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Magnetic Properties of Hydrogen Solid Solutions in Fe–Ni–Mn Alloys

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The magnetization behaviour is investigated in a pulsed magnetic field up to 50 kOe at $80 \leqq T \leqq 220$ K for hydrogen solid solutions in $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ invars containing 0, 4.5, 10, 17, 24, 29, and 35 wt% Mn. The alloys are enriched in hydrogen to hydrogen/metal atomic ratio $n \lessapprox 1$ using exposures to $P_{H_2} \leqq 70$ kbar. The Néel point behaviour is studied at $P_{H_2} \leqq 15$ kbar for the 35% Mn alloy. The dependence of the parameter of the f.c.c. metal sublattice on the hydrogen content is measured for the 29% Mn alloy at $T = 83$ K. The hydrogenation is shown to suppress the antiferromagnetic ordering in manganese-rich alloys. Above a certain hydrogen concentration n_f, each of the studied Me–H solutions becomes ferromagnetic. The Curie points in the ferromagnetic state rise with n increase. At $n \approx 1$, the spontaneous magnetization and Curie points of hydrogen solutions in Fe–Ni–Mn alloys reach magnitudes characteristic of Fe–Ni invars.

В импульсных магнитных полях до 50 kOe при $80 \leqq T \leqq 220$ K исследовано поведение намагниченности растворов водорода в сплавах инварной системы $Fe_{65}(Ni_{1-x}Mn_x)_{35}$, содержащих 0, 4,5; 10; 17; 24; 29 и 35 wt% Mn. Сплавы насыщали водородом до атомного отношения водород/металл $n \lessapprox 1$ путем выдержки при $P_{H_2} \leqq 70$ kbar. У сплава с 35% Mn изучено поведение точки Нееля при $P_{H_2} \leqq 15$ kbar. Для сплава с 29% Mn при $T = 83$ K построена зависимость параметра ГЦК подрешетки металла от содержания водорода. Показано, что внедрение водорода подавляет антиферромагнитное упроядочение в богатых марганцем сплавах. Начиная с определенной концентрации водорода n_f каждый из изученных растворов Me–H становится ферромагнетиком. Точки Кюри сплавов в ферромагнитном состоянии растут при увеличении n. При $n \approx 1$ спонтанная намагниченность и точки Кюри растворов водорода в сплавах Fe–Ni–Mn достигают значений, характерных для инваров Fe–Ni.

1. Introduction

Hydrogenation of transition metals leads to a suppression of magnetic ordering in most cases. For example, as the hydrogen concentration increases, the Curie point T_C drops and the spontaneous magnetization σ_0 at $T = 0$ K decreases for nickel [1 to 3], Ni–Fe alloys with < 60 at% Fe [4, 5], and Ni–Cr alloys [6]. Exchange-enhanced paramagnetic palladium becomes a superconductor at hydrogen/metal atomic ratio $n > 0.8$ [7]. The invar alloys Fe–Ni (disordered f.c.c. alloys with more than 60% Fe) were the first species where an opposite effect was observed [8, 5]. Thus, hydrogen dissolution in the alloy with 67.5 at% Fe at $P_{H_2} = 50$ kbar raised its Curie point by more than 500 K with respect to its magnitude in an inert medium [5]. The alloys of the invar $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ system also appeared to be an interesting object for hydrogenation [9]. We refer to [10, 11] for the *T–P–C* phase diagram and to [12] for the magnetic properties of this system. Substitution of nickel by manganese in the $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ system lowers the Curie point from $T_c = 467$ K for the $Fe_{65}Ni_{35}$ alloy down to helium temperatures for the alloy with $\approx 10\%$ Mn. At higher manganese content, the system undergoes antiferromagnetic ordering, and the Néel point rises steadily up to $T = 442$ K for the $Fe_{65}Mn_{35}$ alloy [11] (see Table 1). The first measurements showed that hydrogenation of 10 and 17% Mn alloys (antiferromagnetic, $T_N \approx 160$ K) caused ferromagnetic ordering [9].

