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High pressure thermoelasticity and sound velocities of Fe-Ni-Si alloys

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Abstract

The Earth’s iron-dominant core is known to contain nickel from cosmochemical analysis and some amount of light elements from geophysical constraints on density and seismic wave velocities. Although there have been several studies to constrain thermoelastic properties of iron-alloys, there has been no systematic study on the effects of nickel and light elements on properties of iron using the same experimental methods and data analysis approach. We conducted nuclear resonant inelastic x-ray scattering and x-ray diffraction experiments on body-centered cubic and hexagonal close-packed (hcp) Fe\textsubscript{0.91}Ni\textsubscript{0.09} and Fe\textsubscript{0.8}Ni\textsubscript{0.1}Si\textsubscript{0.1} up to 104 GPa and 86 GPa, respectively, and compare to similar measurements conducted on hcp-Fe up to 171 GPa. Specifically, we determine the Debye sound velocity from the low-energy transfer region of the (partial) phonon density of states (DOS) using the equation of state determined for each material and a new approach which utilizes information criteria and probability distributions. Nickel decreases the shear velocity of iron, while 10 at% Si has little to no effect on the shear velocity of Fe\textsubscript{0.91}Ni\textsubscript{0.09}. We observe that the shape of the phonon DOS of these alloys remains similar with increasing pressure. In the measured compression range, we therefore apply a generalized scaling law to describe the volume dependence of the phonon DOS and find that the vibrational Grüneisen parameters of hcp-Fe\textsubscript{0.91}Ni\textsubscript{0.09} are nearly indistinguishable from those hcp-Fe and those for Fe\textsubscript{0.8}Ni\textsubscript{0.1}Si\textsubscript{0.1} trend lower. From the vibrational free energy, we constrain the harmonic vibrational component of thermal pressure, which shows a significant positive deviation from theoretical calculations of hcp-Fe at pressures and temperatures of Earth’s core. Collectively, our results demonstrate that the effects of nickel should be considered when modeling iron-rich planetary cores.

Keywords: Earth’s core, sound velocity, Grüneisen parameter, high pressure, nuclear resonant inelastic x-ray spectroscopy

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1. Introduction

Seismological observations place constraints on the shear and compressional sound velocities and density of the inner core (e.g., Dziewonski and Anderson, 1981; Kennett et al., 1995) and the discontinuity in compressional sound velocity and density at the inner core boundary (e.g., Masters and Gubbins, 2003; Deuss, 2008). These observations in conjunction with cosmochemical and mineral physics studies place constraints on the composition and thermal profile of the inner core. The density of the inner core is ~3–5% lighter than hcp-iron at inner core conditions (reviewed in Li and Fei, 2014), which supports the presence of light elements in the inner core. Thus many studies have focused on quantifying the effects of alloying iron with lighter elements on the density of pure iron, lending support to the presence of light elements such as Si, O, S, C, H in the inner core (reviewed in Hirose et al., 2013; Li and Fei, 2014; Vočadlo, 2015; Litasov and Shatskiy, 2016). A plausible inner core composition must also match the compressional and shear velocities of the inner core, which are reported to be respectively ~4–10% slower (e.g., Sakamaki et al., 2016) and >30% slower than hcp-iron (e.g., Martorell et al., 2013a).

A detailed understanding of the effect of composition on the sound velocities and densities of iron alloys at core pressures and temperatures is necessary to constrain the inner core composition and the melting temperature at the inner core boundary, as well as to better constrain outer core composition and to understand the nature of anisotropy and heterogeneity in the inner and outer core. Furthermore, an understanding of the thermoelastic properties of these alloys at core conditions can help constrain geodynamical simulations of the evolution and ongoing processes of the core.

The sound velocities of hcp-iron have been extensively studied through shockwave experiments (Jeanloz, 1979; Brown and Mcqueen, 1986; Nguyen and Holmes, 2004), 300 K static compression experiments (Lubbers et al., 2000; Mao et al., 2001; Giefers et al., 2002; Antonangeli et al., 2004; Liu et al., 2005; Mao et al., 2008, 2012; Murphy et al., 2013; Gleason et al., 2013; Ohtani et al., 2013; Decremps et al., 2014; Liu et al., 2014, 2016; Antonangeli et al., 2018), high temperature static compression experiments (Liu et al., 2005; Sakamaki et al., 2016; Mori et al., 2017), and ab initio studies (Laio et al., 2000; Mao et al., 2001; Steinle-Neumann et al., 2001; Vočadlo et al., 2009; Martorell et al., 2013a; Niu et al., 2015). Similarly, numerous experimental and ab initio studies have investigated hcp-iron’s isothermal equation of state (e.g. Steinle-Neumann et al., 1999; Mao et al., 1990; Dubrovinsky et al., 2000; Dewaele et al., 2006; Boehler et al., 2008; Ono et al., 2010) and thermal equation of state (Wasserman et al., 1996; Stixrude et al., 1997; Dubrovinsky et al., 1998; Uchida et al., 2001; Sha and Cohen, 2010; Garai et al., 2011; Yamazaki et al., 2012; Sakai et al., 2014; Fei et al., 2016).

An important element in constraining the thermal equation of state of hcp-iron is the thermal Grüneisen parameter, which relates thermal pressure to thermal energy per unit volume and can be used to reduce shock data for comparison with isothermal compression studies. As the thermal Grüneisen parameter is composed of vibrational and electronic contributions, constraints on hcp-iron’s vibrational Grüneisen parameter have helped further constrain its thermal equation of state (Dubrovinsky et al., 2000; Uchida et al., 2001; Dewaele et al., 2006; Murphy et al., 2011a; Yamazaki et al., 2012). Furthermore, hcp-iron’s thermal pressure can be estimated by pairing the vibrational component of thermal pressure, directly accessed through phonon density of states (DOS)
measurements (Murphy et al., 2011b), with ab initio constraints on the electronic and anharmonic components of thermal pressure (Wasserman et al., 1996; Alfè et al., 2001; Dewaele et al., 2006; Sha and Cohen, 2010; Martorell et al., 2013a,b).

Despite the presence of nickel in the Earth’s core (Allègre et al., 1995; McDonough and Sun, 1995; McDonough, 2003), the sound velocities and thermoelasticity of hcp-structured iron-nickel alloys have received comparatively little attention. Lin et al. (2003) determined the shear and compressional sound velocities of bcc- and hcp-Fe$_{0.92}$Ni$_{0.08}$ with nuclear resonant inelastic x-ray scattering (NRIXS) and found nickel slightly decreased the compressional and shear velocities of hcp-Fe for a given density. However, there was considerable scatter in the data of iron (Mao et al., 2001) and iron-nickel, such that no effect could also be concluded from these measurements. A variety of experimental studies investigated the equations of state of hcp-iron-nickel at 300 K (Takahashi et al., 1968; Mao et al., 1990; Morrison et al., 2018) as well as at high temperatures (McQueen and Marsh, 1966; Asanuma et al., 2011; Sakai et al., 2014). However, constraints on the thermal equations of state of hcp-iron-nickel are limited and indicate a considerable range of thermal parameters associated with the effects of nickel (Ekholm et al., 2011; Côté et al., 2012; Martorell et al., 2013a).

Silicon is a favored light element in the inner core for a variety of reasons, including its abundance in the Earth’s mantle, the magnesium to silicon ratio in the crust and mantle of Earth compared to chondritic meteorites (Allègre et al., 1995, 2001), observations that silicon partitions into iron in silicate-iron partitioning experiments conducted at high pressure and high temperature (Ricolleau et al., 2011; Fischer and Campbell, 2015), and ab initio and experimental results demonstrating silicon partitions roughly equally between liquid and solid iron at high pressure (Alfè et al., 2002, 2007).

A variety of studies have investigated the sound velocities of iron-silicon alloys at 300 K (Lin et al., 2003; Badro et al., 2007; Mao et al., 2012; Ono, 2013; Liu et al., 2014; Antonangeli et al., 2018). Silicon is found to increase the compressional velocity of hcp-Fe, but the effect of silicon on hcp-Fe’s shear velocity is debated. Recently, Sakairi et al. (2018) investigated the compressional wave velocity of hcp-Fe$_{0.89}$Si$_{0.11}$ up to 1800 K and 84 GPa with inelastic x-ray scattering (IXS), better constraining effect of silicon on compressional velocity at higher temperatures. Fewer studies have investigated the sound velocities of iron-nickel-silicon alloys at 300 K: (Antonangeli et al., 2010) determined the compressional wave velocity from phonon dispersion measurements and (Liu et al., 2016) constrained the shear wave velocities from NRIXS measurements. Most constraints on iron-silicon sound velocities at inner core conditions come from ab initio studies (Vočadlo, 2007; Tsuchiya and Fujibuchi, 2009; Ono, 2013; Martorell et al., 2016). Isothermal equations of state of these alloys include Lin (2003); Hirao et al. (2004); Ono et al. (2007); Sata et al. (2010); Asanuma et al. (2011); Tateno et al. (2015); Morrison et al. (2018), and experimental thermal equations of state studies include Zhang and Gayot (1999); Fischer et al. (2012, 2014); Tateno et al. (2015), all utilizing x-ray diffraction techniques. However, to date, the thermal properties of iron-nickel-silicon alloys, including constraints on the Grüneisen parameter, have not been investigated with techniques sensitive to the vibrational properties of the material.

We present NRIXS measurements on bcc- and hcp-Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ up to 104 GPa and 86 GPa, respectively. To ensure a systematic comparison with hcp-Fe by avoiding differences in analyses methods, we re-analyze hcp-Fe NRIXS data from (Murphy et al., 2011a,b, 2013). We present derived partial (projected) phonon density of states for
each composition. We determine the Debye sound velocity from the low energy region of the phonon density of states using a new analysis method utilizing probability density functions which better constrains the Debye sound velocity and its uncertainty from the measured data. We present two separate constraints on the vibrational component of thermal pressure for the hcp phases. First, we determine the Grüneisen parameter by applying a volume scaling relation to the phonon DOSs. Second, we estimate vibrational thermal pressure from the vibrational free energy derived from the phonon DOS. The thermal expansion is determined using constraints on the bulk modulus from the same alloys (Morrison et al., 2018). Additional parameters are derived from the phonon DOS including the vibrational kinetic energy, vibrational heat capacity and Lamb-Mössbauer factor.

2. Experimental methods

Samples were synthesized by arc-melting individual pieces of Ni, Si, and 95%-enriched $^{57}$Fe in an argon atmosphere to produce Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$. Samples were then cold rolled to $\sim$10 $\mu$m. SEM measurements confirmed the molar sample compositions to be Fe$_{0.91(1)}$Ni$_{0.09(1)}$ and Fe$_{0.8(0)}$Ni$_{0.10(1)}$Si$_{0.10(1)}$, and sample homogeneity was observed at a scale of 1 $\mu$m. Samples from this synthesis batch were previously used to constrain the melting temperature of Fe$_{0.91}$Ni$_{0.09}$ (Zhang et al., 2016) and to constrain the equations of state of Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ (Morrison et al., 2018).

