Raman Spectroscopy of Iron to 152 Gigapascals: Implications for Earth’s Inner Core

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Raman spectra of hexagonal close-packed iron (\(\ce{Fe}\)) have been measured from 15 to 152 gigapascals by using diamond-anvil cells with ultrapure synthetic diamond anvils. The results give a Grüneisen parameter \(\gamma_0 = 1.68 (\pm 0.20)\) and \(q = 0.7 (\pm 0.1)\). Phenomenological modeling shows that the Raman-active mode can be approximated correlated with an acoustic phonon and thus provides direct information about the high-pressure elastic properties of iron, which have been controversial. In particular, the \(C_{44}\) elastic modulus is found to be lower than previous determinations. This leads to changes of about 35% at core pressures for shear wave anisotropies.

Understanding recent geophysical observations of elastic anisotropy, possible superposition, and magnetism of Earth’s inner core (1) requires detailed information about the thermodynamic and elastic properties of core-forming materials under appropriate conditions. High-pressure properties of iron are crucial in this respect because the core is composed primarily of this element. Iron transforms from the body-centered cubic (bcc) phase (\(\alpha\text{-Fe}\)) at ambient conditions to a face-centered cubic (fcc) phase (\(\gamma\text{-Fe}\)) at moderate pressures and temperatures and to a higher-pressure hexagonal close-packed (hcp) phase (\(\varepsilon\text{-Fe}\)) \(\geq 13\) GPa (2). The hcp phase has a wide stability field to more than 300 GPa and high temperatures (3–5). Techniques to measure lattice strains at megabar pressures (6) have determined the elastic properties of \(\varepsilon\text{-Fe}\) to 210 GPa (7). These results show discrepancies with calculations in which first-principles methods were used (8–10), in particular for shear moduli and anisotropy. Measurements and estimates of the Grüneisen parameter, an important thermodynamic property of iron that relates the

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thermal pressure and the thermal energy, show large discrepancies (5, 11–16). Recently, the phonon density of states of $\varepsilon$-Fe at high pressure has been investigated up to 42 GPa (16) and 153 GPa (17) by inelastic nuclear resonance x-ray scattering. Notable differences with the results of first-principles calculations are also found (17). Thus, there is a need to clarify the elastic and thermodynamic properties of iron at core pressures.

For many years, it was thought that vibrational Raman spectroscopy of simple metals was not possible at high pressures because of the weak scattering due to the high reflectivity and strong background from the apparatus (e.g., diamond-anvil cell). The bcc (α-Fe) and fcc (γ-Fe) phases have no first-order Raman spectra because all the atoms sit on inversion centers. The α-Fe fcp phase has one Raman-active mode of $E_g$ symmetry (18). Recent studies have shown that the $E_{2g}$ phonon mode in some hcp metals can be measured at moderate pressure in diamond cells. Measurements have been performed on Zn (19), Si (19), Zr (20), and Mg (21), but the $E_{2g}$ mode of $\varepsilon$-Fe was expected to be particularly weak (22) and has not been reported. Information on the frequency of the $E_{2g}$ mode of $\varepsilon$-Fe and its evolution with pressure provides experimental information on thermodynamic properties of the material because such vibrational frequencies are input data for construction of consistent thermodynamic models (23). Moreover, the mode correlates with a transverse acoustic phonon; thus, its frequency shift provides information on the pressure dependence of shear moduli (i.e., $C_{44}$), which is crucial for constraining the elastic anisotropy of iron at core pressures. We examined the thermal Grüniesen parameter $\gamma_0$, at high pressure. Despite the importance of the Grüniesen parameter of $\varepsilon$-Fe, experimental data have been limited and do not agree (Table 1). The mode-Grüniesen parameter $\gamma_i$ of the Raman mode is defined as

$$\gamma_i = -\left[\left(\frac{\partial \ln \nu}{\partial \ln V}\right)\right]$$

where $\nu$ is the frequency of the mode and $V$ is the volume. It provides an approximate means for calculating $\gamma_0$ with $\gamma_i = \langle \gamma \rangle = \gamma_0$. This assumes that the $\gamma_i$ for the mode is representative of all the vibrations of the crystal (23). We can write

$$\gamma_i \sim \gamma_0 = \gamma_q(V/V_0)^q$$

where $\gamma_0$ represents the extrapolated value of $\gamma_0$ at zero pressure with the volume dependence of $\gamma_0$, explicitly given by the parameter $q$. Using this relation and the equation of state of $\varepsilon$-Fe (3, 29), we calculate $\gamma_0 = 1.68 \pm 0.20$ and $q = 0.7 \pm 0.5$. Assuming $q = 1$, we have $\gamma_0 = 1.81 \pm 0.03$. The results agree with the analysis of recent high-pressure, high-temperature x-ray diffraction measurements (5), which suggests that $\gamma_i$ of the $E_{2g}$ mode provides a good approximation for $\gamma_0$. Our analysis is also compatible with that obtained from measurements of the phonon density of state of $\varepsilon$-Fe between 20 and 40 GPa, where $q = 0$ was assumed (16) (Table 1).

