 pressure than the quasi triple point of $\text{Fe}_{0.9}\text{Ni}_{0.1}$, a trend suggested by ambient
 338 pressure experiments (see Cacciamani et al. 2010 and references therein).

339 3.4. Melting curves of the hcp-phases

340 Two melting experiments are carried out for $\text{Fe}_{0.9}\text{Ni}_{0.1}$ at pressures above
 341 100 GPa. The pressure of the $\text{Fe}_{0.9}\text{Ni}_{0.1}$ sample at room temperature is 109 ± 3
 342 GPa, determined by XRD (Tab. 1). The same sample is melted twice at two
 343 locations, spatially separated by ~ 20 μm . The best-fit melting temperatures of
 344 the two runs are 3383 ± 102 K and 3317 ± 104 K as determined by SIMX. The
 345 thermal contribution according to equation (5) is included to provide pressures

Table 1: Experimental results and melting points of $\text{Fe}_{0.9}\text{Ni}_{0.1}$ determined by synchrotron Mössbauer spectroscopy.

<i>fcc-Fe_{0.9}Ni_{0.1}</i>										
Run number	Volume ^a (cc/mol)	P_{XRD} (GPa)	P_{ruby} (GPa)	P_m (GPa)	Density ^b g/cm ³	Effective thickness	SIMX reduced χ^2	SIMX fitting error (K)	Time window (ns)	T_m (K)
D1R2	6.38±0.02	10.1±0.4	10±1	19.0±2.4	8.93±0.03	89±20	0.7±0.3	72	10.1-124.6	2081±123
D1R1	6.38±0.02	10.1±0.4	10±1	19.2±2.4	8.93±0.03	124±22	0.9±0.2	22	10.1-124.6	2127±102
D10R4	NA	NA	12.5±0.8	22.2±2.8	(9.0±0.1)	100±22	0.9±0.2	26	16.1-136.0	2233±103
D10R1	NA	NA	13.6±0.5	23.3±2.5	(9.07±0.05)	43±15	1.0±0.3	71	18.0-137.3	2246±123
D10R3	NA	NA	13.6±0.5	23.3±2.5	(9.07±0.05)	53±26	1.2±0.2	29	12.3-135.2	2243±104
D10R2	NA	NA	13.6±0.5	23.6±2.5	(9.07±0.05)	70±17	0.7±0.2	22	12.3-135.2	2296±102
D9R2	NA	NA	14.7±0.6	24.7±2.6	(9.12±0.07)	45±26	0.9±0.2	48	12.5-136.2	2279±111
D9R1	NA	NA	14.7±0.6	24.9±2.6	(9.12±0.07)	73±42	0.6±0.2	30	11.2-136.2	2331±104
D7R2	NA	NA	21.3±1	32.0±3	(9.4±0.1)	35±15	1.1±0.4	100	18.9-135.7	2411±141
D7R3	NA	NA	21.3±1	32.0±3	(9.4±0.1)	55±25	0.8±0.4	38	19.0-136.1	2410±107
D7R1	NA	NA	21.3±1	32.1±3	(9.4±0.1)	31±11	1.9±0.6	130	19.6-135.7	2423±164
D9R5	NA	NA	29.3±1	40.7±3	(9.6±0.1)	61±9	1.5±0.3	84	15.8-135.9	2530±131
D9R3	NA	NA	29.3±1	40.9±3	(9.6±0.1)	63±15	0.8±0.1	21	15.9-136.5	2574±103
D9R4	NA	NA	29.3±1	41.0±3	(9.6±0.1)	70±14	1.1±0.2	62	16.1-135.4	2602±112
D1R5	5.95±0.05	30.0±1	30.0±3	41.8±3	9.6±0.1	106±35	2.1±0.3	57	18.2-139.5	2645±115
D1R3	5.92±0.04	36.0±1	38.0±2	47.8±3	9.8±0.1	16±9	1.1±0.3	130	15.8-135.8	2619±164
D1R4	5.92±0.04	36.0±1	38.0±2	48.3±3	9.8±0.1	16±9	2.9±0.4	130	15.8-135.8	2715±164
D3R1	5.76±0.04	37.5±1	39.0±3	49.8±3	9.9±0.1	43±20	1.1±0.3	48	19.3-132.7	2716±111
D8R1	5.76±0.04	39.0±1	37.5±2	50.7±3	9.9±0.1	68±18	1.3±0.2	21	16.4-139.5	2598±102
D8R2	5.76±0.04	39.0±1	37.5±2	51.1±3	9.9±0.1	45±26	1.0±0.2	14	18.0-139.5	2683±101
D1R6	5.62±0.06	50.0±2	52.0±3	63.2±4	10.2±0.2	102±19	1.4±0.2	55	16.1-132.6	2882±114
D8R5	5.44±0.05	61.0±1	63.0±3	74.9±3	10.5±0.1	76±13	1.3±0.2	55	16.1-133.4	2966±114
D1R10	5.38±0.04	66.0±2	66.8±3	79.8±4	10.6±0.1	64±30	1.4±0.2	44	15.9-130.5	2974±109
D1R11	5.38±0.04	66.0±2	66.8±3	80.0±4	10.6±0.1	74±14	1.2±0.1	19	16.0-131.5	3017±102
D8R3	5.37±0.05	69.0±2	63.0±3	83.1±4	10.7±0.1	82±14	0.7±0.2	22	16.0-135.6	3023±102
D8R4	5.37±0.05	69.0±2	63.0±3	83.3±4	10.7±0.1	72±13	1.2±0.2	21	16.0-135.9	3056±102
D4R1	5.34±0.03	71.0±2	71.0±2	85.1±4	10.7±0.1	90±24	4.9±0.4	130	17.9-132.8	3028±164
D1R9	5.28±0.04	74.0±3	74.3±2	88.0±5	10.8±0.2	72±15	1.4±0.1	36	15.9-136.3	3059±106
D1R8	5.28±0.04	74.0±3	74.3±2	88.2±5	10.8±0.2	109±18	1.6±0.2	66	16.0-136.3	3061±114
D1R7	5.28±0.04	74.0±3	74.3±2	88.5±5	10.8±0.2	104±18	1.2±0.1	38	15.7-136.1	3103±107

