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1997 J. Phys.: Condens. Matter 9 2781

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Local magnetic moments in the $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ ($0 \leq x \leq 0.6$) compounds

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Received 23 July 1996, in final form 1 November 1996

Abstract. Mössbauer and magnetic measurements have been performed on the single-phase γ' - Fe_4N and $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ compounds. The local magnetic moments of iron and nickel atoms are evaluated by combining hyperfine fields and saturation magnetizations of $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ compounds. The results confirm that the average magnetic moment per iron atom slightly decreases with increasing nickel content in $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ compounds. The average magnetic moment per nickel atom is approximately 0.3 and 0.9 μ_B for face centre sites and cubic corner sites, respectively.

1. Introduction

The iron–nitrogen system has many interesting magnetic and metallurgical properties. It is well known that γ' - Fe_4N has a saturation magnetization of 208 emu g^{-1} at 0 K, which is very close to the value for α -Fe. The simple structure of Fe_4N offers an ideal case for the study of magnetic properties. The crystal structure of Fe_4N can be visualized as a face centre cubic iron γ -Fe lattice with nitrogen at the body centre position [1]. The corner iron, Fe^c , is surrounded by 12 nearest iron neighbours, while the face centre iron, Fe^f , has two nitrogens as the nearest neighbours. The large magnetic moment of Fe_4N is attributed to the net contribution from Fe^c with electronic configurations $3d^74s^1$ ($\approx 3.0 \mu_B$), and three Fe^f with electronic configurations $3d^84s^1$ ($\approx 2.0 \mu_B$) [2].

In addition, Fe_4N is known to be corrosion and wear resistant [3], and the addition of nickel has been found to noticeably improve the mechanical ductility of the normally brittle Fe_4N compounds [4], which has technological potential. However, some effects of nickel in $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ compounds are still not clearly understood. More interesting is the local magnetic moments of iron and nickel in $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$. As predicted in [5], the average magnetic moments per nickel should be 1.0 and 0.0 μ_B for the corner nickel and face centre nickel, respectively, but this is not verified by experiments so far.

For the reasons given above, we prepared iron–nickel nitrides of different nickel contents, and investigated $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ compounds using Mössbauer spectra and magnetic measurements. The local magnetic moments of nickel and iron were calculated and some effects of nickel in $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ were also studied.

2. Preparation and measurements

The substitution of nickel for iron in Fe_4N can be achieved by starting with a substituted precursor. The procedure began with coprecipitation of a mixed oxalate of iron and nickel

$\text{Fe}_{1-x}\text{Ni}_x \cdot \text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ($0 \leq x \leq 0.6$) through reaction between appropriate amounts of aqueous solutions of oxalic acid and sulphates of iron and nickel. The precipitate was then filtered, washed and dried. The x-ray diffraction patterns of oxalates indicated a single phase of isostructure. Next the dry powder was put into a quartz tube furnace in a gaseous flow of a mixture of ammonia and hydrogen to be nitrogenated with an optimized flow ratio $\text{H}_2/\text{NH}_3 = 1:3$ and temperature $T = 500\text{--}600^\circ\text{C}$. Thus iron–nickel nitrides were obtained. The XRD patterns for different compositions of $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ compounds showed that all compounds are of γ' - Fe_4N type single phase [6]. Mössbauer spectra were recorded using a FH1913 conventional constant-acceleration spectrometer at room temperature (RT) and 77 K. A 10 mCi $^{57}\text{Co}(\text{Rh})$ source was used. The spectrometer was calibrated at room temperature with respect to the standard α -Fe. Magnetic measurements were carried using a vibrating sample magnetometer at 77 K and RT.

3. Results and discussion

3.1. Mössbauer spectra

The Mössbauer spectra of $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ at $T = 77$ K are shown in figure 1. Since the unit cell of γ' - Fe_4N has two non-equivalent sites, i.e. the cubic corner site and face centre site with a ratio of 1:3, the Mössbauer spectra were unfolded into two components corresponding to two iron sites [7]. Because the easy magnetization direction of γ' - Fe_4N is parallel to [100], the iron atoms at face centre sites were split into two groups with a ratio of 2:1. The Mössbauer spectra of γ' - Fe_4N were fitted to three sextets with relative line intensity $\text{Fe}^c:\text{Fe}_{II}^f:\text{Fe}_I^f = 1:2:1$ [8]. The component with largest hyperfine field and zero quadrupole splitting was assigned to the Fe atoms at corner sites, and other components were assigned to Fe_I^f and Fe_{II}^f .

