Structural and magnetic investigations of Sc(Fe$_{1-x}$Ni$_x$)$_2$ compounds by means of Mössbauer effect and neutron diffraction

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Abstract. The structural and microscopic magnetic properties of the pseudobinary Sc(Fe$_{1-x}$Ni$_x$)$_2$ system were studied by XRD and Mössbauer measurements in the range of $0.10 \leq x \leq 0.60$. All investigated samples have the cubic C15-type structure. Both the magnetic hyperfine field on ^{57}Fe and the Curie temperature decrease with increasing Ni content and the system becomes paramagnetic for $x \approx 0.60$ at room temperature. The form and temperature dependences of the Mössbauer spectra for $0.40 \leq x \leq 0.50$ indicate the coexistence of paramagnetic and ferromagnetic regions in the samples and occurrence of magnetic clusters with a wide distribution of the Curie temperatures. As follows from the near to zero values of quadrupole shifts in Mössbauer spectra it results that a <100> direction is a local easy magnetization axis for $x \geq 0.10$.

Key words: hyperfine interactions • Mössbauer effect • quasibinary Laves phase • Sc(Fe$_{1-x}$Ni$_x$)$_2$

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Introduction

The intermetallic pseudobinary compounds Sc(Fe$_{1-x}$Ni$_x$)$_2$ exhibit the C15 cubic Laves phase structure over the whole concentration range except for $x = 0$. Pure ScFe$_2$ shows either the hexagonal C14 or the dihexagonal C36 structure when it crystallizes at high temperatures (1473 < T < 1838 K) [3]. From our earlier investigations, it is known that ScFe$_2$ with the C36 structure (hP24, space group $P6_3/mmc$) is ferromagnet with $T_C = 642$ K. In this structure, Fe atoms occupy three non-equivalent positions: 6g, 6h and 4f (Wyckoff notation) and have magnetic moments equal to 1.31(1), 1.78(1) and 1.52(1) μ_B at RT, respectively. The mean value of hyperfine magnetic field in this compound amounts to 18.2(2) T. The theoretical calculations of band structure for ScFe$_2$ with the C15 cubic structure give the magnetic moment of Fe atom of 1.56 μ_B and predict occurrence of antiparallel induced magnetic moments of about 0.52 μ_B at Sc atoms [1]. NMR ^{45}Sc measurements in the polymorphic C15 form of ScFe$_2$ confirm these predictions giving the significantly larger value of $\mu_{Sc} = 1.05(5)\mu_B$ [6]. In the regular cubic C15 phase (cF24, space group $Fd3m$) Fe/Ni atoms occupy only one type of sites: 16d with the point symmetry $\bar{3}m$ and create regular tetrahedrons (16d positions) connected via their corners. Six Fe and six Sc (8a positions) atoms surround each Fe atom composing its nearest neighbourhood. ScNi$_2$ compound is the Pauli paramagnet [2]. The investigated compounds belong to the class of materials called itinerant magnets. One of the most important characteristics of these materials is that amplitude of the local spin fluctuation

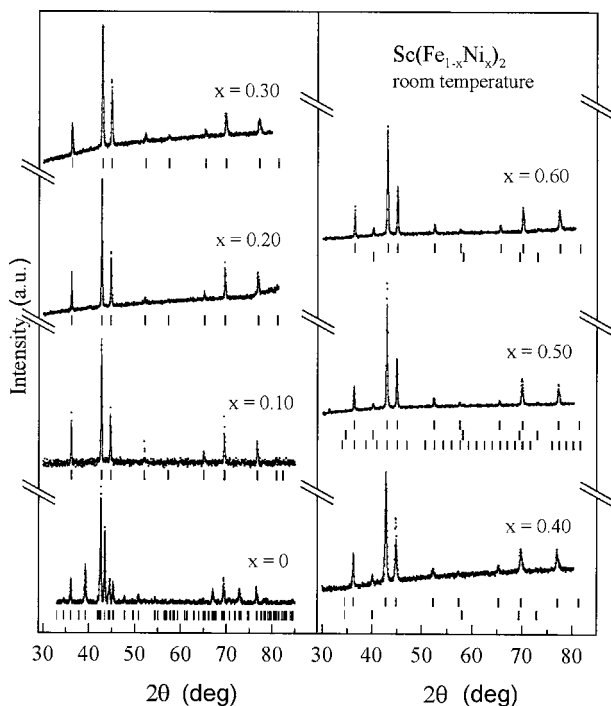**Fig. 1.** XRD patterns of $Sc(Fe_{1-x}Ni_x)_2$ for $x = 0, 0.1, 0.2, 0.3,$ 0.4, 0.5 and 0.6.

varies significantly with temperature, as pointed out by Moriya [4].

