

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

Anastasia P. Kantor, Innokenty Yu. Kantor, Alexander V. Kurnosov, Alexei Yu. Kuznetsov, Natalia A. Dubrovinskaia, Michael Krisch, Alexei A. Bossak, Vladimir P. Dmitriev, Vadim S. Urusov, Leonid S. Dubrovinsky

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Table 1.

	Pressure,	Density,	V_L , km/s	V_T , km/s	K, GPa	<i>G</i> , GPa	ν	Ε,
	GPa	g/cm ³						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
		I	X			1	1	

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2	of inelastic X-ray scattering.
3	
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18	
19	
20	Abstract
21	Knowledge of the high-pressure and high-temperature elasticity of Fe-Ni alloy
22	with low (5-25%) Ni content is crucial for geosciences since it is probably the major
23	component of the cores of the terrestrial planets and the Moon. Here we present a study

24	of a FeNi alloy with 22 at. % of Ni to 72 GPa and 715 K, using inelastic X-ray scattering
25	(IXS) and X-ray powder diffraction from polycrystalline material. The X-ray diffraction
26	(XRD) study revealed stability of the face centred cubic (fcc) over the hexagonal close
27	packed (<i>hcp</i>) phase in the whole investigated pressure-temperature range. The study
28	presents first investigations of elasticity of fcc phase of iron-nickel Fe _{0.78} Ni _{0.22} alloy. The
29	isothermal equations of state were derived at room temperature and at 715 K
30	$(K_{300}=162(1) \text{ GPa}, K'_{300}=4.97(1), V_{300}=6.89(1) \text{ cm}^3/\text{mole}; K_{715}=160(1) \text{ GPa},$
31	K'_{715} =4.97(2), V_{715} =6.96(1) cm ³ /mole). Inelastic X-ray inelastic measurements allow the
32	determination of the longitudinal acoustic wave velocity V_P , and provide, combined with
33	the measured equations of state, the full isotropic elasticity of the material. We found that
34	within experimental errors our data follow the Birch's law. We did not observe any
35	significant deviations for <i>fcc</i> $Fe_{0.78}Ni_{0.22}$ from elastic properties of pure ϵ -iron.
36	Keywords: elasticity, iron-nickel alloy, inelastic scattering, equation of state.
37	1. Introduction
38	Properties of major constituents of the Earth's core, iron and its alloys, have long
39	been of great interest to geophysicists. Cosmochemical data and the composition of iron
40	meteorites suggest that Earth's core contains a significant (5 to 25 %) amount of nickel
41	(Anderson, 1989). Iron-nickel alloy with 5-25% Ni content is also thought to be the main
42	component of the cores of the Mars, Mercury, Moon, satellites of Saturn and Jupiter
43	(Encrenaz et al., 1995; Robbins et al., 1995; Bottke et al., 2006). Information on the
44	behaviour of Fe–Ni alloys at high pressure and temperature $(P-T)$, such as phase relations
45	and thermal equations of state (EoS), is essential for interpreting seismic and
46	geomagnetic observations and for computer modelling of the Earth's deep interior. While

47	pure Fe at high $P-T$ has been the subject of numerous studies (Mao et al., 1990; Saxena et
48	al., 1995; Yoo et al., 1995; Boehler, 1993; Andrault et al., 1997; Dubrovinsky et al.,
49	2000; Crowhurst et al., 2005; Antonangeli et al., 2004), there are far fewer studies on Fe-
50	Ni alloys (Huang et al., 1988; Lin et al., 2003; Mao et al., 2005; Dubrovinsky and
51	Dubrovinskaia, 2003).
52	At ambient conditions, the stable phase of α -Fe has the body-centred cubic (<i>bcc</i>)
53	structure. This phase transforms into a γ -Fe (fcc) phase upon increasing temperature
54	above 1185 K, and then transforms to δ -Fe (another <i>bcc</i> -structured) phase before melting
55	(Saxena et al., 1995). At high pressure, both <i>bcc</i> and <i>fcc</i> phases transform into the ε (or
56	<i>hcp</i>) phase (Takahashi, Basset, 1964). This phase has a broad stability region, and ϵ -Fe is
57	generally considered to be stable at the inner core conditions (Hemley, Mao, 2001; Ma et
58	al., 2004). Some theoretical calculations (Belonoshko et al., 2003) predict the bcc
59	structure of iron in this region near the melting temperature, but it was never confirmed
60	experimentally. Also, the bcc phase of Fe could be stabilized at the inner core conditions
61	by dissolving some amount of "light" elements, in particular, silicon (Vocadlo et al.,
62	2003; Lin et al., 2002). Pure Ni is thought to be in the <i>fcc</i> structure at pressures over 300
63	GPa and up to the melting temperature (Yoo et al., 2000). The ambient pressure phase
64	diagram of Fe-Ni alloys shows the existence of both fcc and bcc phases; the fcc phase,
65	depending on composition, has a complex magnetic behaviour, and is known to exist in
66	different magnetic states (Hausch and Warlimont, 1973; Dubrovinsky et al., 2001; Meyer,
67	Entel, 1995). The lower temperature field (T <400 °C) of the Fe–Ni phase diagram has a
68	complex configuration that includes a paramagnetic low-Ni disordered fcc phase, as well
69	as the ordered compounds FeNi (tetrataenite) and Ni ₃ Fe (Guenzburger and Terra, 2005).

