Sound wave velocities of Fe-Ni alloy at high pressure and temperature by mean of inelastic X-ray scattering

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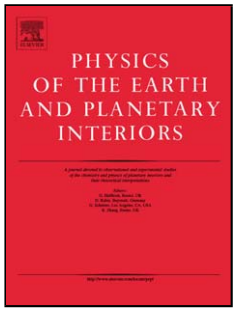

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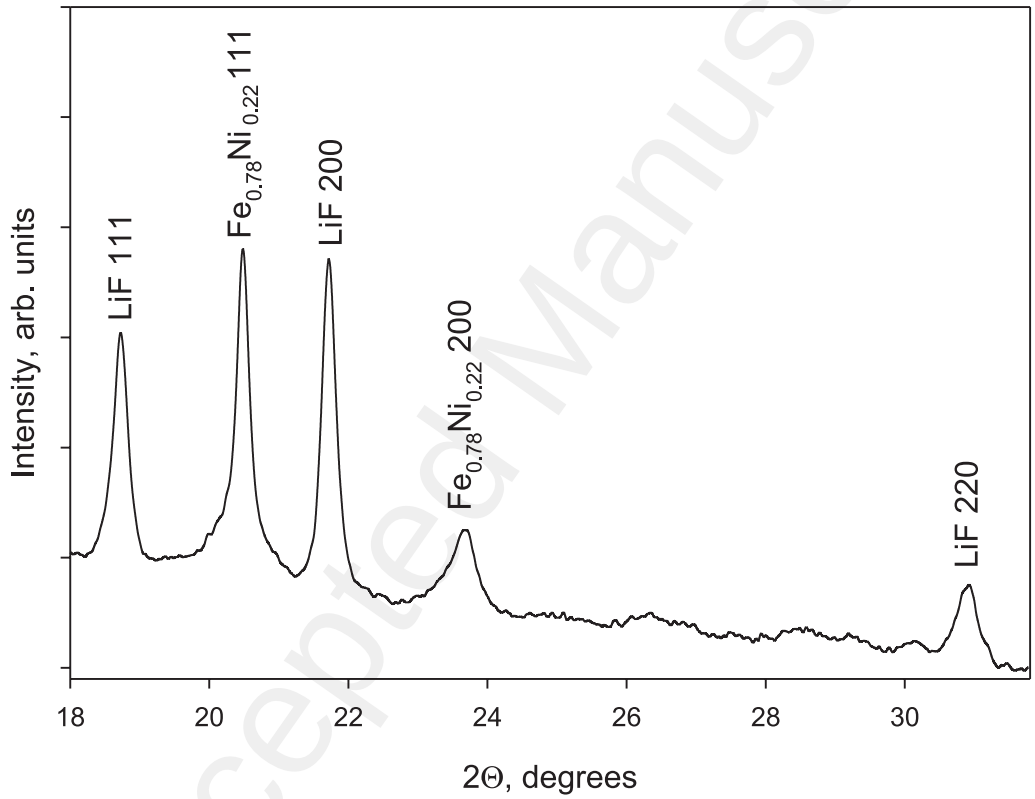

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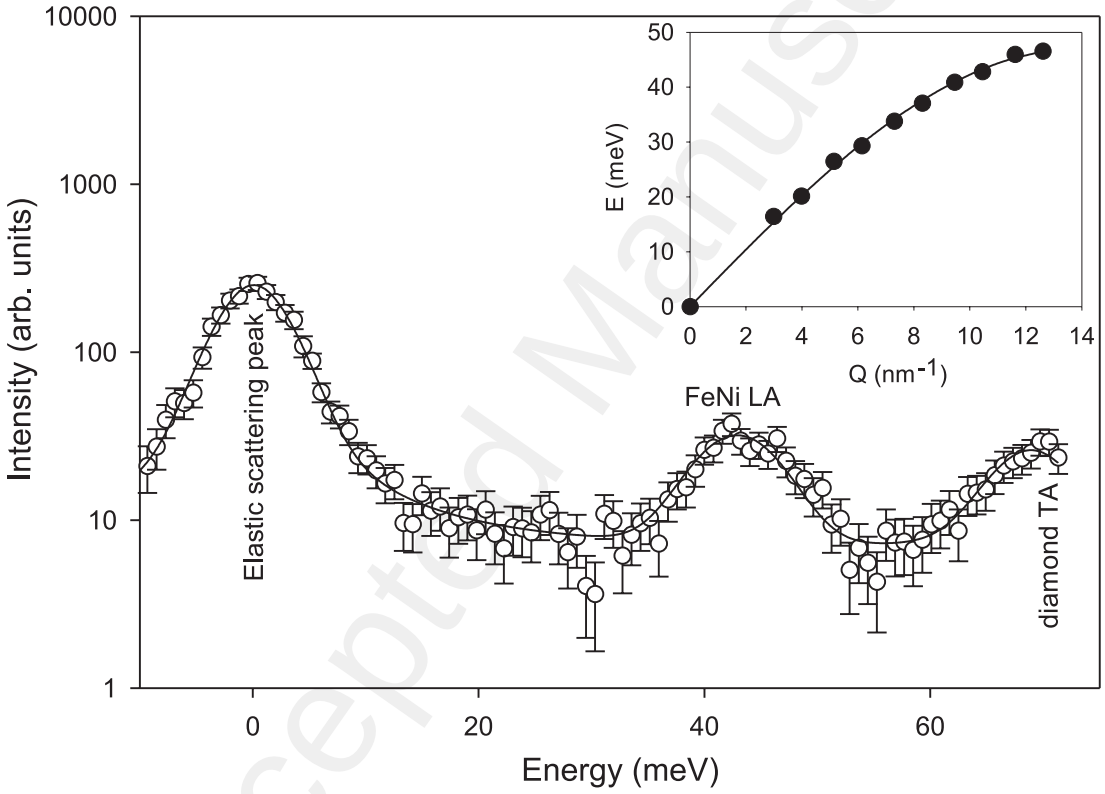

