Magnetic behaviour of Ni-substituted Fe$_2$P

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Abstract. Magnetization and Mössbauer measurements are reported on two alloys, namely $(Fe_{0.99}Ni_{0.01})_2P$ and $(Fe_{0.95}Ni_{0.05})_2P$. Small substitutions of Ni in the ferromagnetic compound Fe_2P strengthen the ferromagnetic order, raising the Curie temperature from 216 K for Fe_2P (value in the literature) to 235 (±10) K and 295 (±5) K in the systems substituted with 1 and 5 at.% Ni, respectively. The magnetic anisotropy decreases. The inverse susceptibility does not follow a strictly linear temperature dependence even up to 800 K. Mössbauer results suggest that Ni has a nearly total preference for the tetrahedral sites. The presence of Ni in the second coordination sphere of iron reduces the ^{57}Fe hyperfine fields at both the crystalline sites.

1. Introduction

The ferromagnetic compound Fe_2P exhibits interesting magnetic properties when iron is substituted by other 3d transition-metal elements (Fruchart *et al* 1969, Nagase *et al* 1973, Wäppling *et al* 1975, Lundgren *et al* 1978, Fujii *et al* 1978, 1982, Ericsson *et al* 1980, Srivastava *et al* 1987, Dolia *et al* 1988, 1991, Bacmann *et al* 1990, Beckman and Lundgren 1991, and references therein). Substitutions of small amounts of Mn or Cr (about 1–3 at.%) destroy ferromagnetism, leading to antiferromagnetism, and also reduce the ordering temperature. Hyperfine fields at the two iron sites—tetrahedral (Fe(1)) surrounded by four P atoms and pyramidal (Fe(2)) surrounded by five P atoms—are drastically reduced. Co and Ni, on the other hand, when substituted for Fe, raise the ordering temperature and thus strengthen the ferromagnetism. However, unlike the cases of Mn and Cr, the studies for Co and Ni have not been made for substitutions smaller than 5 at.% and the effect on the hyperfine fields has not been investigated for any substitution.

This paper is concerned with examining the influence of Ni on the magnetic behaviour of the parent compound Fe_2P. Among the work available in literature on the $(Fe_{1-x}Ni_x)_2P$ systems, Fruchart *et al* (1969) studied magnetization as a function of temperature and reported T_C for various x-values in the range $0.50 \geqslant x \geqslant 0.05$. Maeda and Takashima (1973) studied the Mössbauer spectra of several systems corresponding to $x \geqslant 0.10$ in their paramagnetic states, to learn about the site occupancies. Fujii *et al* (1982) studied the compounds with $x \geqslant 0.10$ in single-crystal form, to determine the variation in Curie temperature, magnetic moment and anisotropy constant as functions of the concentration of Ni.

We have undertaken studies on two polycrystalline samples with small substitutions (1 and 5 at.% Ni) corresponding to $x = 0.01$ and 0.05 in $(Fe_{1-x}Ni_x)_2P$. Magnetization, in both the ferromagnetic and the paramagnetic regions, and ^{57}Fe

Mössbauer measurements have been reported and the results are discussed in the light of the reports in the literature.

2. Experimental details

The two samples in the series $(Fe_{1-x}Ni_x)_2P$ with $x = 0.01$ and 0.05 (hereafter referred to as FNP01 and FNP05, respectively) were prepared by the solid state diffusion technique starting with stoichiometric proportions of elemental Fe (purity, 99.9%) and Ni (purity, 99.99%) powders and phosphorus (purity, 99.999%) flakes. The procedure followed was the same as reported elsewhere (Dolia *et al* 1988). Debye–Scherrer x-ray powder diffraction patterns recorded on a Philips model PW 1840 diffractometer confirmed the formation of a single phase for both alloys. The alloys were found to be hexagonal with the cell parameters $a = 5.84$ Å and $c = 3.45$ Å for FNP01, and $a = 5.89$ Å and $c = 3.43$ Å for FNP05. The reported cell parameters for Fe_2P are $a = 5.859$ Å and $c = 3.453$ Å (Wäppling *et al* 1975). There is no appreciable change in the cell volume.

