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PROCEEDINGS

Mössbauer study of the $Fe_{1-x}Ni_x$ Invar alloys by monochromatic circularly polarized source

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Abstract X-ray diffraction measurements and Mössbauer spectroscopy with and without external magnetic field parallel to beam direction have been performed for $Fe_{1-x}Ni_x$ (x = 0.25, 0.30, 0.35) alloys. The compositions of the studied alloys were chosen in order to cover the concentration range where the fcc ↔ bcc structural transformation appears, as well as where single phase fcc Fe-Ni alloys exhibit the Invar phenomena. Spatial distribution of the iron magnetic moments is discussed. The hyperfine magnetic field (h.m.f.) distribution is analyzed within a scope of two models discussed in the literature. In the first model it is assumed that any hyperfine magnetic filed vector have the same spatial distribution (the same values of ($<\cos\theta>$). In the second, the low field component of the hyperfine magnetic field is ordered antiferomagnetically (or disordered) while the high field component is aligned by an external magnetic field. In order to determine the mean values of cosine of the angle between γ-rays direction and hyperfine field vector of iron, ($<\cos\theta>$), a monochromatic circularly polarized Mössbauer source (MCPMS) was used. The analysis of the MCPMS results show that the shapes of the measured spectra can be explained by single values of $<\cos\theta>$.

Key words Invar alloys • Mössbauer polarimetry • transition metal alloys

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Introduction

The problem of the Invar effect in Fe-Ni alloys at the concentrations close to the fcc ↔ bcc transformation has a long story but the full understanding of the phenomena is still lacking. After discovery of the Invar effect in fcc Fe-Ni alloys, a number of experimental studies were done and theoretical models suggested. The most popular phenomenological model – so-called 2γ state model – was introduced by Weiss [9]. This model assumed the presence of two electronic states of Fe atoms: high spin and high volume (HS) ferromagnetic state and low spin and low volume (LS) state with an antiferromagnetic order. In papers [4, 5] the magnetic model proposed by the authors assumed localized magnetic moments of Fe and Ni with a mixed exchange coupling between them. This can lead to an antiparallel orientation of iron magnetic moments with respect the net magnetization for a certain amount of Fe neighbours. The recent *ab initio* calculations of the volume dependences of magnetic properties, so-called classical Invar ($Fe_{0.65}Ni_{0.35}$), in which the non-collinear spin alignments were allowed, gives a new impulse to the studies of this intriguing phenomena [8]. In this calculations spins may be canted with respect to the average magnetization direction. The results show that the Invar properties could be explained by a continuous transition of Fe spins from nearly ferromagnetic ordering at the large volume to an approximately uniform spatial distribution of spins for small volume. The aim of the presented work is to explore the spatial distributions of the Fe magnetic hyperfine field vectors in fcc Fe-Ni alloys. Because a standard Mössbauer spectroscopy is not sensitive to the sign of the hyperfine magnetic field, the measurements with MCPMS have been used to get information about the spatial distribution of the hyperfine field vectors.

Experimental

The $Fe_{1-x}Ni_x$ (x = 0.25, 0.30, 0.35) alloys were prepared by melting in an arc furnace stoichiometric amounts of iron and nickel elements under a protective argon atmosphere. The ingots were powdered, and then the samples were annealed at 600°C for 2 h and cooled at a rate of 300°C/h. X-ray diffraction measurements were used for the determination of the crystalline structure as well as of the lattice parameters. Standard ^{57}Fe Mössbauer measurements in constant acceleration mode with a commercial ^{57}Co source in the Cr matrix were performed. In the measurements, powder samples of about 12 mg/cm^2 with random grain orientation fixed by an epoxy glue were used. In order to determine the spatial distribution of hyperfine magnetic field of the sample in axial external field of 1.1 T, Mössbauer spectroscopy with monochromatic, circularly polarized radiation was used. Polarized beam was prepared by the filter technique: resonant photons with one polarization were absorbed by the filter. This technique is described in greater detail in [6].