The aim of our study was to examine the influence of Ni substitution for Fe on structural properties and magnetic properties of $Sc(Fe_{1-x}Ni_x)_2$ compounds. In particular, dependence of hyperfine interaction parameters on concentration x, behaviour of T_C in these compounds and critical concentration for the existence of long range magnetic order were the object of our interest.

Experimental details

Intermetallic compounds of $Sc(Fe_{1-x}Ni_x)_2$ for $x \leq 0.60$ in the polycrystalline form were prepared by arc melting appropriate stoichiometric amounts of scandium, iron and nickel of high purity under an inert argon atmosphere. The ingots were annealed in vacuum at about 1000 K for one week to ensure their homogeneity. Phase analysis was carried out by means of X-ray powder diffraction with Cu K_α radiation. The scans were obtained in the range of 24° to 90° (2θ). The Mössbauer spectra of powder samples were recorded using a constant acceleration spectrometer in the 77 to 800 K temperature range with a [57]Co(Rh) source. The Mössbauer spectra were analysed by solving the complete Hamiltonian under the assumption that the energy of the quadrupole interaction is small compared to the hyperfine magnetic splitting. The fast-relaxation limit within the thin absorber approximation was accepted. The isomer shift values are given in relation to α-Fe at room temperature.

For the samples $Sc(Fe_{1-x}Ni_x)_2$ with $x = 0.10$ and 0.20, the neutron powder diffraction measurements were carried out in the temperature range from 10 to 700 K. The DN2 time-of-flight diffractometer at the fast pulsed
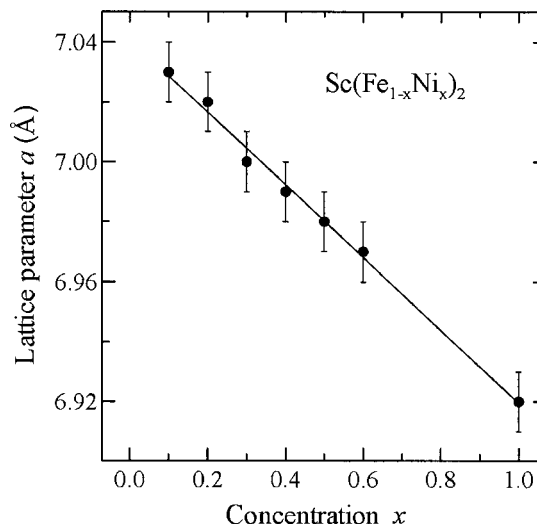

Fig. 2. The lattice constant values vs. the Ni concentration x in the $Sc(Fe_{1-x}Ni_x)_2$ phases from the XRD measurements.

reactor IBR2 at the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research was used. The diffraction patterns were refined by the FULLPROF program for Rietveld refinement. In the final run, the following parameters were refined from the ND data: scale factor, unit cell parameters, positional coordinates of atoms, thermal factors as well as magnitude and orientation of the Fe ordered magnetic moments. The coherent scattering lengths for Sc, Fe and Ni were taken as equal to 12.1, 9.45 and 10.3 fm, respectively.

Results and discussion

The crystallographic structure of the investigated $Sc(Fe_{1-x}Ni_x)_2$ samples was checked by means of X-ray diffraction measurements. The obtained diffraction patterns are shown in Fig. 1. Only small of the order of 2–3% admixtures of Sc_2O_3 and non-stoichiometric $Sc_{0.92}O$ oxides were identified for $x \geq 0.4$.

In Fig. 2 the lattice parameter a dependence on Ni concentration is presented.

The replacement of slightly bigger Fe atoms by Sc atoms in the C15 phase leads to the linear decrease of lattice constant a according to the Vegard's law.

Figure 3 shows the Mössbauer spectra of $Sc(Fe_{1-x}Ni_x)_2$ in the $0.10 \leq x \leq 0.60$ range measured at room temperature.