In the present work, the spontaneous magnetization σ_0 and Curie points of hydrogen solid solutions in the $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys with 0, 4.5, 10, 17, 24, 29, and 35% Mn have been studied at atmospheric pressure. The solutions were obtained by exposure of original Fe–Ni–Mn alloys to high hydrogen pressure. For the 35% Mn alloy, the dependence $T_N(P_{H_2})$ was investigated at $P_{H_2} \leqq 15$ kbar. For the 29% Mn alloy, the dependence of the f.c.c. metal sublattice parameter on hydrogen content was measured at $T = 83$ K.

2. Experimental

The ingots melted from electrolytically pure Ni, Mn, and carbonyl Fe according to [9 to 11] were used for sample preparation. After a 6 h homogenization at 1400 K and water quenching, these ingots were rolled into foils ≈ 0.5 mm thick. Then these foils were subjected to stress-relief annealing at 1400 K for 3 min, water-quenched, and chemically etched to the thickness of ≈ 0.2 mm. The 20 to 30 mg samples for magnetic measurements were assemblies of 10×1.5 mm^2 bands cut from such foils.

Hydrogenation of the samples was conducted by several hours exposure under hydrogen pressures up to 70 kbar and $T = 520$ K. Then the high-pressure chamber was cooled to $T \approx 220$ K, the pressure lowered to atmospheric, the samples were removed from the chamber and immersed into liquid nitrogen to prevent hydrogen loss. At normal pressure the Fe–Ni–Mn–H solid solutions thus obtained are kinetically unstable in regard to the desintegration into metal and molecular hydrogen at temperature above ≈ 240 K [8, 9]. The hydrogen concentration in the Me–H samples was measured with 3% error by collecting the released hydrogen to a scaled glass vessel (silicon being expelled from the vessel) at atmospheric pressure and room temperature.

The magnetization of the samples was measured by the induction method [13] in a pulsed magnetic field up to 50 kOe in the temperature range 80 to 220 K, the pulse duration being ≈ 0.01 s. The results of repetitive measurement at 80 K after covering the whole temperature interval did not differ from the initial ones. This indicates the absence of noticeable hydrogen losses during the measurement.

The Néel points for the $Fe_{65}Mn_{35}$ alloy were determined by controlling the position of the bend of the temperature dependence curve of electrical resistance (Fig. 1), taken with continuous heating and cooling at a rate of about 10 K min^{-1} with an accuracy of ±5 K in an inert medium (silicon) and ±8 K in hydrogen. The fact that this bend corresponds to the Néel point of the $Fe_{65}Mn_{35}$ alloy was proved by means of neutron diffraction investigation in [11]. The temperature was measured by a chromel–alumel thermocouple, the pressure by a manganin wire gauge with an accuracy of ±0.1 and ±0.3 kbar in silicon and in hydrogen, respectively. Then the measurements were performed in hydrogen, the manganin gauge and the thermocouple were insulated against direct exposure to hydrogen.

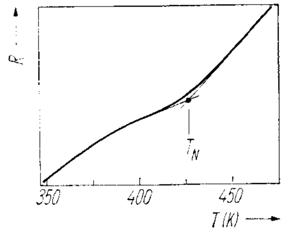

Fig. 1. Isobar ($P = 5.2$ kbar) of the temperature dependence of electroresistance for the $Fe_{65}N_{35}$ alloy near the Néel point

An X-ray measurement was carried out at 83 K using a DRON-2 diffractometer with FeK_α radiation.