Results and disscusion

The X-ray diffraction measurements show that in the sample with x = 0.25 there are two cubic phases, bcc and fcc, while only the fcc structure is present for x = 0.30 and 0.35. The measured lattices parameters are presented in Table 1.

Table 1. Lattices parameters of Fe-Ni alloys.

Lattice parameter (Å)	$Fe_{0.75}Ni_{0.25}$	$Fe_{0.70}Ni_{0.30}$	$Fe_{0.65}Ni_{0.35}$
fcc	3.5839(7)	3.5876(6)	3.5955(5)
bcc	2.8691(6)		

It can be seen that the lattice parameter for the fcc phase increases with increasing Ni concentration. The measured value for $Fe_{0.65}Ni_{0.35}$ agrees well with the data published in [1].

The Mössbauer spectra measured in zero field and in the magnetic field of B = 1.1 T applied parallel to the gamma beam are presented in Figs. 1a and 1b, respectively. The spectra were fitted with a sum of sextets broadened by the Gaussian distribution of magnetic hyperfine field, and a single line, if necessary.

As can be inferred from Fig. 1, the measured shapes of the spectra change drastically with Ni concentration. The shape of the spectrum for x = 0.25 can be explained by one broadened sextet and one single line. The observed sextet comes from Fe in the bcc phase while the single line originates from the Fe atoms in fcc phase. We also note the presence of small amounts of Fe-O for x = 0.25, and 0.30 in all measured spectra. In addition, some slight amounts of Fe_3O_4 appeared after annealing for x = 0.35. Under the applied external magnetic field (B = 1.1. T) the shape of the spectra changes, cf. Figs. 1a and 1b. The magnetic moments belonging to the ferromagnetic phase are aligned and in the axial field geometry this results in a decrease of the line intensities i_2 and i_5 of the Zeeman sextets:

(1) $$i_1:i_2:i_3:i_4:i_5:i_6 = 3:z:1:1:z:3.$$

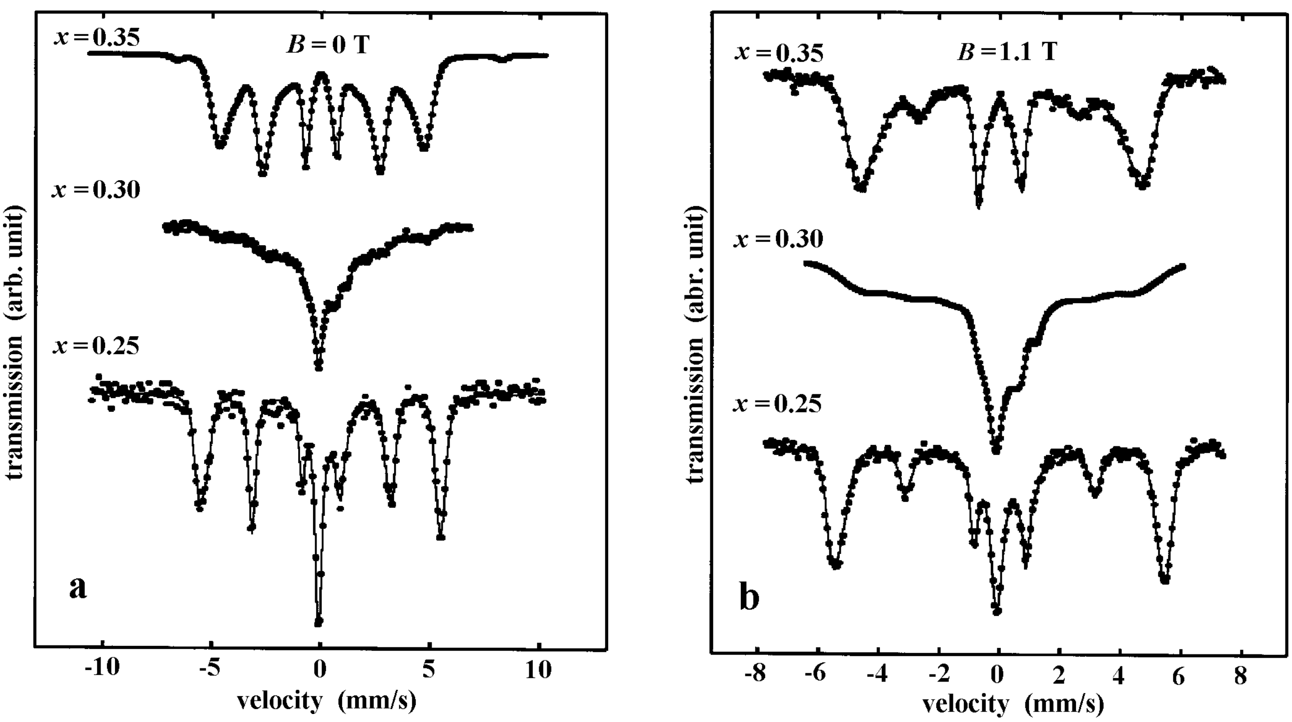

Fig. 1. Mössbauer spectra of $Fe_{1-x}Ni_x$ measured in (a) zero and (b) external applied magnetic field parallel to the direction of photons.

The z value corresponds to the average square of the cosine of an angle θ between the direction of the gamma beam and the direction of the magnetic hyperfine field:

$$\left\langle \cos^2\theta \right\rangle = \frac{4-z}{4+z}. \quad (2)$$

We have found that the external field causes reorientation of magnetic moments only. Within the experimental accuracy the shape of the h.m.f. distribution remains unchanged. Therefore, we performed simultaneous fits to the spectra measured with (Fig. 1a) and without the field (Fig. 1b). The shapes of h.m.f. distributions are shown in Fig. 2. Their main features are the following. The shape for $x = 0.30$ reflects a very broad hyperfine field distribution and a paramagnetic line. The paramagnetic line is well separated from the broad magnetic component (see peak at $B = 0$ T in Fig. 2 for $x = 0.30$). Three weak peaks seen at $B = 9$, 19 and 26 T can be artefacts due to the use of three Zeeman components in the fitting procedure. The shape for $x = 0.35$ can be described by the two peak structure with a very broad low field component (see Fig. 2). This latter shape of hyperfine field distribution is typical for "classical Invar" concentration [2]. Average values of the h.m.f. fcc phase are equal to 0.0 T, 15 ± 2 T and 25 ± 1 T for $x = 0.25$, 0.30, and 0.35, respectively, and agree well with the behavior of the mean magnetic hyperfine field as a function of Ni concentration for fcc phase in the range from 0.25 to 0.38 [3].

Because the standard Mössbauer spectroscopy is not sensitive to the magnetic hyperfine field direction, it is hard to get information about spatial distributions of Fe spins. Some interesting features of the spatial distribution of the hyperfine magnetic field vectors can be obtained from the spectra measured by polarized radiation (see Fig. 3a and 3b). The symbols ↑↑ and ↑↓ at the Fig. 3 refer to two opposite polarizations of the beam. The spectra exhibit characteristic asymmetry [6]. Defining the asymmetry parameters in the intensities between the lines number 1 and 6 or 4 and 3 as:

$$A = \frac{i_1 - i_6}{i_1 + i_6} = \frac{i_4 - i_3}{i_3 + i_4} \quad (3)$$

one can express an average <cos θ> (projection of the iron hyperfine field on the external field direction) by

$$\left\langle \cos\theta \right\rangle = \frac{4 \cdot A}{(4+z)\cdot p} \quad (4)$$

Table 2. The values of the parameters z, A, $<\cos^2\theta>$ and $<\cos\theta>$ for the $Fe_{1-x}Ni_x$ ($x = 0.25, 0.30, 0.35$).

