# Melting of compressed iron by monitoring atomic dynamics

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## ARTICLE INFO

## ABSTRACT

We present a novel method for detecting the solid–liquid phase boundary of compressed iron at high temperatures using synchrotron Mössbauer spectroscopy (SMS). Our approach is unique because the dynamics of the iron atoms are monitored. This process is described by the Lamb–Mössbauer factor, which is related to the mean-square displacement of the iron atoms. Focused synchrotron radiation with 1 meV bandwidth passes through a laser-heated $^{57}Fe$ sample inside a diamond-anvil cell, and the characteristic SMS time signature vanishes when melting occurs. At our highest compression measurement and considering thermal pressure, we find the melting point of iron to be $T_M = 3025 \pm 115$ K at $P = 82 \pm 5$ GPa. When compared with previously reported melting points for iron using static compression methods with different criteria for melting, our melting trend defines a steeper positive slope as a function of pressure. The obtained melting temperatures represent a significant step toward a reliable melting curve of iron at Earth's core conditions. For other terrestrial planets possessing cores with liquid portions rich in metallic iron, such as Mercury and Mars, the higher melting temperatures for compressed iron may imply warmer internal temperatures.

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## 1. Introduction

Seismological and cosmochemical observations indicate that Earth's core consists of a solid inner region surrounded by a liquid outer core, with iron as the main constituent, e.g., (Lehmann, 1936; McDonough and Sun, 1995; Stixrude et al., 1997; McDonough, 2003). The melting temperature of iron at high-pressure provides an important reference point for the temperature distribution within Earth's core and affects a number of important geophysical quantities related to this region: heat flow across the core–mantle boundary (CMB), the temperature gradient within the thermal boundary layer above the CMB, phase relations, and expected wave speeds of candidate phases (e.g., Anderson, 1990; Lay et al., 2008; Hemley and Mao, 2001). More specifically, the melting point of iron at the boundary between the liquid outer core and solid inner core (ICB) provides an upper bound of the temperature at that interface, because studies thus far indicate that all plausible outer core liquids coexist with corresponding inner core alloy solids at or below the melting point of pure iron (e.g., Boehler, 1992; Fei et al., 1995, 1997;

Alfè et al., 2002a; Stewart et al., 2007; Chen et al., 2008; Andrault et al., 2009; Asanuma et al., 2010; Terasaki et al., 2011, and references therein). The melting temperature of iron at high-pressure provides a similarly important reference point for temperature distributions within the cores of other terrestrial planets, such as Mercury and Mars, whose cores are thought to be at least partially molten (e.g., Stevenson, 2001; Fei and Bertka, 2005; Margot et al., 2007; Smith et al., 2012).

Studies of the melting curve of highly compressed iron have been performed dynamically in shock-compression experiments (Brown and McQueen, 1986; Bass et al., 1987; Yoo et al., 1993; Ahrens et al., 2002; Nguyen and Holmes, 2004), statically in diamond-anvil cell experiments, and in calculations (Alfè et al., 1999, 2002b; Laio et al., 2000; Alfè, 2009; Sola and Alfè, 2009). Melting of iron in diamond-anvil cells was achieved by resistive heating monitored by the resistance–temperature curves of the heated wire (Boehler, 1986; Mao et al., 1987), and by laser heating combined with either visual observations (Williams et al., 1987; Boehler, 1993) or with synchrotron x-ray diffraction analysis (Shen et al., 1998; Ma et al., 2004; Boehler et al., 2008). At the ICB, reported melting temperatures of iron range from 4900 to 7600 K. Recently, an internally consistent thermodynamic database was presented for iron up to 360 GPa and 7000 K (Komabayashi and Fei, 2010), based on a newly reported phase

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boundary between the face-centered cubic (fcc or $\gamma$) and hexagonal close-packed (hcp or $\epsilon$) structures (Komabayashi et al., 2009) and existing thermochemical measurements. However, the complete data set of melting observations does not reflect a consensus on the melting curve of iron (see Komabayashi and Fei, 2010, for a recent review).

Here we present a new approach for detecting the melting point of compressed iron using the physical principle of recoilless absorption of x-rays by nuclear resonances (Mössbauer, 1958)—the basis of both conventional Mössbauer spectroscopy and synchrotron Mössbauer spectroscopy (SMS). In these techniques, the observed signal strength is sensitively related to the thermal motion of the resonant nuclei, $^{57}$Fe in our case. This phenomenon is quantitatively described by the Lamb–Mössbauer factor, $f$, which is known to vanish when melting occurs. In this study, we show that the solid–liquid phase boundary of compressed iron can readily be monitored by the disappearance of the SMS signal upon melting. The obtained melting temperatures represent a significant step toward a reliable melting curve of iron at Earth's core conditions. Furthermore, with iron being a dominant component of candidate alloys in Earth's core and a main constituent in the mineralogy of Earth's mantle, this method should provide a unique complement to existing methods for the determination of melting curves of iron-bearing phases under high-pressure conditions.