3. Results

3.1 *X-ray measurements*

Fig. 2 shows the dependence $\Delta V_0 = V(n) - V(0)$ at $T = 83$ K and normal pressure, $V(n)$ and $V(0)$ being the elementary cell volumes for the $Fe_{65}Ni_6Mn_{29}$ alloy with hydrogen content n and without hydrogen. The experimental errors lie within $\delta(\Delta V_0) \approx \approx 0.7$ Å^3 and are mainly due to the diffraction linewidth of this alloy and of the hydrogen solution on its base. It is seen from Fig. 2 that the present data correlate satisfactorily well with the dependence $\Delta V_0(n)$ obtained in [5] at the same temperature for Ni–Fe alloys. The dependence $\Delta V_0(n)$ shown by a dash-dotted line holds for a number of hydrogen solid solutions with f.c.c. sublattice of the transition metal: palladium and its alloys with Ir, Au, Ag, Pt, and Cu, and Ni–Cu alloys [14] ($T = 293$ K). The dependence $\Delta V_0(n)$ for the Ni–Fe and Ni–Fe–Mn alloys differs considerably from that shown by the dash-dotted line; its character, however, does not change: at $n < 0.8$ the slope $\beta = (\partial/\partial n)\,\Delta V_0(n)$ is nearly constant and equals ≈ 9.5 Å^3, and at $n > 0.8$ it decreases considerably (following [14], we approximated the dependence $\Delta V_0(n)$ for Ni–Fe alloys at $n < 0.8$ and > 0.8 by straight lines [5]). Note that the difference between the dependences for alloys on the base of Pd [14], Ni [2], and for Ni–Fe [5] and Ni–Fe–Mn alloys is not due to different measurement temperatures (83 and 220 K): the values $\Delta V_0(0.89)$ for the alloy with 20 at% Fe measured at temperatures 83 and 220 K coincide within the experimental error [5].

3.2 *Magnetization measurements*

The behaviour of the magnetization of our Me–H samples is in qualitative accordance with equations of Wohlfarth's theory of very weak itinerant ferromagnetism [15]. Using these equations, we found σ_0 and T_C for all the alloys. The error in σ_0 determination did not exceed 5%, the Curie points were estimated with an accuracy of ± 5 K when $T_C \leq 200$ K and up to ± 40 K at $T_C \approx 400$ K.

The T_C- and σ_0-values thus obtained are given in Fig. 3 and 4 as functions of the hydrogen content in the specimens. As it is seen from the figures, hydrogenation causes ferromagnetic ordering in all the alloys of the $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ system. However, by contrast to the 10% Mn alloy, in which ferromagnetism arises on dissolving even of the first atomic per cent of hydrogen, for alloys with higher manganese concentration, this occurs only on reaching a "critical" hydrogen concentration n_f. Averaged n_f-values, obtained by extrapolation to $\sigma_0 = 0$ and $T_C = 0$ of the $\sigma_0(n)$ and $T_C(n)$ dependences for the studied Me–H solutions, are listed in Table 1. The slopes of the $\sigma_0(n)$ and $T_C(n)$ dependences for the 35% Mn alloy are chosen like those for the 29% Mn alloy. The Curie points of hydrogen solutions in the $Fe_{65}Ni_{35}$ alloy are too

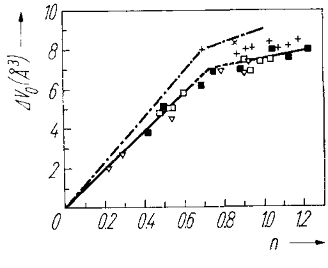

Fig. 2. Dependences $\Delta V_0 = V(n) - V(0)$ (see text). ▽ $Fe_{65}Ni_6Mn_{29}$ alloy, $T = 83$ K; ■, □ Ni–Fe alloys with 20 and 67.5 at% Fe [5], respectively, $T = 83$ K; + Ni [2], $T = 293$ K, × Ni (see references in [14]), $T = 293$ K; dash-dotted line shows the analogous dependence for palladium alloys [14], $T = 293$ K