	$Fe_{0.75}Ni_{0.25}$	$Fe_{0.70}Ni_{0.30}$	$Fe_{0.65}Ni_{0.35}$
z	0.81 ± 0.05	0.4 ± 0.30	0.27 ± 0.05
A	0.59 ± 0.15	0.4 ± 0.20	0.59 ± 0.15
$\cos^2\theta$	0.66 ± 0.02	0.82 ± 0.12	0.87 ± 0.02
$\cos\theta$	0.61 ± 0.14	0.6 ± 0.30	0.69 ± 0.14

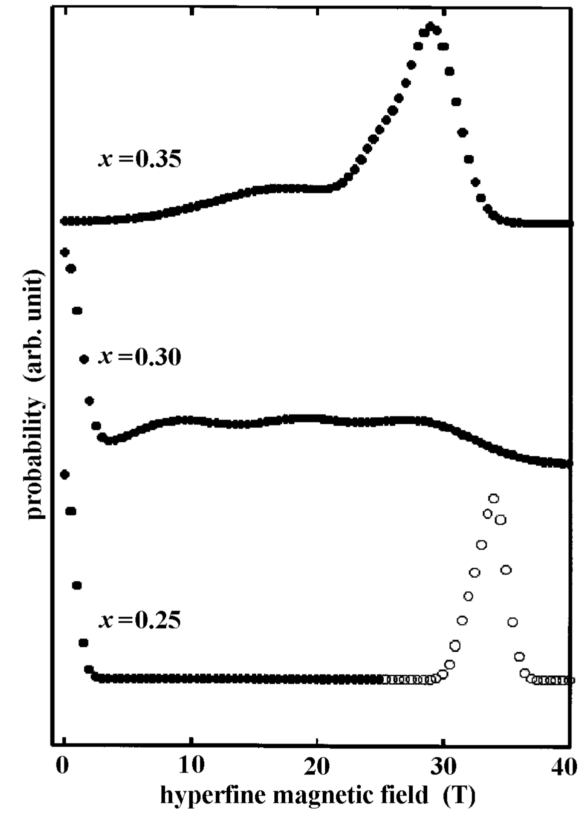

Fig. 2. Hyperfine magnetic field distributions. Full and empty symbols correspond to fcc and bcc phase, respectively.

where the parameter p denotes the polarization of the beam, in our case $p = (80 \pm 2)\%$.

As was already discussed in the literature [2, 9] and is also seen in the presented h.m.f. distributions (see Fig. 2) there are two kinds of iron magnetic moments in the fcc phase: large and small ones. We are interested in response of these moments to the applied field. As a first step, we assume that all the moments in the sample have the same angular distribution. This results in a single value of the <cos θ> (model I). The result of such an assumption is shown in Figs. 3a and 3b and in Table 2. Solid lines in Figs. 3a and 3b correspond to the fit with the same hyperfine parameters as in Fig. 1 (for the in-field experiment) except of the asymmetry between line intensities i_1 and i_6 (or i_4 and i_3). We see that the assumption is confirmed by the experiment.

In the second step we analyzed the spectrum for $x = 0.35$ in greater detail. We assumed that the low field component originates from antiferromagnetic or/and spin disordered phase. In this case the asymmetry parameter A for the low field component is zero. The results of the fitted model are presented in Figs. 3a and 3b (model II). We see that the 'model II' cannot explain the observed asymmetry in the spectra, while the 'model I' describes well the measured spectra.

