

Hydrogen effect on the electronic and structural properties of Nb-Fe alloys

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Abstract The influence of hydrogen on the electronic and structural properties of $\text{Nb}_{1-y}\text{Fe}_y$ alloys has been studied with ^{57}Fe Mössbauer spectroscopy and X-ray diffraction. No ability of hydrogen to creation of the ferromagnetic properties has been observed in this system. The results clearly indicate the $\beta\text{-NbH}_{0.85\pm 0.77}$ hydride formation in place of $\alpha\text{-Nb}$ phase. The quadrupole splitting and the isomer shift of the $\beta\text{-NbH}_x$ subspectrum have been considered in terms of interaction between the interstitials and the Mössbauer atoms within the hydride phase.

Key words Mössbauer spectroscopy of ^{57}Fe • iron-niobium alloys • niobium hydrides

Introduction

Apart from the high-temperature ϵ phase, containing the iron-rich intermetallic compound Fe_3Nb_2 , the niobium and iron can form multiphase alloys that are paramagnetic. Only niobium easily absorbs hydrogen up to the stoichiometric composition of NbH_2 [2]. In contrast to niobium, iron cannot absorb hydrogen unless the giant pressure of H_2 gas is used ($p_{\min} \geq 7$ GPa). In the alloy however, sensible absorption of hydrogen is possible even at the pressure of hydrogen below 10^5 Pa in process of the high temperature synthesis (ca. 1300 K), and is associated with the significant lattice expansion [6]. One of the aims of this work was to check whether the absorbed hydrogen could modify the electronic and crystal structure of the alloy towards the ferromagnetic properties appearance just as in the case of vanadium, zirconium or titanium alloys [3–5]. Due to the lattice distortion near interstitial hydrogen atoms in transition-metal hydrides the intensity and the shape of the Mössbauer pattern are sensitive to the magnitude of the displacements of the probe atoms by neighbouring interstitials, and to the asymmetry in occupancy of interstitials due to hydrogen diffusion. Moreover, the hydrogen interstitials give rise to changes of the electron density and electric field gradient at neighbouring metal nuclei. In disordered, non-stoichiometric hydrides, the probes will usually have a variety of different hydrogen environments. When the diffusion of hydrogen causes the hyperfine interactions to become time independent, as in the fast diffusion case, the resulting Mössbauer patterns should remain sensitive to the asymmetry in the interactions of the probe atoms with interstitials. Thus, the resulting hyperfine patterns reflect therefore structural properties of the hydrides.

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Received: 17 July 2002, Accepted: 18 November 2002

Experiment

The alloys were made from Nb and Fe fine powders supplied by Sigma-Aldrich Co. with a purity of 99.9% and 99.999%, respectively. To obtain Me-H (metal-hydrogen) system the homogenised alloys were placed in a quartz tube and exposed to hydrogen gas at a pressure up to $\sim 10^5$ Pa. The hydrogen absorption took place during slow cooling of the alloy in the temperature range 1300–300 K. The amount of hydrogen absorbed was determined with an accuracy of about 1% from the change of the pressure in an apparatus of known volume. Finally, eight samples of H₂-charged/uncharged niobium-iron alloys, presented in Table 1, have been used in the experiment. The transmission ⁵⁷Fe Mössbauer spectra of all samples were recorded at room temperature with a standard constant-acceleration spectrometer in two ways, at a maximum

Table 1. Atomic concentrations of iron (y) and hydrogen ($x = \text{H/Me}$, where Me denotes an alloy atom) in Nb_{1-y}Fe_yH_x system.

y	0.03	0.05	0.07	0.10	0.30	0.40	0.48	0.70
x	0.85	0.85	0.83	0.77	0.40	0.19	0.06	0.05

velocity of ± 10 mm/s and ± 2 mm/s. The wide scale of velocity was applied to check for additional lines, apart from the contribution of narrow, central lines.