In order to obtain satisfactory fit to the experimental patterns it was assumed in the first approximation that the Ni substitution for Fe is of statistical character. Thus, the number and relative intensity of magnetic components in a spectrum related to a given local environment of [57]Fe nuclear probe may be estimated on the basis of binominal distribution. The right panel of Fig. 3 shows the contributions larger than 5%. Only the nearest neighbours (NN) were taken into account because merely replacement of the Fe atom in NN has a strong influence and may be registered with a high reliability. Moreover, all observed magnetic sextets are symmetric. On the other hand, from the known symmetry of local surroundings of Fe atoms and from the presence
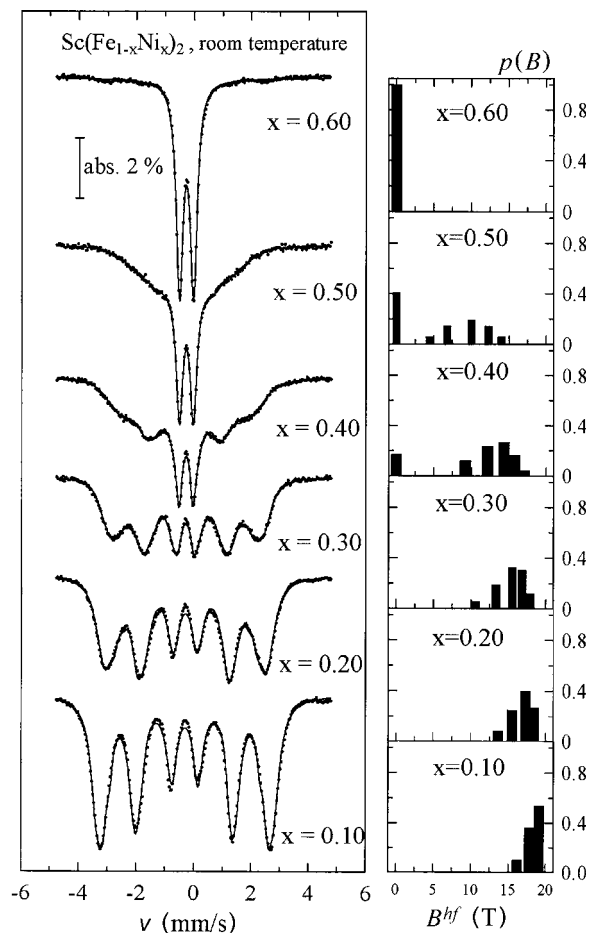
Fig. 3. ^{57}Fe Mössbauer spectra of Sc(Fe$_{1-x}$Ni$_x$)$_2$ for $0.10 \leq x \leq 0.20$ at room temperature (left) and the hyperfine field discrete distribution accepted from a binomial distribution (right).

Fig. 4. The concentration dependences of the ^{57}Fe hyperfine magnetic fields for individual types of local surroundings at room temperature.

magnetic field caused by replacement of 1 Fe atom by Ni atom is 1.5 T on average, and becomes larger for surroundings with more than 4 Ni atoms. The Mössbauer measurements in the wide range of temperature have been also performed. For the illustration of these studies, the spectra for Sc(Fe$_{0.80}$Ni$_{0.20}$)$_2$ recorded at different temperatures are shown in Fig. 5.

of the paramagnetic doublet it is obvious that the quadrupole splitting QS cannot be equal to zero. Its values determined from the paramagnetic component of spectra are the same for all concentrations and equal to 0.49(1) mm/s. In performed fitting procedure quadrupole shifts for all sextets were not been fixed. But obtained values were less than 0.02 mm/s and had both positive and negative signs. This result strongly suggests that for all ^{57}Fe probes located at $16d$ sites the angle θ between HMF and the local principal axis of the EFG tensor is approximately equal to 54.7° and the mean quadrupole shift value defined as $\varepsilon_Q = QS(3\cos^2\theta - 1)/2$ vanishes. The easy axis of magnetization which gives such angles is only the $<100>$ direction. Based on these experimentally established facts, the conclusion that the replacement Ni atoms for Fe atoms in NN of ^{57}Fe probe does not change the direction of local principal axis of the EFG tensor by more than a few degrees can be drawn. This is possible probably due to similarity of the charge states of Ni and Fe atoms in investigated compounds.