Due to the substitution of iron by nickel in Fe_4N , the neighbour configurations of iron atoms are changed, so a good fit with only three subspectra cannot be obtained. A best fit of the spectra of $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ was achieved using five subspectra, corresponding to four groups of six lines for face centre iron and one group of six lines for corner iron. The widths of Lorentz lines were all in the range $0.25\text{--}0.36 \text{ mm s}^{-1}$, and the intensity ratios within each subspectrum (I_2/I_1 and I_3/I_1) were kept the same in all fitted subspectra.

One can see from figure 1 that the outer spectrum is assigned to Fe^c and the other groups of six-lines are assigned to Fe_I^f and Fe_{II}^f . The intensities of outer peaks decrease with increasing nickel content until nearly disappearing at $x = 0.5$, when corner iron atoms are completely replaced by nickel atoms.

The hyperfine fields for different samples of $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ compounds are listed in table 1. The average hyperfine fields \overline{B}_{hf} for iron decrease monotonically with nickel substitution. This is similar to \overline{B}_{hf} of the high-nickel-concentration Fe–Ni bulk alloys, which is always the case in the nickel-substituted alloys. It is interesting that \overline{B}_{hf} for Fe^c increases from $x = 0.0$ to $x = 0.6$ in $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ at 77 K.

The iron magnetic moments μ_{Fe} can be estimated from hyperfine fields by applying a conversion factor A which is the same for all sites [9],

$$\overline{B}_{hf} = A\overline{\mu}_{Fe} \quad (1)$$

where \overline{B}_{hf} is the average hyperfine fields of iron.

In order to calculate iron magnetic moments in $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ ($x \neq 0$), the correct conversion factor is to be decided. According to experimental results, the average magnetic moment per iron atom in Fe_4N is $2.21 \mu_B$ at 0 K and the average hyperfine field is -26.93 T

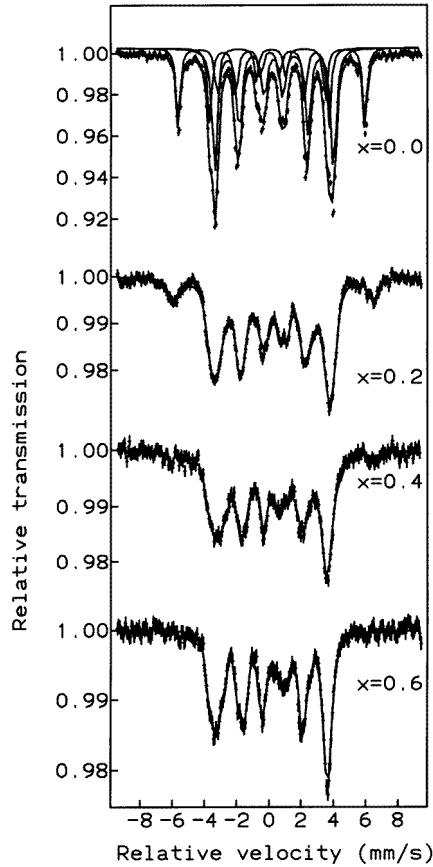


Figure 1. The Mössbauer spectra of $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ compounds at $T = 77$ K.

at 4.2 K [10]. So the conversion factor A is $-12.2 \text{ T } \mu_B^{-1}$. We suppose A is the same for different $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ compounds ($x \neq 0$). Using this conversion constant, the magnetic moments of iron atoms are calculated, and are listed in table 1. The results indicate that the average magnetic moment per iron atom decreases slightly with increasing nickel content.

3.2. Magnetic measurements

In table 2, the magnetic measurement results for $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ compounds at RT and 77 K are given. The magnetizations of $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ compounds decrease as x increases. The average magnetic moment per unit cell decreases with increasing x . The decrease of magnetization of iron–nickel nitrides can be explained with a band structure model of the first long-period fcc transition elements [5]. For alloys with more than one magnetic atom, magnetization measurements cannot provide any information on μ_i of constituent atoms directly. For the ternary ferromagnetic $(\text{A}_x\text{B}_{1-x})_y\text{C}_{1-y}$ with two magnetic transition metal atoms A and B and one non-magnetic atom C, $\bar{\mu}$ can be, in principle, expressed as [11]

$$\bar{\mu} = x\mu_A + (1 - x)\mu_B. \quad (2)$$

Table 1. Mössbauer parameters of ^{57}Fe nuclei for $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$.