Results and discussion

The Mössbauer spectra of ⁵⁷Fe in Nb_{1-y}Fe_y and Nb_{1-y}Fe_yH_x alloys are shown in Figs. 1 and 2. In the iron concentration range 3 at.% Fe – 70 at.% Fe, the transition from a mixture

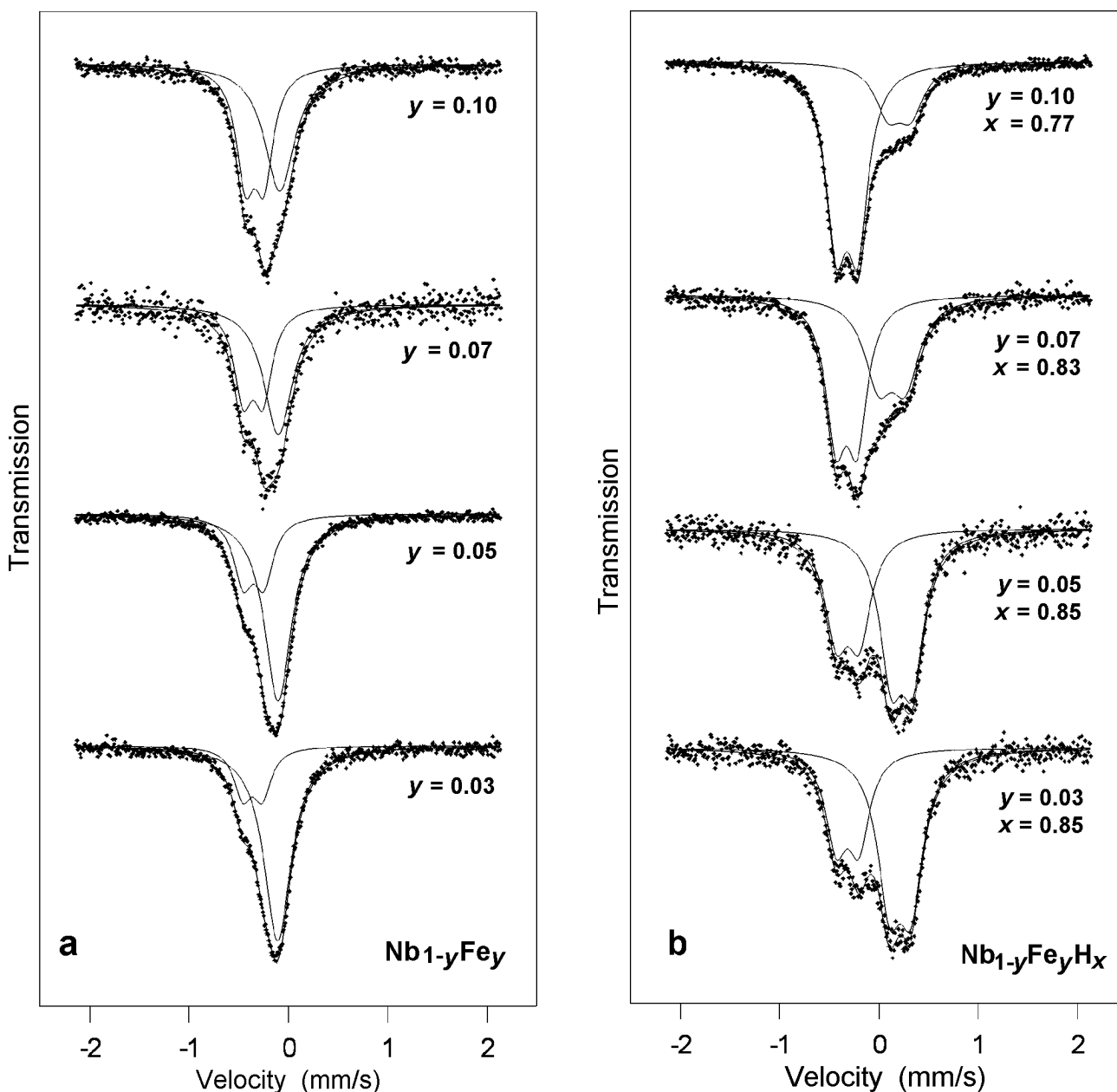


Fig. 1. The central parts of the Mössbauer spectra of ⁵⁷Fe in: a – Nb_{1-y}Fe_y; b – Nb_{1-y}Fe_yH_x alloys in the iron concentration range $y = 0.03 \div 0.10$.