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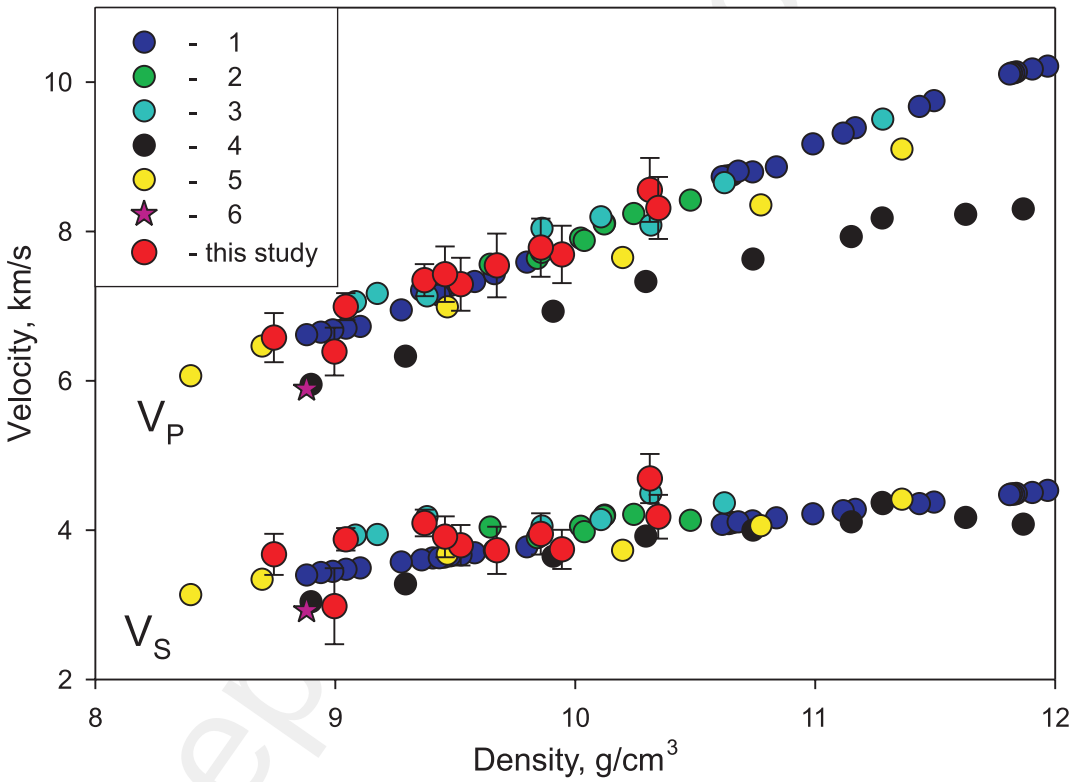

