Grüneisen parameter of hcp-Fe to 171 GPa

Caitlin A. Murphy, Jennifer M. Jackson, Wolfgang Sturhahn, and Bin Chen

Received 2 September 2011; revised 3 November 2011; accepted 6 November 2011; published 20 December 2011.

[1] We measured the phonon density of states (DOS) of hexagonal close-packed iron (\(\varepsilon\)-Fe) with high statistical quality using nuclear resonant inelastic X-ray scattering and in situ X-ray diffraction experiments between pressures of 30 GPa and 171 GPa and at 300 K, with a neon pressure medium up to 69 GPa. The shape of the phonon DOS remained similar at all compression points, while the maximum (cutoff) energy increased regularly with decreasing volume. As a result, we present a generalized scaling law to describe the volume dependence of \(\varepsilon\)-Fe’s total phonon DOS which, in turn, is directly related to the ambient temperature vibrational Grüneisen parameter (\(\gamma_{\text{vib}}\)). Fitting our individual \(\gamma_{\text{vib}}\) data points with \(\gamma_{\text{vib}} = \gamma_{\text{vib,0}}(V/V_0)^\eta\), a common parameterization, we found an ambient pressure \(\gamma_{\text{vib,0}} = 2.0 \pm 0.1\) for the range \(g = 0.8\) to 1.2. We also determined the Debye sound velocity (\(\nu_D\)) from the low-energy region of the phonon DOS and our in situ measured volumes, and used the volume dependence of \(\nu_D\) to determine the commonly discussed Debye Grüneisen parameter (\(\gamma_D\)). Comparing our \(\gamma_{\text{vib}}(V)\) and \(\gamma_D(V)\), we found \(\gamma_{\text{vib}}\) to be \(\sim 10\%\) larger than \(\gamma_D\) at any given volume. Finally, applying our \(\gamma_{\text{vib}}(V)\) to a Mie–Grüneisen type relationship and an approximate form of the empirical Lindemann melting criterion, we predict the vibrational thermal pressure and estimate the high-pressure melting behavior of \(\varepsilon\)-Fe at Earth’s core pressures. Citation: Murphy, C. A., J. M. Jackson, W. Sturhahn, and B. Chen (2011), Grüneisen parameter of hcp-Fe to 171 GPa, Geophys. Res. Lett., 38, L24306, doi:10.1029/2011GL049531.

1. Introduction

[2] Iron is thought to be the main constituent in the Earth’s core [McDonough, 2003], and existing data suggest that hexagonal close-packed iron (\(\varepsilon\)-Fe) is the stable phase at core conditions [Alfè et al., 2001; Ma et al., 2004; Dewaele et al., 2006; Tateno et al., 2010]. Therefore, the accurate determination of \(\varepsilon\)-Fe’s thermophysical properties is of fundamental importance for studies of the deep Earth. For example, accurate measurements of \(\varepsilon\)-Fe’s thermodynamic Grüneisen parameter (\(\gamma_{\text{th}}\)) would aid in the determination of its high-pressure thermal equation of state, because \(\gamma_{\text{th}}\) is the coefficient that relates thermal pressure to thermal

energy per unit volume. In addition, \(\gamma_{\text{th}}\) is used to reduce shock-compression data to isothermal data and to calculate adiabatic gradients [Poirier, 2000], both of which are important applications for furthering our understanding of Earth’s core.

[3] The thermodynamic Grüneisen parameter is made up of electronic and vibrational components, the latter of which is directly related to the volume dependence of the phonon density of states (DOS). The vibrational Grüneisen parameter (\(\gamma_{\text{vib}}\)) of \(\varepsilon\)-Fe is particularly important because it is used to extrapolate available melting data to the inner core boundary, where Earth’s solid inner core and liquid outer core are in contact. However, reported values of \(\gamma_{\text{vib}}\) are not in complete agreement [Jeanloz, 1979; Brown and McQueen, 1986; Dubrovinsky et al., 2000; Lübers et al., 2000; Alfè et al., 2001; Anderson et al., 2001a, 2001b; Ahrens et al., 2002; Giefers et al., 2002; Dewaele et al., 2006], and are often based on indirect or approximate determinations. As a result, uncertainty and confusion surround \(\gamma_{\text{vib}}\) and a wide range of extrapolated melting temperatures have been reported.