High pressure conditions were achieved using modified panoramic diamond anvil cells (DACs) with 90° openings and cubic boron nitride backing seats on the downstream side. These modifications maximize the accessible angle range for in situ x-ray diffraction (XRD). One Fe$_{0.91}$Ni$_{0.09}$ and one Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ experimental run (hereafter referred to as FeNi-Run#1 and FeNiSi-Run#1) were each conducted with beryllium gaskets and loaded with a neon pressure medium at Caltech to ensure nearly hydrostatic conditions. These experimental runs focused on lower pressures where both Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ were in the bcc phase. An Fe$_{0.91}$Ni$_{0.09}$ and an Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ experimental run (FeNi-Run#2 and FeNiSi-Run#2) were each prepared with a beryllium gasket and a boron-epoxy insert to stabilize the chamber at higher pressures, and then loaded with a neon pressure medium. An Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ experimental run (FeNiSi-Run#3) was prepared with a beryllium gasket and a boron-epoxy insert with no additional pressure medium. Additional bcc Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ foil samples were placed on Kapton tape for ambient pressure measurements. Powdered 95%-enriched $^{57}$Fe was also placed on Kapton tape for an ambient pressure measurement of bcc-Fe.

We collected nuclear resonant scattering measurements on each sample at 300 K at Sector 3-ID-B at the Advanced Photon Source. The storage ring was run with 24-bunch top-up mode, with each bunch separated by 153 ns. Incoherent inelastic x-ray scattering was measured with three avalanche photodiode detectors (APDs) positioned radially around the sample, and forward elastic scattering was measured with a single APD downstream from the sample to constrain the resolution function. The x-ray energy was tuned around the nuclear resonance of $^{57}$Fe (14.4125 keV) with a high-resolution monochromator (Toellner, 2000). We varied the scanned energy range depending on the sample and the pressure (a summary is provided in Table S1). For Fe$_{0.91}$Ni$_{0.09}$ measurements, higher counting rates at lower pressures motivated moderately larger scanned energy ranges for the bcc compression points. Compared with Fe$_{0.91}$Ni$_{0.09}$, we...
observed higher energy phonon modes for Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$, which motivated the use of larger scanned energy ranges for some compression points. The higher energy modes observed in Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ are likely due to more dispersive optical phonon branches in the Fe-Ni-Si alloy compared with those in Fe$_{0.91}$Ni$_{0.09}$ and Fe (e.g., Wakabayashi et al., 1982; Muñoz, 2013). The typical energy resolution (full width at half maximum at zero energy transfer) was 1.1 meV. There were four Fe$_{0.91}$Ni$_{0.09}$ compression points between 83 and 104 GPa where we observed large tails around the resolution peak, which severely impacted the quality of the data, so these compression points were discarded. The x-rays were focused to an area of 10 by 14 $\mu$m$^2$ using a Kirkpatrick-Baez mirror system. The nuclear resonant inelastic x-ray scattering (NRIXS) spectra for all compression points are plotted in Figures S1 and S2 in the supplementary material.

In situ x-ray diffraction (XRD) was collected before and after each set of NRIXS scans and averaged to determine the unit-cell volume of the sample at each pressure point (e.g., Gao et al., 2009; Murphy et al., 2013). The x-ray wavelength energy was 14.4125 keV (0.086 nm), corresponding to a nuclear resonance of $^{57}$Fe. The XRD images were calibrated with a powdered CeO$_2$ sample and integrated with the Dioptas software package (Prescher and Prakapenka, 2015). We fit the resulting x-ray diffraction patterns with full-profile Pawley refinement to determine the bcc phase lattice parameter $a$ using reflection (100) and the hcp phase lattice parameters $a$ and $c$ using reflections (100), (101), and (002). We observed the decay/loss of intensity in the (002) reflection in several of the compression points of hcp-Fe$_{0.91}$Ni$_{0.09}$ and hcp-Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ and interpret this as texture development. The remaining diffraction reflections for these compression points were sufficient to determine $a$ and $c$, as the (100) reflection is sensitive to the $a$ lattice parameter and the (101) reflection is sensitive to both the $a$ and $c$ lattice parameters. A preliminary estimate of the lattice parameter uncertainty comes from results of the Pawley refinements. XRD measurements conducted at APS GSECARS sector 13-BM-C ($E = 28.57$ keV) on the same DAC at select compression points showed that the deviations resulting from use of about four times the amount of reflections are within a doubling of the uncertainties provided from the Pawley refinements. We therefore double the uncertainties provided by the Pawley refinements for all Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ compression points. The resulting lattice parameters and unit-cell volumes are reported in Table 1.

Density was determined from the in situ unit-cell volume measurements and accounts for the 95% $^{57}$Fe isotopic enrichment of the samples (Table 1). Throughout most of the NRIXS data analysis, we relied on the measured in situ volumes and densities. We convert the unit-cell volumes to pressure using the equations of state (EOSs) for each sample. For the bcc-Fe data, we use the Vinet EOS for reported in Morrison et al. (2018) based on compression data from Dewaele et al. (2006). For bcc- and hcp-Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$, we use the Vinet EOSs also reported in Morrison et al. (2018). These EOSs were determined from samples synthesized from the same Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ batches used in the NRIXS experiments. All of the EOSs referenced in this study were determined using the same pressure transmitting medium (helium) and the same pressure calibrant (tungsten with the Dorogokupets and Oganov (2006) pressure scale). The experimental conditions and resulting parameters from each EOS study are listed in Table S2. The resulting pressure, $K_T$, and $K'_T$ are listed in Table 1. The conversion to adiabatic bulk moduli utilizes thermodynamic parameters constrained in this study and will be discussed later.
The NRIXS data were analyzed with the PHOENIX software package (version 3.0, www.NRIXS.com) to obtain the partial phonon density of states (DOS) $D(E; V_i)$. Debye sound velocity, and other vibrational-related quantities, including the Lamb-Mössbauer factor, kinetic energy, thermal expansion, and free energy. As detailed in Sturhahn (2000, 2004) and Sturhahn and Jackson (2007), the background and the measured elastic peak were fitted and subtracted from the measured NRIXS spectrum to obtain the pure phonon excitation spectrum, $I'(E)$. The excitation probability density $S(E; V_i)$ was then obtained by applying a normalization procedure to $I'(E)$ based on the property that the first moment of $S(E; V_i)$ is equal to the recoil energy of the resonant isotope $E_R$. For $^{57}$Fe, $E_R = 1.956$ meV. PHOENIX applies the Fourier-log method to decompose $S(E; V_i)$ into $n$-phonon contributions,

$$S_n(E, V_i) = \int E^n S(E, V_i) dE, \quad (1)$$

for $n = 0, 1, 2, 3$. For example, the Lamb-Mössbauer factor and the kinetic energy can be directly determined from the 0th- and 2nd-order moments ($S_0(E, V_i)$ and $S_2(E, V_i)$), respectively (see sections 3 and 5 in the supplementary material).

To obtain the phonon DOS from $S_1(E, V_i)$, the quasi-harmonic approximation was applied, which assumes the interatomic potential is harmonic and accounts for thermal expansion. This approximation is thought to be reasonable for measurements of iron-rich alloys at 300 K (Alfè et al., 2001). The resulting projected partial phonon DOS $D(E, V_i)$ was normalized by $\int D(E, V_i) dE = 3$. The phonon DOS is 'projected' due to the dependency on the direction of incident x-rays and 'partial' as NRIXS is sensitive to the resonant isotope $^{57}$Fe, thus for the $^{57}$Fe samples in this study, the results are simply the projected phonon DOS. For the bcc phase, $D(E, V_i)$ is isotropic (Sturhahn and Kohn, 1999). For samples in the hcp phase, the dependency on the angle of incident x-rays should be minimal as the samples are polycrystalline and in most cases, loaded with neon as a pressure medium. Additionally, anisotropy of the phonon DOS for hcp Fe was found to be minimal in the low energy region used for sound velocity determinations (Giefers et al., 2002) and anisotropy in the compressional elastic components for these iron-alloys was also found to be minimal at 300 K (Morrison et al., 2018). Because the alloys studied here are predominantly iron (using 95%-enriched $^{57}$Fe), the partial phonon DOS is a very close approximation to the total phonon DOS. The resulting phonon DOSs for bcc and hcp phases are plotted in Figures 2 and 3, respectively.

To compare our results to those of hcp-iron in a consistent manner, we re-analyzed data from the NRIXS study on hcp-iron by Murphy et al. (2011a,b, 2013) using the same methods as for Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ described throughout this paper. The resulting phonon DOSs for hcp-iron are plotted in Figure 3. We excluded the 36 GPa hcp-Fe NRIXS dataset from our re-analysis, as we found the statistical quality to be inferior to the other scans in this study. The 36 GPa dataset was collected over a much shorter integration time (18s, compared to an average of 53s), and the number of counts for the highest intensity peak in the Stokes region was much smaller (70 counts, compared to an average of 183 counts).

We compare the phonon DOS of the bcc and hcp phases of Fe, Fe$_{0.91}$Ni$_{0.09}$, and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ in Figure 4. The phonon DOSs for the bcc phases are plotted as measured at 0 GPa. The total phonon DOS for hcp-Fe at 90 GPa, and the partial phonon DOSs
for hcp-Fe$_{0.91}$Ni$_{0.09}$ at 48 GPa and for hcp-Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ at 41 GPa are scaled to 0 GPa using the phonon DOS scaling method outlined in Section 4. Note the difference in relative phonon mode intensity between bcc and hcp-structured iron alloys. Also, note the differences between the phonon DOSs of different compositions. For instance, the phonon DOSs of bcc- and hcp-Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ extend to higher energies than the phonon DOSs of Fe and Fe$_{0.91}$Ni$_{0.09}$.

3. Sound velocities

3.1. Debye sound velocity

The Debye sound velocity ($v_D$) can be determined from the low-energy region of the phonon DOS via

$$v(E) = \left[ \frac{\tilde{m}}{2\pi^2 \hbar^2 \rho D(E)} E^2 \right]^{1/3}$$

(2)

where $\tilde{m}$ is the mass of the resonant isotope, $\rho$ is the density of the material being measured, and $v(E) = v_D$ in the limit where $E$ approaches zero (e.g., Sturhahn, 2004). As an example, we illustrate select phonon DOSs of hcp-Fe, Fe$_{0.91}$Ni$_{0.09}$, and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ scaled according to equation 2 in Figure 5. Two different phonon dispersion models are plotted together with the scaled phonon DOSs. A ‘Debye-like’ model varies quadratically (parabolic) with energy and therefore plots as a constant value in Figure 5. The parabolic ‘Debye-like’ regions of the phonon DOSs of Fe and Fe$_{0.91}$Ni$_{0.09}$ extend to about 15 meV at these pressures, thus a large enough energy range to obtain a suitable constraint on the Debye velocity using this particular model, whereas assuming the parabolic trend above about 15 meV at this pressure would not be appropriate. The parabolic region of Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ at 41 GPa is noticeably smaller than that of Fe$_{0.91}$Ni$_{0.09}$ at the same pressure. A greater amount of data can be included if instead an empirical power law model of the phonon dispersion curve is applied,

$$v(E) = v_D \left[ 1 - (E/A_1)^4 \right],$$

(3)

where the power of 4 is fixed in all cases presented here, and the parameters $v_D$ and $A_1$ are fit. In both models of phonon dispersion, the limit of $v(E)$ as $E$ approaches zero provides $v_D$. For consistency, we apply the phonon dispersion curve in equation 3 to the phonon DOSs of both hcp-Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$, as well as to our re-analysis of hcp-Fe data from Murphy et al. (2013) using a new approach presented here. Note that equation 3 is a Debye-like model for very large values of $A_1$.