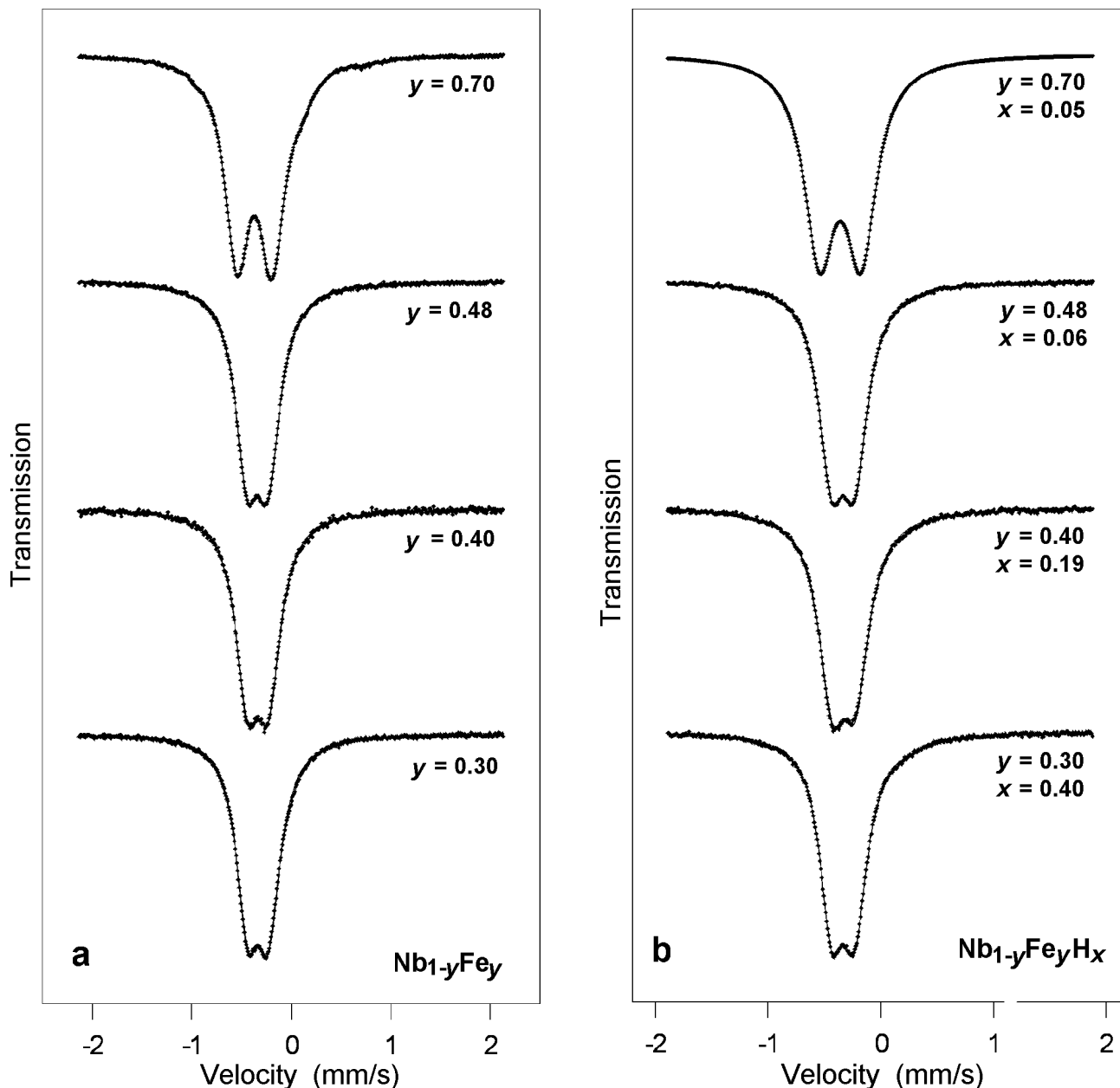


Fig. 2. The central parts of the Mössbauer spectra of ^{57}Fe in: a – $\text{Nb}_{1-y}\text{Fe}_y$; b – $\text{Nb}_{1-y}\text{Fe}_y\text{H}_x$ alloys in the iron concentration range $y = 0.30 \div 0.70$.