[4] An approximate form of \(\gamma_{\text{vib}}\) is the Debye Grüneisen parameter (\(\gamma_D\)), which is based on Debye’s approximation that the entire phonon DOS can be described by its low-energy region, where the dispersion relation is linear. In past studies, \(\gamma_D\) has been approximated from X-ray diffraction experiments via the Rietveld structural refinement method. From this refinement, one obtains an approximate mean-square atomic displacement and in turn, the Debye temperature, which is related to \(\gamma_D\) [Dubrovinsky et al., 2000; Anderson et al., 2001a, 2001b]. In addition, researchers have approximated \(\gamma_D\) from adiabatic decompression experiments via a thermodynamic relationship that relates \(\gamma\) and \((\partial T/\partial P)_S\) [Boehler and Ramakrishnan, 1980].

[5] Here we determine \(\gamma_{\text{vib}}(V)\) from the total phonon DOS, which we measured at eleven compression points between pressures of 30 GPa and 171 GPa using nuclear resonant inelastic X-ray scattering (NRIXS) and in situ X-ray diffraction (XRD) experiments [Sturhahn et al., 1995]. In addition, we determine \(\gamma_D(V)\) for \(\varepsilon\)-Fe from the volume dependence of its Debye sound velocity, which we obtain from the low-energy region of the phonon DOS [Sturhahn and Jackson, 2007]. Our long NRIXS data-collection times and high-energy resolution produced the high statistical quality that is necessary to derive \(\gamma_{\text{vib}}\) and \(\gamma_D\).

2. Experimental Procedure

[6] We prepared three modified panoramic diamond-anvil cells (DACs) with 90° openings on the downstream side and beveled anvils with flat culet diameters of 250 \(\mu\)m or 150 \(\mu\)m. A piece of 10 \(\mu\)m thick 95% enriched \(^{57}\)Fe foil was loaded into beryllium gaskets with boron epoxy inserts, and a neon
The present analysis is performed \( C_1 = 5.57 \pm 0.02 \text{ cm}^{-1} \) and \( C_2 = 171 \pm 11 \text{ GPa} \). We note that results from in Situ E is Boltzmann and Experimental Results From NRIXS and 30(2) 2.62(2) 43.9(5) 4.36(3) E is energy to the vibrational thermal pressure XRD – measured volumes. To present our results on a 1 151(9) 2.30(2) 49.1(6) 5.72(10) 1 121(8) 2.36(2) 48.2(4) 5.33(4) V 69(4) 2.49(2) 46.0(5) 4.80(4) ð 106(6) 2.40(2) 47.5(4) 5.23(3) (GPa) d = 5.15 ± 0.02 cm E [2011] with the k √ C24 = 5.15 ± 0.02 cm “ 133(8) 2.33(2) 48.6(5) 5.47(5) b Sturhahn (k = 5.15 ± 0.02 cm “) 33 GPa). For details of our DAC preparation, experi-

Table 1. Experimental Results From NRIXS and in Situ XRD Measurements of \( \varepsilon \)-Fe