The results obtained for the hyperfine magnetic fields for local surroundings with a different number of Ni atoms are collected in Fig. 4. From these dependences, the critical concentration at RT for the existence of long-range magnetic order may be estimated as $x_c \approx 0.60$. The decrease of the hyperfine
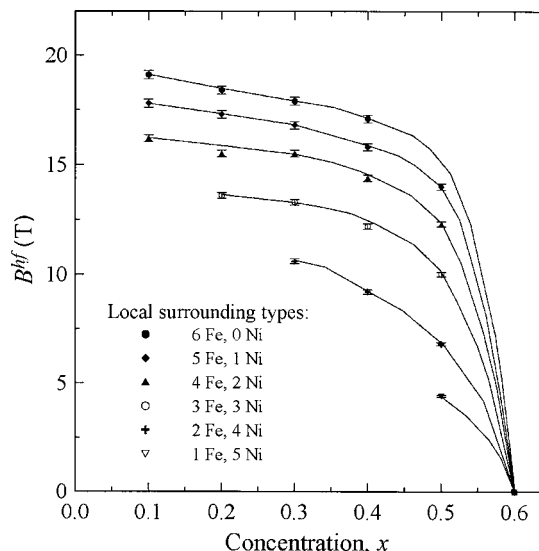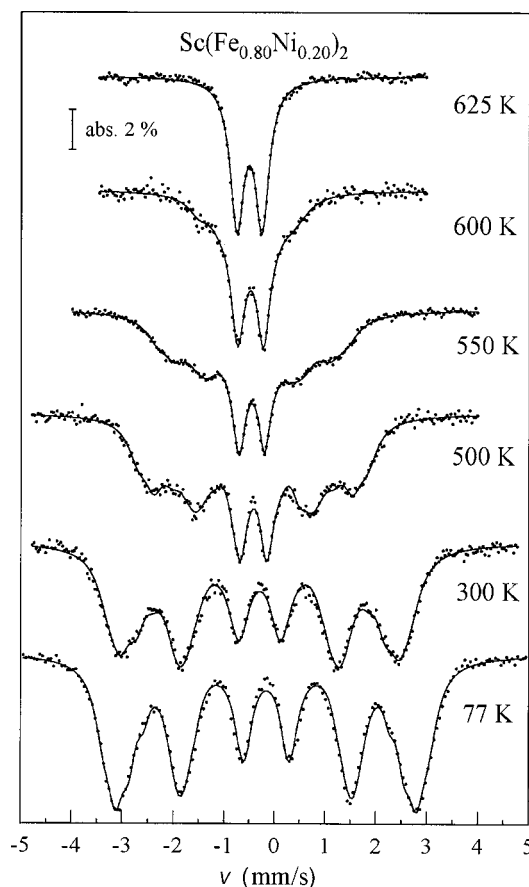

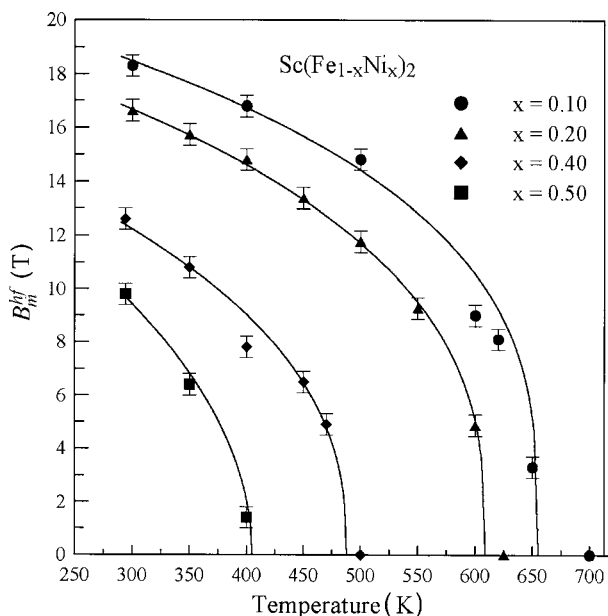**Fig. 5.** ^{57}Fe Mössbauer spectra of Sc(Fe$_{0.80}$Ni$_{0.20}$)$_2$ at various temperatures.

Fig. 6. Temperature dependence of the magnetic hyperfine fields derived from the computer fits to the ^{57}Fe Mössbauer spectra obtained for $Sc(Fe_{1-x}Ni_x)_2$. The continuous line represents the least-squares fit of the Brillouin function.

The spectra in Figs. 3 and 5 exhibit a property characteristic of $Sc(Fe_{1-x}Ni_x)_2$. At fixed temperature for the samples with $0.40 \leq x \leq 0.60$, the paramagnetic doublet appears with the intensity increasing with increase of concentration. In this range paramagnetic parts coexist with a ferromagnetic matrix. Similarly, such components appear when the sample is heated and the coexistence takes place considerably below the Curie temperature of ferromagnetic matrix. Since there is no indication of the segregation of a different phase from the crystallographic point of view, the paramagnetic parts should be ascribed to local concentration fluctuations which result in a wide distribution of the Curie temperatures. Formation of magnetic clusters and micromagnetic behaviour at low temperatures were observed earlier in analogical pseudobinary phases many a time [5, 7].

The thermal evolution of the mean ^{57}Fe magnetic hyperfine field B_m^{hf} derived from the numerical analysis is shown in Fig. 6 together with the Brillouin curve fitted to the experimental points.