x	$B_{hf}^{Fe^c}$	$\overline{B_{hf}^{Fe}}$	$A = -12.2 \text{ T } \mu_B^{-1}$	
			$\overline{\mu_{Fe}} (\mu_B)$	
293 K	0.0	34.1 (± 0.2)	24.8 (± 0.2)	2.03 (± 0.02)
	0.1	34.8 (± 0.2)	23.8 (± 0.2)	1.95 (± 0.02)
	0.2	35.6 (± 0.2)	21.8 (± 0.2)	1.79 (± 0.02)
	0.3	36.3 (± 0.2)	21.0 (± 0.2)	1.72 (± 0.02)
	0.4	35.9 (± 0.2)	20.0 (± 0.2)	1.64 (± 0.02)
	0.5	—	18.7 (± 0.2)	1.54 (± 0.02)
	0.6	—	16.9 (± 0.2)	1.39 (± 0.02)
77 K	0.0	36.2 (± 0.2)	26.4 (± 0.2)	2.16 (± 0.02)
	0.1	36.8 (± 0.2)	26.0 (± 0.2)	2.13 (± 0.02)
	0.2	38.8 (± 0.2)	24.9 (± 0.2)	2.05 (± 0.02)
	0.3	39.3 (± 0.2)	23.5 (± 0.2)	1.93 (± 0.02)
	0.4	39.7 (± 0.2)	22.4 (± 0.2)	1.84 (± 0.02)
	0.5	—	21.7 (± 0.2)	1.79 (± 0.02)
	0.6	—	21.7 (± 0.2)	1.79 (± 0.02)

Table 2. The saturation magnetizations (σ_s (emu g^{-1})) and magnetic moment per unit cell (M_s) of $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$.

x	77 K		293 K	
	σ_s (emu g^{-1})	M_s ($\mu_B \text{ FU}^{-1}$)	σ_s (emu g^{-1})	M_s ($\mu_B \text{ FU}^{-1}$)
0.0	197.8 (± 0.5)	8.41 (± 0.02)	179.9 (± 0.5)	7.65 (± 0.2)
0.1	182.3 (± 0.5)	7.79 (± 0.02)	165.1 (± 0.5)	6.60 (± 0.2)
0.2	166.3 (± 0.5)	7.16 (± 0.02)	144.9 (± 0.5)	6.24 (± 0.2)
0.3	146.4 (± 0.5)	6.32 (± 0.02)	129.2 (± 0.5)	5.56 (± 0.2)
0.4	130.6 (± 0.5)	5.66 (± 0.02)	115.2 (± 0.5)	5.44 (± 0.2)
0.5	109.7 (± 0.5)	4.78 (± 0.02)	91.8 (± 0.5)	4.00 (± 0.2)
0.6	96.7 (± 0.5)	4.23 (± 0.02)	87.3 (± 0.5)	3.80 (± 0.2)

Thus for $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ compounds, we have

$$\overline{\mu} = x\overline{\mu_{Ni}} + (1-x)\overline{\mu_{Fe}}. \quad (3)$$

Bringing values for $\overline{\mu_{Fe}}$ and $\overline{\mu}$ into (3), the values $\overline{\mu_{Ni}}$ can be calculated for the different x , and are listed in table 3. The average magnetic moment per nickel atom is approximately $0.7 \mu_B$ at 77 K, and $0.6 \mu_B$ at RT, which is close to the value for pure nickel. Supposing that magnetic moments of nickel atoms at different sites do not vary with nickel content, we have

$$\overline{\mu_{Ni}} = P(x)\mu_{Ni}^c + (1-P(x))\mu_{Ni}^f \quad (4)$$

where $P(x)$ is the occupation factor of the nickel atoms at cubic corner sites with different x , which has been evaluated in a previous paper [6]. μ_{Ni}^c and μ_{Ni}^f represent the magnetic moments of nickel atoms at face centre sites and cubic corner sites, respectively.

By applying the least-squares method to equation (4), the values of μ_{Ni}^c and μ_{Ni}^f could be obtained. The results are about $0.3 \mu_B$ and $0.9 \mu_B$ for the face centre nickel atoms and cubic corner nickel atoms, respectively. They are in good agreement with the prediction in [5], while a small magnetic moment is found for the face centre nickel atoms.

Table 3. The average magnetic moment per nickel atom in $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$.

	$x = 0.2$	$x = 0.3$	$x = 0.4$	$x = 0.5$	$x = 0.6$
293 K	0.62 (± 0.06)	0.62 (± 0.06)	0.68 (± 0.06)	0.46 (± 0.06)	0.67 (± 0.06)
77 K	0.75 (± 0.06)	0.76 (± 0.06)	0.78 (± 0.06)	0.60 (± 0.06)	0.60 (± 0.06)

4. Conclusions

By combining Mössbauer spectra and magnetic measurements, the magnetic moments of iron and nickel were calculated. The conversion factor for iron magnetic moments to the hyperfine field is $-12.2 \text{ T } \mu_B^{-1}$, and the average magnetic moment per iron atom decreases with increasing x for $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ compounds. The average magnetic moment per nickel atom is close to 0.3 and $0.9 \mu_B$ for the face centre nickel atom and cubic corner nickel atom, respectively.

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