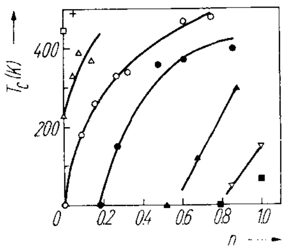

Fig. 3

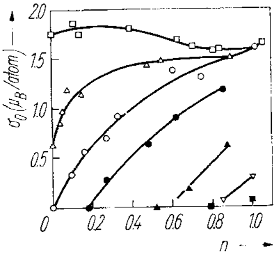

Fig. 4

Fig. 3. Dependences of the Curie point T_C on hydrogen concentration n for the $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys. □ for the 0%, △ 4.5%, ○ 10%, ● 17%, ▲ 24%, ▽ 29%, ■ 35% Mn alloys. T_C ($n = 0.05$) value for the $Fe_{65}Ni_{35}$ alloy denoted by a cross is found from the difference $\Delta T_C = T_C(P_{H_2}) - T_C(P)$ at $P = 20$ kbar [8] (see text)

Fig. 4. Spontaneous magnetization σ_0 at $T = 0$ K in dependence on hydrogen concentration n for the $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys. Notations are the same as in Fig. 3. (Magnetization is given in μ_B/atom of the Fe–Ni–Mn alloy)

Table 1

wt% Mn	T_C*) (K)	T_N*) (K)	N^e (el./atom)	$N_f^e - N^e$ (el./atom)	n_f	ζ (el./atom)
0	467	—	8.68	−0.33	—	—
4.5	228	—	8.54	−0.19	—	—
10	—	—	8.38	−0.03	0	—
17	—	160	8.17	0.18	0.18	1.00
24	—	253	7.97	0.38	0.58	0.66
29	—	341	7.82	0.53	0.81	0.65
35	—	442	7.65	0.70	0.94	0.74

$\zeta = (N_f^e - N_e)/n_f$; $N_f^e = 8.35$ electrons/atoms of Fe–Ni–Mn alloy.
*) Data of [10, 11].

high to be reliably estimated from magnetic measurements at $T \leq 220$ K. The T_C ($n = 0.05$) position for this alloy (denoted by a cross in Fig. 3) is evaluated using the difference $\Delta T_C = T_C(P_{H_2}) - T_C(P) \approx 40$ K at $P = 20$ kbar [8]. As one can see from Fig. 3, the Curie points of all the Me–H solutions investigated rise as hydrogen content increases.

The magnetization σ_0 of the alloys containing more than 10% Mn also rises steadily with increasing n (Fig. 4). Alloys with smaller concentration of manganese have a more complicated $\sigma_0(n)$ behaviour. For the 4.5% Mn alloy, σ_0 increases rapidly at $n \leq 0.5$ and then remains nearly constant. For the $Fe_{65}Ni_{35}$ alloy, σ_0 depends weakly on hydrogen content up to $n \approx 0.5$ and then decreases.

3.3 The effect of hydrogen pressure on T_N for the $Fe_{65}Mn_{35}$ alloy

Fig. 5 shows that in an inert medium, the Néel point of the 35% Mn alloy falls linearly with a slope $dT_N/dP = (-0.85 \pm 0.15)$ K kbar^{-1} in good agreement with the data of [11]. Due to the diffusional nature of the formation of Me–H solid solutions the time drift $T_N(\tau)$ occurs after pressure change in hydrogen atmosphere. Exposure of

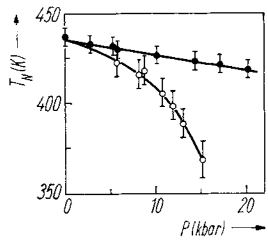

Fig. 5. Dependence of the Néel point T_N on pressure for the $Fe_{65}Ni_{35}$ alloy. ● in an inert medium, ○ in hydrogen

the $Fe_{65}Mn_{35}$ sample at $T = 400$ K during $\Delta\tau \leqq 1$ h proved to be sufficient for T_N to cease varying within experimental error. Fig. 5 shows ultimate values $T_N(P_{H_2})$. As it is seen from the figure, hydrogenation leads to a monotonic decrease of T_N with respect to its value in an inert medium at the same pressure, the effect reaching $\Delta T_N = T_N(P_{H_2}) - T_N(P) \approx -50$ K at $P = 15$ kbar. Chemical analysis of a quenched $Fe_{65}Mn_{35}$–H sample showed $n = (3.9 \pm 0.2) \times 10^{-2}$ to be the equilibrium hydrogen content for $P_{H_2} = 15$ kbar and $T = 400$ K. The anomaly of the electroresistance isobar corresponding to T_N (Fig. 1), is highly smoothed at $P_{H_2} > 15$ kbar, and the Néel point determination by our method becomes impossible.