<table>
<thead>
<tr>
<th>Volume (V)</th>
<th>Pressure (P)</th>
<th>C_vib (k_B/atom)</th>
<th>U_vib (meV/atom)</th>
<th>V_0 (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.92(2)^a</td>
<td>30(2)</td>
<td>2.62(2)</td>
<td>43.9(5)</td>
<td>4.36(3)</td>
</tr>
<tr>
<td>5.81(1)^a</td>
<td>36(2)</td>
<td>2.60(4)</td>
<td>44.3(9)</td>
<td>4.37(6)</td>
</tr>
<tr>
<td>5.56(1)^a</td>
<td>53(3)</td>
<td>2.54(3)</td>
<td>45.2(6)</td>
<td>4.57(4)</td>
</tr>
<tr>
<td>5.36(1)^a</td>
<td>69(4)</td>
<td>2.49(2)</td>
<td>46.0(5)</td>
<td>4.80(4)</td>
</tr>
<tr>
<td>5.27(2)</td>
<td>77(5)</td>
<td>2.47(2)</td>
<td>46.3(5)</td>
<td>4.93(3)</td>
</tr>
<tr>
<td>5.15(2)</td>
<td>90(5)</td>
<td>2.44(2)</td>
<td>46.8(6)</td>
<td>5.13(3)</td>
</tr>
<tr>
<td>5.00(2)^a</td>
<td>106(6)</td>
<td>2.40(2)</td>
<td>47.5(4)</td>
<td>5.23(3)</td>
</tr>
<tr>
<td>4.80(2)^a</td>
<td>121(8)</td>
<td>2.36(2)</td>
<td>48.2(4)</td>
<td>5.33(4)</td>
</tr>
<tr>
<td>4.81(2)^a</td>
<td>133(8)</td>
<td>2.33(2)</td>
<td>48.6(5)</td>
<td>5.47(5)</td>
</tr>
<tr>
<td>4.70(2)^a</td>
<td>151(9)</td>
<td>2.30(2)</td>
<td>49.1(6)</td>
<td>5.72(10)</td>
</tr>
<tr>
<td>4.58(2)^a</td>
<td>171(11)</td>
<td>2.25(3)</td>
<td>50.0(9)</td>
<td>5.64(7)</td>
</tr>
</tbody>
</table>

\( ^a \)Volume (V) was measured with in situ XRD and converted to pressure (P) using the Vinet EOS [Dewaele et al., 2006]; the vibrational specific heat capacity (C_vib) and vibrational energy (U_vib) per \( ^{57} \text{Fe} \) atom were determined from the integrated phonon DOS (equations (1) and (2)); and the Debye sound velocity (v_D) was obtained using the low-energy region of the measured phonon DOS and our in situ measured volumes, and accounts for \( ^{57} \text{Fe} \) enrichment levels. Values in parentheses give uncertainties for the last significant digit(s). Reported uncertainties for Dewaele et al.’s [2006] EOS parameters account for ~75% to 90% of the total pressure uncertainties.

\( ^b \)For these measurements, neon was loaded as the pressure transmitting medium.

\( ^c \)Texturing was observed at these compression points in the form of a loss of intensity in the (002) diffraction peak.

Pressure transmitting medium was loaded for measurements made at atomic volumes of \( \varepsilon \)-Fe greater than 5.27 cm\(^3\)/mol (\( P \leq 69 \text{ GPa} \)). For details of our DAC preparation, experimental procedures, and data analysis, see auxiliary material or Murphy et al. [2011].\(^1\) The present analysis is performed on the dataset presented by Murphy et al. [2011], in addition to a recently acquired higher-pressure point (\( V = 4.58 \pm 0.02 \text{ cm}^3/\text{mol}, P = 171 \pm 11 \text{ GPa} \)). We note that results from the analysis presented by Murphy et al. [2011] with the addition of this new largest compression point agree with the original results within uncertainty.

\( ^1 \)From our in situ XRD experiments, we obtained the atomic volume (V) of our sample at each of our eleven compression points. To derive \( \gamma_{vib} \) and \( \gamma_D \), we rely on these in situ measured volumes. To present our results on a common scale and for discussion, we convert our measured volumes to pressures using the Vinet equation of state (EOS) [Dewaele et al., 2006] (Table 1).