The goal is to accurately determine the Debye velocity with an appropriate uncertainty from a measured phonon DOS. An ideal method should be repeatable, consistent, and produce meaningful uncertainties. Previous selection criteria have involved selecting an energy range that corresponds to a low reduced goodness of fit ($\chi^2$) and a stable $v_D$ (e.g., Murphy et al., 2013). The metric $\chi^2$ is meaningful in that it detects deviations in the model from the data (i.e., it is sensitive to under-fitting of the data). However, $\chi^2$ is not sensitive to over-fitting of the data, as only a few data points may yield a very good (low) $\chi^2$. A better choice would be a metric that prefers both a good fit of the model to the data and an energy range with more data points (i.e., a criteria that disfavors both
under-fitting and over-fitting of the data). Essentially, an energy range choice should yield the maximum information from the data.

There are a variety of methods of estimating information, some more computationally intensive than others. Two common information estimates that are easily computationally accessible are the Akaike Information Criteria (AIC) and the Bayesian Information Criteria (BIC). Both of these criteria assume a large number of data points. When selecting between energy fit ranges, the number and quality of data points will vary, so it is important to not assume the number of data points is large. A common correction to the AIC (known as the AICc) corrects for the case where the number of data points is small (Hurvich and Tsai, 1989). The AICc has the form

$$AICc = \chi^2 + 2M + \frac{2M(M+1)}{N-M-1},$$

where $\chi^2$ is the goodness of fit of the model to the data, $M$ is the number of model parameters, and $N$ is the number of data points. In our case, $M = 2$ for a power law model (equation 3) where the model parameters are $v_D$ and $A_1$, and $N$ is the number of data points in the selected energy range. The third term of equation 4 is critical, as it provides a sensitivity to over-fitting of the data, which a traditional goodness of fit lacks.

As an example, we plot the effective probability $\exp(-AICc/2)$ of each fit as a function of the start and end of the fit range ($E_{min}$ and $E_{max}$, respectively) for Fe$_{0.91}$Ni$_{0.09}$ at 41 GPa in the top panel of Figure 6. Low values of $\exp(-AICc/2)$, e.g., where the number of data points is too small or where $E_{max}$ is too large, provide a poor constraint on the Debye velocity $v_D$, whereas high values of $\exp(-AICc/2)$ provide a better constraint on $v_D$. This plot demonstrates there are many choices of $E_{min}$ and $E_{max}$ that are equally favorable, e.g., choices that yield equally large values of $\exp(-AICc/2)$. We also plot the $v_D$ as a function of $E_{min}$ and $E_{max}$ in the middle panel of Figure 6. Depending on the quality of the NRIXS spectrum and the phonon dispersion, the value of $v_D$ obtained from a given data set may vary widely for different fit ranges, even for fit ranges with similar AICc values. As a result, two different fit ranges may yield equal values of $\exp(-AICc/2)$ but noticeably different Debye velocities. By accounting for many possible fit ranges in the calculation of $v_D$, this method provides a more reasonable constraint on the uncertainty of $v_D$ than would be obtained by using a single energy range. For example, in Figure 6 we include all fit ranges that fall within $E_{min}=0.0-27.0$ meV and $E_{max}=1.0-28.0$ meV. This is a demonstration that using this approach leads to a $v_D$ that doesn’t depend on the choice of $E_{min}$. The results we present throughout the manuscript are for $E_{min}=3.5-27.0$ meV and $E_{max}=4.5-28.0$ meV. The $v_D$ of these fits are weighted by their corresponding $\exp(-AICc/2)$ and binned to produce a probability distribution function of $v_D$ (bottom panel of Figure 6). The most probable value is then obtained by using two asymmetric functions to fit the probability distribution. The reported Debye velocity and its uncertainty is the peak and FWHM of the best-fit asymmetric function, respectively.

We compare the obtained probability distribution functions for hcp-Fe, Fe$_{0.91}$Ni$_{0.09}$, and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ in Figure 7, each at three different pressures. These probability distribution functions illustrate that the uncertainty on $v_D$ can vary noticeable depending on the quality of the NRIXS data. The increase in $v_D$ with pressure is clearly resolvable given the $v_D$ probability distributions and $v_D$ uncertainty. The Debye velocities for
bcc- and hcp-Fe, Fe$_{0.91}$Ni$_{0.09}$, and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ computed via this method are listed in Table 2 and plotted as a function of density and pressure in Figure 8.

We find measurable differences in the Debye velocities of iron and iron-nickel. Alloying hcp-iron with 9 at\% nickel decreases the Debye velocity for a given density or pressure. Interestingly, alloying Fe$_{0.91}$Ni$_{0.09}$ with 10 at\% silicon produces Debye velocities very similar to those of pure iron as a function of density, but as a function of pressure, $v_D$ values of Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ are similar to those of Fe$_{0.91}$Ni$_{0.09}$ (Figure 8). To understand why, we first look to constraints at the lattice level. (Morrison et al., 2018), using samples from the same syntheses as those studied here, investigated Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ to $\sim$170 GPa in a helium pressure medium using powder X-ray diffraction. Within the experimental resolution, the XRD patterns are consistent with the hcp structure for both compositions. Specifically, there are no additional reflections that would indicate a super-structure, arising from Ni (and Si) substituting on an interstitial site. Thus, one may conclude that the samples investigated here are in a solid solution, implying that Ni (and Si) substitute for Fe.

Therefore, the reduction in Debye velocity of Fe$_{0.91}$Ni$_{0.09}$ compared with that of pure iron (as a function of density and pressure) can be understood by substituting Fe with a heavier element, such as Ni. The case for Si appears more complicated, and we return to this discussion at the end of Section 3.2.

### 3.2. Compressional and shear sound velocities

We combine the Debye velocities of the iron-alloys obtained from their probability distribution functions with their independently determined equations of state (Dewaele et al., 2006; Morrison et al., 2018) to constrain the compressional and shear sound velocities $v_P$ and $v_S$ via

$$\frac{3}{v_P^3} = \frac{1}{v_P^3} + \frac{2}{v_S^3}$$

and

$$\frac{K_S}{\rho} = v_P^2 - \frac{4}{3} v_S^2,$$

where $K_S$ is the isentropic bulk modulus and $\rho$ is the density of our $^{57}$Fe enriched samples. $K_S$ is related to the isothermal bulk modulus $K_T$ via the following relation,

$$K_S = K_T(1 + \gamma \alpha T),$$

where $\gamma$ is the Grüneisen parameter and $\alpha$ is the thermal expansion. For a given composition and volume, $K_T$ is determined from existing 300 K equations of state. For bcc-Fe data, we apply the Vinet EOS for bcc-Fe reported in Morrison et al. (2018) based on compression data from Dewaele et al. (2006). For hcp-Fe, we apply the hcp-Fe EOS from Dewaele et al. (2006). For bcc- and hcp-Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$, we apply the Vinet EOSs also reported in Morrison et al. (2018). Experimental details for each equation of state are summarized in Table S2 in the supplementary material. The EOS studies for Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ were conducted using samples from the same synthesis batches as the samples in this study. For samples in the bcc phase, we assume $K_S \approx K_T$. For samples in the hcp phase, we calculate $K_S$ using our reported $\gamma_{vib}$ and $\alpha_{vib}$ determined from the phonon DOS of each composition (see sections 4 and 6).
shear modulus $G$ is then calculated via

$$G = \frac{v_S^2 \rho}{2}.$$ \hspace{1cm} (8)

The determined $K_E$, $v_p$, $v_S$, and $G$ are reported in Table 2, and $v_p$, $v_S$ are plotted as a function of density and pressure in Figure 8. The density and sound velocities in Table 2 and Figure 8 account for the $^{57}$Fe enrichment of the samples.

From equation 5, one can see that the Debye velocity is mostly sensitive to shear velocity, rather than to compressional velocity. Thus, it is not surprising that the compositional trends in the shear velocity follow those observed for the Debye velocity: alloying hcp-iron with 9 at% nickel decreases the shear velocity by ~6% for a given density (or pressure). Further alloying with 10 at% silicon has a negligible effect on the shear velocity of iron as a function of density, but trends similar to Fe$_{0.91}$Ni$_{0.09}$ with pressure (Figure 8).

As noted previously, NRIXS measurements are better suited for constraining shear velocities, and the resulting compressional sound velocities are more strongly affected by the applied equation of state (Sturhahn and Jackson, 2007). It is therefore not surprising that for a given pressure, alloying iron with nickel has a minimal effect on compressional velocity, as their equations of state are similar in this pressure range (Morrison et al., 2018) (see also Table S2). Further alloying Fe$_{0.91}$Ni$_{0.09}$ with silicon also has a minimal effect on compressional velocity as a function of pressure, as differences in their equations of state compensate for their differences in density. Because Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ is less dense than iron or Fe$_{0.91}$Ni$_{0.09}$ when plotted as a function of density, Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ has a greater $v_p$ than that of hcp-Fe or Fe$_{0.91}$Ni$_{0.09}$ (e.g., Martorell et al., 2016).

These findings suggest that nickel decreases the shear velocity of iron but not the compressional velocity of iron, while silicon has little to no effect on the compressional and shear velocities of Fe$_{0.91}$Ni$_{0.09}$ for a given pressure (Figure 8). Our findings for Fe$_{0.91}$Ni$_{0.09}$ are in qualitative agreement with ab initio studies at 360 GPa and 0 K by (Martorell et al., 2013a) which predict a ~5% shear velocity decrease when ~10 at% nickel is alloyed to hcp-iron. For the case of Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$, the combined effects of substituting a lighter element (increasing average vibrational frequency) and a heavier element (decreasing average vibrational frequency) for Fe appear to cancel one another, leading to essentially no effect on the shear velocity of pure iron as a function of density. Differences in the equation of state could then explain why $v_s$ values of Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ are similar to those of Fe$_{0.91}$Ni$_{0.09}$, as a function of pressure. (Martorell et al., 2016) studied the effects of alloying Si to Fe on the sound velocities of hcp-Fe at 360 GPa and found that hcp-Fe$_{0.9375}$Si$_{0.0625}$ has 2.9% lower shear velocities than hcp-Fe at 0 K. Thus, qualitatively, there is agreement in finding lower shear velocities in Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ compared with that of pure Fe. Although, based upon the individual studies of (Martorell et al., 2013a, 2016), one may suspect that the shear velocity of Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ could be lower than Fe$_{0.91}$Ni$_{0.09}$. However, (Martorell et al., 2013a, 2016) did not study the combined effects of Ni and Si. Nevertheless, (Martorell et al., 2013a, 2016) show that with increasing temperature from 0 K, the effects of alloying Ni (and Si) to Fe on the compressional and shear velocities decrease and become minimal at 5500 K and 360 GPa.
3.3. Comparison with previous studies

To compare with geophysical observations and studies using samples of natural isotopic enrichment, our reported density and sound velocities can be corrected to values corresponding to natural isotopic enrichment with the following relation,

$$\rho_{\text{nat}} = \rho_{\text{enr}} (M_{\text{nat}} / M_{\text{enr}})$$  \hspace{1cm} (9)

and the following approximation,

$$v_{\text{nat}} = v_{\text{enr}} \sqrt{M_{\text{enr}} / M_{\text{nat}}},$$  \hspace{1cm} (10)

where $M$ is the molecular mass of the alloy. The subscripts $\text{nat}$ and $\text{enr}$ denote samples with natural isotopic enrichment and samples enriched in $^{57}\text{Fe}$, respectively. Values of $M_{\text{enr}}$ and $M_{\text{nat}}$ are listed in Table S3.