70	The high-pressure phase diagram of Fe-Ni alloys is still not well constrained, and details
71	of stability fields of <i>bcc</i> , <i>fcc</i> and <i>hcp</i> phases are not clear even for low-Ni (below 25 at%)
72	alloys (Mao et al., 1990; Huang et al., 1988; Lin et al., 2003; Mao et al., 2005;
73	Dubrovinsky et al., 2003).
74	Seismological observations provide us constraints concerning pressure, density
75	and sound wave velocities in the outer liquid and inner solid core, but experimental data
76	of Fe-Ni elasticity at appropriate conditions are missing. Although sound wave velocities
77	in pure ε -iron were measured at high pressures and temperatures (Lin et al., 2005), the
78	effect of its transition to the γ -phase and on the Ni content were not known so far.
79	However even relatively small amounts of additional components could change phase
80	relations and thermophysical properties of iron alloys (Boehler, 1993; Mao et al., 2005;
81	Lin et al., 2002; Dubrovinsky et al., 2001; Schilfgaarde et al., 1999; Vidale and Earle,
82	2000): addition of Ni is thought to increase the fcc phase stability field. Therefore, the
83	understanding and interpretation of composition and properties of the Earth's core (such
84	as seismic anisotropy, fine-scale heterogeneity, super-rotation (Vidale and Earle, 2000;
85	Breger et al., 2000)) require detailed studies of the Fe-Ni system at high pressure and
86	temperature. Here we present the first in situ measurements of the longitudinal sound
87	velocity V_P in fcc Fe _{0.78} Ni _{0.22} alloy at high pressure and temperature by means of inelastic
88	X-ray scattering from polycrystalline material. The composition was chosen as one of the
89	high-end probable Ni-concentrations in the Earth's core in order to see the strongest
90	possible effect of it on the bulk sound velocities in the alloy. Combined with the
91	determination of the EoS by X-ray diffraction, we derive as well the transverse velocity
92	V_{S} .

93 **2. Experimental details**

94 A single-crystal of iron-nickel alloy containing 22 at% Ni, commercially available 95 from the IBS company (Germany), was synthesized by the Chochralski method. The 96 metastable *fcc* crystal, guenched from high temperature, completely transformed to the 97 polycrystalline bcc phase during crystal cutting and polishing, as confirmed by XRD 98 studies. The sample was polished to a thin plate of about 19 µm thickness, loaded into a 99 diamond anvil cell and compressed above 12 GPa, so it completely transformed to the 100 polycrystalline high-pressure *fcc* phase used for further measurements. 101 A four-pin modified Merrill-Basset type DAC (Dubrovinskaia and Dubrovinsky, 102 2003) equipped with an internal miniature platinum resistive heater was used to compress 103 and heat the sample. Diamonds with 250 µm culet diameter were used as anvils. A 104 rhenium gasket with 260 µm initial thickness was preindented to ~45 µm and a hole of 105 125 µm in diameter was drilled. A Fe-Ni sample was loaded along with a large amount 106 (~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 107 108 LiF. Several small ruby chips were loaded into the sample chamber for pressure 109 measurements (Mao et al., 1986). Temperature dependence of the ruby fluorescence was 110 taken from Rekhi et al., (1999). Temperature was measured using an ultra-thin R-type 111 thermocouple, located close (within less than 1 mm) to the sample chamber. The 112 thermocouple was fixed with a ceramic bond on the surface of the metal gasket right near 113 the diamond/gasket interface. 114 IXS measurements were performed on the ID28 beamline at the European