\( ^2 \)From our NRIXS experiments, we obtained \( \varepsilon \)-Fe’s total phonon DOS, D(E, V) [Sturhahn, 2000; Sturhahn and Jackson, 2007], from which we directly determined two parameters that relate \( \gamma_{vib} \) to the vibrational thermal pressure via a Mie-Grüneisen type relationship. The vibrational component of the specific heat capacity per \( ^{57} \text{Fe} \) atom (C_vib) is given by

\[ C_vib(V) = k_B \int \left( \frac{\beta E}{2 \sinh(\beta E/2)} \right)^2 D(E, V) dE, \]  \( ^{2} \) and the vibrational energy per \( ^{57} \text{Fe} \) atom (U_vib) is given by

\[ U_vib(V) = \frac{1}{2} \int E \coth\left( \frac{\beta E}{2} \right) D(E, V) dE \] (2)

\( ^{3} \)Qualitative inspection of our data reveals that our phonon DOS are similar in shape at all compression points, and that any pair of phonon DOS appears to be related by a single overall scaling parameter. This suggestion can be evaluated in Figure 1, where we plot our measured phonon DOS at each compression point in black, along with the phonon DOS at \( V_1 = 5.15 \pm 0.02 \text{ cm}^3/\text{mol} (P = 90 \pm 5 \text{ GPa}) \) that has been scaled using

\[ D(E, V) = \xi(V/V_1) \cdot D(\xi(V/V_1), E, V_1) \] (3)

and the appropriate scaling parameter (\( \xi \)) for each pair of phonon DOS in green. We note that \( \xi \) is energy-independent and \( \xi(1) = 1 \).

\( ^{10} \)To determine the appropriate scaling parameter for each pair of phonon DOS, we assign one spectrum to be an initial reference phonon DOS, D(E, V_1), to which we apply equation (3). We then minimize the least-squares difference between this scaled reference phonon DOS and each of the other ten unscaled phonon DOS, D(E, V_j) (Figure 1). This process is repeated with each phonon DOS serving as the reference, resulting in eleven datasets that each contain ten data points. To incorporate our entire scaling parameter

![Figure 1](image-url)

Figure 1. Comparison of measured and scaled phonon DOS of \( \varepsilon \)-Fe. Black open circles show the measured phonon DOS at each compression point with uncertainties; green curves show the phonon DOS at \( V_1 = 5.15 \pm 0.02 \text{ cm}^3/\text{mol} (P = 90 \pm 5 \text{ GPa}) \), scaled to each other measured phonon DOS using equation (3) and the appropriate scaling parameter for each pair of phonon DOS, following the procedure described in section 3.

1Auxiliary materials are available in the HTML. doi:10.1029/2011GL049531.
V = 5.15 cm$^3$/mol

$V_i = 5.15 \pm 0.02$ cm$^3$/mol ($P = 90 \pm 5$ GPa). All scaling analysis data have been included, following equation (4).

Analysis into each dataset, we then rescale all of our data to each reference volume ($V_i$) by

$$\xi\left(\frac{V_k}{V_i}\right) = \xi\left(\frac{V_k}{V_r}\right) \cdot \xi\left(\frac{V_r}{V_i}\right).$$

[11] In Figure 2, we show the result of this scaling analysis for an example reference phonon DOS: ($V_i/V_k$) for $V_i = 5.15 \pm 0.02$ cm$^3$/mol. Given the smooth trend and small errors, we find that a generalized scaling law successfully describes the volume dependence of $\varepsilon$-Fe’s phonon DOS. We note that a similar analysis was previously performed by Alfè et al. [2001], who investigated the volume dependence of dispersion curves for $\varepsilon$-Fe using ab initio density-functional theory (DFT) calculations. Alfè et al. [2001] reported $\xi(1244) = 1.409$ for $V_i = 4.20$ cm$^3$/mol, which agrees fairly well with the value predicted by extrapolating our results to the same volume ratio. However, this comparison is largely qualitative because Alfè et al.’s [2001] scaling parameter was determined for dispersion curves calculated at $T = 4000$ K, and $V_i = 4.20$ cm$^3$/mol is beyond the compression range of our measurements.