3.4. Iron

We plot the 300 K Debye, compressional, and shear sound velocities of our bcc-Fe data and our re-analyzed hcp-Fe data from Murphy et al. (2013) in Figure 9. We plot these as a function of pressure to compare with other NRIXS, inelastic x-ray scattering (IXS), and ultrasonic interferometry bcc- and hcp-Fe studies, some of which do not report unit-cell volumes determined in situ. We compare to NRIXS studies by Mao et al. (2001), Lin et al. (2005), Gleason et al. (2013), and Liu et al. (2016); IXS studies by Mao et al. (2012), Ohtani et al. (2013), Liu et al. (2014), and Antonangeli et al. (2018); a combined NRIXS and IXS study by Mao et al. (2008); and a picosecond ultrasonic study by Decremps et al. (2014).

Unlike NRIXS studies, IXS and ultrasonic sound velocity studies do not require $^{57}\text{Fe}$ sample enrichment. Therefore, the plotted $v_D$, $v_P$, and $v_S$ values for bcc-Fe from this study and our re-analysis of hcp-Fe from Murphy et al. (2013) have been corrected to natural enrichment via equation 10. We have also corrected the reported $v_D$, $v_P$, and $v_S$ from Lin et al. (2005), Liu et al. (2016), Mao et al. (2001), and Gleason et al. (2013) to natural isotopic enrichment using equation 10. As Mao et al. (2008) report $v_P$ from samples with natural isotopic enrichment and $v_D$ from samples enriched in $^{57}\text{Fe}$, we correct their reported $v_D$ to natural isotopic enrichment and re-calculate $v_S$ for natural isotopic enrichment.

The $v_D$ for hcp-Fe re-analyzed from Murphy et al. (2013) agrees well with Liu et al. (2016) that conducted experiments using a neon pressure medium and the singular value reported by Mao et al. (2008) at 50 GPa using helium as a pressure medium. These $v_D$ trends are in reasonable agreement with the three data points reported in Gleason et al. (2013) below 85 GPa, and it is only the data point at 136 GPa (Gleason et al., 2013) that is about about 2–4% higher than these aforementioned studies. The data sets of Mao et al. (2001) (no pressure medium) and Lin et al. (2005) (NaCl pressure medium) show more scatter, making it difficult to make precise comparisons.

The compressional sound velocities from IXS studies trend above those from NRIXS studies. It is therefore important to discuss the differences in the methods. In NRIXS studies, the measured quantity is the self-correlation function, where the one-phonon contribution is used to determine the phonon DOS. In the polycrystalline IXS studies of iron-alloys discussed here, the measured quantities are points along the phonon branch
of the longitudinal acoustic mode (compressional wave). A fit to these points using a dispersion relation yields $v_p$. As discussed previously, the Debye sound velocity from NRIXS studies is obtained from the material's density and fits to the low energy region of the phonon DOS. In this study, we improve this method by determining a probability distribution function and report the most probable value given a wide range of energies and their ranges used to fit a particular spectrum. Nevertheless, there is little sensitivity to compressional wave velocity in NRIXS studies (see Starhahn and Jackson (2007) for a discussion of the relative sensitivities of NRIXS to $v_p$, $v_p$, and $v_S$). The difference in $v_p$ values between those of IXS and NRIXS studies will also be due to differences in the equations of state used, as well as the energy range used to constrain the respective sound velocities in each method. In NRIXS studies, it is common to use data starting as low as about 3 meV to determine the sound velocity.

Similar to the trends in $v_p$, our reported $v_S$ for hcp-Fe agrees well with Mao et al. (2001), Lin et al. (2005), Mao et al. (2008), Liu et al. (2016), and it is only the 136 GPa data point of Gleason et al. (2013) that appears to deviate significantly from these trends. The IXS studies by Antonangeli et al. (2018) and Ohtani et al. (2013) report $v_S$ curves based on their determined $v_p$ and existing equations of state (Dewaele et al., 2006; Sakai et al., 2014). The $v_S$ of Antonangeli et al. (2018) and Ohtani et al. (2013) trend respectively ~5% and ~11% above our reported $v_S$ for hcp-Fe, which is a significant deviation. As discussed above, differences from NRIXS results can be partially attributed to the fact that the IXS studies are measuring the longitudinal acoustic branch of the phonons, not the transverse (shear) branch, and differences between the two IXS studies could be explained by different choices of equations of state used to compute $v_S$.

3.5. Iron-nickel

Debye, compressional, and shear sound velocities of bcc- and hcp-Fe$_{0.91}$Ni$_{0.09}$ are plotted in Figure 10 and compared to results from Lin et al. (2003) for Fe$_{0.92}$Ni$_{0.08}$ at 300 K. Velocities from both studies have been corrected to natural enrichment via equation 10. The wave velocities from both studies are generally in close agreement, with the exception of the data points around 25 GPa and 50 GPa. Improved statistics due to smaller energy step sizes (0.25 meV compared to 0.5 meV), energy resolution (1.1 meV compared to 2.2 meV), and equation of state constraints from the same sample batch (Morrison et al., 2018), along with our improved Debye velocity analysis method have allowed us to improve the constraints on hcp-Fe$_{0.91}$Ni$_{0.09}$ wave velocities. We robustly show that nickel decreases the shear velocity of hcp-iron. As described in Section 3.1, the reduction in shear wave velocity can be understood by substituting iron with a heavier element, such as nickel.

3.6. Iron-nickel-silicon

In Figure 11, we compare our Debye, compressional, and shear sound velocities of bcc- and hcp-Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ at 300 K with existing sound velocity studies on Fe-Si and Fe-Ni-Si alloys. Previous studies include an NRIXS study on bcc- and hcp-Fe$_{0.85}$Si$_{0.15}$ (Lin et al., 2003); a combined NRIXS and IXS study on hcp-Fe$_{0.86}$Ni$_{0.08}$Si$_{0.06}$ (Liu et al., 2016); and IXS studies on hcp-Fe$_{0.89}$Ni$_{0.06}$Si$_{0.07}$ (Antonangeli et al., 2010), hcp-Fe$_{0.91}$Si$_{0.09}$ (Antonangeli et al., 2018), and hcp-Fe$_{0.87}$Si$_{0.11}$ (Sakairi et al., 2018), bcc- and hcp-Fe$_{0.83}$Si$_{0.15}$ (Liu et al., 2014), and hcp-Fe$_{0.82}$Si$_{0.15}$ (Mao et al., 2012).
from this study and those from Lin et al. (2003) and Liu et al. (2014) have been corrected to natural enrichment via equation 10. The \( v_S \) from IXS studies by Antonangeli et al. (2010, 2018) are from their reported \( v_p \) curves, which are based on their measured \( v_p \) paired with their choice of equations of state.

Our reported \( v_D \) and \( v_S \) of hcp-Fe\(_{0.8}\)Ni\(_{0.1}\)Si\(_{0.1}\) are lower than those of hcp-Fe\(_{0.85}\)Si\(_{0.15}\) (Lin et al., 2003). Based on our findings that nickel decreases the shear velocity of iron and that silicon has a minimal effect on the shear velocity of Fe\(_{0.91}\)Ni\(_{0.09}\) for a given pressure (Figure 8), we would expect hcp-Fe\(_{0.85}\)Si\(_{0.15}\) to instead have even higher shear velocity than hcp-Fe\(_{0.8}\)Ni\(_{0.1}\)Si\(_{0.1}\). Our determined \( v_D \) and \( v_S \) of hcp-Fe\(_{0.8}\)Ni\(_{0.1}\)Si\(_{0.1}\) deviate from those of hcp-Fe\(_{0.868}\)Ni\(_{0.086}\)Si\(_{0.046}\) (Liu et al., 2016), especially at higher pressures where hcp-Fe\(_{0.868}\)Ni\(_{0.086}\)Si\(_{0.046}\) is noticeably lower than hcp-Fe\(_{0.8}\)Ni\(_{0.1}\)Si\(_{0.1}\). Based on our finding that silicon has a minimal effect on the shear velocity of Fe\(_{0.91}\)Ni\(_{0.09}\) for a given pressure, we would expect the values reported by Liu et al. (2016) and our study to more closely agree. Both Lin et al. (2003) and Liu et al. (2016) apply a parabolic ‘Debye-like’ phonon dispersion model to the low energy region of their phonon DOSs. Lin et al. (2003) use a fixed energy range of 3.5–14 meV for the entire pressure range. Liu et al. (2016) used \( E_{\text{min}} = 3.5 \) meV and varied \( E_{\text{max}} \) according to the goodness of fit \( \chi^2 \) (\( E_{\text{max}} = 13 \) meV for 30 GPa and \( E_{\text{max}} = 16.5 \) meV for 133 GPa). Because alloying iron with silicon appears to decrease the parabolic ‘Debye-like’ region of the phonon DOS (see Figure 5), a ‘Debye-like’ fit to Fe-Si and Fe-Ni-Si alloys, if extended to too large of an energy range, would produce artificially lower Debye velocities, resulting in systematically lower shear velocities. This could explain in part why the Debye and shear velocities of hcp-Fe\(_{0.85}\)Si\(_{0.15}\) (Lin et al., 2003) and hcp-Fe\(_{0.868}\)Ni\(_{0.086}\)Si\(_{0.046}\) (Liu et al., 2016) are lower than would be expected given our findings. The \( v_D \) and \( v_S \) from (Lin et al., 2003) are constrained by combining \( v_D \) with existing equations of state on hcp-Fe\(_{0.85}\)Si\(_{0.15}\) from Lin (2003), although specific EOS values were not cited in Lin (2003).

When comparing with previous NRIXS studies on similar compositions, the largest deviations from our results are those of Liu et al. (2016), with reported \( v_D \) and \( v_S \) values significantly lower than our results. As mentioned previously, \( v_p \) and \( v_S \) from our study are calculated by combining NRIXS determined \( v_D \) and in-situ unit-cell volume measurements with the Vinet hcp-Fe\(_{0.8}\)Ni\(_{0.1}\)Si\(_{0.1}\) equation of state from Morrison et al. (2018), which were all conducted with samples from the same Fe\(_{0.8}\)Ni\(_{0.1}\)Si\(_{0.1}\) synthesis batch. Liu et al. (2016) combines NRIXS constrained \( v_D \) with IXS constrained \( v_p \) to determine \( v_S \), and pressure is determined with an equation of state for samples from their synthesis batch. Although the sample compositions are similar between our study and Liu et al. (2016), other aspects of the data are noticeably different. The equation of state obtained in Liu et al. (2016) produces pressure differences of around +4 GPa around 50 GPa, compared to the EOS we obtain for our sample (Morrison et al., 2018); the bcc-hcp transition in Liu et al. (2016) is around 21 GPa, whereas we observe the transition around 16 GPa (Morrison et al., 2018); the NRIXS spectra are qualitatively different (the phonon modes around 25 meV produce a noticeable peak in our spectra, whereas this region is relatively flat in the spectra of Liu et al. (2016)). Further, if one uses the EOS reported in Liu et al. (2016) to compute the bulk modulus at 136 GPa, \( K_{T,136\text{GPa}} = 726 \) GPa, whereas \( K_{S,136\text{GPa}} = 835 \) GPa from their reported density, \( v_p \) and \( v_S \) at this condition, after correcting for natural enrichment. Note that the minimum energy used for constraining \( v_p \) from the IXS spectra was 30 meV Liu et al. (2016), a value that is relatively high for use in constraining wave velocities.
The computed $v_S$ from IXS studies by Antonangeli et al. (2010, 2018) are significantly higher than NRIXS determined $v_S$. Again, this could be partially attributed to the facts that the IXS studies are measuring the longitudinal acoustic branch of the phonons, not the transverse (shear) branch, and that the sampled data points on these phonon branches begin at relatively larger energy-transfers compared to NRIXS studies. Differences between the two IXS studies (and from the NRIXS values) could be explained by different choices of equations of state used to compute $v_S$.

