Sound velocities and density measurements of solid hcp-Fe and hcp-Fe-Si(9wt.%) alloy at high pressure: Constraints on the Si abundance in the Earth's inner core

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Abstract

We carried out sound velocity and density measurements on solid hcp-Fe and an hcp-Fe-Si alloy with 9 wt.% Si at 300 K up to ~170 and ~ 140 GPa, respectively. The results allow a precise determination of the dependence on density (ρ) of the compressional sound velocity (V_P) and of the shear sound velocity (V_S) for pure Fe and the Fe-Si alloy. The established V_P-ρ and V_S-ρ relations are used to address the effect of Si on the velocities in the Fe-FeSi system in the range of Si concentrations 0 to 9wt.% applicable to the Earth's core. Assuming an ideal linear mixing model, velocities vary with respect to those of pure Fe by ~ +80 m/s for V_P and ~ -80 m/s for V_S for each wt.% of Si at the inner core density of 13000 kg/m^3. The possible presence of Si in the inner core and the quantification of its amount strongly depend on anharmonic effects at high temperature and on actual core temperature.

Keywords: seismic wave velocities; iron; iron-silicon alloys; high pressure; high temperature; Earth's inner core

1. Introduction

The physical properties of iron and iron alloys at high pressure are crucial to refine the chemical composition and dynamics of the Earth's core. To this respect, density (ρ), compressional–wave (V_P) and shear-wave (V_S) sound velocities are of particular importance, as those parameters can be directly compared to the seismological observations.

Over the last twenty years, a great effort has been devoted to the development of experiments capable of probing sound velocity of metallic samples at high pressure, with a specific focus on iron (see *Antonangeli and Ohtani [2015]* for a recent review). Ab initio calculations have been extensively applied as well to assess material's properties at core pressures and temperatures [e.g. *Vočadlo et al., 2009; Sha and Cohen, 2010; Martorell et al., 2013*]. Yet, a consensus has not been reached, not only concerning the absolute values of velocities of solid iron at inner core conditions, but also the dependence of velocities upon pressure and temperature.

Since the seminal work of *Birch [1952]* it has been well established that light elements are alloyed to iron in the Earth's core to account for the density difference between pure Fe and seismological observations (e.g. model PREM by *Dziewonski and Anderson [1981]*). For the solid inner core, many recent experimental studies suggest silicon as one of the major candidates, based on its physical properties (density and sound velocity) and/or affinity for the metallic phase during Earth's differentiation [e.g. *Lin et al., 2003; Badro et al., 2007; Antonangeli et al., 2010; Mao et al. 2012; Siebert et al., 2013; Fischer et al., 2015; Tateno et al., 2015*]. However, different works propose different amount of Si alloyed to Fe in the inner core, ranging from ~2wt.% [*Badro et al., 2007; Antonangeli et al., 2010*] up to ~8% [*Mao et al. 2012; Fischer et al., 2015*]. One of the causes for such a discrepancy is the large pressure and temperature extrapolation necessary to compare experimental results with inner core seismological models. For instance, results based on linear extrapolations of V_P-ρ relation argued for about 2 wt% Si alloyed to Fe in the inner core [*Badro et al., 2007; Antonangeli et al., 2010*], while a model using a power law for the V_P-ρ extrapolation proposed 8 wt% Si [*Mao et al. 2012*]. In contrast with the bulk of the experimental results, a very recent computational work on silicon alloys at inner core conditions [*Martorell et al., 2016*] suggested that both the P-wave and the S-wave velocities of any hcp-Fe-Si alloy would be too high to match the seismically observed values at inner-core density.

To shed light on this ongoing debate, we carried out sound velocity and density measurements on pure Fe and a Fe-Si alloy with 9 wt.% Si in the hexagonal close-packed structure (hcp) from ~40 GPa up to ~170 GPa, using inelastic x-ray scattering (IXS) and x-ray diffraction (XRD). IXS allows a clear identification of longitudinal aggregate excitations in polycrystalline samples [*Fiquet et al., 2001, 2009; Antonangeli et al., 2004, 2010, 2012, 2015; Badro et al., 2007; Mao et al., 2012; Ohtani et al., 2013*] and the derivation of V_P from a sine fit of the phonon dispersion. Combining the measured V_P with the bulk modulus derived from the equation of state, V_S can be determined as well, while the density is directly obtained from the collected diffraction patterns. In this study, we aim to establish precise relations between velocities (both V_P and V_S) and density for Fe and a representative Fe-Si alloy with 9 wt.% Si over a wide pressure range at room temperature. The results will provide a reference benchmark for calculations and will serve as basis for further studies of increased compositional complexity and evaluating the temperature effects on the velocities.

2. Materials and Methods

Starting materials consisted in commercially available polycrystalline samples of Fe (99.998%, Alpha Aesar) and a Fe-Si alloy with 9 wt.% Si (Goodfellow, hereafter Fe-Si9). Nominal composition and chemical homogeneity at micrometric scale of the Fe-Si alloy has been verified by electron microprobe analysis.