[12] Finally, we derive an expression for the relationship between $\gamma_{vib}$ and the volume dependence of the scaling parameter, $\xi(V/V_i)$, by combining the commonly used parameterization

$$\gamma_{vib} = \gamma_{vib,i}\left(\frac{V}{V_i}\right)^q,$$

with the definition of the vibrational Grüneisen parameter

$$\gamma_{vib} = g \frac{\partial \ln \xi(V/V_i)}{\partial \ln V_i},$$

where $\gamma_{vib,i}$ and $V_i$ are the vibrational Grüneisen parameter and volume at a reference compression, and $q$ is a fitting parameter. Substituting equation (5) into equation (6) and integrating, we obtain

$$\xi\left(\frac{V}{V_i}\right) = \xi\left(\frac{V}{V_r}\right) \cdot \xi\left(\frac{V_r}{V_i}\right) \cdot \left\{ -\frac{\gamma_{vib,i}}{q} \left[ \left(\frac{V}{V_i}\right)^q - 1 \right] \right\}$$

when $q \neq 0$. At the reference compression, $V = V_i$ and $\xi = \xi(1) = 1$, so equation (7) simplifies to

$$\xi\left(\frac{V}{V_i}\right) = \exp\left\{ -\frac{\gamma_{vib,i}}{q} \right\} \exp\left\{ \gamma_{vib,i}\left(\frac{V_r}{V_i}\right)^q \right\}. \quad (8)$$

[13] Fitting each of our eleven ($\xi(V_i/V_k)$) datasets with equation (8) and allowing both $\gamma_{vib,i}$ and $q$ to vary freely, we found large uncertainties in $q$, with the most tightly constrained fit being $q(5.15 \text{ cm}^3/\text{mol}) = 0.8 \pm 0.7$. Therefore, we re-performed the fits with $q$ fixed to one of three assigned values: first, $q(5.15 \text{ cm}^3/\text{mol}) = 0.8$; second, the commonly assumed $q = 1$; and third, $q = 1.2$. Finally, we fit the resulting three sets of $\gamma_{vib}(V_i)$ with equation (5) and obtained ambient pressure $\gamma_{vib,0} = 1.88 \pm 0.02$ for $q = 0.8$; $\gamma_{vib,0} = 1.98 \pm 0.02$ for $q = 1.0$, and $\gamma_{vib,0} = 2.08 \pm 0.02$ for $q = 1.2$. These results can be combined and presented as $\gamma_{vib,0} = 2.0 \pm 0.1$, where we assign the error to reflect fitting parameter uncertainties and the range associated with our fixed $q$ values.

4. Debye Grüneisen Parameter

[14] The low-energy region of a material’s phonon DOS is related to its Debye sound velocity ($v_D$), provided it is parabolic (“Debye-like”). We determined $v_D$ for $\varepsilon$-Fe at each of our eleven compression points (Table 1) by using an exact relation for the dispersion of low-energy acoustic phonons with our in situ measured volumes, and determining the best energy range to use for this fit [see Sturhahn and Jackson, 2007, equation 9]. The large compression range and high statistical quality of our data allow us to calculate a very accurate $v_D(V_i)$, which is related to $\gamma_D$ by

$$\gamma_D = 1 - \frac{V}{v_D} \frac{\partial v_D}{\partial V}.$$

[15] Combining equations (9) and (5) and integrating, we obtain the expression

$$v_D = v_{D,0}\left(\frac{V}{V_i}\right)^{1/3} \exp\left\{ -\frac{\gamma_{D,0}}{q} \left[ \left(\frac{V}{V_i}\right)^q - 1 \right] \right\}, \quad (10)$$

which depends on the ambient pressure Debye sound velocity ($v_{D,0}$), Debye Grüneisen parameter ($\gamma_{D,0}$), and volume ($V_0$) [Dewaele et al., 2006], and the fitting parameter $q$ [Sturhahn and Jackson, 2007]. Therefore, to determine $\gamma_D(V_i)$, we fit our $v_D(V)$ with equation (10), fixing $q$ as in section 3, and found $\gamma_{D,0} = 1.70 \pm 0.07$ and $v_{D,0} = 3.66 \pm 0.06$ km/s for $q = 0.8$; $\gamma_{D,0} = 1.78 \pm 0.07$ and $v_{D,0} = 3.63 \pm 0.06$ km/s for $q = 1.0$, and $\gamma_{D,0} = 1.87 \pm 0.08$ and $v_{D,0} = 3.60 \pm 0.06$ km/s for $q = 1.2$. Combining these results as in section 3, we find $\gamma_{D,0} = 1.8 \pm 0.1$ and $v_{D,0} = 3.63 \pm 0.09$ km/s.