3.7. Other light elements

We compare our reported $v_D$, $v_P$, $v_S$ for bcc- and hcp-Fe, Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ at 300 K to the sound velocities of other candidate core compositions in Figure 12. We include NRIXS studies on Fe$_3$S (Lin et al., 2004), Fe$_3$C (Gao et al., 2008; Chen et al., 2018), Fe$_7$C$_3$ (Chen et al., 2014), FeO, (Mg$_{0.06}$Fe$_{0.94}$)O$_6$[(Mg$_{0.16}$Fe$_{0.84}$)O (Wicks et al., 2017), FeH$_x$ (Mao et al., 2004), and FeH$_x$ (Thompson et al., 2018). We also include IXS studies on Fe$_3$S (Fiquet et al., 2009) and FeH$_x$ (Shibazaki et al., 2012). Although these compounds do not have the same crystal structures nor are they strict metallic alloys, it is informative to draw comparisons of their sound velocities with respect to discussions on iron-rich planetary cores. Note that most of the phases being compared in this section were studied using NRIXS, thus the sound velocities are plotted as reported, without a correction to natural enrichment.

When plotted as a function of pressure, the computed $v_P$ of Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ from NRIXS results show negligible differences with our re-analysis of similar data for hcp-Fe (Murphy et al., 2013). The computed $v_P$ of Fe$_3$S (Lin et al., 2004) trends $\sim$4% below hcp-Fe, while the $v_P$ of iron-hydrides (computed from NRIXS (Mao et al., 2004; Thompson et al., 2018); constrained from phonon dispersion measurements (Shibazaki et al., 2012)) trend above hcp-Fe. Although the $v_P$ values of Fe$_3$C also trend higher than hcp-Fe (Fiquet et al., 2009; Gao et al., 2008; Chen et al., 2018), the value constrained from phonon dispersion measurements around 70 GPa (Fiquet et al., 2009) is significantly higher than the trend computed from NRIXS (Gao et al., 2008). The compressional velocities of Fe$_7$C$_3$ computed from an NRIXS study (Chen et al., 2014) shows a noticeably different $d v_P / d P$ slope than Fe$_3$C. As a result, the $v_P$ of Fe$_3$C falls above that of Fe above $\sim$25 GPa, while the $v_P$ of Fe$_7$C$_3$ falls below iron above $\sim$70 GPa. The calculated $v_P$ values for iron-rich (Mg,Fe)O (Wicks et al., 2017) deviates from that of hcp-Fe above $\sim$50 GPa, as the $d v_P / d P$ slope of (Mg,Fe)O is noticeably different from that of hcp-Fe and Fe$_3$C.

As $v_D$ is predominately influenced by $v_S$ rather than by $v_P$ in NRIXS studies, the trends of $v_P$ are similar to those of $v_S$ in Figure 12. Therefore we focus the following discussion on $v_S$. The constraints on $v_S$ as a function of pressure suggest that silicon has a negligible effect on the $v_S$ of hcp-Fe and that iron-hydrides (Mao et al., 2004; Shibazaki et al., 2012; Thompson et al., 2018) have a higher $v_S$ than hcp-Fe. The elements nickel, silicon, oxygen, and carbon all appear to decrease $v_S$ when alloyed with hcp-Fe, so it is reasonable that one or a combination of these elements may help explain the relatively low $v_S$ of the inner core. The $v_S$ of Fe$_{0.91}$Ni$_{0.09}$ trends $\sim$6.5% below that of hcp-Fe at 100 GPa. Fe$_3$S (Lin et al., 2004) falls $\sim$10% below hcp-Fe at 60 GPa, although the $d v_S / d P$ of Fe$_3$S is slightly steeper than hcp-Fe, so this difference may decrease at higher pressures. At 100 GPa, the $v_S$ of iron-rich (Mg,Fe)O (Wicks et al., 2017) is $\sim$26% lower than that of hcp-Fe. The $v_S$ of Fe$_7$C$_3$ (Chen et al., 2014) is noticeably slower than
that of Fe$_3$C (Gao et al., 2008). From 30–50 GPa, the $v_S$ of Fe$_3$C is ~7–10% slower than that of hcp-Fe, while the $v_S$ of Fe$_7$C$_3$ is ~31% slower than that of hcp-Fe. The $dE_S/dP$ slope of Fe$_7$C$_3$ is slightly lower than that of hcp-Fe, so the difference between Fe$_7$C$_3$ and hcp-Fe may increase with pressure.

We plot bulk sound speed $v_\phi$ for hcp-Fe, Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.6}$Ni$_{0.4}$Si$_{0.1}$ at 300 K in Figure 13. We note that the trends of hcp-Fe, Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.6}$Ni$_{0.4}$Si$_{0.1}$ are all remarkably linear, suggesting the validity of Birch’s law for these compositions, at least at 300 K in the pressure range investigated. We compare to $v_\phi$ from other NRIXS iron-light element studies, including Fe$_3$S (Lin et al., 2004), Fe$_3$C (Gao et al., 2008), Fe$_7$C$_3$ (Chen et al., 2014), FeO, (Mg$_{0.06}$Fe$_{0.94}$)O, (Mg$_{0.16}$Fe$_{0.84}$)O (Wicks et al., 2017), FeH$_2$ (Mao et al., 2004), and FeH$_3$ (Thompson et al., 2018). There is noticeable scatter in the FeH$_x$ data sets. We note that although (Mg,Fe)O exhibits a smoothly varying trend, it noticeably deviates from Birch’s law. This can be explained by a spin pairing transition that occurs around a density of 8.3 g/cm$^3$ at 300 K for (Mg$_{0.96}$Fe$_{0.04}$)O (Wicks et al., 2010).

3.8. Limits to extrapolations

The extrapolation of $v_P$ and $v_S$ of candidate iron alloys to inner core conditions requires a fairly accurate constraint on the pressure and temperature derivatives of these quantities. Due to necessary long integration times and technique requirements for IXS and NRIXS studies, the number of data points and compression range in $v_P$ and $v_S$ data sets are typically much less than in, for instance, equation of state studies using x-ray diffraction. This hinders the ability to make an informed extrapolation of $v_P$ and $v_S$ to pressures relevant to the inner core. Furthermore, the thermal effects $dv_P/dT$ and $dv_S/dT$ are more poorly constrained, even for hcp-Fe. For example, a value for $dv_S/dT$ for hcp-Fe was constrained to be $-4.6 \times 10^{-4}$ km s$^{-1}$ K$^{-1}$ from a high-pressure high-temperature NRIXS study (Lin et al., 2005). A more recent constraint based on hcp-Fe ab initio constraints from Mardovoll et al. (2013a) gives $dv_S/dT = -3.2 \times 10^{-4}$ km s$^{-1}$ K$^{-1}$.

Chen et al. (2014) suggest an inner core composed entirely of Fe$_7$C$_3$ would explain the $\rho$, $v_P$, and $v_S$ of the inner core without invoking large sound velocity temperature effects. However, cosmochemical and iron-silicate melt partitioning studies have suggested the carbon content of the inner core is <0.7–1 wt% (Wood et al., 2013; Zhang and Yin, 2012). An ab initio study suggested the density of Fe$_7$C$_3$ was too low to be a substantial component of the inner core (Li et al., 2016), and, in the analysis of equations of state and seismic observations, Morrison et al. (2018) find a carbon content of less than 1 wt%. FeO and iron-rich (Mg,Fe)O also have a low $v_S$ compared to that of hcp-Fe, suggesting a large oxygen content could explain the low $v_S$ of the inner core. However, solid-liquid iron partitioning studies have suggested oxygen is largely incompatible in the inner core (Alfè et al., 2002, 2007). Additionally, Morrison et al. (2018) found the bulk sound speed of FeO limited the oxygen content of the inner core to 2 wt%. It is of course recognized that these constraints were obtained from mixing end-member components which do not have the same crystal structures, and thus more realistic candidate core-forming alloys must be examined in the future. Nevertheless, constraining the effect of large compression and very high temperatures (~4000–5000 K) on the sound velocities of realistic iron-nickel alloys, combined with tighter seismic constraints, will be essential to take the next steps in constraining inner core composition using mineral elasticity data.
4. Vibrational Grüneisen parameter

The vibrational component of the Grüneisen parameter $\gamma_{\text{vib}}$ for a given phonon mode can be defined as the volume dependence of energy of that phonon mode,

$$\gamma_{\text{vib}} = -\frac{\partial \ln \omega}{\partial \ln V} = -\frac{\partial \ln E}{\partial \ln V},$$

(11)

where $\omega$ is the frequency corresponding to the given phonon mode, and $E$ is the corresponding energy. As we have measured the phonon DOS for each composition as a function of volume, we can evaluate constraints for the vibrational Grüneisen parameter, such as using a phonon DOS scaling relation Murphy et al. (2011a). We plot our phonon DOSS for each hcp phase in Figure 14. Upon visual inspection, the phonon DOSs for a given composition appear to be related by a single scaling parameter. For a given hcp-phase, we scale a single phonon DOS $D(E, V_i)$ to all other phonon DOSs $D(E, V)$ using the relation

$$D(E, V) = \xi(V, V_i)D\left[\xi(V, V_i)E, V_i\right],$$

(12)

where $V_i$ is the volume of the reference phonon DOS, $V$ is the volume to which the reference phonon DOS is scaled, $\xi(V, V_i)$ is an energy independent scaling parameter, and $\xi(V, V_i) = 1$ when $V = V_i$. For hcp-Fe$_{0.91}$Ni$_{0.09}$, we compare the measured phonon DOSs to the scaled phonon DOS measured at $V_i = 18.72 \pm 0.04 \text{ Å}^3$ ($P = 48 \pm 1 \text{ GPa}$) in the left panel of Figure 14. Similarly, for hcp-Fe$_{0.8}Ni_{0.1}Si_{0.1}$, we compare the measured phonon DOSs to the scaled phonon DOS measured at $V_i = 19.09 \pm 0.06 \text{ Å}^3$ ($P = 41 \pm 1 \text{ GPa}$) in the middle panel of Figure 14. For our re-analysis of hcp-Fe, we compare the measured phonon DOSs to the scaled phonon DOS measured at $V_i = 17.10 \pm 0.07 \text{ Å}^3$ ($P = 90 \pm 3 \text{ GPa}$) in the right panel of Figure 14.

For a given hcp-phase, we apply equation 12 to scale a reference phonon DOS $D(E, V_i)$ to all other phonon DOSs $D(E, V)$ using a linear least squares regression, thereby obtaining a scaling parameter corresponding to each pair of phonon DOSs. We repeat this process with the other phonon DOS acting as the reference to obtain a total of $7 \times 8 = 56$ scaling parameters for hcp-Fe$_{0.91}Ni_{0.09}$, $5 \times 6 = 30$ scaling parameters for hcp-Fe$_{0.8}Ni_{0.1}Si_{0.1}$, and $9 \times 10 = 90$ scaling parameters for hcp-Fe. These scaling parameters are plotted as a function of $V/V_i$ in Figure S3. The near-linear trend of the scaling parameter $\xi$ with respect to $V/V_i$ demonstrates the applicability of the scaling law in equation 12.