4. Discussion

4.1 Dependence $V_0(n)$

In the Ni–H system at $T < T_{cr}$ ($620\text{ K} < T_{cr} < 700$ K [4, 2]), the separation into two isomorphic phases γ_1 and γ_2, poor and rich in hydrogen, occurs, the compositions of phases γ_1 and γ_2 in thermodynamical equilibrium at $P = 1$ atm and $T < 250$ K being $n_{\gamma_1}^{max} < 0.02$ and $n_{\gamma_2}^{min} = 0.7 \pm 0.05$ [3]. Addition of ≈ 20 to 40% Fe to nickel lowers T_{cr} below room temperature [4], and hydrogen dissolving in Fe–Ni invars forms solid solutions over the whole concentration range ($n \leqq 1$) investigated [8, 5, 9].

X-ray measurement confirms the existence of a continuous hydrogen solubility also for the invars $Fe_{65}(Ni_{1-x}Mn_x)_{35}$. Really, firstly, the invars Fe–Ni–H [5] and $Fe_{65}Ni_6Mn_{28}$–H proved to be single-phase over a wide range of concentration, the parameter of the f.c.c. metal sublattice increasing with increasing n (Fig. 2). Secondly, Me–H samples, obtained by exposure to high hydrogen pressure during a time insufficient for the hydrogen concentration to reach equilibrium, are single-phase and homogeneous (a similar situation was already observed at the formation of Co–H solid solutions [16]). The latter not only indicates that the rate of hydrogen solid solution formation is defined mainly by surface processes, but also that no isomorphic transformation ($\gamma_1 \to \gamma_2$) occurs in these solutions since, otherwise, the samples would be two-phase.

Of considerable interest is a change in the $\Delta V_0(n)$ dependence at $n \approx 0.8$ for the Me–H solutions studied (Fig. 2). At $n \leqslant 1$, hydrogen atoms occupy in all these solutions likely the octahedral interstitial sites (octapores), that was stated experimentally for the systems Ni–H, Pd–H, Pd–Au–H (see [14] for references). Since there is one octapore only per each lattice point in the f.c.c. crystal lattice, in the Me–H solutions with $n > 1$ (Fig. 2, data from [2, 5]) hydrogen must occupy, only partially, interstitial sites of the second tetrahedral type (tetrapores).

It is reasonable to associate [2] the n-value at which the occupation of tetrapores takes place with $n \approx 0.8$ at which the character of the $\Delta V_0(n)$ dependence changes. This suggestion needs, indeed, a direct experimental test.

4.2 Magnetic properties

Thus, the following picture is observed on hydrogenation of the $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys. The Néel points of antiferromagnetic alloys become lower, antiferromagnetic ordering is suppressed, and ferromagnetism arises at a certain hydrogen concentration. The Curie points of the samples in the ferromagnetic state rise with increasing n (Fig. 3).

A characteristic feature of invars is the abnormally strong dependence of physical properties on volume. It is shown in [8, 5] that at $n \ll 1$ the behaviour of the $T_C(n)$ dependences for hydrogen solutions in the Fe–Ni alloys is in qualitative agreement with the assumption that the effect due to the metal lattice extension is predominant on hydrogen dissolution. In this case [8]

$$\Delta T_C^V = \frac{(\mathrm{d}T_C/\mathrm{d}P)_{\mathrm{in}} \left(\dfrac{\beta}{kV}\right)}{(1 + \mathrm{d}T_C/\mathrm{d}P)_{\mathrm{in}} \left(\dfrac{3\alpha}{k}\right)}, \tag{1}$$

where k is the compressibility, V the volume of the alloy unit cell, α the linear expansion coefficient at $T \approx T_C$, the index "in" denotes an inert medium. It was shown in [17] that the behaviour of Curie points on hydrogenation of intermetallics Y–Fe and Ce–Fe can be also explained if the $T_C(V)$ dependence is taken into account. Qualitative correlation with (1) is observed for the 4.5% Mn alloy studied in the present work (Fig. 3), too.