Conclusions

The X-ray diffraction experiments show that the sample with $x = 0.25$ consists of two crystallographic phases (fcc

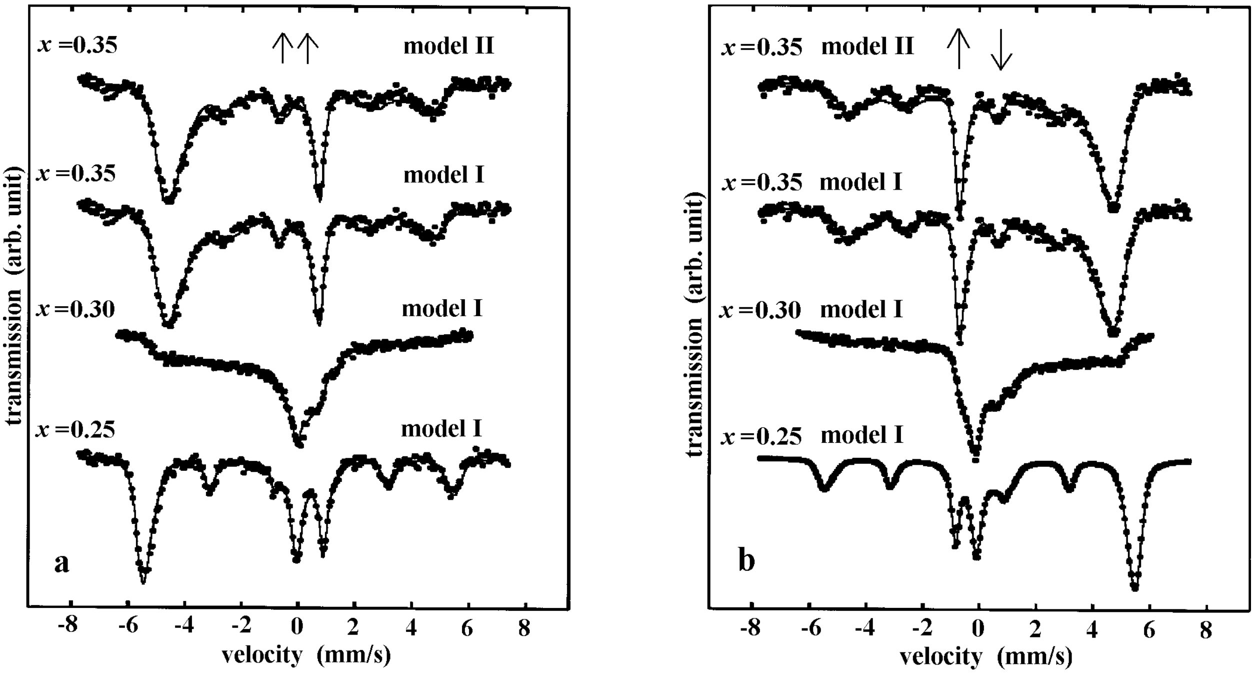

Fig. 3. Mössbauer spectra of $Fe_{1-x}Ni_x$ measured using MCPMS source for both polarizations (a) and (b).

and bcc), while for $x = 0.30$, 0.35 only a single fcc phase was detected. The measured parameters of the lattices agree well with the data presented in [1].

The measured shapes of the Mössbauer spectra show remarkable changes with increasing nickel concentration. The mean values of magnetic hyperfine field for fcc phase are equal to 0.0 T, 15 ± 2 T and 25 ± 1 T for $x = 0.25$, 0.30, 0.35, respectively.

The monochromatic circularly polarized Mössbauer source has been used to measure spatial distributions of hyperfine field vectors of Fe atoms. The conclusion from the MCPMS measurements is that the average cosine between local iron magnetic moment and the average magnetization direction in the Invar $Fe_{65}Ni_{35}$ is the same for the whole sample. This conclusion is in contradiction with the Weiss 2γ state model where the LS antiferromagnetic state is postulated. Because of the relatively large uncertainty of the measured $\langle\cos\theta\rangle$ and $\langle\cos^2\theta\rangle$, it is hard to say whether some minor part of iron hyperfine vectors are not antiparallel to the net magnetization as detected in [2, 7].

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