We combine a rephrasing of equation 11,

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

(13)

with the commonly applied empirical relation,

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

(14)

where $q$ is a fitting parameter, and the subscript $i$ refers to a reference phonon DOS.
Combining equations 13 and 14 and integrating yields

\[ \xi(V, V_i) = \exp \left\{ \frac{\gamma_{\text{ vib.}i}}{q} \left[ \left( \frac{V}{V_i} \right)^q - 1 \right] \right\}, \tag{15} \]

where \( q \neq 0 \). Substituting an analogous relation to equation 14,

\[ \gamma_{\text{ vib.}i} = \gamma_{\text{ vib.}0} \left( \frac{V}{V_0} \right)^q, \tag{16} \]

into equation 15 yields

\[ \xi(V, V_i) = \exp \left\{ \frac{\gamma_{\text{ vib.}0}}{q} \left( \frac{V}{V_0} \right)^q \left[ \left( \frac{V}{V_i} \right)^q - 1 \right] \right\}, \tag{17} \]

where \( \xi \) is the scaling parameter as a function of volume \( V \) and reference volume \( V_i \). \( V_0 \) is the volume at 0 GPa, as determined with an equation of state (Morrison et al., 2018). The vibrational Grüneisen parameter at 0 GPa, \( \gamma_{\text{ vib.}0} \), and \( q \) are fitting parameters. We applied equation 17 to the scaling parameters in Figure S3 using a linear least squares regression to determine \( \gamma_{\text{ vib.}0} \) and \( q \). Then equation 16 was applied to determine the vibrational Grüneisen parameter as a function of volume \( V_i \).

We applied a grid search to the regression of equation 17, and we found the scaling parameter values shown in Figure S3 do not constrain \( q \). Therefore, we fix \( q \) at the commonly assumed value of 1, and obtain values of \( \gamma_{\text{ vib.}0} = 2.04 \pm 0.01 \) for hcp-Fe, \( \gamma_{\text{ vib.}0} = 2.07 \pm 0.02 \) for hcp-Fe\(_{0.91}\)Ni\(_{0.09}\), and \( \gamma_{\text{ vib.}0} = 2.03 \pm 0.05 \) for hcp-Fe\(_{0.8}\)Ni\(_{0.1}\)Si\(_{0.1}\). The resulting vibrational Grüneisen parameters are plotted as lines with shaded uncertainties in Figure 15.

To test the robustness and validity of the above method, we approximate the vibrational Grüneisen parameter with a second method outlined in the supplemental material. While this second method is a coarse approximation for \( \gamma_{\text{ vib.}i} \), we note that it does not rely on the application of the empirical relation in equation 14, on a linear least squares fit, or on fixing the fitting parameter \( q \). Therefore, it serves as a check of the validity of equation 17. Both methods of determining \( \gamma_{\text{ vib.}i} \) agree well within error bars within the measured volume region (Figure S9).

The \( \gamma_{\text{ vib}} \) for hcp-Fe\(_{0.91}\)Ni\(_{0.09}\) and our re-analysis of hcp-Fe data from Murphy et al. (2011a) are in close agreement and nearly indistinguishable within our reported error bars, and those for Fe\(_{0.8}\)Ni\(_{0.1}\)Si\(_{0.1}\) trend lower (Figure 15). We compare to previously reported values of \( \gamma_{\text{ vib}} \) for hcp-Fe. Ab initio calculations by Sha and Cohen (2010) computed at 500 K are similar to our results, although the slope of \( \gamma_{\text{ vib}} \) with respect to volume is noticeably different. The \( \gamma_{\text{ vib}} \) reported by Dewaele et al. (2006) is determined with shock-wave and 300 K static compression XRD data and is in close agreement with our results. Merkel et al. (2000) estimate \( \gamma_{\text{ vib}} \) with Raman spectroscopy at 300 K, and Dubrovinsky et al. (2000) estimate \( \gamma_{\text{ vib}} \) with static compression XRD data.

Fei et al. (2016) calculate \( \gamma_{\text{ vib}} \) from the results of Murphy et al. (2011a), much as we do in this study. In Figure 16, we compare \( \gamma_{\text{ vib}} \) reported in Murphy et al. (2011a), Fei et al. (2016), and our study, which all use the same NRIXS hcp-Fe data set from Murphy et al. (2011a). We plot our \( \gamma_{\text{ vib}} \) results for hcp-Fe calculated using equation 17. Note that each study applies the same empirical constraint of equation 14. Our analyses...
are internally consistent and in close agreement with published results from Murphy et al. (2011a) with \( q = 1 \). Small differences between our analysis using equation 17 and reported values from Murphy et al. (2011a) are likely due to our exclusion of the NRIXS data set at 36 GPa. However, our results of \( \gamma_{\text{vib}} \) trend significantly higher than the trend reported in Fei et al. (2016).

We investigate the difference between our \( \gamma_{\text{vib}} \) analysis and that of Fei et al. (2016), and we estimate the effect of this difference on the extrapolation of an EOS to inner core conditions. We apply equation 15 to the \( \gamma_{\text{vib}} \) of Fei et al. (2016), and we compare the resulting scaled phonon DOS to ours in Figure 17 and Figures S4 and S5 in the supplementary material. Figure 17 illustrates the scaling using the 30 GPa phonon DOS, and Figures S4 and S5 illustrate the scaling using the 90 and 171 GPa phonon DOS, respectively. The scaling fit in this study weights the phonon modes roughly evenly, whereas the scaling fit in Fei et al. (2016) preferentially fits the lower energy region of the phonon DOS. This is particularly evident in Figures 17 and Figure S5 in the supplementary material. The \( \gamma_{\text{vib}} \) from Fei et al. (2016) appears to be closer to the so-called Debye Grüneisen parameter, defined as

\[
\gamma_D = \frac{1}{3} \left( V \frac{\nu_D}{v_D} \right) T. \tag{18}
\]

This is also supported by the close agreement between the \( \gamma_{\text{vib}} \) from Fei et al. (2016) and the \( \gamma_D \) from Murphy et al. (2011a).

We estimate the impact of \( \gamma_{\text{vib}} \) from Murphy et al. (2011a), Fei et al. (2016), and this study on isothermal EOS extrapolation to inner core conditions. We extrapolate the 300 K hcp-iron EOS from Dewaele et al. (2006) to 5500 K using the methods described in Morrison et al. (2018). We apply \( \Theta_0 = 417 \) K and each of the \( \gamma_{\text{vib}} \) from Murphy et al. (2011a), Fei et al. (2016), and this study. The resulting density, bulk modulus, and bulk sound speed are compared in Figure 18. The bars to the right represent the estimated uncertainty as reported in Morrison et al. (2018), where contributions from electronic or anharmonic contributions to thermal pressure are excluded in order to isolate the effect of different \( \gamma_{\text{vib}} \) and \( q \) values used. The seismic model AK135-F is plotted for reference (Kennett et al., 1995) with uncertainties for \( \rho \) (2%), \( K_S \) (2.3%), and \( v_\phi \) (0.6%) (Masters and Gubbins, 2003; Deuss, 2008).

The \( \gamma_{\text{vib}} \) from Murphy et al. (2011a), Fei et al. (2016), and this study produces densities, bulk modulus, and bulk sound speed at 5500 K and inner core pressures that agree within 0.5%. In comparison to the current equation of state uncertainty and seismic uncertainty, this difference is negligible. This is before taking into account the contributions from electronic or anharmonic terms to thermal pressure. Morrison et al. (2018) estimated the electronic and anharmonic contributions to thermal pressure with theoretical calculations from Dewaele et al. (2006) and found a combined \( P_{\text{el}} + P_{\text{ahn}} \) of 14.5 GPa at 5500 K. At 5500 K and 13.7 g/cm\(^3\) density, the formulation from Fei et al. (2016) estimates \( P_{\text{el}} + P_{\text{ahn}} = 14.8 \) GPa, in close agreement with Dewaele et al. (2006). Therefore, adding electronic and anharmonic contributions to thermal pressure to Figure 18 would not noticeably change the difference between the three compared thermal equations of state for hcp-iron.

Morrison et al. (2018) applied the \( \gamma_{\text{vib}} \) from Murphy et al. (2011a) and \( \Theta_0 = 417 \) K (Dewaele et al., 2006) to isothermal equations of state of hcp-Fe\(_{0.91}\)Ni\(_{0.09}\) and Fe\(_{0.8}\)Ni\(_{0.1}\)Si\(_{0.1}\)
to determine thermal equations of state. They then reported the corresponding $\rho$, $K_S$, and $v_0$. We find the differences between the $\gamma_{vib}$ of hcp-Fe, Fe$_{0.91}$Ni$_{0.09}$, and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ to be within mutual uncertainty, and our re-analysis of $\gamma_{vib}$ of hcp-Fe is in close agreement with that of Murphy et al. (2011a). Therefore, we conclude that our application of the $\gamma_{vib}$ of hcp-Fe from Murphy et al. (2011a) to hcp-Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ in Morrison et al. (2018) is a reasonable approximation.

5. Vibrational free energy

In Section 4, we determined the vibrational Grüneisen parameter for the suite of iron-alloys investigated here from a scaling approach to the measured phonon DOS. We showed the application of the vibrational Grüneisen parameter to estimates of hcp-iron’s thermoelastic properties at inner core conditions using Mie-Grüneisen-Debye thermal equation of state. Another approach to estimating the thermal properties of a solid is to evaluate the volume dependence of the vibrational free energy of the material, as outlined in Murphy et al. (2011a,b, 2013).

The harmonic (h) vibrational free energy $F_{vib}^h$ is accessible from the phonon DOS with

$$F_{vib}^h = \frac{1}{\beta} \int \ln \left( 2 \sinh \frac{\beta E}{2} \right) D(E,V)dE,$$

where $\beta = (k_BT)^{-1}$. When combined with the electronic and anharmonic components of pressure, $P_{el}$ and $P_{vib}^{anh}$, this yields the total thermal pressure $P_{th}$,

$$P_{th} = P_{vib}^h + P_{el} + P_{vib}^{anh} = -\left( \frac{\partial F_{vib}^h}{\partial V} \right)_T - \left( \frac{\partial F_{el}}{\partial V} \right)_T - \left( \frac{\partial F_{vib}^{anh}}{\partial V} \right)_T.$$

Constraints on the thermal properties of hcp-iron have also come from shock-compression experiments using the thermodynamic Grüneisen parameter and Mie-Grüneisen theory (Jeanloz, 1979; Brown and Mcqueen, 1986), theoretical studies have also (Wasserman et al., 1996; Stixrude et al., 1997; Vociadlo et al., 2000; Alfè et al., 2001; Sha and Cohen, 2010; Bouchet et al., 2013), in addition to those discussed in Section 4. By comparison, the thermal pressure of iron-nickel and iron-silicon alloys has received little attention. Zhang et al. (2014) investigate the thermal pressure of iron-nickel-silicon alloys with shock compression, and Côté et al. (2010, 2012) apply theoretical calculations to study the thermal pressure of iron-silicon and iron-nickel alloys, respectively. Here, we apply the methods of Murphy et al. (2011b) to Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$. For consistency, we also re-analyze NRIXS data from Murphy et al. (2011a) to ensure a systematic comparison of the alloys.