As the $\mathrm{d}T_C/\mathrm{d}P$ value changes weakly on Ni substitution by Mn in the $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys [10, 11], the arising of ferromagnetism and the rapid increase of T_C of manganese-rich alloys with increasing hydrogen concentration may in principle be due to the strong dependence of their Curie points on volume. However, formula (1) does not describe even the sign of the hydrogen effect on the Néel points of antiferromagnetic alloys Fe–Ni–Mn. Under the assumption that the compressibility of the $Fe_{65}Mn_{35}$ alloy is as large as for the invar $Fe_{65}Ni_{35}$, formula (1) yields $\Delta T_N^V \geqq +8$ K at $n = 3.9 \times 10^{-2}$ whereas the experimental value is $\Delta T_N \approx -50$ K (Section 3.3). Taking into consideration the effects due to volume expansion of alloys at hydrogenation only, one failed to describe the $\sigma_0(n)$ behaviour for the studied hydrogen solid solutions, too. For example, $(1/\sigma_0)_{\mathrm{in}} (\partial\sigma_0/\partial P) = -0.9 \times 10^{-2}\ \mathrm{kbar}^{-1}$ for the $Fe_{65}Ni_{35}$ alloy [18], and at $n = 0.1$ we have

$$\Delta\sigma_0^V = \left(\frac{\partial\sigma_0}{\partial P}\right)_{\mathrm{in}} \frac{\beta}{kV} \approx +0.34\mu_B/\mathrm{atom}\,.$$

As it is seen from Fig. 4, the σ_0-value for this alloy does not vary within experimental error at $n \leqq 0.5$. Moreover, for Fe–Ni invars it is shown [5] that the effect of hydrogen on σ_0 cannot be described as a sum of two components associated with changes in volume and electron concentration, under the assumption of [19] that the hydrogen atom supplies its electron to the conduction band of the metal.

Thus, hydrogen essentially distorts the Ni–Fe–Mn alloy band structure. This is in accordance with the band structure calculations for the hydrides of a number of transition metals, and particularly, of nickel and palladium [20, 21]. According to these calculations, an increase of the number of protons in interstitial sites of the above metals distorts the energy spectrum so that the number of states below the Fermi level increases. Thus, only a part of electrons (0.4 to 0.1 electron/proton for Pd and Ni [20]), supplied by hydrogen atoms to the conduction band, populates states above the Fermi level, and the rest occupies the mentioned additional states below it.

Then, despite of the great magnitude and complication of the effects caused by hydrogen dissolution in transition metals, a possibility exists to describe, although only qualitatively, the hydrogen effect on the magnetic properties of our alloys, considering hydrogen as a donor of a fractional quantity of electrons. This approach allowed a semi-quantitative description of the behaviour of the Curie point in hydrogen atmosphere for Fe–Ni alloys using the dependence of the Curie point on iron concentration $T_C(x_{Fe})$ in the system Fe–Ni and the coefficients $\xi = -x_{Fe}/n$ for a "recalculation" of the hydrogen content into a change of iron concentration, which were derived from the magnetization measurements [5]. In this case, the "effective" number of electrons supplied by hydrogen atom to the metal band $\zeta = 2\xi$ was within the limits $\zeta = 0.6$ for 10% Fe to $\zeta \approx 0.37$ for invars [5]. The sign and the order of magnitude of these ζ-values are in agreement with the calculations of [20, 21].