The DC magnetization measurements were made using a PARC vibrating-sample magnetometer, a flow-control-type liquid-nitrogen cryostat and a high-temperature oven. Mössbauer spectra were recorded in transmission geometry, in constant-acceleration mode using a $^{57}Co(Rh)$ source. Low-temperature spectra were recorded with a flow-control-type cryostat and the spectra above room temperature were recorded using a temperature-controlled oven.

3. Results and discussion

3.1. Magnetization measurements

Figure 1 shows the magnetization M as a function of applied field for the two samples at 90 K. The magnetization recorded as a function of temperature, in a low applied field of 100 Oe, is plotted in figure 2. The trend of saturation in M with the field and the hysteresis (figure 1) and the Brillouin-type temperature dependence of M (figure 2) suggest that the two samples are ferromagnetically ordered. The transition region is rather broad in FNP01. This may be because, at such a low level of substitution, there would be an inherent chemical inhomogeneity in the sense that, while some Fe atoms will have a neighbouring Ni, others will not. The Curie temperatures T_C can be taken as about $235(\pm 10)$ K and $295(\pm 5)$ K for FNP01 and FNP05, respectively.

Figure 3 shows a plot of the Curie temperature versus x. The values for Fe_2P and for $x = 0.10$ are taken from the work of Fujii *et al* (1978). It should be noted that T_C increases almost linearly up to $x \simeq 0.10$, where Fujii *et al* (1978) and also Fruchart *et al* (1969) observed it to begin to decrease. It is interesting to compare this with the substitution of Mn and Cr which destroy ferromagnetism when substituted in Fe_2P. On substitution of Mn, the ordering temperature T_o shows a considerable fall linearly with $x \simeq 0.03$, flattening thereafter and showing an upward trend only above $x \simeq 0.15$ (Srivastava *et al* 1987). For Cr substitution, T_o drastically decreases in a linear way up to $x \simeq 0.01$ and then only slowly up to $x \simeq 0.05$ (Dolia *et al* 1988, 1991); studies on the systematic variation in T_o have not been made for higher Cr content. Thus we find that the influence of small amounts of Ni in strengthening
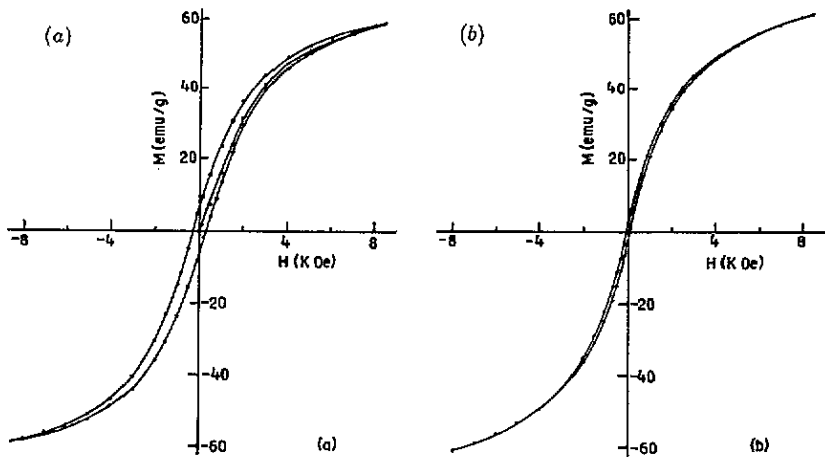
Figure 1. Magnetization as a function of applied field for (a) $(Fe_{0.99}Ni_{0.01})_2P$ and (b) $(Fe_{0.95}Ni_{0.05})_2P$ at 90 K.