IXS and XRD measurements have been carried out at the European Synchrotron Radiation facility (ESRF) at ID28 and ID27 beamlines, respectively. IXS measurements have been performed on polycrystalline specimens compressed in a diamond anvil cell (DAC) using the Si(9,9,9) instrument configuration, which yields an overall energy resolution of 3 meV full width half maximum (FWHM). Absolute energies have been calibrated prior to the experiment comparing IXS diamond phonon dispersion with that obtained by inelastic neutron and Raman scattering. Specific to this experiment, we double-checked the energy calibration by comparing the sound velocity measured by IXS on iron powders at ambient conditions with the Voigt−Reuss−Hill average of ultrasonic determination on single crystal [*Guinan and Beshers, 1968*]. We also calibrated the scattering angle at the small working values of our IXS measurements by collection of diffraction from a silver behenate standard. Optics in Kirkpatrick-Baez configuration allowed focusing the x-ray beam at sample position at 30x70 μm^2 (horizontal x vertical, FWHM) or down to 12x7 μm^2 (horizontal x vertical, FWHM) depending upon DAC configuration. Momentum resolution was set by slits in front of the analyzers to 0.28 nm^{-1} and to 0.84 nm^{-1}, in the scattering plane and perpendicular to it. A vacuum chamber was used to minimize the quasi-elastic scattering contribution from air. Good-statistic data have been obtained with typical integration time of ~300 s per point for Fe, and ~500-600 s per point for Fe-Si9.

Pressures were generated by symmetric type, MAO DAC, using composite Re/c-BN gaskets, with either 150/300 µm beveled anvils, or 40/100/300 µm beveled anvils prepared by focus ion beam (FIB) technique [*Fei et al., 2016*]. Diamonds were pre-aligned and oriented to select the fastest transverse acoustic phonon of the diamond in the scattering plane and to minimize its intensity. The focused beam of 12x7 μm^2 FWHM at sample position granted collection of clean spectra on specimens down to ~35 µm in diameter. Such a small beam also permitted to probe phonons across moderate pressure gradients (as determined from the fine diffraction mesh, see below), while the composite gasket ensured relatively thick samples (8 to 12 μm at the highest pressure), and hence proper IXS signal, averaged over a reasonably large number of grains. Pressure was increased off line by monitoring the Raman spectra at the tip of the diamonds, and more precisely measured by the x-ray diffraction according to known samples equation of state. Specifically we used a third-order Birch-Murnaghan formalism, with V_0 = 22.47 Å^3/unit cell [*Dewaele et al. 2006*], K_0 = 155 GPa and K'= 5.37 [*Sakai et al., 2014*] for hcp-Fe and V_0 = 23.50 Å^3/unit cell, K_0 = 129 GPa and K'= 5.24 for hcp-Fe-Si9 [*Fei, 2017*].

At each investigated pressure point, we mapped the aggregate longitudinal acoustic phonon dispersion throughout the entire first Brillouin zone collecting 6 to 9 spectra in the 3-12.5 nm^{-1} range. The energy positions of the phonons were extracted by fitting a set of Lorentzian functions convolved with the experimental resolution function to the IXS spectra. Figure 1 shows an example of the collected IXS spectra and the fitted result. We derived V_P from a sine fit to the phonon dispersion [*Antonangeli et al., 2004*] (Figure 1), with error bars between ±1 and ±3% for Fe and between ±2 and ±4% for Fe-Si9. The errors account for statistical errors, finite energy and momentum resolution, as well as deviation from ideal random orientation of the polycrystalline samples. Combining the measured V_P with bulk modulus from the equation of state (the difference between isothermal and adiabatic bulk modulus at 300 K is negligible), we also derived V_S [*Antonangeli et al., 2004*], with uncertainties, obtained by propagating uncertainties on V_P and on K (the contribution from uncertainties on density was observed to be negligible), between ±5 and ±6% for pure-Fe, and between ±8 and ±10% for Fe-Si9 (assuming different equation of state leads to effects on V_S within reported error bars).

For both samples, we collected angle dispersive 2D diffraction patterns at each investigated pressure point, with a monochromatic wavelength of 0.3738Å (iodine K edge).

This allowed for clear structure determination and direct measurements of samples' density. Taking advantage of the 3x3 μm^2 beam, we mapped the entire sample area, monitoring pressure gradients across the sample chamber. Diffraction data are also used to detect any developed texture. An example of the collected diffraction patterns are shown in Figure 2 and Figure 3. The diffraction patterns of the compressed hcp-Fe (Figure 2) show rather smooth rings, indicating the small sizes of the diffracting crystallites (average size ~25 nm at 167 GPa) and the good orientation averaging (only 100 reflection shows some variation in intensity with the azimuthal angle). Two-dimensional detector images caked into rectilinear projection show negligible dependence of the d spacing on the azimuthal angle around 2θ=0 direction (Figure 2), and hence a negligible deviatoric stress [*Wenk et al., 2006*]. Furthermore, the (002) reflection, although weak, is still visible up to the highest attained pressure, further highlighting the overall marginal preferential orientation. Such observations support the overall validity of the random orientation approximation, critical to the analysis and interpretation of the IXS results [*Antonangeli et al., 2004; Bosak et al., 2007;2016*]. The diffraction patterns collected for the Fe-Si9 alloy (Figure 3) are somewhat less favorable than those on pure Fe, in particular in term of sizes of crystallites (average size ~40 nm at 117 GPa) and randomness of the distribution (intensity variation are quite visible for both 100 and 101 reflections), but they are still acceptable. The (002) reflection, still visible at all probed pressure, is very weak, as a direct consequence of a small preferential orientation fully developed already at 59 GPa and not significantly evolving with pressure, with the c-axis preferentially aligned along the main compression axis of the cell. Similar texture has been already reported in previous experiments on iron [*Wenk et al., 2000*] and other metals with hcp structure [*Merkel et al., 2006*]. Such a moderately increased deviation from the ideal random distribution is reflected into the fairly increased error bars on the velocities derived from the IXS data (deviation from ideal average up to 2%).

At the highest compression the maximum observed difference in pressure across the sample chamber (~35 μm) is <7 GPa for Fe and <10 GPa for Fe-Si9. Over the volume seen by IXS we obtain an average pressure of 167 GPa (Fe), with a standard deviation of 2 GPa and a standard error of 1 GPa, and an average pressure of 144 GPa (Fe-Si9), with a standard deviation of 2 GPa and a standard error of 1 GPa.