The vibrational free energy $F_{vib}^h$ of Fe$_{0.91}$Ni$_{0.09}$, Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$, and Fe at 300 K is plotted in Figure S6, and we fit empirical second-order polynomials to the $F_{vib}^h$ of the hcp phases to calculate the derivative $(\partial F_{vib}^h/\partial V)_T$. The polynomials are listed in Figure S6, where volume $V$ is in Å$^3$ and $F_{vib}^h$ is in meV/atom. We find the curvature of $F_{vib}^h$ for hcp-Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ is poorly constrained due to the smaller compression range explored for the Fe-Ni-Si alloy. We find for hcp-Fe that $P_{vib}^h = -0.29V + 7.5$, for hcp-Fe$_{0.91}$Ni$_{0.09}$ that $P_{vib}^h = -0.21V + 6.2$, and for that hcp-Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ $P_{vib}^h = -0.07V + 3.6$, where $V$ is in Å$^3$ and $P_{vib}^h$ has been converted to units of GPa. The resulting $P_{vib}^h$ are plotted
in Figure S7, and the $P_{vib}^h$ and corresponding $P_{vib}^h$ for each hcp volume can be found in Table 4.

As can be seen in equation 19, $F_{vib}^h$ is directly proportional to temperature. Therefore, our 300 K data can be used to inform the temperature dependence of the harmonic $P_{vib}^h$ with the following relation:

$$ P_{vib}^h(V, T) = \left( \frac{T}{300 \text{ K}} \right) P_{vib}^h(V, 300 \text{ K}). $$

We plot the temperature dependent harmonic $P_{vib}^h$, in Figure 19, and compare to the harmonic $P_{vib}^h$ calculated by Alfè et al. (2001). We note that the slope of $P_{vib}^h$ with volume of hcp-Fe is steeper than that previously published by Murphy et al. (2011b), due in part to our exclusion of the NRIXS data at 36 GPa, which had much lower statistical quality compared with the other compression points in the same data set. Our re-analysis of $P_{vib}^h$, for hcp-Fe deviates significantly, especially at lower volumes (higher pressures) from theoretical calculations reported in Alfè et al. (2001) (Fig. 19). The $P_{vib}^h$ for hcp-Fe$_{0.91}$Ni$_{0.09}$ is nearly indistinguishable from that of hcp-Fe. The slope of $P_{vib}^h$, for hcp-Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ is more shallow than that of hcp-Fe or Fe$_{0.91}$Ni$_{0.09}$, although we note the slope of hcp-Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ is not as well constrained due to the smaller compression range explored.

Our above discussion does not include the anharmonic $P_{an}^h$ and the electronic $P_{el}$ contributions to the thermal pressure $P_{th}$, as the phonon DOSs at 300 K for these alloys are insensitive to these components. The $P_{an}^h$ and $P_{el}$ for iron alloys are not well constrained by experimental data. Murphy et al. (2011b) and Sakai et al. (2014) used the $P_{an}^h$ and $P_{el}$ of hcp-Fe reported in Dewaele et al. (2006). These values are based on hcp-Fe ab initio calculations by Alfè et al. (2001) and use the $P_{vib}^h$ and $P_{el}$ formulation from Dorogokupets and Oganov (2006). As similar ab initio calculations are not available for hcp-Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$, we applied the hcp-Fe $P_{vib}^h$ and $P_{el}$ terms from Dewaele et al. (2006) to each of our hcp compositions to estimate $P_{th}$. For modeling metallic materials at very high temperatures, the electronic term becomes significant. For example, at 104 GPa and 5500 K, the contributions from $P_{vib}^h$, $P_{an}^h$, $P_{el}$ for hcp-Fe$_{0.91}$Ni$_{0.09}$ are as follows: 49 GPa, 3 GPa, and 13 GPa, respectively. The estimated contributions of $P_{vib}^h$, $P_{an}^h$, and $P_{el}$ for hcp-Fe$_{0.91}$Ni$_{0.09}$, Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$, and Fe at 5500 K are tabulated in Table 4, and the corresponding total thermal pressures $P_{th}$ for 300, 2000, 4000, and 5500 K are plotted in Figure S8.

6. Vibrational entropy and thermal expansion

The volumetric thermal expansion coefficient $\alpha_{vib}$ can be obtained from the volume dependence of the vibrational entropy and the isothermal bulk modulus. The vibrational entropy per $^{57}$Fe resonant atom, $S_{vib}$, is accessible via the phonon DOS,

$$ S_{vib} = \frac{k_B \beta}{2} \int E \coth \left( \frac{\beta E}{2} \right) D(E, V) dE - k_B \int \ln \left( 2 \sinh \left( \frac{\beta E}{2} \right) \right) D(E, V) dE. $$

The $S_{vib}$ for bcc- and hcp-Fe$_{0.91}$Ni$_{0.09}$, Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$, and Fe are plotted in Figure S11.
The derivative of $S_{vib}$ with respect to volume is related to volumetric $\alpha_{vib}$ with

$$\alpha_{vib} = \frac{1}{K_T} \left( \frac{\partial S_{vib}}{\partial V} \right)_T,$$

where $K_T$ is the isothermal bulk modulus, accessible with equations of state (EOSs). For hcp-Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$, we use the corresponding Vinet EOSs from Morrison et al. (2018). For hcp-Fe, we use the Vinet EOS from Dewaele et al. (2006). The EOS experimental conditions and parameters are listed in Table S2. To calculate $(\partial S_{vib}/\partial V)_T$, we apply linear fits to the hcp data. These fits and their corresponding equations are displayed in Figure S11. Our resulting $\alpha_{vib}$ for the hcp phases at 300 K are plotted in Figure 20 and tabulated in Table S5. The $\alpha_{vib}$ of hcp-Fe and Fe$_{0.91}$Ni$_{0.09}$ are in close agreement, while Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ has a slightly higher thermal expansion at large volumes. At smaller volumes, $\alpha_{vib}$ of Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ seems to approach that of hcp-Fe and Fe$_{0.91}$Ni$_{0.09}$.

7. Conclusions

We performed high pressure nuclear resonant inelastic x-ray scattering (NRIXS) measurements on bcc- and hcp-Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ at 300 K with in situ x-ray diffraction. From these data, we determine the partial phonon density of states for each composition. To ensure a systematic comparison to pure iron, we re-analyze the hcp-iron NRIXS data presented in Murphy et al. (2011a), Murphy et al. (2011b), and Murphy et al. (2013) using the same methods used to analyze our Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ data sets.

We demonstrate a new method of determining the Debye sound velocity from the low energy region of the phonon DOS. This method applies the corrected Akaike Information Criteria and uses a binning of many possible fit ranges to determine a probability distribution function of the Debye sound velocity. Unlike previous methods, this method does not depend on picking an energy fit range for the phonon DOS, and it provides an improved estimate on the Debye sound velocity uncertainty. Using this new method, Debye sound velocities were determined for bcc- and hcp-Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$. Using the equations of state constrained for the same compositions (Morrison et al., 2018), the compressional and shear sound velocities, as well as the shear modulus, of bcc- and hcp-Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ were calculated at 300 K. We find that 9 at% nickel decreases the shear velocity of hcp-iron by ~6%, and that silicon has a minimal effect on the shear velocity of hcp-Fe$_{0.91}$Ni$_{0.09}$.

From the volume scaling of the phonon DOS, we constrain the 300 K vibrational component of the Grüneisen parameter for hcp-Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$. Within the compression range of the measurements, we find that the Grüneisen parameters of hcp-Fe$_{0.91}$Ni$_{0.09}$ are similar to those of hcp-Fe, whereas those of Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ trend lower. Extrapolation using a Mie-Grüneisen-Debye model with these newly determined values to inner core conditions leads to insignificant deviations from the assumption that these particular alloys have the same Grüneisen parameter and scaling value as hcp-Fe (Morrison et al., 2018). More importantly, we find that the volume dependence of the vibrational free energy of hcp-Fe, which is directly related to the vibrational component of thermal pressure, shows a significant positive deviation from theoretical calculations.
for hcp-Fe at pressures and temperatures of Earth’s core (Fig. 19). The total thermal pressure for iron-alloys under core conditions, most importantly at thousands of kelvin, must consider the electronic component and to lesser extent, the anharmonic component \cite{Morrison2018}. These terms, in particular for hcp-iron alloys, are thus far only available from theoretical studies, and thus far only reported for hcp-Fe. By combining our experimentally constrained vibrational component with theoretical estimates of the anharmonic and electronic contributions by Alfé \textit{et al.} \cite{Alfe2001}, we provide an estimate for the total thermal pressure of hcp-Fe, hcp-Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ at core pressures and temperatures Table 4.

The phonon DOS also provides access to the vibrational component of entropy per $^{57}$Fe atom, the volume derivative of which is directly related to the product of isothermal bulk modulus and thermal expansion. Therefore, we can apply the isothermal bulk modulus constrained by Morrison \textit{et al.} \cite{Morrison2018} to determine the vibrational component of thermal expansion for hcp-Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$. The vibrational thermal expansion of hcp-Fe$_{0.91}$Ni$_{0.09}$ is indistinguishable from that of hcp-iron. Silicon slightly increases the vibrational thermal expansion of Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ at low compressions, but at compressions above 65 GPa, the effect becomes negligible.

Other vibrational properties have been derived from the phonon DOS, including constraints on the mean-square displacement of the iron atoms. We find that adding 9 at% nickel decreases the Lamb-Mössbauer factor of hcp-iron by $\sim$1\%, and that silicon has a minimal impact on the Lamb-Mössbauer factor of hcp-Fe$_{0.91}$Ni$_{0.09}$. With increasing pressure, the vibrational kinetic energy per $^{57}$Fe atom of hcp-Fe$_{0.91}$Ni$_{0.09}$ trends lower than that of hcp-Fe, whereas Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ is indistinguishable from that of hcp-Fe. Furthermore, we constrain the vibrational component of specific heat from the phonon DOS. The vibrational specific heat of hcp-Fe$_{0.91}$Ni$_{0.09}$ trends slightly higher than that of hcp-Fe, while that of Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ is indistinguishable from that of hcp-iron. In summary, we present a systematic approach to provide improved constraints on the effects of nickel and silicon on a range of thermoelastic and vibrational properties of iron, including the sound velocities, all of which are important in modeling the core of Earth and other iron-rich cores of planets.

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Figure 1: Comparison of raw (unnormalized) NRIXS spectra for bcc-Fe$_{0.91}$Ni$_{0.09}$, Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$, and Fe at 0 GPa and 300 K collected around the resonance energy of $^{57}$Fe at 14.5125 keV with a step size of 0.25 meV. The numbers in the upper left of each panel indicate the collection time per data point.