<i>hcp-Fe_{0.9}Ni_{0.1}</i>										
Run number	Volume ^a (cc/mol)	P_{XRD} (GPa)	P_{ruby} (GPa)	P_m (GPa)	Density ^b g/cm ³	Effective thickness	SIMX reduced χ^2	SIMX fitting error (K)	Time window (ns)	T_m (K)
D4R3	4.96±0.04	109.0±3	112.0±5	124.8±5	11.5±0.1	61±12	1.1±0.1	27	19.6-132.5	3317±104
D4R2	4.96±0.04	109.0±3	112.0±5	125.0±5	11.5±0.1	64±13	1.1±0.1	19	19.6-132.4	3383±102

quasi γ - ϵ -I triple point

P: 116±5 GPa

T: 3260±120 K

DXRY = DAC X Run Y. ^a: In some melting runs the limited angular access of backing plates prevented diffraction peaks to be observed (NA: not applicable), therefore pressures are determined from fluorescence of ruby spheres. ^b: Values in parentheses are calculated from pressure via the *fcc*-Fe (Komabayashi (2014)) or *hcp*-Fe (Dewaele et al. (2006)) equations of state. P_m is determined by adding the thermal contribution (Eq. 5) at the melting temperature to the pressure at 300 K.

Table 2: Experimental results and melting points of Fe determined by synchrotron Mössbauer spectroscopy.

<i>fcc</i> -Fe										
Run	Volume ^a	P _{XRD}	P _{ruby}	P _m	Density ^b	Effective	SIMX	SIMX fitting	Time window	T _m
number	(cc/mol)	(GPa)	(GPa)	(GPa)	g/cm ³	thickness	reduced χ^2	error (K)	(ns)	(K)
D10R5	6.42±0.04	10.0±0.5	11.1±1	19.0±2.5	8.88±0.05	49±12	1.7±0.4	25	15.8-135.7	2116±103
D10R6	6.42±0.04	10.0±0.5	11.1±1	19.1±2.5	8.88±0.05	53±12	2.2±0.4	43	15.8-135.8	2123±119
D6R1	NA	NA	28.0±1	39.8±3	(9.6±0.1)	27±11	0.9±0.2	190	17.8-136.4	2614±215
D6R2	NA	NA	28.0±1	39.8±3	(9.6±0.1)	28±10	0.6±0.2	150	18.0-135.6	2614±180
D6R3	NA	NA	28.0±1	40.0±3	(9.6±0.1)	18±11	1.4±0.3	230	17.8-135.7	2650±251
D6R6	5.70±0.03	43.0±1	42.3±2	55.9±3	10.0±0.1	49±14	1.5±0.2	54	21.1-136.3	2835±114
D6R5	5.69±0.03	44.0±2	42.3±2	57.1±4	10.0±0.2	47±15	0.9±0.2	29	21.0-136.5	2858±104
D6R4	5.65±0.03	47.0±1	42.3±2	59.8±3	10.1±0.1	53±14	0.5±0.1	45	21.2-135.6	2792±110