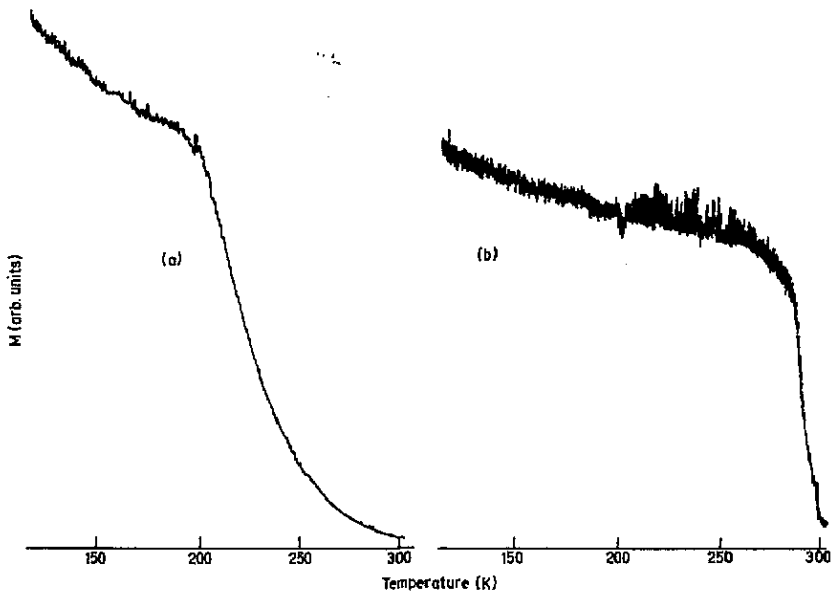**Figure 2.** Magnetization as a function of temperature for (a) $(Fe_{0.99}Ni_{0.01})_2P$ and (b) $(Fe_{0.95}Ni_{0.05})_2P$ in an external field of 100 Oe.

the ferromagnetic order is not as drastic as that of small amounts of Mn or Cr in destroying the ferromagnetic order.

The moment at 8 kOe and 90 K is 59 emu g^{-1} for FNP01 and 62 emu g^{-1} for FNP05 (figure 1) which compare well with that of pure Fe_2P (about 48 emu g^{-1}; figure 2 in the work of Fujii *et al* (1978)) at the same field and at a lower temperature of 4.2 K. Fe_2P has a saturation moment of 120 emu g^{-1} but its high uniaxial magnetic anisotropy ($K_1 = 2.4 \times 10^7$ erg cm^{-3} (Fujii *et al* 1982)) results in a low value of the moment for the powdered sample. Now, for the two alloys under study, if one
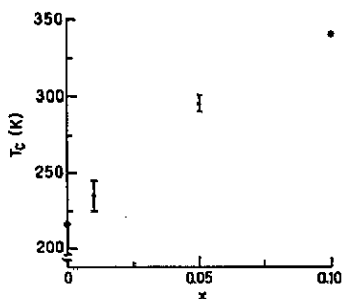
Figure 3. Plot of the Curie temperature T_C as a function of x for the system $(Fe_{1-x}Ni_x)_2P$. T_C for Fe_2P and for $x = 0.10$ are taken from the work of Fujii *et al* (1978).
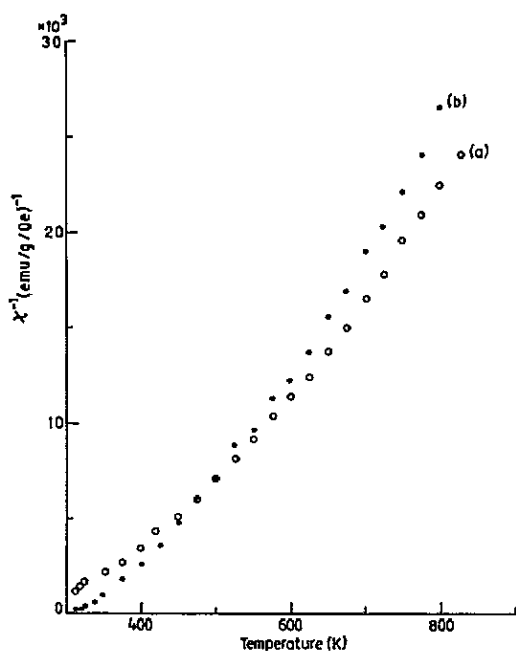
Figure 4. Inverse susceptibility as a function of temperature for $(Fe_{0.99}Ni_{0.01})_2P$ (O) and $(Fe_{0.95}Ni_{0.05})_2P$ (●) at $T \geqslant 300$ K.