3. Results

The experimentally determined densities and velocities for hcp-Fe and hcp-Fe-Si9 are summarized in Table 1. The details are presented in the following subsections.

3.1. Hcp-Fe

The measured compressional and shear sound velocities as a function of density are plotted in Figure 4. These new measurements of V_P are in very good agreement with the V_P-ρ linear relationship recently proposed by fitting a combined datasets derived from multiple techniques [*Antonangeli and Ohtani, 2015*], extending the data coverage at extreme pressures. We notice that the extrapolation of the established trend to higher density is in remarkable agreement with ab initio calculations at 0 K [*Vočadlo et al., 2009; Sha and Cohen, 2010*], clearly supporting a linear dependence of V_P on density. The derived V_S-ρ linear relationship is also in general agreement with results of ab initio calculations at 0 K. We also noticed the good agreement between the slope of our V_S-ρ trend with that obtained by the most recent nuclear resonant inelastic x-ray scattering (NRIXS) experiments [*Murphy et al., 2013; Gleason et al., 2013; Liu et al., 2016*], even if actual V_S values derived by NRIXS are somewhat lower, between 3 to 8% depending upon datasets. Such a difference is at least partially due to the enrichment in heavier Fe isotopes of samples used for NRIXS studies with respect to sample of natural isotopic abundance used here.

3.2 Hcp-Fe-Si9

The measured compressional and shear sound velocities as a function of density are shown in Figure 5. Our V_P measurements on samples with 9 wt.% Si are very close to previous IXS measurements on samples with 8 wt.% Si [*Mao et al., 2012*], but they are systematically higher than early determination by NRIXS on samples with 8 wt.% Si [*Lin et al., 2003*]. Similar to the case of pure Fe, our measurements support a linear dependence of V_P on ρ for Fe-Si9. The derived V_S-ρ relationship can be well described by a second order polynomial (Figure 5).

Comparison of results obtained for Fe and Fe-Si9 (Figure 6) show that Si alloying systematically increases V_P at constant density over the investigated pressure range. Linear fits indicate that, even if V_P of the Fe-Si9 alloy increases with density slower than pure Fe, Fe-Si9 is still expected to have significantly higher V_P than Fe at inner core density (~12390 m/s vs. ~11680 m/s at 13000 kg/m^3). On the other hand, the derived density evolution for V_S of Fe-Si9 is such that the Si-bearing alloys is expected to have higher V_S than pure Fe only up to $\rho \approx 11200$ kg/m^3, with V_S of Fe larger than V_S of Fe-Si9 at inner core density (~5130 m/s vs. ~5890 m/s at 13000 kg/m^3). This trend (i.e V_P increasing with Si content and V_S decreasing) has been reported as well by recent ab initio calculations of Fe-Si alloys at core pressures [*Martorell et al., 2016*]. On the contrary to the case of pure Fe, the extrapolation of our experimental results for Fe-Si9 does not agree with the calculations.

4. Discussion

Concerning hcp-Fe, we note a remarkable agreement between our new measurements, previous measurements by various techniques and ab initio calculations for V_P, and an overall agreement for V_S. The established consensus provides very strong constraints on the linear dependence of velocities on density and on actual values of velocities of hcp-Fe at inner core densities and 300 K (Figure 4), which can by now be considered known within few percent (with V_P better constrained than V_S).

Somewhat less evident is the case for Si bearing hcp Fe-alloys. Literature data obtained in the ~40 to ~100 GPa range on samples of the same nominal composition [*Lin et al., 2003; Mao et al., 2012*] are in evident disagreement (Figure 5). Reasons for the discrepancy between NRIXS [*Lin et al., 2003*] and IXS [*Mao et al., 2012*] data possibly include systematic differences due to the techniques, or due to the sample's texture. The V_P measured in this study is in a good agreement with previous IXS determination at lower pressures [*Mao et al., 2012*] and significantly extend the probed pressure range. In view of our new data, the sub linear evolution of V_P with density according to the empirical power-law function proposed by *Mao et al., [2012]* on the basis of V_P-ρ data over a more restricted pressure range, seems not justified. Linear extrapolation of experimental results to inner core density and comparison with calculations [*Tsuchiya and Fujibuki, 2009; Martorell et al., 2016*] show however a disagreement, more important for V_P than for V_S. The difference would be even more striking when considering a power-law extrapolation. In particular, the calculations seem to overestimate the effect of Si on V_P of the Fe-Si alloys. We noticed that ab initio calculations on Fe-Si alloys, even when performed at 0 K, give quite conflicting results [*Tsuchiya and Fujibuki, 2009; Martorell et al., 2016*], highlighting the difficulty in performing calculations taking into account the configurational order/disorder inherent to alloys. Further investigation by both experiments and theoretical calculations is necessary to resolve the discrepancy.

The direct comparison between results obtained on Fe and on Fe-Si9 allows us to address the effect of Si content on the velocities of a hcp $Fe_{1-x}Si_x$ alloy in the limit of low to moderate Si concentration (0 to 9wt.%). The simplest approach is to use an ideal linear mixing model [e.g. *Badro et al., 2007; Antonangeli et al., 2010*]. Using the reference relations established here for pure Fe and the extrapolation of our measurements on Fe-Si9, at the inner core density of 13000 kg/m^3 we get a variation ~ +80 m/s on V_P and ~ -80 m/s on V_S for each wt.% of Si (Figure 6). Measurements of V_P on an Fe-Ni-Si alloy with 4.3wt.% Ni and 3.7wt.% Si [*Antonangeli et al., 2010*] extrapolated to 13000 kg/m^3 yield V_P~12100 m/s, in good agreement with our estimate of V_P~11980 m/s for a Fe-Si alloy with 3.7wt.%Si (difference ~ -1%). This agreement on one side argues in favor of the suitability of the here-proposed estimate, and on the other suggests that the effect on the compressional sound velocity due to Ni inclusion at level of 4 to 5 wt.% is minor. Further independent support comes from the good agreement also observed between our predicted value of V_P~12160 m/s and the extrapolation of very new measurements on a Fe-Si alloy with 6wt.% Si [*Sakairi et al., Am. Min. in press.*] yielding V_P~11940 m/s (difference ~ +1.8%).