γ - ϵ -I triple point

P: 110±5 GPa

T: 3345±120 K

DXY = DAC X Run Y. ^a: In some melting runs the limited angular access of backing plates prevented diffraction peaks to be observed (NA: not applicable), therefore pressures are determined from fluorescence of ruby spheres. ^b: Values in parentheses are calculated from pressure via the *fcc*-Fe (Komabayashi (2014)) or *hcp*-Fe (Dewaele et al. (2006)) equations of state. P_m is determined by adding the thermal contribution (Eq. 5) at the melting temperature to the pressure at 300 K.

at melting as 125 ± 3 GPa and 124.8 ± 3 GPa, respectively (Fig. 8). These melting points are at higher pressures and temperatures than the quasi γ - ϵ -I triple point, and we can infer that melting of the *hcp*-phase of Fe_{0.9}Ni_{0.1} was observed in these two melting runs. In order to extrapolate the high pressure melting curves of *hcp*-structured Fe and Fe_{0.9}Ni_{0.1} to inner core conditions, we apply the Simon-Glatzel equation (6) and the (quasi) triple points determined earlier as anchor points, T_{m0} and P_{m0}. The other two parameters in the Simon-Glatzel equation are obtained from the phonon density-of-states of *hcp*-Fe measured by nuclear resonant inelastic X-ray scattering by a procedure outlined in section 4 of Murphy et al. (2011). This method makes the reasonable assumption that the vibrational behavior of *hcp*-structured Fe and Fe_{0.9}Ni_{0.1} are very similar. Then the best-fit parameters in the Simon-Glatzel equation are: $x = 171\pm20$ GPa, $y = 0.63\pm0.08$ for *hcp*-Fe_{0.9}Ni_{0.1}, and $x = 167\pm20$ GPa, $y = 0.64\pm0.08$ for *hcp*-Fe. These melting curves, which are shown in Figure 8, predict for *hcp*-Fe_{0.9}Ni_{0.1} a melting temperature of 3370 ± 120 K at 125 GPa, demonstrating

361 consistency with the measured values of 3383 ± 102 K and 3317 ± 104 K.

362 Melting curves of Fe-Ni alloys at high pressures were not reported previ-
363 ously, but a comparison of the obtained melting curves for Fe with previous
364 studies is possible. A wide range of criteria were used in those studies to deter-
365 mine melting: Liu and Bassett (1975) and Boehler et al. (1990) measured the
366 resistivity of Fe at different temperatures; Williams et al. (1987), Boehler et al.
367 (1990), and Boehler (1993) monitored the surface properties of Fe, such as op-
368 tical reflectivity, texture and convective motion; diffuse scattering observed in
369 an XRD setup has been used recently (Shen et al., 1998, 2004; Anzellini et al.,
370 2013); X-ray absorption spectroscopy is used to monitor the phase transitions
371 of Fe (Aquilanti et al., 2015).

372 These methods have different sensitivities to the onset of melting. Moni-
373 toring the surface properties is not sensitive to the interior of the sample, and
374 can be dependent on sample-specific surface and interface properties. X-ray
375 based methods, such as monitoring diffuse scattering (X-ray diffraction), short-
376 range coordination environment (X-ray absorption), and atomic dynamics (syn-
377 chrotron Mössbauer spectroscopy), are more sensitive to the entire scattering
378 volume of the sample. Thermal diffuse scattering is sensitive to the average
379 electronic arrangement of the material during the X-ray diffraction exposure
380 time (Shen et al., 2004; Dewaele et al., 2007, 2010; Anzellini et al., 2013). The
381 presence of melt is identified by the appearance of broad diffuse rings in the
382 X-ray diffraction pattern characterizing the disappearance of long range coordi-
383 nation environments in the melt. The thermal diffuse scattering signal must be
384 discriminated against a relatively large background signal and likely requires a
385 large volume of melt in the scattering volume. X-ray absorption spectroscopy
386 monitors the average short-range coordination of the absorbing atoms rendering
387 a subtle change upon melting.