could obtain an estimate of their saturation moments, the corresponding values in their polycrystalline state relative to that of Fe_2P could be interpreted in terms of an increase or decrease in anisotropy due to Ni substitution. In this context, it is found that the internal hyperfine fields at the two Fe sites (surrounded by all Fe in their second coordination spheres (SCSS)) of the two compounds, as measured by their Mössbauer spectra, are very similar to those for pure Fe_2P (see discussions below). This indicates that the saturation moments of these compounds should be nearly the same as that of Fe_2P. Thus our results on the magnetic moments of polycrystalline FNP01 and FNP05 would suggest that the magnetic anisotropy has decreased in these two compounds. Indeed the measurements of K_1 at 4.2 K for higher x (> 0.10) in single-crystal $(Fe_{1-x}Ni_x)_2P$ compounds by Fujii *et al* (1978) show a rapid decrease in K_1 with increasing x, becoming almost zero near $x = 0.3$.

The values of coercivity are about 300 Oe for FNP01 and about 50 Oe for FNP05 at 90 K. These also suggest that the magnetic anisotropy decreases with increasing Ni substitution. Values of remanence for the two respective samples are 6.3 emu g^{-1} and 1.5 emu g^{-1}.

Figure 4 shows a plot of inverse susceptibility χ^{-1} as a function of temperature in the paramagnetic region. Earlier studies on Fe_2P and Mn-substituted and Ni-substituted analogues (Nagase *et al* 1973, Fujii *et al* 1982, 1978) report a linear χ^{-1}–T relationship at higher temperatures, establishing the validity of the Curie–Weiss law. The paramagnetic Curie temperatures for substitutions up to 10 at.% are reported to be in the range 300–400 K. However, in the present study, the χ^{-1}–T plot up to 800 K does not show evolution of a strictly linear dependence. It is worth

mentioning that, in recent polarized neutron scattering work on the ferromagnetic compound Fe$_2$P, spin correlations have been found to persist up to 3.7 times the Curie temperature and $\chi^{-1}-T$ has been noticed to be non-linear (Wilkinson *et al* 1989). The present work shows that the introduction of Ni does not change this character.
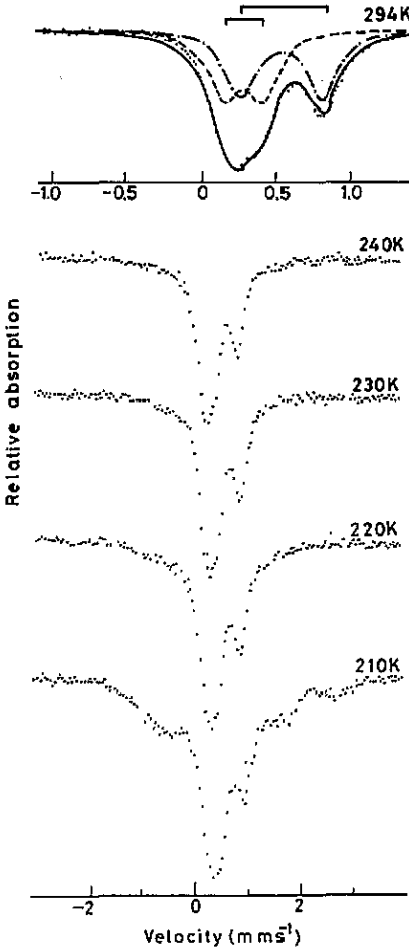

Figure 5. ^{57}Fe Mössbauer spectra of (Fe$_{0.99}$Ni$_{0.01}$)$_2$P at different temperatures. For the 294 K spectrum, the analysed components and the total fitted envelope are also shown.