of $\alpha\text{-Nb}$ phase and $\eta\text{-Fe}_2\text{Nb}_3$ phase to the pure ϵ phase composed of Fe_3Nb_2 takes place. The plots covering an expanded velocity scale show no magnetic components even in the spectra of hydrogenated samples and, therefore, the magnetic aspect of hydrogenation will not be discussed in this work. The plots of the central parts of the spectra reveal the mixed pattern composed of singlet and/or symmetric doublets. Some of hyperfine parameters of the individual components, fitted in compliance with suitable phases that may be formed before and after hydrogenation, are shown in Table 2. It seems that the formation of the niobium β -hydride in place of bcc solid solution of Fe in Nb is the only effect of hydrogen interference in the phase structure of the alloy. This conclusion results from the absence of the single line responsible for this contribution after hydrogenation and, on the other side, that the doublets expected due to intermetallic compounds of Fe_3Nb_2 and Fe_2Nb_3 distorted by Fe solutes are well visible both, in

unloaded and hydrogenated system almost without any change. Furthermore, the hyperfine parameters of the right doublet in the spectra of $\text{Nb}_{0.97}\text{Fe}_{0.03}\text{H}_{0.85 \div 0.77}$ (Fig. 1b) are exactly the same within experimental error as obtained for the $\text{NbH}_{0.84}$ in [8]. However, in [8] the Mössbauer atoms were substitutional probes rather than the normal lattice atoms. So, it would seem that in our hydrogenated niobium-based samples ($y \leq 0.1$) the Fe atoms are simultaneously the lattice atoms in the intermetallic compounds and the substitutional probes in the hydride sublattice. The resulting hyperfine pattern may, therefore, reflect the structural properties of the hydride as well.

In order to verify the phase composition the X-ray diffraction method was employed. These results are collected in Table 3 and confirm, in general, the outcome of the Mössbauer spectra analysis. Furthermore, there is a characteristic decrease of the intensity of the β -hydride phase with iron concentration. This is probably due to the enthalpy of

Table 2. The measured isomer shift (IS) (with respect to α -Fe) and the quadrupole splitting (QS) of the components fitted in the ^{57}Fe Mössbauer spectra of $\text{Nb}_{1-y}\text{Fe}_y$ and $\text{Nb}_{1-y}\text{Fe}_y\text{H}_x$ alloys.

Phase	$\text{Nb}_{1-y}\text{Fe}_y$		$\text{Nb}_{1-y}\text{Fe}_y\text{H}_x$	
	IS (mm/s)	QS (mm/s)	IS (mm/s)	QS (mm/s)
α -Nb (bcc), $y = 0.03 \div 0.10$	0.003(5) \div 0.023(5)	–	–	–
β - $\text{NbH}_{0.85 \div 0.77}$	–	–	0.321(6)	0.22(2)
β - $\text{NbH}_{0.40}$ orthorhombic; tetrahedral H-site	–	–	0.186(5)	0.29(3)
η - Fe_2Nb_3 (bcc)	–0.224(4)	0.21(3)	–0.220(2)	0.21(2)
ϵ - Fe_3Nb_2 (hcp) MgZn_2 -type	–0.259(4)	0.36(2)	–0.257(5)	0.37(2)

Table 3. The X-ray diffraction phase analysis in $\text{Nb}_{1-y}\text{Fe}_y$ and $\text{Nb}_{1-y}\text{Fe}_y\text{H}_x$ alloys. (J – relative reflection intensity of K^α – Co; TA – trace amount.)

y	$\text{Nb}_{1-y}\text{Fe}_y$			x	$\text{Nb}_{1-y}\text{Fe}_y\text{H}_x$		
	α -Nb (J, %)	Fe_2Nb_3 (J, %)	Fe_3Nb_2 (J, %)		Nb_x (J, %)	Fe_2Nb_3 (J, %)	Fe_3Nb_2 (J, %)
0.03	76	17		0.85	63	33	
0.05	64	29		0.85	57	36	
0.07	56	41		0.83	29	64	
0.10	40	45		0.77	19	76	
0.30	TA	95		0.40	5	91	
0.40		99		0.19	TA	98	
0.48		87		0.06	TA	95	TA
0.70			96	0.05		TA	95

formation of niobium hydrides NbH_x (-59 kJ/mol H_2) that becomes less negative than for almost all of compounds of Nb_mFe_n ($-66 \div -71$ kJ/mol formula unit) [2]. Moreover, going from the solid solution to the compound, i.e. since the Fe atoms substitute the Nb ones, they become more lattice atoms in the η phase or/and in α -Nb phase than the body-centred substitutions in the hydride. In other words, an iron atom reflects the alloy structure missing thereby the role of the Mössbauer probe in the hydride cage. Thus, the hydride fraction decreases and finally escapes observation.