In $\varepsilon$-Fe, the $C_{44}$ elastic modulus and the $E_{2g}$ Raman mode are properties of the same phonon branch. Specifically, the $E_{2g}$ mode correlates with a transverse acoustic phonon

### Table 1. Thermal Grüniesen $\gamma_0$ parameter of $\varepsilon$-Fe and its volume dependence $q$

<table>
<thead>
<tr>
<th>Pressure range (GPa)</th>
<th>$\gamma_0$</th>
<th>$q$</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 to 100</td>
<td>2.2</td>
<td>1</td>
<td>Shock compression (11)</td>
</tr>
<tr>
<td>15 to 100</td>
<td>2.2 (±0.5)</td>
<td>1.62 (±0.37)</td>
<td>Shock compression (12)</td>
</tr>
<tr>
<td>20 to 250</td>
<td>2.75</td>
<td>1.5</td>
<td>First-principles (13)</td>
</tr>
<tr>
<td>0 to 240</td>
<td>1.7</td>
<td>0.7</td>
<td>Theory (15)</td>
</tr>
<tr>
<td>15 to 300</td>
<td>1.78 (±0.06)</td>
<td>0.69 (±0.10)</td>
<td>X-ray diffraction (5)</td>
</tr>
<tr>
<td>20 to 42</td>
<td>1.5 (±0.2)</td>
<td>0</td>
<td>Phonon density of states (16)</td>
</tr>
<tr>
<td>15 to 150</td>
<td>1.68 (±0.20)</td>
<td>0.7 (5)</td>
<td>This study*</td>
</tr>
</tbody>
</table>

*If we fix different values of $q$, we obtain the following: $q = 0$, $\gamma_0 = 1.44 \pm 0.03; q = 1$, $\gamma_0 = 1.81 \pm 0.03; q = 1.5$, $\gamma_0 = 2.02 \pm 0.04$. 

![Fig. 1. Raman spectra of $\varepsilon$-Fe at selected pressures. The strong band is identified as the $E_{2g}$ optical phonon, a weaker feature is observed at higher frequencies and lower pressures. Solid line, Lorentzian fit to the peak, which suggests a homogeneous line shape.](image1)

![Fig. 2. Pressure shift of $E_{2g}$ Raman phonon in $\varepsilon$-Fe. Open squares, first set of experiments; filled and open circles, second set of experiments during loading and unloading, respectively; solid line, second-order polynomial fit to experimental data; dashed line, fit to the results of first-principles calculations by the techniques described in (28) but for ambient temperature (27); open diamond, result of an empirical model (28).](image2)
and $C_{64}$ represents the slope of this branch at the center of the Brillouin zone. With a phenomenological model, they may be related as

$$C_{64} = 2\pi^2 M(31/2)\bar{c}^2/(6a^2)v^2 \quad (3)$$

where $M$ is the atomic mass of iron, $c$ and $a$ are unit cell parameters, and $v$ is the frequency of the optical phonon (30). Applying this relation to our data, we deduce the pressure dependence of the $C_{64}$ of $\varepsilon$-Fe (Fig. 3). Notably, our data are lower than the results of lattice-strain experiments (7). The analysis used in these experiments assumes that the state of stress on all unit cells is the same. Assuming no difference in the estimation of the other elastic moduli (7) arising from the change of $C_{64}$, we calculate $\Delta \omega_1 \approx 0.65$ and $\Delta \omega_2 \approx 1.44$ at 39 GPa, corresponding to changes of about 35%. This also improves the agreement with the first-principles calculations (33).

Finally, we can compare the results with those of other hcp structured transitions metals that have been studied recently by high-pressure Raman spectroscopy—for example, Zn (19), Si (19), Zr (20), and Mg (21). The behavior of the $E_{2g}$ phonon with pressure differs appreciably from one to another. Zn, Si, and Mg show an increase in frequency with pressure that linearly extrapolate to zero from about 3.3, 3.1, and 3 cm$^{-1}$/GPa, respectively. In contrast, $\varepsilon$-Fe shows a positive pressure shift with a $d\omega/dP$ of about 1.7 GPa. Comparing $\omega_1$ values, we find $\gamma_0$ (Zn) $\approx 2.4$ between ambient pressure and 12 GPa, $\gamma_0$ (Mg) $\approx 1.6$ at ambient pressure, and $\gamma_0$ (Si) $\approx 6$ near 40 GPa compared with $\gamma_0$ (Fe) $\approx 1.44$ ($\pm 0.03$) between 20 and 150 GPa. Zirconium appears to be a unique case: mode softening is observed for the $E_{2g}$ phonon of $\alpha$-Zr, with $d\omega/dP = -0.7$ cm$^{-1}$/GPa (20). Moreover, the relation between elastic modulus $C_{64}$ and the frequency of the $E_{2g}$ mode (Eq. 3) can be examined for Zr, Mg, and Zn because they crystallize in the hcp structure at zero pressure and 12 GPa, respectively. The first-principles results (44) indicate that the hcp phase is stable to at least 300 GPa and 150 K.