Extrapolation of this curve to the zero field value allows determining of Curie temperatures. The T_C dependence on concentration is given in Fig. 7. The determined T_C is related to ferromagnetic matrix. Critical temperatures for magnetic clusters are lower and may lie in a very wide range of temperatures. For the samples with $x = 0.10$ and $x = 0.20$, Curie temperatures were determined also from the temperature dependences of magnetic moments of Fe atoms obtained in the ND measurements. They are equal to 657(5) K and 610(5) K, respectively, and remain in a good accordance with respective values from the Mössbauer measurements.

In Table 1, the results for magnetic moments of Fe atoms and hyperfine magnetic fields measurements at room temperature are collected. Due to the fact that
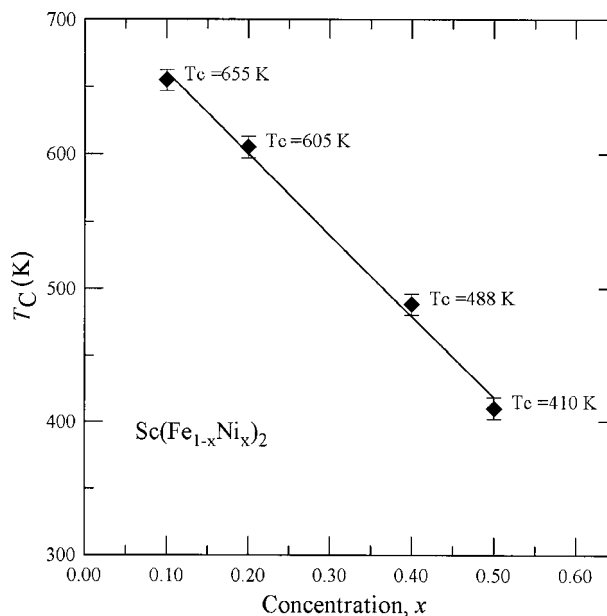

Fig. 7. The variation of the Curie temperature T_C values with Ni concentration determined by extrapolation of the Brillouin curve to the zero fields.

Fe magnetic moments and hyperfine magnetic fields for $Sc(Fe_{0.90}Ni_{0.10})_2$ and $Sc(Fe_{0.80}Ni_{0.20})_2$ were determined by two independent methods MS and ND, it was possible to estimate a hyperfine coupling constant A.

The obtained value of 12 T/μ_B is independent of temperature and concentration.

Summary

The concentration dependence of the hyperfine magnetic fields in $Sc(Fe_{1-x}Ni_x)_2$ and the decrease of Fe magnetic moments may be qualitatively explained by the increase of 3d band occupation. Each atom of nickel introduces approximately 2.2 of 3d electrons more than iron atom.

The transition from the ferromagnetic state to the paramagnetic one in $Sc(Fe_{1-x}Ni_x)_2$ compounds takes place over a large temperature range due to the occurrence of clusters coming from the short range magnetic order. With increasing temperature more and more magnetic Fe atoms form clusters with only a short range magnetic order. The magnetic interaction between them becomes weak. At some critical concentration ($x \approx 0.60$), the volume of such clusters becomes so large that the long range magnetic order in the sample disappears at room temperature. There exist a few

Table 1. ^{57}Fe hyperfine magnetic fields, Fe magnetic moments and a hyperfine coupling constant A for $Sc(Fe_{1-x}Ni_x)_2$ with $x = 0.10$ and $x = 0.20$

x	T (K)	B^{hf} (T)	$\mu_{Fe}(16d)$ (μ_B)	A (T/μ_B)
0.10	77	19.1(2)	1.53(13)	12(1)
	300	18.3(2)	1.47(13)	12(1)
0.20	77	18.2(2)	1.51(19)	12(2)
	300	16.7(2)	1.44(13)	12(1)

factors promoting the cluster formation and the magnetic order instability in the investigated samples. The first is topology of the triangular Kagomé lattice on which the iron atoms are located and which favours topologic frustration. The second is the form of the function of local density of states near the Fermi level [2]. Even not large changes of the $3d$ electrons number in a common Fe and Ni $3d$ band may drastically violate stability of magnetic long range order. Eventually, it should be remembered that in such type compounds the amplitude of local spin fluctuations varies significantly with temperature and it seems that simultaneously they are strongly dependent on local defects. Defects like antisite occupation of Sc ($8a$) by Ni atom cannot be detected in our diffraction investigations due to similar Z of all three elements and also very near values of coherent scattering lengths for nuclear neutron scattering. On the other hand, interstitial positions are rather excluded because in the whole range of concentration x the widths of diffraction peaks remain unbroadened.

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