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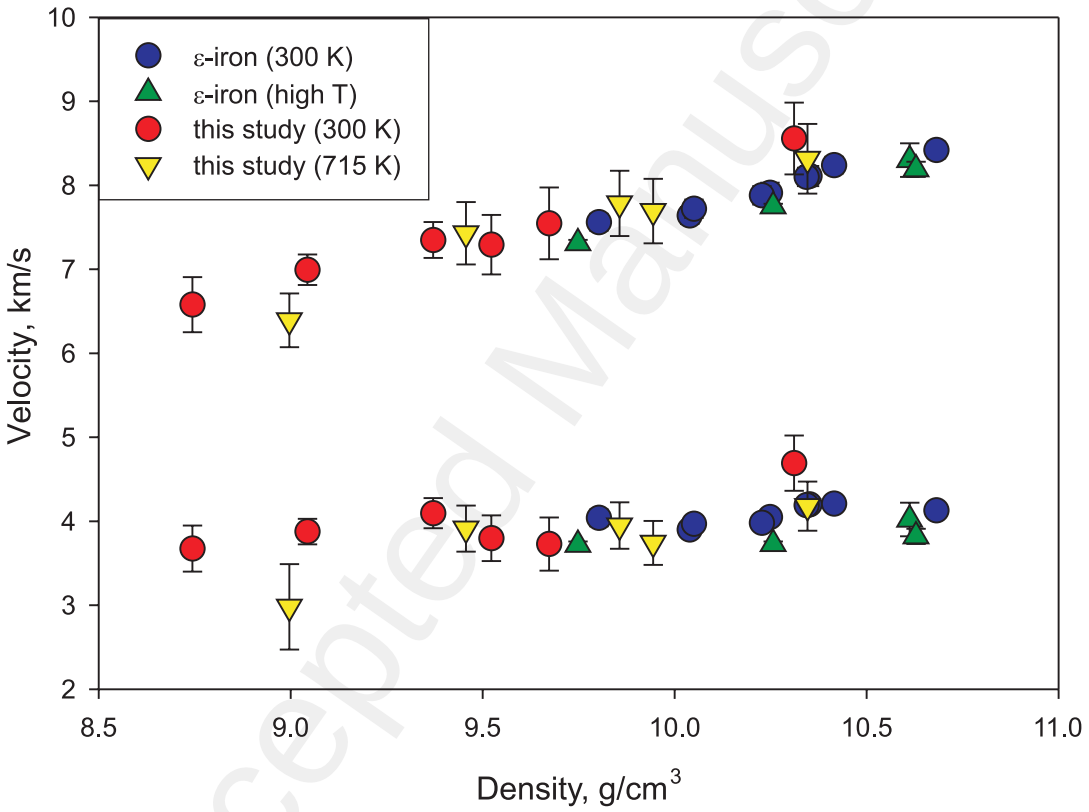

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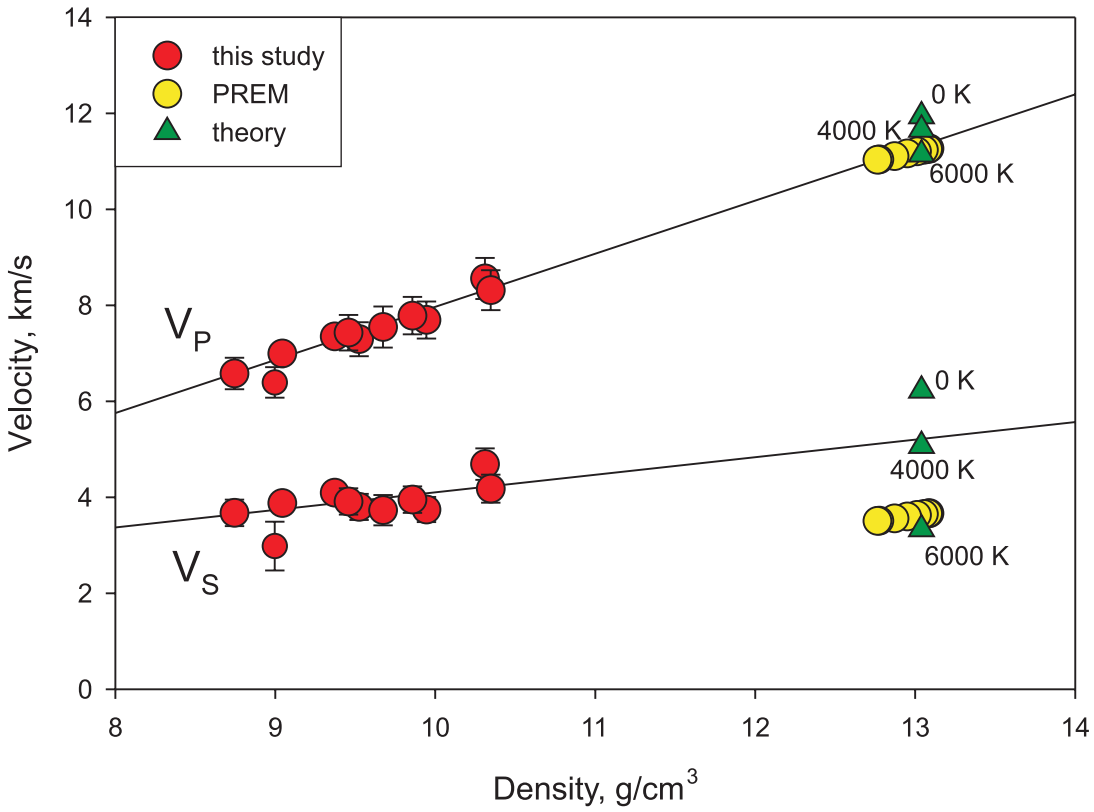

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Table 1.