6. The gasket material was W for the first experiment and Rh for the second experiment. There was no evidence of a degenerate $E_{2g}$ mode in the 488- and 514.5-nm lines of an argon-ion laser. Direct comparison of the measured and calculated frequency of the $E_{2g}$ phonon at different pressures is possible for Mg (35) and Zr (36). In both cases, we find that the measured frequency is lower than that calculated by first-principles methods, which is consistent with results obtained for $\varepsilon$-Fe (Figs. 2 and 3). This study and analysis open the possibility of Raman investigations of the vibrational dynamics of other metals, including planetary core-forming materials at megabar to multi-megabar pressures.
sure, which suggests increased ordering of the hcp lattice and that the high-frequency weak band is disorder induced. The high-frequency band remained in the spectra on pressure release to 7 GPa, unlike the hcp Raman phonon, which disappears at the phase transition back to bcc α-Fe.

27. L. Vocadlo, personal communication.


33. For example, at a reference pressure of 210 GPa [see (10)], the lattice-strains experiments (7) lead to $\Delta_{31} = 0.60$ and $\Delta_{32} = 1.70$, the first-principles LDA calculations (9) give $\Delta_{31} = 1.27$ and $\Delta_{32} = 0.99$, and the first-principles OP calculations (10) give $\Delta_{31} = 1.03$ and $\Delta_{32} = 1.02$. If we extrapolate the $C_{44}$ calculated here and substitute it into the lattice-strains results (7), we would deduce $\Delta_{31} = 0.91$ and $\Delta_{32} = 1.12$, which is closer to theory.


38. We thank L. Vocadlo for communicating unpublished results and very helpful correspondence; we are grateful to V. V. Struzhkin, E. Gregoryanz, and R. E. Cohen for useful discussions and P. McMillan and other reviewers for their comments.

13 March 2000; accepted 19 April 2000

Reports

**Accretion of Primitive Planetesimals: Hf-W Isotopic Evidence from Enstatite Chondrites**

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Enstatite chondrites have often been considered to be closely related to the material from which Earth accreted. However, tungsten isotopic data reveal clear differences. Moreover, the silicate and metal fractions define distinct initial $^{182}$Hf/$^{180}$Hf corresponding to a 13.8 ± 5.3 million year apparent age difference. Internal reequilibration does not provide a ready explanation for this result. Larger scale redistribution of tungsten is more likely, such as may have occurred during collisions between planetesimals.

Enstatite chondrites formed in a highly reduced environment, possibly in the inner regions of the solar nebula (1, 2). They are the only group of chondrites whose silicate fractions have oxygen isotopic compositions similar to those of Earth and the moon (3), prompting some to suggest a genetic relationship (4). The Mn-Cr isotopic data for enstatite chondrite leachates and residues define an initial Cr isotopic composition that is similar to that of silicate Earth and the moon (5, 6), and this has been used to argue that the enstatite chondrite parent body (ECPB) may have formed at the same heliocentric distance. However, many features of enstatite chondrites are enigmatic and hard to explain. There are substantial compositional gaps between the enstatite chondrites and the Earth-moon system (2, 7), and chemical evidence for heterogeneous accretion of the ECPB has been presented (8). Furthermore, the relationship with Earth is unlikely to be straightforward. For example, dynamic simulations suggest that localized feeding zones for the growth of planetesimals and planets are unrealistic (9). Rather, planetary accretion can sample a broad provenance (9, 10).

The recently developed $^{182}$Hf-$^{182}$W chronometer (half-life = 9 million years) is well suited for studying accretion in the inner solar system (11–15). Both Hf and W are highly refractory. However, chemically they are quite different, with Hf being strongly lithophile (“silicate-loving”) and W moderately siderophile (“metal-loving”), such that fractionation between Hf and W occurs during metal-silicate differentiation and partial melting (11, 12). Hence, excess $^{182}$W in the W atomic abundance is found in meteorites that sample high Hf/W silicate reservoirs formed within the life-span of $^{182}$Hf. This is as found in some ecumrites, Martian meteorites, lunar samples, and the silicate phases of ordinary chondrites (13–15). Conversely, a deficit in $^{182}$W is found in early metals such as iron meteorites and the metal fractions of ordinary chondrites (13–15). The initial $^{182}$Hf/$^{180}$Hf at the start of the solar system is thought to lie in the range (1.87 ± 0.16) × 10^{-4} to (2.75 ± 0.24) × 10^{-4} (15). On this basis, the metals in the enstatite chondrites formed within a few million years, at most, of the start of the solar system.

In contrast, the nonmagnetic fractions (predominantly silicates) for each sample lie to the right of and below the best-fit line defined by the magnetic (metal) fractions (Fig. 1). The data for the nonmagnetic frac-

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