In order to be able to use our data to discuss the Si abundance in the inner core by comparison with seismological models, the effects of high temperature have to be accounted for. A velocity vs. density representation, as the one proposed here, implicitly accounts for quasi-harmonic effects. Anharmonic effects might be important as well, in particular on V_S and for temperatures approaching melting. Sound velocity measurements at simultaneous high pressure and high temperature conditions are at the cutting edge of current technical capabilities and only few datasets are available, mostly for pure Fe [e.g. *Antonangeli et al., 2012; Mao et al., 2012; Ohtani et al., 2013; Sakamaki et al., 2015*]. If we model high-temperature effects for Fe following *Sakamaki et al. [2015]*, V_P is expected to lower by ~ -0.09 m/s K^{-1} at the constant density of 13000 kg/m^3. The orange arrow in Figure 4 highlights the magnitude of the expected reduction of V_P for T up to ~7000 K. Alternatively we can model temperature-induced softening (in this case for both V_P and V_S) following calculations by *Martorell et al., [2013]*. As these calculations have been performed at constant pressure, while here we are interested in the effects at constant density, we corrected the computed values according to the measured density dependence of sound velocities to compensate for the effects due to density variation with increasing temperature. Once limiting to T up to 7000 K, the estimated lowering of V_P and V_S are, respectively, ~ -0.12 m/s K^{-1} and ~ -0.32 m/s K^{-1} at the constant density of 13000 kg/m^3. The violet arrows in Figure 4 highlights the magnitude of the expected reduction of V_P and V_S for T up to ~7000 K. In qualitative agreement with recent calculations, for Fe, temperature effects alone seem enough to explain inner core velocities (but not densities, too high for pressures in the 330 to 360 GPa range). In the case of Fe-Si alloys we can only rely on calculations [*Martorell et al., 2016*], which, once corrected as in the case of Fe, yield for a sample with 3.2 wt% Si a reduction of V_P and V_S of, respectively, ~ -0.12 m/s K^{-1} and ~ -0.34 m/s K^{-1}, and for a sample with 6.7 wt% Si a reduction of ~ -0.20 m/s K^{-1} and ~ -0.23 m/s K^{-1}, at the constant density of 13000 kg/m^3. We note that theoretical estimates for pure Fe and a Fe-Si alloy with 3.2wt.% Si are very close, while those for a Fe-Si with 6.7wt.% Si differ, with an effect on V_P almost double and an effect on V_S about 30% smaller. The arrows in Figure 5 highlights the magnitude of the expected reduction of V_P and V_S for T up to ~7000 K if we apply to the extrapolation to our measurements on Fe-Si9 the correction estimated for samples with 3.2wt.% Si or that for samples with 6.7 wt.% Si (the dark blue arrows in the first case, and green arrows in the second case). Similarly to the case of Fe, if temperature effects are as large as expected according to calculations, temperature alone might be enough to explain inner core velocities (but again, not the densities, too low for pressures in the 330 to 360 GPa range for samples with 9 wt.% Si [*Tateno et al., 2015*]).

If we assume temperature effects at the constant density of 13000 kg/m^3 of ~ -0.20 m/s K^{-1} for V_P and ~ -0.23 m/s K^{-1} for V_S (as from estimates from calculations on a sample with 6.7 wt% Si) we match PREM values of V_P and V_S for a Si concentration of 10±1 wt.% and T between 6500 and 6700 K. This solution however is not acceptable, as such Fe-Si alloy is expected to have the right density only for pressures well above 360 GPa [*Tateno et al., 2015*]. If we assume temperature effects at the constant density of 13000 kg/m^3 of ~ -0.12 m/s K^{-1} for V_P and ~ -0.33 m/s K^{-1} for V_S (as from estimates from calculations on pure Fe and on a sample with 3.2 wt% Si) we obtain PREM values of V_P and V_S for a Si concentration of 3±1 wt.% and T between 6200 and 6500 K. P-V-T relation for a Fe-Si alloy with ~3 wt.% Si has not been experimentally determined yet, but calculations suggest such an alloy to have a density of ~13160 kg/m^3 at 360 GPa and 6400 K [*Martorell et al., 2016*], thus making this solution acceptable. Furthermore, an inner core temperature of 6200-6500 K is well compatible with estimates based on measurements of the Fe and Fe-Si alloys melting curve [*Anzellini et al., 2013; Morard et al., 2011*]. However, as already mentioned, the most recent experimental determination of temperature dependence of V_P for Fe by *Sakamaki et al. [2016]* argues for a less important temperature-induced lowering with respect to that proposed by calculations. If we assume temperature effects at the constant density of 13000 kg/m^3 of ~ -0.09 m/s K^{-1} for V_P as from *Sakamaki et al. [2016]*, we match PREM value of V_P for ~1 wt.% Si at 6300 K and ~2 wt.% Si at 7300 K. The last solution is not acceptable as a Fe-Si alloy is not solid at such a high temperatures [*Morard et al., 2011; Anzellini et al., 2013*]. Furthermore, irrespectively whether we assume a temperature effect on V_S of ~ -0.33 m/s K^{-1} (as from estimates from calculations on pure Fe and a Fe-Si alloy with 3.2 wt.% Si), or ~ -0.23 m/s K^{-1} (as from estimates from calculations on Fe-Si alloy with 6,7 wt.% Si), or ~ -0.24 m/s K^{-1} for V_S (scaling the estimates from calculations on pure Fe in line with the reduced effect on V_P), there is no obvious solution matching PREM values of V_P and V_S for a fixed Si content. Further, improved constraints on temperature effects on sound velocities remain crucial to reliably estimate the Si content in the inner core.