## 2. Methods

### 2.1. Melt detection using Mössbauer spectroscopy

The physical principles of synchrotron Mössbauer spectroscopy (SMS) have been studied previously in great detail (e.g., Sturhahn, 2004, and references therein). The observed time-delayed signal is caused by the coherent elastic scattering of synchrotron x-rays while traversing a sample containing $^{57}$Fe or a similar resonant isotope. The emission of the SMS signal occurs into the direction of the incident x-rays, the forward direction, and is therefore independent of the spatial configuration of atoms. The strength of the SMS signal is primarily determined by the "effective thickness" of the sample traversed by the x-rays. The effective thickness, $\eta$, is a dimensionless number given as the product of the numerical density of the $^{57}$Fe nuclei, $\rho$, the physical thickness of the sample, $d$, the nuclear resonant cross-section, $\sigma = 2.56 \times 10^{-22}$ m$^2$, and the dimensionless Lamb–Mössbauer factor $f$

$$\eta = f\sigma\rho d. \tag{1}$$

The relation between SMS intensity and effective thickness is complex but can be numerically calculated in every detail (Sturhahn, 2000). Here our strategy is to determine all relevant parameters that influence the SMS signal strength with the exception of the Lamb–Mössbauer factor.

Typical values for the Lamb–Mössbauer factor for solids at room-temperature range from 0.05 to 0.9 (Sturhahn and Chumakov, 1999). A value of $0.796 \pm 0.002$ has been reported for body-centered cubic (bcc or $\alpha$) iron at ambient conditions (Toellner et al., 1997), and an increase with pressure is commonly observed (Murphy et al., 2011b; Mao et al., 2001; Giefers et al., 2002). With increasing temperature, $f$ typically decreases (Sturhahn and Chumakov, 1999; Bergmann et al., 1994; Shen et al., 2004). However at the solid–liquid phase transition a discontinuous drop to zero has been observed for tin metal at ambient pressure (Boyle et al., 1961). Mechanisms for this abrupt change in $f$ upon melting have been discussed (Singwi and Sjölander, 1960), and may be best understood by expressing the

Lamb–Mössbauer factor as $f = \exp[-k^2 \langle u^2 \rangle]$, where $k$ is the wave number of the resonant x-rays and $\langle u^2 \rangle$ is the mean-square displacement of the nuclear resonant atoms. In this expression, it is implicitly assumed that the time scale for the positional averaging is determined by the lifetime of the nuclear state excited in the SMS scattering process. For example, the lifetime and the energy of the first excited state for $^{57}$Fe are 141 ns and 14.4 keV, respectively. If the iron atoms stray from their equilibrium positions much farther than $1/k = 0.14$ Å during the nuclear lifetime, the value of $f$ becomes exponentially small. This rarely happens for solids, but in the liquid state atoms are very mobile and move 10's of Å during 100 ns. For all practical purposes, the Lamb–Mössbauer factor therefore becomes zero for liquids leading to zero effective thickness and a collapse of the SMS signal.

The disappearance of the SMS signal is strictly based on the dynamical behavior of the atoms in a time window comparable to the nuclear lifetime. The spatial arrangement of the atoms such as crystalline order is not relevant for the collapse of the SMS signal. This is in clear contrast to the common application of x-ray diffraction techniques to determine melting. In x-ray diffraction, the x-ray scattering process is non-resonant and extremely fast, i.e., of the order of $10^{-19}$ s, and atomic motions become irrelevant. An x-ray diffraction pattern represents a series of snapshots of atomic positions. Each snapshot clearly reflects the spatial order of the sample. In this situation, the disappearance of features such as diffraction lines and the appearance of diffuse scattering upon melting are caused by the loss of long-range order not by a change in atomic mobility.

In the method we present here, we observe the time-integrated SMS signal $I(\eta)$ which can be expressed in terms of the theoretical time spectrum appropriate for the sample $S(t,\eta)$

$$I(\eta) = Ae^{-\mu d} \sum_{n=0}^{\infty} \int_{t_1 + nt_B}^{t_2 + nt_B} S(t',\eta) \, dt'. \tag{2}$$

Here $t_1$ and $t_2$ are the beginning and end of the time window accessible in the experiment, $t_B$ is the time between x-ray pulses ($n$) given by the synchrotron operation mode (where $n=0$ refers to the most recent x-ray pulse), $A$ is a scaling factor that depends on experimental conditions such as x-ray spectral flux incident on the sample, $d$ is the physical thickness of the sample, and $\mu$ is the electronic absorption coefficient of the sample material. The analysis of measured data reduces to an inversion problem with respect to the effective thickness, $\eta$. An important input to the required modeling is the shape of $S(t,\eta)$ which depends on the level splitting of the resonant nuclei. For fcc and hcp phases of iron, it is well known that the nuclear levels of $^{57}$Fe are unsplit. Then the time spectrum is given as

$$S(t,\eta) = \eta^2 \, e^{-t/\tau} \frac{J_1^2(x)}{x^2} \quad \text{with } x = \sqrt{\eta t/\tau}, \tag{3}$$

where $J_1$ is the first-order Bessel function of the first kind and $\tau$ is the lifetime of the excited nuclear state (Kagan et al., 1979). The linear behavior of the Bessel function for small arguments, $J_1(x) \approx x/2$, is followed by a regime of aperiodic oscillations and eventually by the asymptotic form for large arguments, $J_1(x) \approx (\sin x - \cos x)/\sqrt{\pi x}$. In our data analysis, we numerically solve the integration in (2) with the shape of the time spectrum given by (3) for a series of reasonable effective thickness values using the CONUSS software (Sturhahn, 2000). The effect of electronic attenuation, the exponential in (2), is important if the thickness of the sample changes during the heating cycle. Otherwise, it may be assimilated into the scaling factor. In all successful melting experiments, a continuous decrease in thickness was observed over the duration of the heating cycle ($\sim 0.25$ μm/min, with a starting sample thickness of typically 9 μm and cycle