	Pressure, GPa	Density, g/cm^3	V_L, km/s	V_T, km/s	K, GPa	G, GPa	ν	E, GPa
300 K	12.4 (0.7)	8.74	6.579 (0.3)	3.675 (0.3)	221 (2)	118 (3)	0.2733	301
	20.4 (1.0)	9.04	6.994 (0.2)	3.877 (0.2)	258 (2)	136 (3)	0.2757	347
	30.4 (1.5)	9.37	7.348 (0.2)	4.095 (0.2)	302 (3)	157 (4)	0.2783	402
	35.3 (1.8)	9.52	7.293 (0.4)	3.797 (0.3)	323 (2)	137 (3)	0.3141	361
	40.6 (2.0)	9.67	7.545 (0.4)	3.729 (0.3)	346 (3)	135 (3)	0.3281	357
	65.9 (2.1)	10.31	8.557 (0.4)	4.691 (0.3)	452 (4)	227 (2)	0.2496	583
715 K	21.5 (0.6)	8.997	6.392 (0.3)	2.981 (0.2)	261 (3)	80 (2)	0.2984	218
	37.1 (0.8)	9.457	7.428 (0.4)	3.912 (0.3)	329 (3)	145 (3)	0.2650	379
	52.0 (1.3)	9.857	7.783 (0.4)	3.948 (0.3)	392 (3)	154 (3)	0.2771	408
	54.3 (1.2)	9.945	7.692 (0.4)	3.743 (0.3)	403 (4)	139 (3)	0.2885	375
	71.7 (1.7)	10.35	8.315 (0.4)	4.179 (0.3)	474 (4)	181 (3)	0.2798	481

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Sound wave velocities of *fcc* Fe-Ni alloy at high pressure and temperature by mean of inelastic X-ray scattering.

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Abstract

Knowledge of the high-pressure and high-temperature elasticity of Fe-Ni alloy with low (5-25%) Ni content is crucial for geosciences since it is probably the major component of the cores of the terrestrial planets and the Moon. Here we present a study

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of a FeNi alloy with 22 at. % of Ni to 72 GPa and 715 K, using inelastic X-ray scattering (IXS) and X-ray powder diffraction from polycrystalline material. The X-ray diffraction (XRD) study revealed stability of the face centred cubic (*fcc*) over the hexagonal close packed (*hcp*) phase in the whole investigated pressure-temperature range. The study presents first investigations of elasticity of *fcc* phase of iron-nickel $Fe_{0.78}Ni_{0.22}$ alloy. The isothermal equations of state were derived at room temperature and at 715 K (K_{300}=162(1) GPa, K'_{300}=4.97(1), V_{300}=6.89(1) cm^3/mole; K_{715}=160(1) GPa, K'_{715}=4.97(2), V_{715}=6.96(1) cm^3/mole). Inelastic X-ray inelastic measurements allow the determination of the longitudinal acoustic wave velocity V_P, and provide, combined with the measured equations of state, the full isotropic elasticity of the material. We found that within experimental errors our data follow the Birch's law. We did not observe any significant deviations for *fcc* $Fe_{0.78}Ni_{0.22}$ from elastic properties of pure ε–iron.

Keywords: elasticity, iron-nickel alloy, inelastic scattering, equation of state.

1. Introduction

Properties of major constituents of the Earth's core, iron and its alloys, have long been of great interest to geophysicists. Cosmochemical data and the composition of iron meteorites suggest that Earth's core contains a significant (5 to 25 %) amount of nickel (Anderson, 1989). Iron-nickel alloy with 5-25% Ni content is also thought to be the main component of the cores of the Mars, Mercury, Moon, satellites of Saturn and Jupiter (Encrenaz et al., 1995; Robbins et al., 1995; Bottke et al., 2006). Information on the behaviour of Fe–Ni alloys at high pressure and temperature (*P–T*), such as phase relations and thermal equations of state (EoS), is essential for interpreting seismic and geomagnetic observations and for computer modelling of the Earth's deep interior. While

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pure Fe at high *P–T* has been the subject of numerous studies (Mao et al., 1990; Saxena et al., 1995; Yoo et al., 1995; Boehler, 1993; Andrault et al., 1997; Dubrovinsky et al., 2000; Crowhurst et al., 2005; Antonangeli et al., 2004), there are far fewer studies on Fe–Ni alloys (Huang et al., 1988; Lin et al., 2003; Mao et al., 2005; Dubrovinsky and Dubrovinskaia, 2003).