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Table 1: Results from x-ray diffraction and 300 K equations of state

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<th>Phase</th>
<th>(a)</th>
<th>(c)</th>
<th>Volume Density(^a)</th>
<th>Pressure(^b) (K_T)</th>
<th>(\frac{\partial K_T}{\partial \bar{V}})</th>
<th>(K_T)</th>
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<td>2.863(1)</td>
<td>23.46(3)</td>
<td>8.062(9) 0</td>
<td>168(8)</td>
<td>4.7(1.3)</td>
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<tr>
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<td>23.73(2)</td>
<td>7.99(1) 0</td>
<td>147(3)</td>
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<td>8.11(1) 1.7(1)</td>
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\(^a\)Density calculations account for sample enrichment

\(^b\)Pressure, isothermal bulk modulus \((K_T)\), and pressure derivative of bulk modulus \((\frac{\partial K_T}{\partial \bar{V}})\) were calculated from volumes paired with Vinet EOSs listed in Table S2 in the supplementary material (Morrison et al., 2018).
Table 2: Results from NRIXS sound velocity analysis

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$^a$The tabulated values for density, Debye sound velocity, bulk sound speed, compressional velocity, and shear velocity all account for $^{57}$Fe enrichment

$^b$Re-analyzed from Murphy et al. (2013)
Figure 2: Partial phonon density of states (DOS) of bcc-Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$. Phonon DOSs are offset for visibility. Pressures were determined from unit-cell volumes measured in situ.
Figure 3: Partial phonon density of states (DOS) of hcp-Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ and total phonon DOS of hcp-Fe re-analyzed from Murphy et al. (2013). Spectra are offset for visibility. Pressures were determined from unit-cell volumes measured in situ.
Figure 4: Partial phonon DOS (PDOS) of bcc-Fe\(_{0.91}\)Ni\(_{0.09}\), Fe\(_{0.8}\)Ni\(_{0.1}\)Si\(_{0.1}\), and total PDOS of Fe at 0 GPa are compared to PDOSs scaled to 0 GPa of hcp-Fe\(_{0.91}\)Ni\(_{0.09}\) (scaled from 48 GPa), Fe\(_{0.8}\)Ni\(_{0.1}\)Si\(_{0.1}\) (scaled from 41 GPa), and Fe (scaled from 90 GPa, re-analyzed from Murphy et al. (2013)). The scaling was accomplished using our determined \(\gamma_{0,vib}\) and \(q\) for each composition and the scaling procedure detailed in section 4.
Figure 5: Phonon DOSs of hcp-Fe, Fe$_{0.91}$Ni$_{0.09}$, and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ scaled according to equation 2 to allow for visual representation of the low energy region used to constrain the Debye sound velocity. Examples of two typical phonon dispersion models used to constrain the Debye sound velocity are plotted: the Debye-like model (flat black solid line) and the power law model (equation 3, black dashed line). The hcp-Fe data is from our re-analysis of Murphy et al. (2013), and all other data is from this study. Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ data were conveniently collected at the same pressure of 41 GPa. The flat region at low energy appropriate for fitting a constant Debye-velocity model is much larger for hcp-Fe$_{0.91}$Ni$_{0.09}$ than for hcp-Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$. We note that the fit models plotted here are purely demonstrative and do not directly reflect our reported Debye velocities. See text for a detailed description of our Debye velocity determination method.
Figure 6: To illustrate our Debye velocity determination, the power law function (equation 3) is applied to the low energy region of the phonon DOS of hcp-Fe$_{0.91}$Ni$_{0.09}$ at 41 GPa. In the top panel, we plot the fit quality of the model as a function of starting energy range $E_{\text{min}}$ and ending energy range $E_{\text{max}}$. Fit quality is assessed as $\exp(-\text{AICc}/2)$, where the corrected Akaike Information Criteria (AICc) is defined in equation 4. Larger values of $\exp(-\text{AICc}/2)$ represent higher quality fits. In the middle panel, we plot the resulting Debye velocity as a function of $E_{\text{min}}$ and $E_{\text{max}}$. These variations in Debye velocity highlight the advantage of our Debye velocity analysis method over a fixed energy range, which may influence the resulting Debye velocity. In the bottom panel, we plot the probability distribution of the Debye velocity as calculated from the top two panels using a bin size of 10 m/s. The red line and shaded region represent the most probable $v_D$ and its uncertainty, respectively. See section 3.1 for a detailed description of the analysis methods used.
Figure 7: Debye velocity ($v_D$) probability distribution functions of hcp-Fe, Fe$_{0.91}$Ni$_{0.09}$, and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ at 300 K using a bin size of 10 m/s. The hcp-Fe data is from our re-analysis of Murphy et al. (2013), and all other data is from this study. The red line and shaded region represent the most probable $v_D$ and its uncertainty, respectively. The uncertainty of $v_D$ can vary noticeably depending on the NRIXS spectra and the phonon dispersions.
Figure 8: Debye velocity ($v_D$), compressional velocity ($v_P$), and shear velocity ($v_S$) for Fe (gray), Fe$_{0.91}$Ni$_{0.09}$ (orange), and Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ (blue) as a function of density and pressure. The bcc-phase (open circles) is distinguished from the hcp-phase (filled circles). The hcp-Fe data is from our re-analysis of Murphy et al. (2013), and all other data is from this study. Sound velocity and density values account for the $^{56}$Fe enrichment of the samples.
Figure 9: A comparison of Debye ($v_D$), compressional ($v_P$), and shear ($v_S$) sound velocities for bcc- and hcp-Fe from NRIXS, IXS, and ultrasonic experimental studies at 300 K. Data from Murphy et al. (2013) has been re-analyzed. For NRIXS studies conducted with $^{57}$Fe enriched samples, we plot sound velocities that have been corrected to those of natural enrichment via equation 10, except for velocities from (Liu et al., 2016), where their reported natural enrichment correction was applied.
Figure 10: A comparison of Debye ($v_D$), compressional ($v_P$), and shear ($v_S$) sound velocities for bcc- and hcp-Fe-Ni alloys from NRIXS experimental studies at 300 K. Both studies were conducted with $^{57}$Fe enriched samples, and we plot sound velocities that have been corrected to those of natural enrichment via equation 10.

Table 3: Grüneisen parameters from this study, Murphy et al. (2011a), and Fei et al. (2016)

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Figure 11: A comparison of Debye ($v_D$), compressional ($v_P$), and shear ($v_S$) sound velocities for Fe-Si and Fe-Ni-Si alloys from NRIXS and IXS studies at 300 K. For NRIXS studies conducted with $^{57}$Fe enriched samples, we plot sound velocities that have been corrected to those of natural enrichment via equation 10, except for velocities from (Liu et al., 2016), where their reported natural enrichment correction was applied.
Figure 12: Debye ($v_D$), compressional ($v_P$), and shear ($v_S$) sound velocities at 300 K of hcp-Fe$_{0.91}$Ni$_{0.09}$ and Fe$_{0.9}$Ni$_{0.1}$Si$_{0.1}$ and our re-analysis of hcp-Fe data from Murphy et al. (2013). We compare to other iron-light-element compositions. The sound velocities are plotted as reported without a correction to natural enrichment.
Figure 13: Birch plot showing the bulk sound speed $v_\phi$ at 300 K plotted as a function of density for hcp-Fe_{0.91}Ni_{0.09} and Fe_{0.8}Ni_{0.1}Si_{0.1} and our re-analysis of hcp-Fe data from Murphy et al. (2013). We compare to other iron-light element compositions. The sound velocities are plotted as reported without a correction to natural enrichment.
Figure 14: Examples of scaled phonon DOSs (red) compared to measured phonon DOS (black with gray error bars) for hcp-structured Fe$_{0.91}$Ni$_{0.09}$, Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$, and our re-analysis of Fe data from Murphy et al. (2011a). The hcp-Fe$_{0.91}$Ni$_{0.09}$ phonon DOS at 48 GPa and the hcp-Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$ phonon DOS at 41 GPa are scaled to each compression point according to equation 12. Similarly, our re-analyzed phonon DOS of hcp-Fe from Murphy et al. (2013) at 90 GPa is scaled to each compression point following the same method.
Figure 15: Vibrational Grüneisen parameter $\Gamma_{\text{vib}}$ for hcp-Fe$_{0.91}$Ni$_{0.09}$, Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$, and Fe calculated with equation 17 compared to $\Gamma_{\text{vib}}$ for hcp-Fe determined from results of NRIXS measurements by Murphy et al. (2011a) re-analyzed by Fei et al. (2016), ab initio calculations at 500 K (Sha and Cohen, 2010), shock-wave and 300 K static compression XRD data (Dewaele et al., 2006), static compression Raman spectroscopy at 300 K (Merkel et al., 2000), and static compression XRD data (Dubrovinsky et al., 2000).
Figure 16: Various reported $v_{\text{ vib}}$ determined from the hcp-Fe NRIXS data reported in Murphy et al. (2011a). Our analysis using equation 17 and $q = 1$ are internally consistent and in agreement with published results from Murphy et al. (2011a) with $q = 1$. Our analysis is not in agreement with results from Fei et al. (2016).
Figure 17: Scaled phonon DOSs (red) compared to measured phonon DOS (black with gray error bars) for hcp-structured Fe. The hcp-Fe phonon DOS at 30 GPa is scaled to each compression point according to equation 12. On the left is our analysis of Murphy et al. (2011a), and on the right is the phonon DOS scaling calculated from $\gamma_{\text{vib}}$ from Fei et al. (2016).
Figure 18: Thermal EOSs for hcp-Fe (Dewaele et al., 2006) are extrapolated to inner core conditions to calculate density $\rho$, adiabatic bulk modulus $K_S$, and bulk sound speed $v_\phi$ as a function of pressure at 5500 K (see text for details). Estimated electronic and anharmonic contributions to thermal pressure are not included. Bars (right) represent uncertainty due to EOS parameters for hcp-Fe. We compare to the seismic model AK135-F (red line) (Kennett et al., 1995) with estimated uncertainties for $\rho$ (2%), $K_S$ (2.3%), and $v_\phi$ (0.6%) (Masters and Gubbins, 2003; Deuss, 2008).
Table 4: Thermal pressure components for hcp phases: harmonic vibrational free energy ($F_{vib}^h$) and pressure ($P_{vib}^h$), anharmonic ($P_{vib}^{anh}$) and electronic pressures ($P_{el}$) at 300 K and 5500 K

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<th>V ($\text{Å}^3$)</th>
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<th>$F_{vib}^h$ (meV/atom)</th>
<th>$P_{vib}^h$ (GPa)</th>
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$^{a}$Re-analyzed from Murphy et al. (2011a, b, 2013)

$^{b}$Taken from Dewaele et al. (2006)
Figure 19: Harmonic vibrational thermal pressure $P_h^{vib}$ as a function of volume and temperature for hcp-Fe$_{0.91}$Ni$_{0.09}$, Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$, and Fe at 2000, 4000, and 5500 K (circles). The hcp-Fe data is a re-analysis of data from Murphy et al. (2011b). We compare to ab initio calculations of the harmonic thermal pressure for hcp-Fe by Alfè et al. (2001) at 2000, 4000, and 6000 K (solid lines).
Figure 20: Vibrational harmonic component of thermal expansion for hcp-Fe$_{0.91}$Ni$_{0.09}$, Fe$_{0.8}$Ni$_{0.1}$Si$_{0.1}$, and Fe at 300 K. The data for hcp-Fe is a re-analysis of data from Murphy et al. (2013). If not shown, error bars are smaller than the displayed symbol.
High pressure thermoelasticity and sound velocities of Fe-Ni-Si alloys: Highlights

- Nuclear resonant inelastic x-ray scattering on Fe-Ni and Fe-Ni-Si to 104 and 86 GPa
- New Debye velocity determination method yields improved results and uncertainties
- Nickel decreases the shear velocity of iron, and 10 at% Si has little to no effect
- Vibrational Grüneisen parameters of hcp-Fe-Ni-Si trend lower than Fe and Fe-Ni
- hcp-Fe harmonic vibrational thermal pressure deviates from theoretical calculations