388 Synchrotron Mössbauer spectroscopy is sensitive only to the resonant nuclei
389 in the sample and is a background free diagnostic method when used in combi-
390 nation with time discrimination techniques. The intensity of the time-integrated
391 signal from synchrotron Mössbauer spectroscopy reflects the microscopic range

Figure 8: Phase boundaries of Fe and $\text{Fe}_{0.9}\text{Ni}_{0.1}$. Dashed curves and solid curves are for Fe and $\text{Fe}_{0.9}\text{Ni}_{0.1}$, respectively (this study), where the γ - ϵ boundaries of Fe and $\text{Fe}_{0.9}\text{Ni}_{0.1}$ are adapted from Komabayashi et al. (2009, 2012). The empty circles are for $\text{hcp-Fe}_{0.9}\text{Ni}_{0.1}$ (this study, error bars are smaller than the symbols). Dash-dotted curves: Fe ϵ -l boundary (dark green: Anzellini et al. 2013, cyan: Boehler 1993). Black dots: Fe solid-liquid boundary, (Boehler et al., 2008). Empty square: hcp-Fe in LH-DAC, XRD (Ma et al., 2004). Diamonds: hcp-Fe , shock compression experiments (orange: Nguyen and Holmes 2004, magenta: Brown and McQueen 1986, green: Bass et al. 1987, empty: Yoo et al. 1993).

392 of movement of the iron nuclei. As the solid sample transitions to a liquid state,
 393 atoms experience an enhanced freedom of motion. For the iron nuclei this re-
 394 sults in the absence of recoil-free scattering events. The Mössbauer signal, which
 395 is a consequence of recoil-free scattering, consequently disappears in the liquid
 396 state and drops markedly in a solid-liquid mixture (Singwi and Sjölander, 1960;
 397 Boyle et al., 1961; Jackson et al., 2013; Zhang et al., 2015). These significant
 398 differences in criteria may explain the higher melting temperatures reported for
 399 Fe using thermal diffuse scattering (Figs. 7, 8), as they are likely to represent
 400 upper bounds. The marked drop in the Mössbauer signal reliably captures the
 401 first melt to form in the sampled volume. In combination with well-calibrated
 402 temperature data from the FasTeR instrument, high-quality melting tempera-
 403 tures for Fe and $\text{Fe}_{0.9}\text{Ni}_{0.1}$ can be obtained.

Figure 9: Proposed thermal profiles of Earth’s interior and melting points of minerals. Blue curves: proposed geotherms (dotted: Brown and Shankland 1981; dashed: Stacey 1977). Red solid curve: outer core temperature profile calculated from inferred melting temperature of $hcp\text{-Fe}_{0.9}\text{Ni}_{0.1}$ at 330 GPa, this study, red shaded region gives error estimate. Red dashed curve: outer core temperature profile calculated from our study and accounting a 700 K melting point depression at the ICB from light elements (Alfè et al., 2002). Dark green dash-dotted curve: outer core temperature profile calculated from inferred melting temperature of $hcp\text{-Fe}$ at 330 GPa (Anzellini et al., 2013). Circle: bridgmanite melting point (Akins et al., 2004). Gray cross: peridotite containing about 50% melt (Tateno et al., 2014). Reversed triangle: peridotite solidus (Fiquet et al., 2010). Triangle: chondrite solidus (Andrault et al., 2011). Green cross: MORB solidus (Pradhan et al., 2015), extrapolated value from data between 44 and 128 GPa. Green asterisk: MORB solidus (Andrault et al., 2014). Square: wüstite melting point (Fischer and Campbell, 2010), extrapolated value from data between 0 and 77 GPa. Diamond: alkali pyroxene solidus (Nomura et al., 2014). The depth scale is taken from the Preliminary Reference Earth Model (Dziewonski and Anderson, 1981).