At ambient conditions, the stable phase of α-Fe has the body-centred cubic (*bcc*) structure. This phase transforms into a γ–Fe (*fcc*) phase upon increasing temperature above 1185 K, and then transforms to δ-Fe (another *bcc*–structured) phase before melting (Saxena et al., 1995). At high pressure, both *bcc* and *fcc* phases transform into the ε (or *hcp*) phase (Takahashi, Basset, 1964). This phase has a broad stability region, and ε–Fe is generally considered to be stable at the inner core conditions (Hemley, Mao, 2001; Ma et al., 2004). Some theoretical calculations (Belonoshko et al., 2003) predict the *bcc* structure of iron in this region near the melting temperature, but it was never confirmed experimentally. Also, the *bcc* phase of Fe could be stabilized at the inner core conditions by dissolving some amount of "light" elements, in particular, silicon (Vocadlo et al., 2003; Lin et al., 2002). Pure Ni is thought to be in the *fcc* structure at pressures over 300 GPa and up to the melting temperature (Yoo et al., 2000). The ambient pressure phase diagram of Fe-Ni alloys shows the existence of both *fcc* and *bcc* phases; the *fcc* phase, depending on composition, has a complex magnetic behaviour, and is known to exist in different magnetic states (Hausch and Warlimont, 1973; Dubrovinsky et al., 2001; Meyer, Entel, 1995). The lower temperature field (T<400 °C) of the Fe–Ni phase diagram has a complex configuration that includes a paramagnetic low-Ni disordered *fcc* phase, as well as the ordered compounds FeNi (tetrataenite) and Ni_3Fe (Guenzburger and Terra, 2005).

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The high-pressure phase diagram of Fe-Ni alloys is still not well constrained, and details of stability fields of *bcc*, *fcc* and *hcp* phases are not clear even for low-Ni (below 25 at%) alloys (Mao et al., 1990; Huang et al., 1988; Lin et al., 2003; Mao et al., 2005; Dubrovinsky et al., 2003).

Seismological observations provide us constraints concerning pressure, density and sound wave velocities in the outer liquid and inner solid core, but experimental data of Fe-Ni elasticity at appropriate conditions are missing. Although sound wave velocities in pure ε–iron were measured at high pressures and temperatures (Lin et al., 2005), the effect of its transition to the γ-phase and on the Ni content were not known so far. However even relatively small amounts of additional components could change phase relations and thermophysical properties of iron alloys (Boehler, 1993; Mao et al., 2005; Lin et al., 2002; Dubrovinsky et al., 2001; Schilfgaarde et al., 1999;Vidale and Earle, 2000): addition of Ni is thought to increase the *fcc* phase stability field. Therefore, the understanding and interpretation of composition and properties of the Earth's core (such as seismic anisotropy, fine-scale heterogeneity, super-rotation (Vidale and Earle, 2000; Breger et al., 2000)) require detailed studies of the Fe-Ni system at high pressure and temperature. Here we present the first in situ measurements of the longitudinal sound velocity V_P in *fcc* $Fe_{0.78}Ni_{0.22}$ alloy at high pressure and temperature by means of inelastic X-ray scattering from polycrystalline material. The composition was chosen as one of the high-end probable Ni-concentrations in the Earth's core in order to see the strongest possible effect of it on the bulk sound velocities in the alloy. Combined with the determination of the EoS by X-ray diffraction, we derive as well the transverse velocity V_S.

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2. Experimental details

A single-crystal of iron-nickel alloy containing 22 at% Ni, commercially available from the IBS company (Germany), was synthesized by the Chochralski method. The metastable *fcc* crystal, quenched from high temperature, completely transformed to the polycrystalline *bcc* phase during crystal cutting and polishing, as confirmed by XRD studies. The sample was polished to a thin plate of about 19 μm thickness, loaded into a diamond anvil cell and compressed above 12 GPa, so it completely transformed to the polycrystalline high-pressure *fcc* phase used for further measurements.

A four-pin modified Merrill-Basset type DAC (Dubrovinskaia and Dubrovinsky, 2003) equipped with an internal miniature platinum resistive heater was used to compress and heat the sample. Diamonds with 250 μm culet diameter were used as anvils. A rhenium gasket with 260 μm initial thickness was preindented to ~45 μm and a hole of 125 μm in diameter was drilled. A Fe-Ni sample was loaded along with a large amount (~50 % of volume) of pure polycrystalline LiF. One of the loadings was performed without LiF and we didn't observe any difference between experiments with and without LiF. Several small ruby chips were loaded into the sample chamber for pressure measurements (Mao et al., 1986). Temperature dependence of the ruby fluorescence was taken from Rekhi et al., (1999). Temperature was measured using an ultra-thin R-type thermocouple, located close (within less than 1 mm) to the sample chamber. The thermocouple was fixed with a ceramic bond on the surface of the metal gasket right near the diamond/gasket interface.