5. Conclusions

We carried out sound velocity and density measurements on solid hcp-Fe and an hcp-Fe-Si alloy with 9 wt.% Si up to ~170 and ~ 140 GPa, respectively. The experimentally established V_P-ρ and V_S-ρ relations for pure Fe are in good agreement with results from ab initio calculations and clearly show that within uncertainties both compressional and shear velocity at 300 K scale linearly with density (Figure 4). At 300 K and at the inner core density of 13000 kg/m^3 reference values for V_P and V_S are respectively 11680±250 m/s and 5890±360 m/s. Measurements on the Fe-Si alloy with 9 wt.% Si allowed us to discriminate between previous inconsistent datasets (Figure 5) and to propose V_P-ρ and V_S-ρ relations for Fe-Si9. These results are used to address the presence and abundance of Si in the Earth's inner core.

From a methodological standpoint, constraints coming only from density [e.g. *Tateno et al., 2015*] or even by combined density and compressional sound velocity [e.g. *Badro et al., 2007; Mao et al., 2012; Ohtani et al., 2013*] can be used to exclude possibilities, but it is necessary to simultaneously consider V_P, V_S and ρ to propose a consistent composition for the Earth's inner core. Qualitatively, at inner core conditions, high temperature reduces sound velocities, even at constant density, while Si alloying at level of 9 wt.%, besides reducing ρ, increases V_P and decreases V_S with respect to pure Fe. These same effects have been very recently suggested by calculations on Fe-Si alloys [*Martorell et al., 2016*], as well as for carbon alloying [*Caracas, 2017*]. Assuming an ideal linear mixing model to be valid for low to moderate Si concentration (<10wt.%), we quantitatively evaluate the effect in ~ +80 m/s on V_P and ~ -80 m/s on V_S for each wt.% of Si at the inner core density of 13000 kg/m^3. Studies on samples of intermediate compositions will allow further refinement of this estimation.

We explored the possible solutions for an hcp-Fe-Si alloy whose density, compressional and shear sound velocities would match PREM values for pressures in the 330 to 360 GPa range and temperatures in the 4000 to 7500 K range. The existence of a solution and the amount of Si justifying the seismological observations strongly depends on the way we model anharmonic effects on sound velocities at high temperature and on core temperature. In particular we obtain possible solutions only for large temperature corrections, relatively high core temperatures (T between 6200 and 6500 K) and for Si content not exceeding 3±1 wt.% Si. Accordingly, the current results do not support presence of Si in the inner core at level of 6 to 8 wt.% [*Mao et al., 2012; Fischer et al., 2015; Tateno et al., 2015*], while on the solely basis of density and sound velocities, we cannot discriminate between results proposing little (up to 4 wt.%) [e.g. *Badro et al., 2007; Antonangeli et al., 2010*] to no presence [*Martorell et al., 2016*] of Si in the inner core. More experimental and theoretical work on Fe-Si alloys to extend the directly probed pressure and temperature range and to check the limit of the ideal mixing approximation remains to be performed. We also encourage performing calculations not only at actual core conditions, but as well at conditions where experimental data exist, so as to validate theoretical treatments of alloys.

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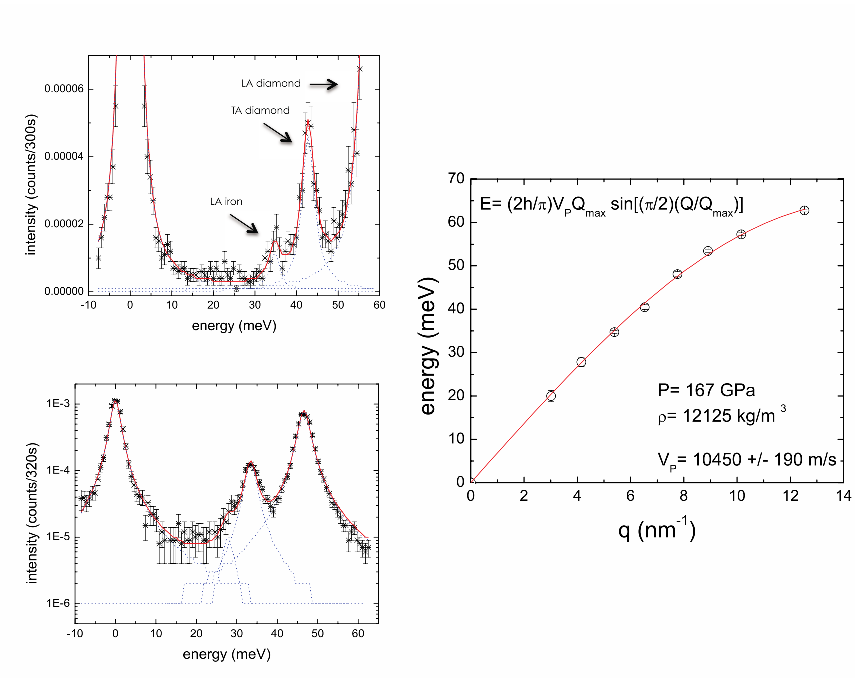