More interesting problem seems to be, therefore the behaviour of the quadrupole splitting (QS) that is almost invariable with iron concentration excluding the case of $y = 0.40$ (Fig. 3). It goes to show that the Fe atoms interact alike with surrounding interstitials, as long as the hydride stoichiometry is not changed significantly. The explanation of such interaction and hence the hyperfine parameters seems to be possible taking into account the diffusion of hydrogen within the hydride superlattice. In the β phase of NbH_x , the structurally allowed interstitial sites form a plane rectangle around each metal atom (Fig. 4). In stoichiometric β - $\text{NbH}_{1.0}$ each metal atom is surrounded by four hydrogen atoms [7]. In the sub-stoichiometric hydride, some of these nearest neighbours will be missing and the diffusion of hydrogen is supposed to take place mainly between sites allowed by the structure [1]. At a hydrogen-to-metal ratio of $x = 0.75$ three of these sites should be occupied on the average, unless the environment of the impurities is modified by a repulsive or attractive interaction with the interstitials. Such interactions have been found to be small in the hydrides of niobium [8]. To simplify the situation somewhat we assume that three of these four

sites are always occupied, and that the hydrogen diffusion can be described as a hopping of the vacancy on the fourth corner of the rectangle around the Fe probe. Configurations with zero or four nearest neighbours will not disturb the central metal atom.

For ^{57}Fe in palladium hydride it was found [8] that the hydrogen-induced isomer shift is, with good approximation, proportional to the number of nearest hydrogen neighbours around the probe atoms. If the same is true in the present case, the mean isomer shift relative to the unloaded alloys can be used as a measure of the mean number of hydrogen atoms next to the Fe probes. The isomer shift and quadrupole interactions observed indicate that in this case mainly a configuration with three nearest neighbours occurs. In fact, the isomer shift of about $+0.3$ mm/s with respect to the near pure α -Nb is relatively large. According to this interpretation the mean isomer shift per nearest hydrogen neighbour is about 0.1 mm/s and hence quite similar to the shift per nearest neighbour found in palladium hydride [8]. The planar arrangement of the nearest hydrogen neighbours around the metal atoms in the β phase of NbH_x explains why the electric field gradient at the iron nuclei does not disappear when the diffusion becomes sufficiently fast for motional averaging, that is certainly above 300 K. According to the conclusions drawn from the isomer shifts, this should be a configuration in which a single hydrogen atom is missing on the four nearest interstitial sites that are allowed by the superlattice structure. Configurations with two nearest neighbours would have not much influence on the electric field gradient unless the hydrogen occupies mostly two of interstitials on the same side of the rectangle. From the statistical point of view this is unlikely in the case of fast diffusion. Thus, no reasonable explanation was found