IXS measurements were performed on the ID28 beamline at the European Synchrotron Radiation Facility in Grenoble, France (Fiquet et al., 2004). The instrument

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was operated in the Si(888) configuration, with an incident photon energy of 15.817 keV and a total instrumental energy resolution of 5.5 meV full width at half maximum (FWHM). The transverse dimensions of the focused X-ray beam of 25×60 μm^2 (horizontal×vertical, FWHM) were further reduced by slits to approximately 10×15 μm^2. The momentum transfer $Q=2k_i\sin(\theta_s/2)$, where k_i is the incident photon wave vector and θ_s is the scattering angle, was selected by rotating the spectrometer around a vertical axis passing through the scattering sample in the horizontal plane. The momentum resolution was set by slits in front of the analyzers to 0.25 nm^{-1}. Energy scans were performed by varying the monochromator temperature while the analyzer temperature was kept fixed. Conversion from the temperature scale to the energy scale is accomplished by using the known thermal expansion coefficient of silicon: $\alpha(T) = \alpha_0 +\beta(T-T_0)$ with $\alpha_0 = 2.581\times10^{-6}$ 1/K and $\beta = 0.016\times10^{-6}$ $1/K^2$, T_0 = 22.5 ºC (Bergamin et al., 1997). The validity of this conversion has been checked by comparing the measured diamond dispersion curve for longitudinal acoustic phonons with well-established inelastic neutron scattering results. Two sets of experiments, at room temperature and at 715 (10) K, have been performed. Before and after each measurement (taking about 10 hours) an in-situ 1-D monochromatic X-ray diffraction pattern was collected for lattice parameter determination exactly from the same sample. The final pressure value was calculated from the lattice parameters (see below).

High-pressure and high-temperature angle-dispersive XRD study of the same Fe-Ni alloy compressed in LiF pressure-transmitting medium was performed using the high-resolution powder diffractometer of the Swiss-Norwegian BM01 beamline at the ESRF (Kuznetsov et al., 2002). Sample loading and experimental protocol was exactly the same

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as for the IXS measurements, in order to avoid any systematic uncertainty. A monochromatic beam with 0.7995 Å wavelength was used, and the diffracted intensities were registered with a MAR345 image plate. Experimentally measured pressure-volume relations at room temperature and at 715 K were reduced to the isothermal third order Birch-Murnaghan equations of state with a least-square minimization routine. Detailed results of the XRD study will be given elsewhere.

3. Results and discussion

Powder X-ray diffraction reveals that $Fe_{0.78}Ni_{0.22}$ alloy is stable in the *fcc* phase throughout the whole studied *P*, *T* range. An example of the analysed integrated pattern of the spectrum collected at 24.4(2) GPa and room temperature is shown in Fig. 1. The Debye-Scherrer rings of the studied sample show no evidence of "spotty" diffraction or inhomogeneous intensity distribution, indicating the absence of notable preferred orientation. The measured volume in the 20 to 72 GPa pressure range was fitted to the third order isothermal equations of state at 300 K and at 715 K with the following coefficients:

K_{300}=161 (1) GPa, K'_{300}=4.97(1), V_{300}=6.89(1) cm^3/mole

K_{715}=160 (1) GPa, K'_{715}=4.97(2), V_{715}=6.96(1) cm^3/mole

All the parameters were fitted, since ambient pressure volume at 300 and 715 K cannot be measured and is estimated from the obtained EOS. These parameters were used to calculate the pressure and bulk modulus *K* from the measured volume for every *P-T* point of the IXS experiment.

Fig. 2 shows an example of the IXS spectra collected at the highest reached pressure (71.7 GPa) and 715 K. It is characterized by an elastic contribution centred

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around zero energy, and two inelastic features, corresponding to the longitudinal acoustic phonons of Fe-Ni and the transverse acoustic phonon of diamond (see Fig. 2). Due to the much higher sound velocity (~11 km/s) the diamond contribution moves rapidly out of the spectral window of interest with increasing momentum transfer. The energy position $E(Q)$ (Q is the wave vector) of the phonons was extracted using a model function composed of several Lorentzians plus Gaussian peak functions, and the number of peak components was kept constant for each fit. The origin of small Gaussian smearing of inelastic peaks is probably small fluctuations of pressure and temperature during data collection, as well as possible pressure gradients and non-systematic instrumental errors. This model function was fitted to the IXS spectra, utilizing a standard χ^2 minimization routine. In the case of loading with LiF we also saw its LA phonon, but the contribution was clearly apparent due to the higher sound speed in LiF. Transverse phonon modes of the $Fe_{0.78}Ni_{0.22}$ alloy cannot be distinguished in our experiment, and only longitudinal sound velocities could be obtained directly from IXS measurements. Six to ten $E(Q)$ (for Q from 3 to 12.6 nm^{-1}) values were used to describe the LA phonon dispersions at every measured P,T condition.