404 3.5. Implications for the temperature in Earth’s core

405 The high pressure melting curves of *fcc* and *hcp* structured Fe and Fe_{0.9}Ni_{0.1}
 406 constrained in this study allow us to predict the temperature in Earth’s core. It
 407 is commonly assumed that addition of light elements to Fe depresses the melting
 408 point of iron alloys (Alfè et al., 2002). Therefore the melting temperatures of
 409 *hcp*-Fe and *hcp*-Fe_{0.9}Ni_{0.1} at 330 GPa serve as an upper bound for the tem-
 410 perature at Earth’s inner core-outer core boundary (T_{ICB}) (Lehmann, 1936;
 411 Terasaki et al., 2011). An extrapolation of our melting curves for *hcp*-Fe and
 412 *hcp*-Fe_{0.9}Ni_{0.1} predicts upper bounds for T_{ICB} of 5700±200 K and 5500±200
 413 K, respectively (Fig. 8). In this study, we assume that *hcp*-Fe_{0.9}Ni_{0.1} is a
 414 more likely base composition for the core than pure *hcp*-Fe, and consequently
 415 we proceed with *hcp*-Fe_{0.9}Ni_{0.1}’s melting curve to constrain the upper bound of
 416 T_{ICB} .

417 The thermal profile in the core is commonly derived from an adiabatic model,
 418 for which the temperature gradient in the outer core is given by (Poirier, 2000)

$$\frac{\partial T}{\partial z} = \frac{g\gamma_{th}}{\Phi} T \quad , \quad (7)$$

419 where T is temperature, z is depth, g is gravitational acceleration, γ_{th} is the ther-
 420 modynamic Grüneisen parameter, and Φ is the seismic parameter. We use the
 421 gravitational acceleration data from the PREM model (Dziewonski and Anderson,
 422 1981) and the seismic parameter from the AK135 global seismic model (Kennett et al.,
 423 1995). For compressed liquid iron, γ_{th} was reported as ranging between 1.56 at
 424 257 GPa and 1.47 at the ICB from shock-compression experiments (Brown and McQueen,
 425 1986) and calculated as ranging between 1.5 and 1.53 in the outer core (Alfè et al.,
 426 2002). After combining these results into an average, we use $\gamma_{th} = 1.51$ and,
 427 with *hcp*-Fe_{0.9}Ni_{0.1}’s melting point of 5500±200 K at the ICB, we obtain a tem-
 428 perature of 4000±200 K at the core side of the CMB at $z = 2891$ km, $P = 136$
 429 GPa (Fig. 9).

430 The temperature of 4000±200 K that we obtain for the core side of the
 431 CMB is slightly lower than the solidus temperature of peridotitic (4180±150

432 K, Fiquet et al. 2010) and chondritic lower mantle assemblages (4150 ± 150 K,
 433 Andraut et al. 2011) at 135 GPa (albeit in the mutual uncertainties). The ex-
 434 trapolated melting point of wüstite at $P = 136$ GPa is 3690 K (Fischer and Campbell,
 435 2010). A very low solidus temperature of an alkali-rich pyrolitic sample was re-
 436 ported to be 3570 ± 200 K at the CMB (Nomura et al., 2014). The alkalic pyro-
 437 lite starting material contains a significant amount of volatile elements (400 ppm
 438 water, ~ 0.4 wt% Na_2O and ~ 0.05 wt% K_2O) not present in other experiments
 439 (Fiquet et al., 2010; Andraut et al., 2011), and volatile elements are known
 440 to depress the solidus temperatures of mantle assemblages (Hirschmann et al.,
 441 1998; Corgne et al., 2003; Andraut et al., 2011).

442 We conduct similar calculations with the melting curve of *hcp*-Fe reported
 443 by Anzellini et al. (2013). Their melting temperature at 330 GPa is 6230 ± 500
 444 K, which corresponds to a temperature of 4560 K at the core-mantle boundary
 445 using the adiabat described above. This temperature is much higher than the
 446 solidus of peridotitic (Fiquet et al., 2010; Nomura et al., 2014) and chondritic
 447 (Andraut et al., 2011) phase assemblages at the CMB, suggesting that roughly
 448 half of the base of the mantle should be molten (Tateno et al., 2014) (Fig. 9).

449 Although the Earth’s core is mainly composed of an iron-nickel alloy, the
 450 seismologically inferred density requires the presence of light elements to balance
 451 the density deficit. Therefore, the lower bound on the temperature profile in the
 452 core depends on the species of light elements and how these elements affect the
 453 melting behavior of iron and iron-nickel alloys. Experimental and theoretical
 454 investigations suggest that light elements such as S, O, and Si alloyed with iron
 455 could depress the melting point of iron by up to 700 K at the ICB (e.g., Alfè et al.
 456 2002). If one considers a relatively extreme melting point depression of 700 K
 457 on the temperature at the ICB inferred from *hcp*- $\text{Fe}_{0.9}\text{Ni}_{0.1}$ ’s melting point of
 458 5500 K (this study), then the temperature at the ICB would be 4800 K. If the
 459 adiabat is unchanged with the addition of light elements, then the core-side
 460 CMB temperature could be as low as 3500 K (Fig. 9). Terasaki et al. (2011)
 461 measured the phase relations of a candidate core-alloy of atomic composition
 462 $\text{Fe}_{75}\text{O}_5\text{S}_{20}$ up to 157 GPa and concluded that, assuming its existence in Earth’s