Note that qualitatively hydrogenation of the $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys results in the same change of T_N and T_C as the substitution of manganese by nickel in the original ternary system (in this case the number of s + d electrons increases). As it was shown in [22], on hydrogenation of the $Fe_{66}Ni_{31}Mn_3$ alloy (at%), its ^{57}Fe Mössbauer absorption spectrum approaches the spectrum observed for the $Fe_{65}Ni_{35}$ alloy. So, the ζ-values for the considered Fe–Ni–Mn alloys are of useful sign. Let us see now whether the behaviour of magnetic properties of hydrogen solutions in the $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys can be described using reasonable ζ-magnitudes.

Assume that at hydrogen content nearly "critical" for ferromagnetic ordering to arise (n_f), the band structures of Fe–Ni–Mn–H solutions are similar. That is a "critical" electron concentration N_f^e exists which is common for all the alloys and has such a value that for $N^e + \zeta n > N_f^e$ the hydrogen solutions in $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys become ferromagnetic (N^e is the total number of s + d electrons per atom in the original Fe–Ni–Mn alloy). Assuming that ζ-values do not differ strongly for the investigated alloys from

$$N^e + \langle\zeta\rangle\, n_f = N_f^e\,,$$

using the N^e- and n_f-values listed in Table 1, we obtain by a least-squares procedure $\langle\zeta\rangle = 0.7$ electrons/atom and $N_f^e = 8.35$ electrons/atom. $N_f^e - N^e$ and $\zeta = (N_f^e - N^e)/n_f$ calculated for each alloy are also listed in Table 1. As one can see, sign and order of ζ-values thus obtained are in agreement with the calculations [20, 21].

It is worth pointing out that this approach does not contradict the previous conclusion about the predominant role of volume effects in T_C varying under hydrogenation, since volume expansion due to hydrogen dissolving was taken into account when the calculations of [20, 21] were performed. More than this, the description in terms of electron concentration changes (hydrogen being a donor of a fractional number of electrons) is quite phenomenological and cannot elucidate the question about the actual reasons for the observed behaviour of magnetic properties of the Me–H solid solutions studied.

Under the assumption that the major effect upon T_C and T_N at manganese substitution by nickel in the original ternary system Fe–Ni–Mn is due to the change in s + d electron concentration, one can carry out additional estimations. Let us consider the effect of hydrogen on the Curie point of the 4.5% Mn alloy. When going over from this alloy to the $Fe_{65}Ni_{35}$ alloy the s + d electron concentration increases by $\Delta N^e = 0.14$ electrons/atom and the Curie point increases by $\Delta T_C^e = 239$ K (see Table 1). Dissolving hydrogen up to $n = 0.1$ in the 4.5% Mn alloy raises the Curie point by $\Delta T_C^n = 130$ K (see Fig. 3). Then

$$\zeta_C = \left(\frac{\Delta T_C^n}{n}\right)\Big/\left(\frac{\Delta T_C^e}{\Delta N^e}\right) \approx 0.76 \text{ electrons/atom}\,,$$

that is also a reasonable estimate.

However, this approach fails to describe the Néel point behaviour for the $Fe_{65}Mn_{35}$ alloy in hydrogen atmosphere. Indeed, $\Delta N^e = 0.17$ electrons/atom and $\Delta T_N^e = -101$ K (Table 1) for the 35 and 29% Mn alloys, and $\Delta T_N^n = -50$ K for the 35% Mn alloy at $n = 0.039$ (Section 3.3). Then

$$\zeta_N = \left(\frac{\Delta T_N^n}{n}\right) \Big/ \left(\frac{\Delta T_N^e}{\Delta N^e}\right) \approx 2.2 \text{ electrons/atom}\,.$$

Thus, hydrogenation of the $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ invar alloys changes their magnetic properties drastically. Estimations show that in these alloys the strong Curie point dependence upon volume may be a dominant factor for ferromagnetism to arise with increasing hydrogen content. Like for the Fe–Ni alloys [5], a qualitative description of the $T_C(n)$ dependence is possible for the Fe–Ni–Mn alloys considering hydrogen as an electron donor with $\zeta \approx 0.7$. The effect of hydrogen on σ_0 and T_N is more complicated. Nevertheless, it proves to be qualitatively analogous to that observed in substitution of manganese by nickel.

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