Within the framework of the Born–von Karman lattice-dynamics theory (Ashcroft and Mermin, 1976), the solution of the dynamical matrix can be written as:

$$M\omega^2 = \sum_n \Phi_n \left(1 - \cos\left(\pi \frac{Q}{Q_{\max}}\right)\right), \qquad (1)$$

where M is the atomic mass, ω is the angular frequency and Q is the wave vector of the considered normal mode, Q_{max} is half the distance to the nearest reciprocal lattice point in the direction of Q, and Φ_n is the interplanar force constants (the force between an atom

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and the *n*th neighbour plane normal to *Q*). Taking into account only the first term (nearest-neighbours interactions) and substituting $\omega=E/h$ where h is the Plank constant, it can be rewritten as

$$E^2 = \frac{h^2\Phi}{M}\left[1-\cos\left(\pi\frac{Q}{Q_{\max}}\right)\right], \qquad (2)$$

or, equally

$$E = \sqrt{\frac{2h^2\Phi}{M}}\sin\left(\frac{\pi Q}{2Q_{\max}}\right). \qquad (3)$$

Taking into account that in long-wavelength limit $V_P = \frac{2\pi}{h}\frac{\partial E}{\partial Q}$ with Q equals to zero, the final result is

$$E = \frac{h}{\pi^2}Q_{\max}V_P\sin\left(\frac{\pi Q}{2Q_{\max}}\right), \qquad (4)$$

or, equally

$$V_P = \frac{\pi^2}{h}E\left[Q_{\max}\sin\left(\frac{\pi Q}{2Q_{\max}}\right)\right]^{-1}, \qquad (5)$$

where V_P is the longitudinal (compressional) sound wave velocity. Values for V_P were consequently derived from the equation 5, with Q_{max} left as a free parameter (Fig.2, inset). Although intrinsic anisotropy of the material could still produce some anisotropy even in an orientationally averaged polycrystalline sample, this effect is probably negligible, and we consider our sample as an isotropic polycrystalline material. In this case, the measured V_P is the bulk longitudinal sound velocity, and the transverse (shear) sound velocity V_S was obtained according to the relation:

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$$V_S^2 = \frac{3}{4}\left(V_P^2 - \frac{K}{\rho}\right), \qquad (6)$$

where ρ is the density and K is the adiabatic bulk modulus. In this equation the isothermal (instead of adiabatic) bulk modulus was used. Numerical estimates show that the difference between K_T and K_S in our case is negligible (less than 2 %). Values of the isothermal bulk modulus K for a given density ρ were calculated from measured EoS parameters (see above). The values of other generally used isotropic elastic moduli (shear modulus G, Young's modulus E, and Poisson's ratio ν) could be easily calculated and are listed in table 1 along with V_P and V_S values.

Sound wave velocities, plotted against density, are shown in Fig. 3. Our data for *fcc* $Fe_{0.78}Ni_{0.22}$ are in good agreement with those for ε–iron and iron-nickel alloy measured by Lin et al. (2003) (Fig. 3A). The sound velocities for pure *hcp*-Co and Ni are systematically lower at the same density. This difference cannot be explained by the atomic mass difference only, implying that simple mass corrections to the alloys elastic properties are invalid.

The well-known linear relation between longitudinal velocities and density (so called "Birch's law") (Birch, 1961) that is usually used in geosciences for extrapolations to the Earth's inner core conditions is generally satisfied within the uncertainties of our measurements. Our IXS study shows no detectable difference between room and high temperature results when normalized to density (Fig. 3B). The only exception is one high-temperature point at pressure 21.5 GPa, which is notably lower. This point could accidentally fall into narrow pressure and temperature region with anomalous compressibility in FeNi alloy also known as the invar effect (Dubrovinsky et al., 2001)

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and thus the elastic behaviour of *fcc* $Fe_{0.78}Ni_{0.22}$ alloy at low pressure (<25 GPa) region require additional studies. The absence of a significant temperature effect on V_P agrees with theoretical calculations (Steinle-Neumann et al., 2001): even at temperatures about 4000 K, longitudinal sound wave velocities in ε-iron are thought to decrease only by 2-3% (Fig. 3C). We can suppose that at T<1000 K the temperature effect is not detectable with the present experimental accuracy. In contrast to this, a recent nuclear-resonant inelastic x-ray scattering study (Lin et al., 2005) reported that ε-iron does not follow Birch's law at high temperatures, and that sound velocities significantly decrease with temperature for a given density. Our results could not confirm such anomaly for Fe-Ni alloy in studied pressure – temperature range.