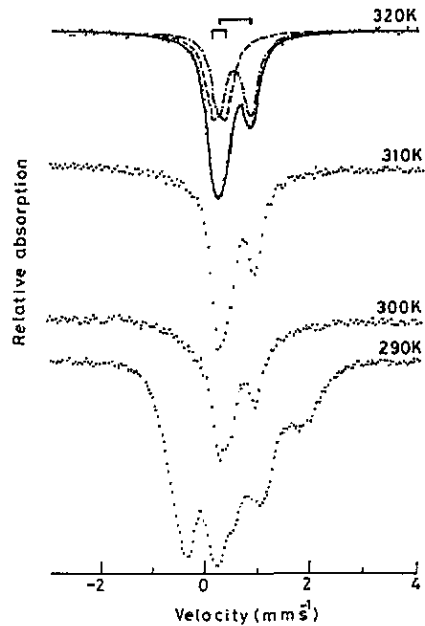**Figure 6.** ^{57}Fe Mössbauer spectra of (Fe$_{0.95}$Ni$_{0.05}$)$_2$P at different temperatures. For the 320 K spectrum the analysed components and the total fitted envelope are also shown.

3.2. Mössbauer measurements

Figures 5 and 6 show the ^{57}Fe Mössbauer spectra for the two samples at different temperatures along the magnetic transition. One finds transition temperatures of about 230 K for FNP01 and about 310 K for FNP05, in reasonable agreement with the values obtained in the DC magnetization measurements. We have analysed one spectrum for each of the two samples in their paramagnetic states, i.e. at 294 K for FNP01 and at 320 K for FNP05. The spectra were resolved into two doublets each:

one corresponding to iron at the tetrahedral site Fe(1) and the other corresponding to iron at the pyramidal site Fe(2). The resolved patterns are also shown in figures 5 and 6. The central shifts (CSS) and quadrupole splittings (QSS) within uncertainty limits are the same as those for Fe_2P (Ericsson *et al* 1980). The CS values (with respect to iron metal at 300 K) for the two respective sites Fe(1) and Fe(2) are 0.30 mm s^{-1} and 0.56 mm s^{-1} for FNP01 and 0.25 mm s^{-1} and 0.54 mm s^{-1} for FNP05 as against 0.28 mm s^{-1} and 0.58 mm s^{-1} for Fe_2P. The QS values are 0.28 mm s^{-1} and 0.58 mm s^{-1} for FNP01, 0.27 mm s^{-1} and 0.60 mm s^{-1} for FNP05, and 0.25 mm s^{-1} and 0.59 mm s^{-1} for Fe_2P. The uncertainties involved in the intensity parameters do not allow any inference about the site occupancy in the case of FNP01. However, in the case of FNP05 the data suggest that Ni has a preference for M(1), the intensities being 46% and 54% for Fe(1) and Fe(2) sites, respectively (complete preference of Ni for M(1) should give the intensities as 47.4% and 52.6%, respectively; total preference for M(2) would give the intensities the other way round).
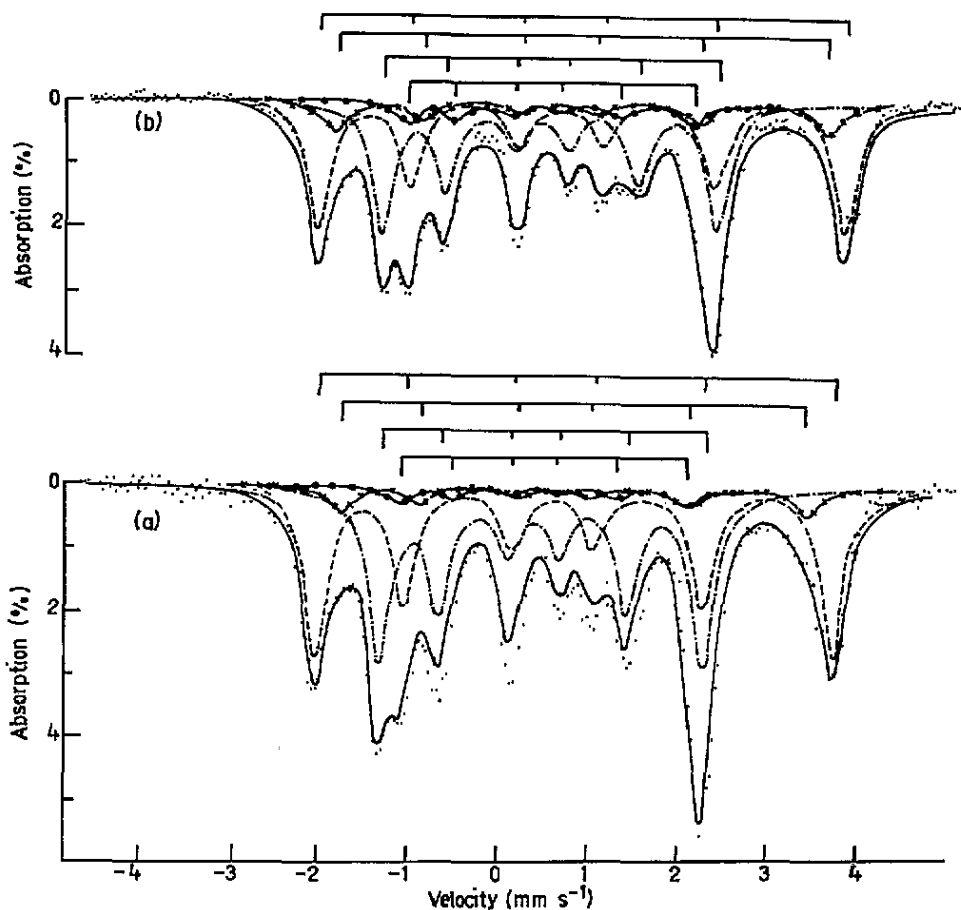

Figure 7. ^{57}Fe Mössbauer spectra of (a) $(Fe_{0.99}Ni_{0.01})_2P$ and (b) $(Fe_{0.95}Ni_{0.05})_2P$ at 7 K. The analysed components and the total fitted envelope are also shown.

Table 1. Mössbauer parameters for $(Fe_{1-x}Ni_x)_2P$ ($x = 0.01$ and 0.05) at 7 K: cs, central shift with reference to metallic Fe; qs, quadrupole splitting; B_{hf}, hyperfine field; I, intensity; lw, full width at half-maximum. The accuracies in cs and lw are within ± 0.01 mm s^{-1}, qs within ± 0.02 mm s^{-1}, B_{hf} within ± 0.1 T and I within 2%. The parameters for Fe$_2$P at 15 K (Wäppling *et al* 1975) are also given for comparison.

	Fe(1)[a]				Fe(2)[a]				
x	cs (mm s^{-1})	qs (mm s^{-1})	B_{hf} (T)	I (%)	cs (mm s^{-1})	qs (mm s^{-1})	B_{hf} (T)	I (%)	lw (mm s^{-1})
0	0.41	0.10	11.4	49	0.68	0.19	18.0	51	0.33
0.01[b]	0.39	0.09	11.2	45	0.69	0.25	17.9	44	0.32
	0.38	0.10	9.9	4	0.67	0.20	15.9	7	
0.05[c]	0.39	0.09	11.5	41	0.68	0.23	18.2	40	0.30
	0.37	0.16	9.9	8	0.67	0.26	16.9	11	