115 Synchrotron Radiation Facility in Grenoble, France (Fiquet et al., 2004). The instrument

116	was operated in the Si(888) configuration, with an incident photon energy of 15.817 keV
117	and a total instrumental energy resolution of 5.5 meV full width at half maximum
118	(FWHM). The transverse dimensions of the focused X-ray beam of $25 \times 60 \ \mu m^2$
119	(horizontal×vertical, FWHM) were further reduced by slits to approximately $10 \times 15 \ \mu m^2$.
120	The momentum transfer $Q=2k_i\sin(\theta_s/2)$, where k_i is the incident photon wave vector and
121	θ_s is the scattering angle, was selected by rotating the spectrometer around a vertical axis
122	passing through the scattering sample in the horizontal plane. The momentum resolution
123	was set by slits in front of the analyzers to 0.25 nm ⁻¹ . Energy scans were performed by
124	varying the monochromator temperature while the analyzer temperature was kept fixed.
125	Conversion from the temperature scale to the energy scale is accomplished by using the
126	known thermal expansion coefficient of silicon: $\alpha(T) = \alpha_0 + \beta(T-T_0)$ with $\alpha_0 = 2.581 \times 10^{-10}$
127	6 1/K and β = 0.016x10 ⁻⁶ 1/K ² , T ₀ = 22.5 °C (Bergamin et al., 1997). The validity of this
128	conversion has been checked by comparing the measured diamond dispersion curve for
129	longitudinal acoustic phonons with well-established inelastic neutron scattering results.
130	Two sets of experiments, at room temperature and at 715 (10) K, have been performed.
131	Before and after each measurement (taking about 10 hours) an in-situ 1-D
132	monochromatic X-ray diffraction pattern was collected for lattice parameter
133	determination exactly from the same sample. The final pressure value was calculated
134	from the lattice parameters (see below).
135	High-pressure and high-temperature angle-dispersive XRD study of the same Fe-
136	Ni alloy compressed in LiF pressure-transmitting medium was performed using the high-
137	resolution powder diffractometer of the Swiss-Norwegian BM01 beamline at the ESRF
138	(Kuznetsov et al., 2002). Sample loading and experimental protocol was exactly the same

as for the IXS measurements, in order to avoid any systematic uncertainty. A

140 monochromatic beam with 0.7995 Å wavelength was used, and the diffracted intensities

141 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

143 Birch-Murnaghan equations of state with a least-square minimization routine. Detailed

144 results of the XRD study will be given elsewhere.

145

3. Results and discussion

146 Powder X-ray diffraction reveals that Fe_{0.78}Ni_{0.22} alloy is stable in the *fcc* phase 147 throughout the whole studied P, T range. An example of the analysed integrated pattern 148 of the spectrum collected at 24.4(2) GPa and room temperature is shown in Fig. 1. The 149 Debye-Scherrer rings of the studied sample show no evidence of "spotty" diffraction or 150 inhomogeneous intensity distribution, indicating the absence of notable preferred 151 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 152 153 coefficients:

154 $K_{300}=161 (1)$ GPa, $K'_{300}=4.97(1)$, $V_{300}=6.89(1)$ cm³/mole

155 $K_{715}=160 (1)$ GPa, $K'_{715}=4.97(2)$, $V_{715}=6.96(1)$ cm³/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

162 around zero energy, and two inelastic features, corresponding to the longitudinal acoustic 163 phonons of Fe-Ni and the transverse acoustic phonon of diamond (see Fig. 2). Due to the 164 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 165 E(O) (O is the wave vector) of the phonons was extracted using a model function 166 167 composed of several Lorentzians plus Gaussian peak functions, and the number of peak 168 components was kept constant for each fit. The origin of small Gaussian smearing of 169 inelastic peaks is probably small fluctuations of pressure and temperature during data 170 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 171 routine. In the case of loading with LiF we also saw its LA phonon, but the contribution 172 173 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 174 175 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 176 177 measured *P*, *T* condition.

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

180
$$M\omega^2 = \sum_n \Phi_n \left(1 - \cos\left(\pi \frac{Q}{Q_{\text{max}}}\right) \right), \qquad (1)$$

181 where *M* is the atomic mass, ω is the angular frequency and *Q* is the wave vector of the 182 considered normal mode, Q_{max} is half the distance to the nearest reciprocal lattice point in 183 the direction of *Q*, and Φ_n is the interplanar force constants (the force between an atom

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

187
$$E^{2} = \frac{h^{2}\Phi}{M} \left[1 - \cos\left(\pi \frac{Q}{Q_{\text{max}}}\right) \right], \qquad (2)$$

188 or, equally

189
$$E = \sqrt{\frac{2h^2\Phi}{M}}\sin\left(\frac{\pi Q}{2Q_{\max}}\right).$$

190 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

(3)

191 final result is

192
$$E = \frac{h}{\pi^2} Q_{\max} V_P \sin\left(\frac{\pi Q}{2Q_{\max}}\right), \qquad (4)$$