Figure 1. Examples of IXS spectra (left) and aggregate phonon dispersion (right) obtained for pure-Fe at the highest investigated pressure *(ρ=12125 kg/m^3, corresponding to ~167 GPa). Up left: IXS spectrum for q=5.39 nm^{-1}; bottom left IXS spectrum for q=4.15 nm^{-1}. IXS spectra are characterized by an elastic line, centered around zero, and inelastic features, assigned for increasing energy to the longitudinal acoustic (LA) aggregate phonon of iron and the transverse acoustic (TA) and longitudinal acoustic (LA) phonons of diamond. The experimental points and error bars are shown together with the best-fit (red line) and individual excitations (dashed blue lines). Sample phonons for q of 5.39 nm^{-1} and higher are well resolved and visible in linear scale, while for smaller q values, sample phonons and TA phonon of diamonds get very close, and sample phonons become a shoulder on the low-energy side of the TA phonon of diamond, better visible in logarithmic scale.*

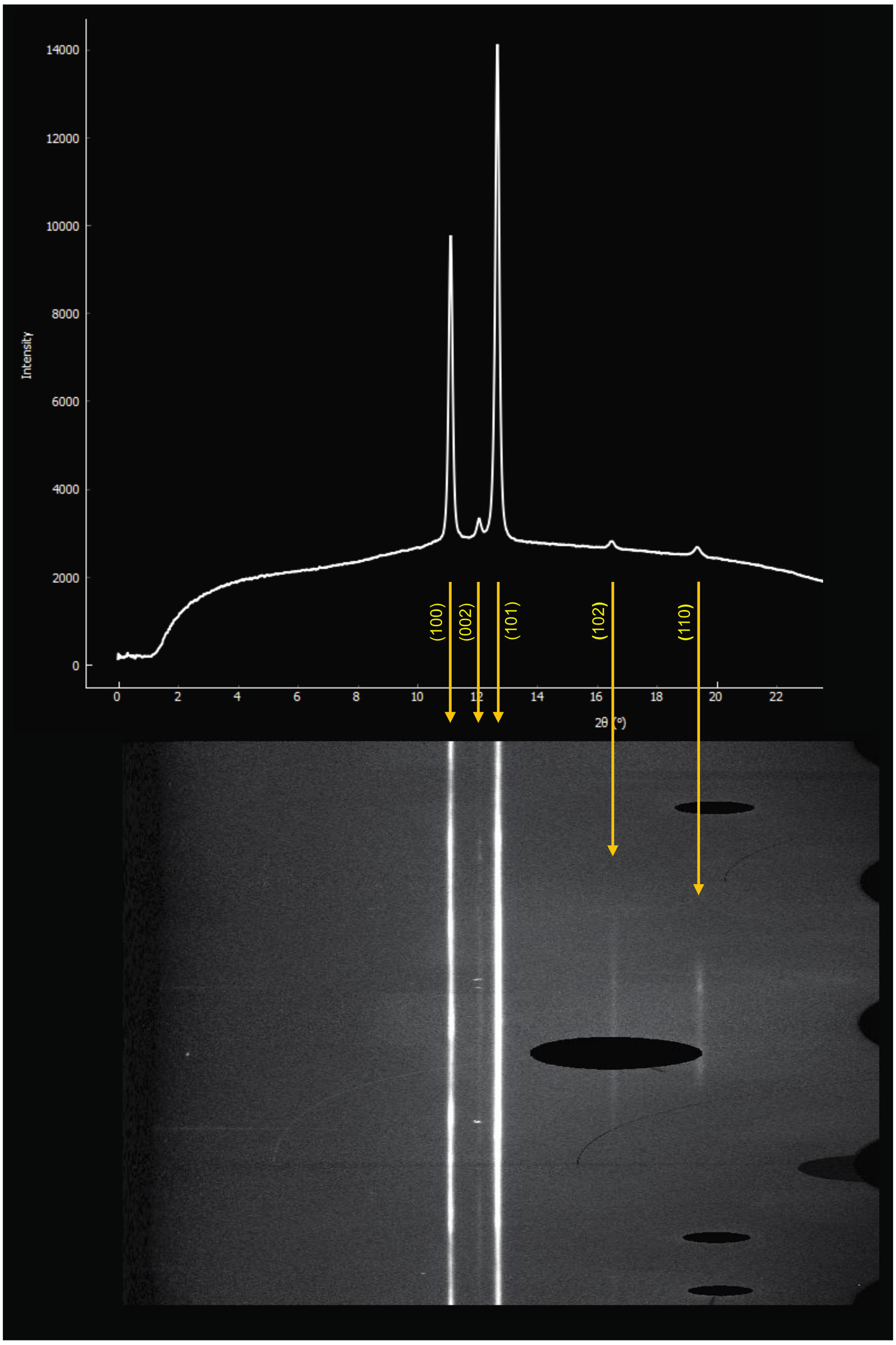

Figure 2. Example of integrated diffraction pattern collected on pure hcp-Fe at P~167 GPa (top) and caked into a rectilinear projection (bottom)*. 2D diffraction images have been integrated using Dioptas [Prescher and Prakapenka, 2015].*