5. Discussion

[16] A generalized scaling law describes the volume dependence of $\varepsilon$-Fe’s phonon DOS fairly well. However,
it is important to note that the relative intensity of the middle vibrational mode decreases with respect to the low- and high-energy vibrational modes with compression (Figure 1). This slight deviation from perfectly generalized scaling could contribute to the poorly constrained nature of \( q \), which is the parameter that controls the rate at which \( \gamma_{vib} \) and \( \gamma_D \) decrease with decreasing volume.

17 Our \( \gamma_{vib,i} \) and \( \gamma_D \) at each compression point are listed in Table S1 in the auxiliary material, and are plotted with their fitted curves in Figure 3. We find that \( \gamma_{vib} \) is systematically \( \sim 10\% \) larger than \( \gamma_D \), which may be explained in part by the fact that \( \gamma_{vib} \) is derived from the entire phonon DOS, while \( \gamma_D \) depends only on the acoustic regime (i.e., the low-energy region). There is not enough information to determine whether this discrepancy is related to sample texturing, which we observed in our five largest compression points.

18 Our \( \gamma_{vib} \) for \( q = 0.8 \) agree fairly well with Anderson et al.’s [2001a, 2001b] \( \gamma_{vib} \), determined from intensity changes in static-compression XRD lines with compression. In addition, the slope for \( q = 0.8 \) agrees fairly well with that of Dewaele et al.’s [2006] \( \gamma_D \), which was determined from a combination of previously reported shock-compression data, an assumed volume dependence of \( \gamma \), and their static-compression XRD experiments. However, Dewaele et al.’s [2006] \( \gamma_D \) is \( \sim 10\% \) larger than our \( \gamma_D \). Finally, two previous NRIXS experiments on \( \varepsilon \)-Fe reported volume-independent \( \gamma_D \) up to 42 GPa; our \( \gamma_D \) agree well with Giefers et al.’s [2002] \( \gamma_D \), but are significantly lower than Lübbers et al.’s [2000] \( \gamma_D \) (Figure 3).

19 Although \( \gamma_{vib} \) is only one component of the total \( \gamma \), we compare our results with reported values for \( \varepsilon \)-Fe’s \( \gamma_{vib} \). Merkel et al. [2000] used Raman spectroscopy experiments to determine \( \gamma_{vib} = 1.68 \pm 0.2 \) for \( q = 0.7 \pm 0.5 \), which is very similar to our \( \gamma_D \) for \( q = 0.8 \). Sha and Cohen [2010] performed DFT calculations to find \( \gamma_{vib} \) for nonmagnetic \( \varepsilon \)-Fe at 500 K. Their result agrees fairly well with our high-pressure \( \gamma_{vib} \), but has a steeper slope than our fitted curves, possibly due to different EOS parameters (Figure 3). Finally, Brown and McQueen [1986] found \( \gamma = 1.56 \) at a density of 12.54 g/cm³ using shock-compression experiments, which is larger than our predicted value at the same density (\( \sim 1.3 \)). However, we note that the Brown and McQueen [1986] data point is for liquid iron, whereas our results are for solid \( \varepsilon \)-Fe at 300 K.

20 To explore the geophysical applications of \( \gamma_{vib} \), we first investigate the volume-dependent vibrational thermal pressure \( (P_{vib}) \) of \( \varepsilon \)-Fe by applying our \( \gamma_{vib} \) to a Mie-Grüneisen type relationship:

\[
P_{vib} = \left( \frac{C_{vib} \gamma_{vib}}{C_{vib} + C_{el}} \right) \frac{U_{vib}}{V^3}.
\]