core and comparing to previous studies on pure iron, the CMB temperature could be 3600 ± 200 K. We have observed that alloying about 10wt% nickel to iron could result in a melting point depression relative to pure iron of about 290 K or about 5 % at the ICB. Thus it is conceivable that the melting temperatures of light element alloys of *hcp*-Fe_{0.9}Ni_{0.1} would be further depressed than the values considered in Terasaki et al. (2011) .

One major implication of the temperature constraints considered here is the effect on phase relations at the base of the mantle. Fits to seismic waves that sample the base of the mantle suggest ultra-low velocity zones ranging from 10's to 100 km in width and height (Berryman, 2000; Ni and Helmberger, 2001; Lay et al., 2004; McNamara et al., 2010; Sun et al., 2013; Thorne et al., 2013). These features are often attributed to partial melt of lower mantle materials (Williams and Garnero, 1996; Berryman, 2000; Lay et al., 2004; Labrosse et al., 2007; Hier-Majumder, 2008). A recent dynamic compression study suggests that a peridotitic lowermost mantle rock is unlikely to produce an equilibrium partial melt that is sufficiently dense to match seismic inferences of about +5 to 14 % density anomalies (Thomas and Asimow, 2013). A similarly compelling explanation of seismic observations is solid material with low seismic velocities, such as Fe-rich (Mg,Fe)O magnesiowüstite (Wicks et al., 2010; Bower et al., 2011; Sun et al., 2013; Rost, 2013). These hypotheses could be assessed by examination of the solidus temperatures reported for candidate mantle phases and assemblages at the CMB in comparison with the temperature ranges reported for this region. The presence of partial melts at the base of the mantle is feasible if a sufficient amount of light elements would depress the solidus of silicate phase assemblages, so that the geotherm of the lowermost mantle intersects the solidus at just the right value and angle to generate a reasonable amount of melt.

490 4. Conclusion

491 The melting points of *fcc*- and *hcp*-structured $\text{Fe}_{0.9}\text{Ni}_{0.1}$ and Fe have been
492 measured up to 125 GPa. We carried out these measurements with LH-DACs us-
493 ing newly developed techniques involving synchrotron Mössbauer spectroscopy,
494 the FasTeR spectrometer, and the MINUTI software package. The SIMX mod-
495 ule in MINUTI is used to reliably fit a melting point to the observed signal. We
496 place the γ - ϵ -I triple point of Fe at 110 ± 5 GPa and 3345 ± 120 K, and the quasi
497 triple point of $\text{Fe}_{0.9}\text{Ni}_{0.1}$ at 116 ± 5 GPa and 3260 ± 120 K. With the (quasi) γ - ϵ -I
498 triple points and the thermophysical parameters of *hcp*-Fe determined from a
499 nuclear resonant inelastic X-ray scattering dataset (Murphy et al., 2011), we
500 constructed high pressure melting curves of *hcp*-structured Fe and $\text{Fe}_{0.9}\text{Ni}_{0.1}$.
501 We suggest that the upper bound of Earth’s inner-core outer-core boundary
502 temperature is given by *hcp*- $\text{Fe}_{0.9}\text{Ni}_{0.1}$ ’s melting point, rather than by pure
503 iron. With an ICB temperature of 5500 ± 200 K for *hcp*- $\text{Fe}_{0.9}\text{Ni}_{0.1}$, we use an
504 adiabatic thermal model to derive the upper bound for the temperature on the
505 core side of the CMB as 4000 ± 200 K. This temperature is lower than the solidus
506 of typical lower mantle assemblages. With the addition of light elements such
507 as a combination of sulfur, oxygen, and silicon, the core-side CMB temperature
508 could be as low as 3500 K. Therefore, given the melting curves of candidate
509 dominant core materials presented here, light element melting point depression-
510 s, and reported phase relations of volatile-free lower mantle assemblages, we find
511 that solid-state assemblages are more likely to be present at Earth’s core-mantle
512 boundary.

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