When extrapolate our data to Earth's inner core conditions and compare with PREM (Dziewonski and Anderson, 1981), almost no difference can be seen in longitudinal wave velocities, but V_s is significantly higher than the values expected in Earth's core (Fig. 3C). If we assume similar temperature corrections as for pure ε-iron (Steinle-Neumann et al., 2001), both V_P and V_S would be below the PREM model for *fcc* $Fe_{0.78}Ni_{0.22}$ alloy. Could this difference be attributed to the presence of "light" elements, such as oxygen or sulphur, in the inner core? It is known that the density of the core is somewhat lower than what is expected for pure iron or iron-nickel alloy at corresponding conditions (Dziewonski and Anderson, 1981; Dubrovinsky et al., 2001). Incorporation of a few percent of "light" elements to the core could solve the problem. At the same time "light" elements would influence elastic properties of the core, and also increase sound velocities. For example, numeric estimations for addition of silicon in form of FeSi-alloy

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247 to pure iron would result in decreasing density and increasing sound wave velocities (Lin
248 et al., 2003).

249 Previous studies (Mao et al., 2005; Huang et al., 1992) in combination with the
250 present work show that there is still no unambiguous answer about phase stability fields
251 of *bcc*, *fcc* and *hcp* structures of FeNi alloys with different content of Ni under high
252 pressure. It is clear that even small changes in Ni content result in dramatic changes of
253 the *fcc* stability field. In our case (22 at. % of Ni) the stability field of the *fcc* phase is
254 larger than was reported by Mao et al. (2005) for $Fe_{0.95}Ni_{0.05}$, $Fe_{0.85}Ni_{0.15}$, $Fe_{0.80}Ni_{0.20}$ and
255 by Huang et al. (1992) for $Fe_{0.70}Ni_{0.30}$.

256 **4. Conclusions**

257 High-pressure and high-temperature (up to 72 GPa and 715 K) study of *fcc*
258 $Fe_{0.78}Ni_{0.22}$ alloy was performed. The X-ray diffraction study revealed stability of the *fcc*
259 over *hcp* phase in the whole studied *P, T* range. An isothermal equation of state was
260 derived at room temperature and at 715 K. X-ray inelastic scattering measurements
261 allowed the longitudinal acoustic wave velocity to be measured that gives, combined with
262 measured EoS, the full isotropic elasticity of the material. We did not observe a
263 significant deviation of the elastic properties from those of pure ε–iron and furthermore
264 no deviation from Birch's law. Although the bulk elasticity of *fcc* Fe-Ni alloy and ε–Fe
265 seem to be very similar, the elastic anisotropy (directions of the fast and slow waves) of
266 the hexagonal e-Fe and cubic Fe-Ni should be quite different (Cohen et al., 1997). If the
267 metal phase in the inner core is not hexagonal, but cubic (or a mixture of the two phases
268 exists) anisotropy may provide a better way to discriminate between the two.

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Figure and table captions.

Fig.1. Typical example of analysed integrated XRD patterns of the spectrum collected at 24.4 GPa and room temperature.

Fig. 2. Representative IXS spectrum of polycrystalline $Fe_{0.78}Ni_{0.22}$ alloy, collected at 71.7 GPa and 715 K (Q=10.45 nm^{-1}). Inset: an example of the sinusoidal fit to the experimental $E(Q)$ relation.

Fig. 3. Sound velocities of $Fe_{0.78}Ni_{0.22}$ alloy at ambient and high temperature (red circles) in comparison with: A - data for pure ε–iron: 1 – Dubrovinsky et al. (2001), 2 – Lin et al. (2005), 3- Antonangeli et al. (2004), *hcp* Co – 4 (Antonangeli et al., 2005), $Fe_{0.87}Ni_{0.13}$ alloy – 5 (Lin et al., 2003) and 6 - sound wave velocities for pure *fcc* Ni at ambient conditions; B –high and room temperature data for ε–iron (Lin et al., 2005) and *fcc* $Fe_{0.78}Ni_{0.22}$ alloy (this study); C - our data (line shows linear fit to our data extended to the inner core conditions) in comparison with the seismic observations (PREM) (Dziewonski and Anderson, 1981) and calculated sound wave velocities for ε–iron at different temperatures (Steinle-Neumann et al., 2001).

Table 1. Aggregate longitudinal and transverse velocities, bulk, shear, Young's moduli and Poisson ratio of *fcc* $Fe_{0.78}Ni_{0.22}$ alloy as obtained from IXS and X-ray diffraction measurements.

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