\( C_{vib} \) and \( U_{vib} \) are obtained from our measurements (equations (1) and (2)), and we use approximate values for the electronic component of the specific heat capacity \( (C_{el}) \) from Alfé et al. [2001]. Applying these values and our \( \gamma_{vib} \) to equation (11), we find \( P_{vib}(300 \text{ K}) = 2.39 \pm 0.08 \text{ GPa} \) and \( 2.75 \pm 0.1 \text{ GPa} \) at our smallest (30 GPa) and largest (171 GPa) compression points, respectively. Reported errors account for the previously mentioned uncertainties in \( \gamma_{vib} \) and our measured uncertainties in \( V, C_{vib}, \) and \( U_{vib} \). These values agree very well with our \( P_{vib} \) calculated directly from the integrated phonon DOS [Murphy et al., 2011], which were \( 2.31 \pm 0.06 \text{ GPa} \) and \( 2.74 \pm 0.06 \text{ GPa} \) at our smallest and largest compression points. Finally, accounting for electronic and anharmonic contributions at high-temperatures following Murphy et al. [2011], we find the total thermal pressure \( (P_{th}) \) of \( \varepsilon \)-Fe at our new, largest compression point \( (V' = 4.58 \text{ cm}^3/\text{mol}) \) to be \( P_{th}(2000 \text{ K}) = 16 \text{ GPa}, P_{th}(4000 \text{ K}) = 37 \text{ GPa}, \) and \( P_{th}(5600 \text{ K}) = 56 \text{ GPa}. \)

21 Next, we use our \( \gamma_{vib} \) to estimate the high-pressure melting behavior of \( \varepsilon \)-Fe by applying it to a commonly used, approximate form of the empirical Lindemann melting criterion

\[
T_m(V) = T_m^{\text{ref}} \left( \frac{V}{V_m^{\text{ref}}} \right)^{2/3} \exp \left\{ \frac{2 \gamma_{vib} q}{q \left[ 1 - \left( \frac{V}{V_m^{\text{ref}}} \right)^q \right]} \right\}.
\]

where \( T_m^{\text{ref}}, V_m^{\text{ref}}, \) and \( \gamma_{vib} \) are the melting temperature, volume, and vibrational Grüneisen parameter at a reference melting point. We take the melting point measured by Ma et al. [2004] using laser-heated synchrotron X-ray diffraction experiments as the reference: \( T_m^{\text{ref}} = 3510 \pm 100 \text{ K} \) at \( P_{300 \text{ K}} = 105 \text{ GPa}, \) or \( T_m^{\text{ref}} = 5.01 \text{ cm}^3/\text{mol} \) using the Vinet EOS [Dewaele et al., 2006]. From equation (5) and our results in section 3, we find \( \gamma_{vib} = 1.47 \pm 0.1 \). Applying these reference point values to equation (12), we estimate \( T_m(4.70 \text{ cm}^3/\text{mol}) = 4100 \pm 100 \text{ K} \) and \( T_m(4.58 \text{ cm}^3/\text{mol}) = 4300 \pm 100 \text{ K} \) for \( \varepsilon \)-Fe. We note that replacing \( \gamma_{vib}^{\text{ref}} \) with \( \gamma_{vib} \) results in melting temperatures that are \( \sim 3\% \) smaller at these compressions.
Finally, we account for thermal pressure at the melting temperatures of our two largest compression points following Murphy et al. [2011], which gives 40 GPa and 40 GPa, respectively. Applying the corresponding thermal pressure correction assuming constant volume, we find T_m(186 GPa) = 4100 ± 100 K and T_m(208 GPa) = 4300 ± 100 K. These estimated melting points agree very well with our previously reported high-pressure melting behavior of ε-Fe, determined from the mean-square displacement of 182 Fe atoms which we obtained directly from the integrated phonon DOS [Murphy et al., 2011].

Acknowledgments. We would like to thank D. Zhang, H. Yavas, and J.K. Wicks for assistance during the experiments, and NSF-CAREER-0956166 and Caltech for support of this research. We thank two anonymous reviewers for their comments that helped improve our manuscript. Use of the Advanced Photon Source was supported by the U.S. D.O.E., O.S., O.B.E.S. (DE-AC02-06CH11357). Sector 3 operations and the GSE-CARS gas-loading facility are supported in part by COMPRES (NSF EAR 06-49658). The Editor thanks two anonymous reviewers for their assistance in evaluating this paper.

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