193 or, equally

194
$$V_{P} = \frac{\pi^{2}}{h} E \left[Q_{\text{max}} \sin \left(\frac{\pi Q}{2Q_{\text{max}}} \right) \right]^{-1}, \qquad (5)$$

195

196 where V_P is the longitudinal (compressional) sound wave velocity. Values for V_P were

197 consequently derived from the equation 5, with Q_{max} left as a free parameter (Fig.2,

198 inset). Although intrinsic anisotropy of the material could still produce some anisotropy

- 199 even in an orientationally averaged polycrystalline sample, this effect is probably
- 200 negligible, and we consider our sample as an isotropic polycrystalline material. In this
- 201 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:

203
$$V_s^2 = \frac{3}{4} \left(V_P^2 - \frac{K}{\rho} \right),$$
 (6)

224

204 where ρ is the density and K is the adiabatic bulk modulus. In this equation the isothermal 205 (instead of adiabatic) bulk modulus was used. Numerical estimates show that the 206 difference between K_T and K_S in our case is negligible (less than 2 %). Values of the 207 isothermal bulk modulus K for a given density ρ were calculated from measured EoS 208 parameters (see above). The values of other generally used isotropic elastic moduli (shear 209 modulus G, Young's modulus E, and Poisson's ratio v) could be easily calculated and are 210 listed in table 1 along with V_P and V_S values. 211 Sound wave velocities, plotted against density, are shown in Fig. 3. Our data for 212 fcc Fe_{0.78}Ni_{0.22} are in good agreement with those for ε -iron and iron-nickel alloy 213 measured by Lin et al. (2003) (Fig. 3A). The sound velocities for pure hcp-Co and Ni are 214 systematically lower at the same density. This difference cannot be explained by the 215 atomic mass difference only, implying that simple mass corrections to the alloys elastic 216 properties are invalid. The well-known linear relation between longitudinal velocities and density (so 217 218 called "Birch's law") (Birch, 1961) that is usually used in geosciences for extrapolations 219 to the Earth's inner core conditions is generally satisfied within the uncertainties of our 220 measurements. Our IXS study shows no detectable difference between room and high 221 temperature results when normalized to density (Fig. 3B). The only exception is one 222 high-temperature point at pressure 21.5 GPa, which is notably lower. This point could 223 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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225	and thus the elastic behaviour of fcc Fe _{0.78} Ni _{0.22} alloy at low pressure (<25 GPa) region
226	require additional studies. The absence of a significant temperature effect on V_P agrees
227	with theoretical calculations (Steinle-Neumann et al., 2001): even at temperatures about
228	4000 K, longitudinal sound wave velocities in ϵ -iron are thought to decrease only by 2-
229	3% (Fig. 3C). We can suppose that at T<1000 K the temperature effect is not detectable
230	with the present experimental accuracy. In contrast to this, a recent nuclear-resonant
231	inelastic x-ray scattering study (Lin et al., 2005) reported that ε-iron does not follow
232	Birch's law at high temperatures, and that sound velocities significantly decrease with
233	temperature for a given density. Our results could not confirm such anomaly for Fe-Ni
234	alloy in studied pressure – temperature range.

235 When extrapolate our data to Earth's inner core conditions and compare with 236 PREM (Dziewonski and Anderson, 1981), almost no difference can be seen in 237 longitudinal wave velocities, but V_s is significantly higher than the values expected in 238 Earth's core (Fig. 3C). If we assume similar temperature corrections as for pure ε -iron 239 (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, 240 241 such as oxygen or sulphur, in the inner core? It is known that the density of the core is 242 somewhat lower than what is expected for pure iron or iron-nickel alloy at corresponding 243 conditions (Dziewonski and Anderson, 1981; Dubrovinsky et al., 2001). Incorporation of 244 a few percent of "light" elements to the core could solve the problem. At the same time 245 "light" elements would influence elastic properties of the core, and also increase sound 246 velocities. For example, numeric estimations for addition of silicon in form of FeSi-alloy

to pure iron would result in decreasing density and increasing sound wave velocities (Linet al., 2003).

Previous studies (Mao et al., 2005; Huang et al., 1992) in combination with the present work show that there is still no unambiguous answer about phase stability fields of *bcc*, *fcc* and *hcp* structures of FeNi alloys with different content of Ni under high pressure. It is clear that even small changes in Ni content result in dramatic changes of the *fcc* stability field. In our case (22 at. % of Ni) the stability field of the *fcc* phase is 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 by Huang et al. (1992) for Fe_{0.70}Ni_{0.30}.

256

4. Conclusions

High-pressure and high-temperature (up to 72 GPa and 715 K) study of fcc 257 258 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 no deviation from Birch's law. Although the bulk elasticity of *fcc* Fe-Ni alloy and ε -Fe 264 265 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.