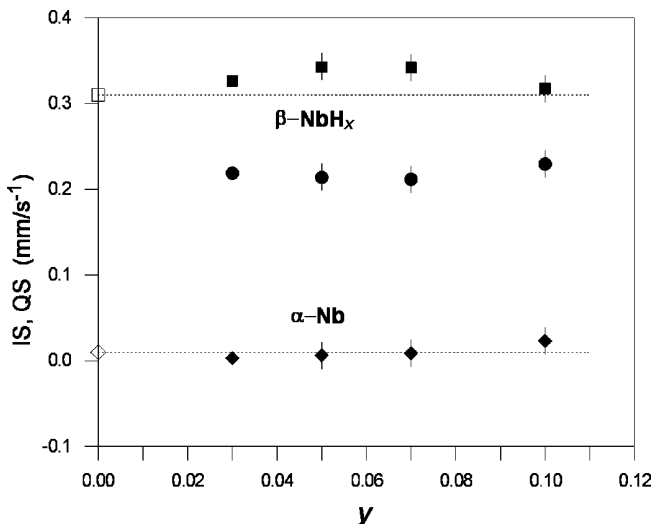


Fig. 3. The ^{57}Fe isomer shift (■) and quadrupole splitting (●) of the doublet representing $\beta\text{-NbH}_{0.85\pm 0.77}$ in the Mössbauer pattern of ^{57}Fe in $\text{Nb}_{1-y}\text{Fe}_y\text{H}_x$ ($y \leq 0.1$) alloys. The isomer shift of the single line representing the $\alpha\text{-Nb}$ phase in $\text{Nb}_{1-y}\text{Fe}_y$ alloys is shown by (◆). Also the values of the isomer shift of ^{57}Fe in $\text{NbH}_{0.84}$ and in pure Nb taken from [8] are indicated on the left-side axis by (□) and (◇) symbols and dashed lines, respectively. The isomer shift values are given with respect to the $\alpha\text{-Fe}$.

for the relatively large quadrupole splitting of the sub-spectrum of the β -hydride in the $\text{Nb}_{70}\text{Fe}_{30}\text{H}_{0.40}$ alloy, all the more that the basic metallic phase of $\alpha\text{-Nb}$ almost does not exist in this region of the alloy components concentration.

At the end, it is worthy of notice shortly the problem of displacement of the Fe atom in the hydride cage coming from hydrogen diffusion, and then the probability of quasi-elastic contribution to the Mössbauer spectrum. In general, the relatively large displacements of Fe in NbH_x may be due to the fact that the $4d$ elements have larger atomic radii than the $3d$ analogues, and hence the Fe solutes should fit rather loosely into the Nb hydride lattice. The displacement geometry in the β phase is expected to be anisotropic. One should note that, due to the anisotropic displacement geometry in the β phase the quadrupole doublet observed in β phase of NbH_x should, therefore, be asymmetric. This asymmetry is, however, not seen in the spectra, perhaps because it is small. Regarding the quasi-elastic line observation when the Mössbauer nuclei are subject to motions, the Mössbauer lineshape should be broadened due to fluctuations of the hyperfine interaction parameters. When the diffusion of the interstitials becomes very fast the quasi-elastic lines merge into the background and no longer contribute to the observed intensity of the Mössbauer pattern. In the limit of fast diffusion, one thus expects to observe the truly elastic component with a motionally averaged isomer shift and an electric quadrupole interaction.

Conclusions

The shapes and centre shifts of the Mössbauer patterns reflect the structure of the hydride β -phase, the interactions between the Fe probes and the interstitials, as well as the motional averaging of the isomer shifts and electric quadrupole

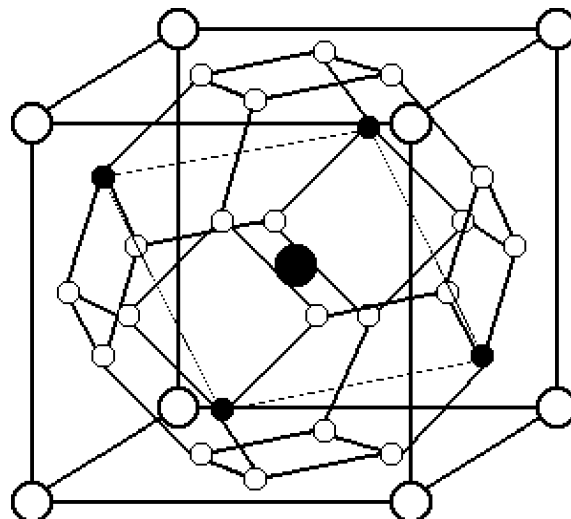


Fig. 4. The lattice structure of the NbH_x hydride, with large circles for the metal atoms and small ones for 24 nearest interstitial sites surrounding a Mössbauer atom in the body-centred position. Full circles indicate the four hydrogen positions allowed in the β phase of NbH_x .

pole splitting. Moreover, the results for samples with different hydrogen concentrations indicate that the structure of the spectra also depends sensitively on the hydrogen content. When more data for different hydrogen concentrations become available, such data will also provide additional information on the jump processes in the vicinity of the probe atoms in different regions of the phase diagrams.

Acknowledgment This work was supported by the University of Wrocław under the grant No. 2016/IFD/2001.

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