[a] Two patterns each for the two sites are assigned to Fe atoms having their scs consisting of all Fe and all Fe but one Ni except for the Fe(2) site of the $x = 0.05$ sample (for details see text).
[b] Predicted intensities for the two components, assuming complete preference of Ni for M(1), are 47.5% and 2% for Fe(1) and 45% and 5.5% for Fe(2), respectively. Assuming complete preference for M(2) sites, the predictions would be 45% and 5.5% for the Fe(1) site and 45.8% and 3.7% for the Fe(2) site.
[c] The predicted intensities for the Fe(1) site are 39% and 8.5% assuming a preference for M(1) and 35% and 15% assuming an equal preference for the two sites. For predictions on the Fe(2) site, see text.

Figure 7 shows the Mössbauer spectra of the two samples at 7 K. Attempts to analyse the spectra into two six-line patterns, corresponding to the two crystalline sites, did not succeed. Eventually four patterns were fitted, as in the cases of Cr- and Mn-substituted systems (Srivastava *et al* 1987, Dolia *et al* 1988, 1991). In this analysis two patterns are assigned to each of the two crystalline sites. The resulting linewidths, which were constrained to be equal for all the patterns, are quite reasonable. The resolved components are also shown in figure 7. It is seen that in the central part of the spectrum the fitting is not as good as in the outer parts, suggesting that the internal magnetic fields may have some distribution. The analysed parameters are tabulated in table 1 together with those for pure Fe$_2$P at 15 K, from the work of Wäppling *et al* (1975), for the purpose of comparison. The two patterns assigned to a given site, say Fe(1), would correspond to the scs of Fe consisting of only Fe atoms and all Fe but one Ni atom, respectively, except for those corresponding to the Fe(2) site in FNP05 (see the following discussion). The experimental values of intensities seem to match well those calculated† assuming a complete preference of Ni for the M(1) site. However, uncertainties in the intensities of the weaker Mössbauer components, in particular due to poor fitting in the central part of the spectrum, do not permit an inference about the site occupancy in FNP01 (see footnote to table 1). In the case of FNP05 an inference can be made and the intensity data for site Fe(1) suggest a strong preference of Ni for the M(1) site (see footnote to table 1). This is in good agreement with our results on the 320 K spectrum of the same sample and also the findings of Maeda and Takashima (1973) based on their analysis of Mössbauer spectra of samples with 25 at.% Ni or more substituted, which

† Using the binomial distribution and considering the scs of Fe(1) to have two M(1) and six M(2) and that of Fe(2) to have six M(1) and four M(2) atoms (atoms with interatomic separation of 3.46 Å do not seem to contribute; otherwise for example there are four M(1) instead of two M(1) in the scs of Fe(1) (Wäppling *et al* 1975)).

are in their paramagnetic states. As regards the Fe(2) site components of FNP05, the binomial calculation predicts about 28%, 19% and 5% intensities for the components corresponding to the SCS formed of only Fe, all Fe but one Ni atom, and all Fe but two Ni atoms respectively. Experimentally, however, it is not possible to resolve into more components and the results for this site may be treated as representing some average values.

Comparing the internal hyperfine fields B_{hf}, one notices that in going from Fe_2P to FNP01 to FNP05 the values for the sites with the SCS formed of only Fe atoms show little change. However, when Ni enters the SCS, the internal fields decrease. This reduction is very similar for the two crystalline sites. It is worthwhile mentioning that Mn as well as Cr which, unlike Ni, destroy ferromagnetism, also lower B_{hf} and do so much more severely (Srivastava et al 1987, Dolia et al 1988). B_{hf} is lowered by as much as 70% when one Cr atom enters the SCS of Fe(1) and even for the sites having no Cr atom in the SCS it is lowered by up to 15%.

Acknowledgments

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