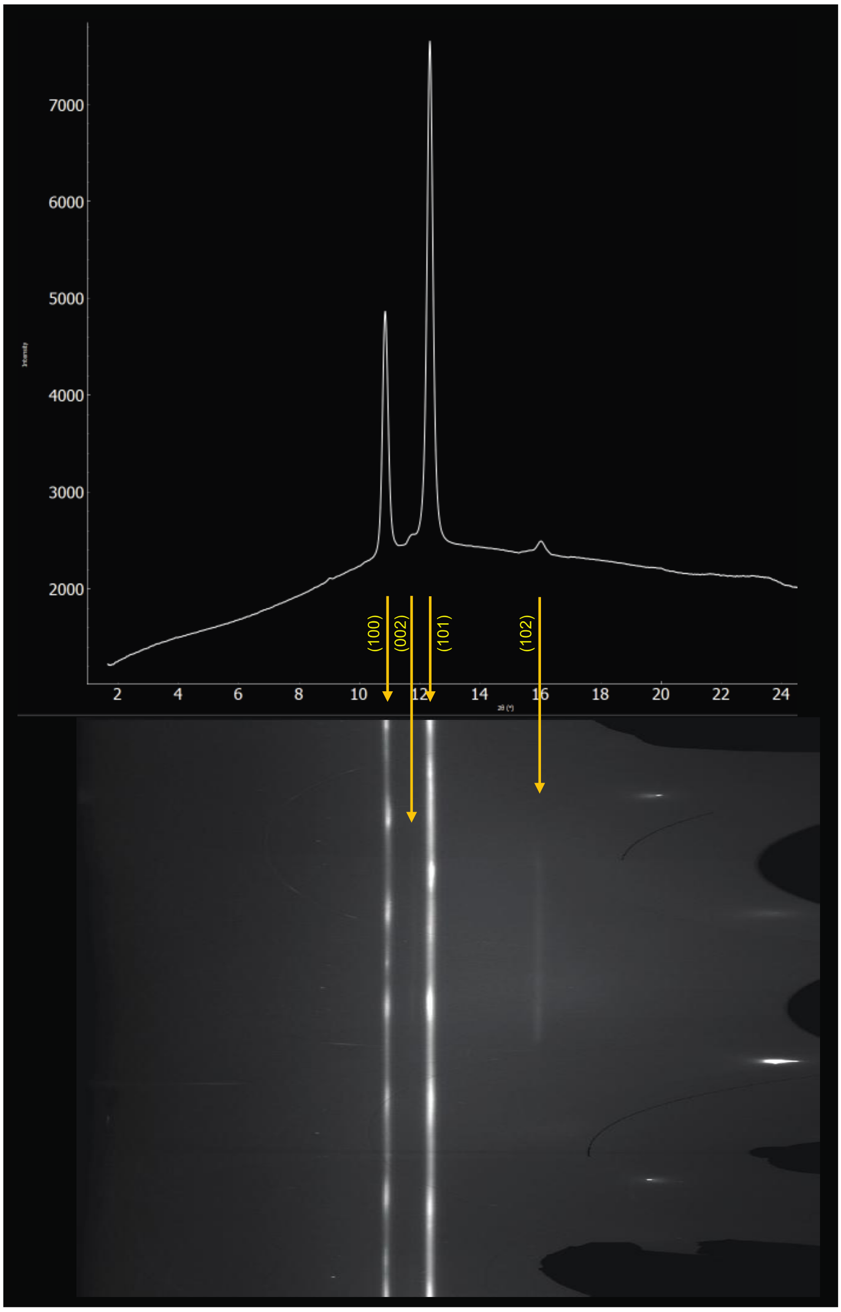

Figure 3. Example of integrated diffraction pattern collected on hcp-FeSi9 at P~117 GPa (top) and caked into a rectilinear projection (bottom). *2D diffraction images have been integrated using Dioptas [Prescher and Prakapenka, 2015].*

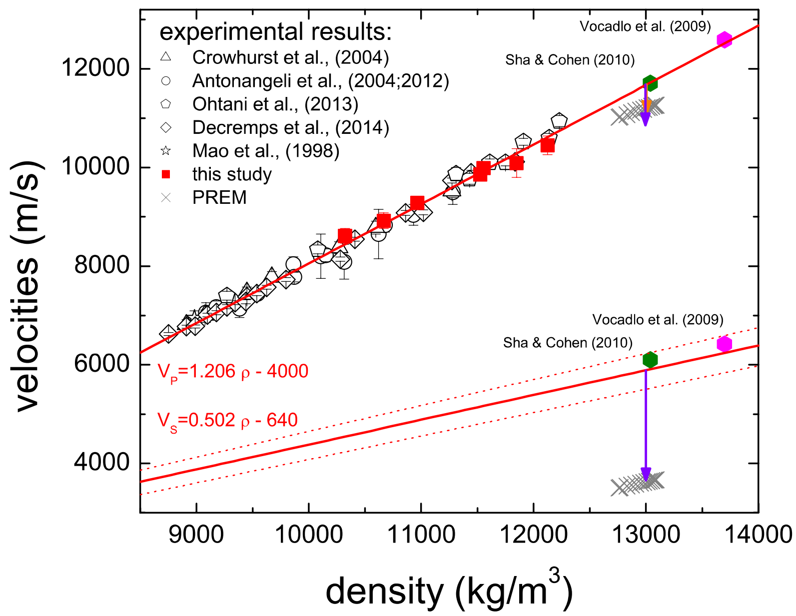

Figure 4. Aggregate compressional (V_P) and shear (V_S) sound velocities of hcp-Fe at 300 K as a function of density*. Results of this study are compared with a selection of published measurements at 300 K [Mao et al., 1998; Crowhurst et al., 2004; Antonangeli et al., 2004, 2012; Ohtani et al., 2013; Decremps et al., 2014] (for further details see Antonangeli and Ohtani [2015]), ab initio calculations at 0 K and 295 GPa [Vočadlo et al., 2009] and at 0 K and 13040 kg/m^3 [Sha and Cohen, 2010]. PREM [Dziewonski and Anderson, 1981] is reported as crosses. Solid lines show the established linear V_P-ρ and V_S-ρ relationships. Dotted lines show confidence level on the derived V_S. Arrows indicate possible magnitude of anharmonic effects up to 7000 K (see text).*

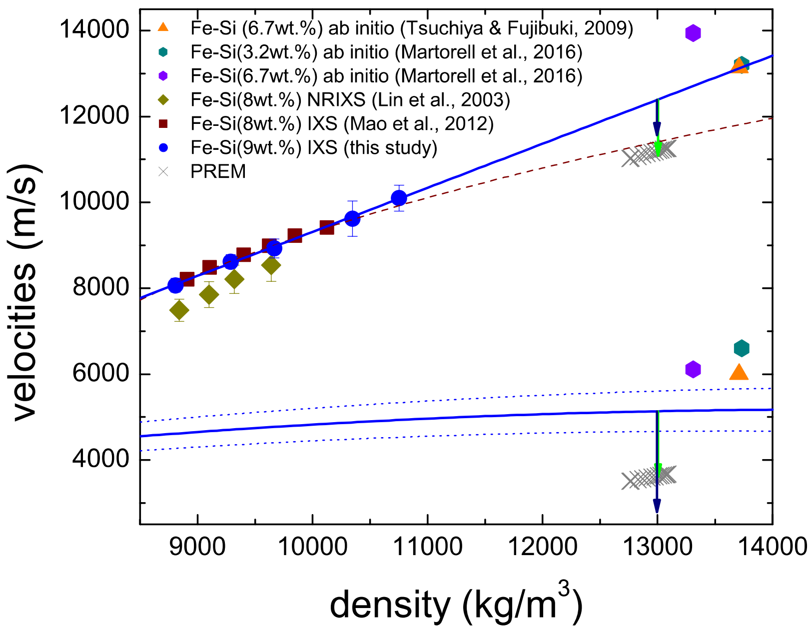

Figure 5. Aggregate compressional (V_P) and shear (V_S) sound velocities of hcp-Fe-Si9 at 300 K as a function of density. *Results of this study are compared with measurements at 300 K on a hcp-Fe-Si alloy with 8 wt.% Si by NRIXS [Lin et al., 2003] and by IXS [Mao et al., 2012] as well as with results of ab initio calculations at 0 K and 360 GPa on an hcp-Fe-Si alloy with 6.7 wt.% Si [Tsuchiya and Fujibuki, 2009] and at 0 K and 360 GPa on hcp-Fe-Si alloys with 3.2 and 6.7 wt.% Si [Martorell et al., 2016]. PREM [Dziewonski and Anderson, 1981] is reported as crosses. Solid lines show the proposed V_P-ρ ($V_P=1.026\times\rho-946$) and V_S-ρ ($V_S=1530+0.503\times\rho-1.736\times10^{-5}\times\rho^2$) relationships. Dotted lines show confidence level on the derived V_S. The dashed line is the empirical power-law function used by Mao et al., [2012] to describe their V_P-ρ data. Arrows indicate possible magnitude of anharmonic effects up to 7000 K (see text).*

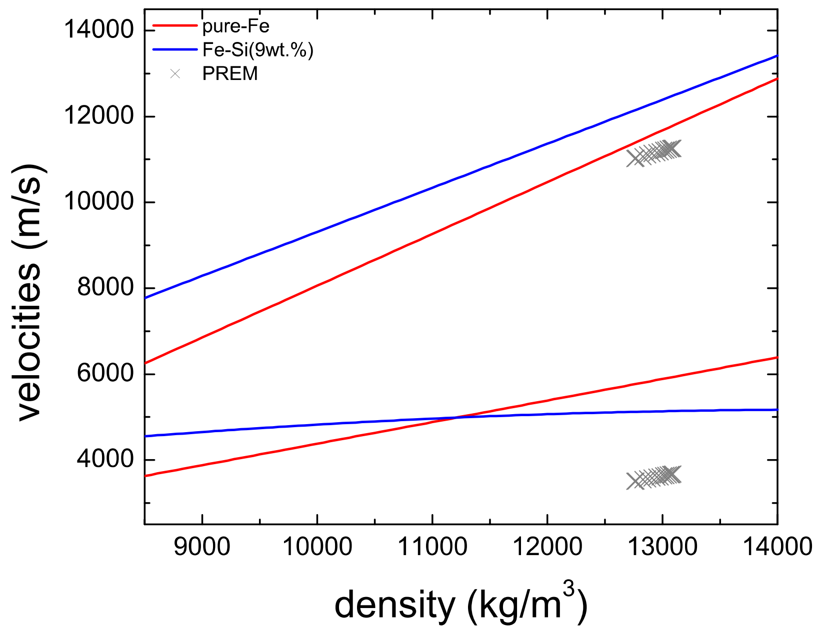

Figure 6. Comparison of the here-proposed density dependence of the aggregate compressional (V_P) and shear (V_S) sound velocities of hcp-Fe and hcp-FeSi9 extrapolated to core density. *PREM [Dziewonski and Anderson, 1981] is reported as crosses.*

Table 1. Measured densities and compressional sound velocities (V_P). *Pressure estimated from measured diffraction patterns are reported as well. See text for discussion of pressure uncertainties and pressure gradients. Assuming different equation of state for hcp-Fe leads to a maximum difference in the reported pressure of less than 10 GPa at the highest density when using equation of state from Mao et al., [1990] .*

Sample	**Density (kg/m^3)**	**Pressure (GPa)**	**V_P (m/s)**
hcp-Fe	10325	63	8610±150
hcp-Fe	10665	79	8920±160
hcp-Fe	10965	96	9280±90
hcp-Fe	11525	124	9860±110
hcp-Fe	11555	126	9990±120
hcp-Fe	11850	146	10090±290
hcp-Fe	12125	167	10450±190
hcp-Fe-Si9[a]	8805	42	8070±170
hcp-Fe-Si9	9285	59	8620±160
hcp-Fe-Si9	9665	79	8930±220
hcp-Fe-Si9	10350	117	9620±410
hcp-Fe-Si9	10755	144	10100±300

[a] This point have been collected on decompression.