^{57}Fe Hyperfine Interactions in the Sc(Fe$_{1-x}$Ni$_x$)$_2$ Laves Phases Synthesized under High Pressure

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　　The structural and microscopic magnetic properties of the pseudobinary Sc(Fe$_{1-x}$Ni$_x$)$_2$ system prepared under high pressure of 8 GPa were studied by X-ray diffraction and Mössbauer measurements in the range of $0.0 \leq x \leq 0.60$. The samples for $0.0 \leq x \leq 0.10$ have the hexagonal C14-type structure and those for $0.30 \leq x \leq 0.60$ crystallize in the C15-type structure. Both the magnetic hyperfine field on ^{57}Fe and the Curie temperature decrease with the 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. It is interesting that T_{C} for the compounds obtained under high pressure are by about 100 K smaller in comparison with those for the isostructural samples produced under normal pressure even though interatomic distances are practically equal in the both types of compounds.

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1. Introduction

　　In our earlier investigations the intermetallic pseudobinary compounds Sc(Fe$_{1-x}$Ni$_x$)$_2$ produced in an arc furnace under an atmosphere of argon gas have been studied [1]. They exhibit the cubic C15 (cF24, space group $Fd\bar{3}m$) Laves phase structure over the whole concentration range except for $x = 0$. Pure ScFe$_2$ shows the dihexagonal C36 structure (hP24, space group $P6_3/mmc$). It is a ferromagnet in which Fe atoms occupy the three non-equivalent positions: 6g, 6h,

and 4f (the Wyckoff notation). Magnetic moments at these sites measured by neutron diffraction are equal to 1.31(1), 1.78(1) and 1.52(1)μ_B at room temperature (RT), respectively. The mean value of hyperfine magnetic field in this compound amounts to 18.2(2) T. It was possible to estimate a hyperfine coupling constant A in investigated intermetallics. The obtained value of 12 T/μ_B is independent of temperature and concentration. The theoretical calculations of band structure for $ScFe_2$ with the $C15$ cubic structure give the magnetic moment of Fe atom of 1.56μ_B and predict the occurrence of antiparallel induced magnetic moments of about 0.52μ_B at Sc atoms [2]. NMR ^{45}Sc measurements in the polymorphic $C15$ form of $ScFe_2$ confirm these predictions giving the significantly larger value of $\mu_{Sc} = 1.05(5)\mu_B$ [3]. In the regular cubic $C15$ phase Fe/Ni atoms occupy only one type of sites: 16d with the point symmetry $\bar{3}m$ and create a lattice of regular tetrahedrons (16d positions) connected via their corners. Six Fe and six Sc (8a positions) atoms surround each Fe atom composing its nearest neighborhood. There are two magnetically non-equivalent types of Fe positions in this structure for which an easy magnetization axis makes the angles of 70° and 0° with the principal axis of the electric field gradient. A population ratio of these sites is equal to 3:1, respectively. It is known that the stoichiometric sample $ScFe_2$ prepared under a high hydrostatic pressure crystallizes in a hexagonal $C14$ structure [3]. In this structure the composition of the Fe nearest neighborhood is the same as in the $C15$ phase but Fe atoms form a lattice of regular tetrahedrons linked alternately by apexes (2a positions) or by their bases (6h positions) and occupy the two crystallographic and magnetic non-equivalent positions: 6h and 2f. Moreover, the application of a high pressure in the process of melting similar pseudobinary $Y(Fe_{1-x}Ni_x)_2$ compounds makes it possible to obtain single-phase $C15$ samples in the whole range of Ni concentration [4]. This is connected with the pressure induced changes of the occupation number n_{3d} of the Ni $3d$-based band which lead to the changes in the total energy of a crystal structure.

The $Sc(Fe_{1-x}Ni_x)_2$ 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 varies significantly with temperature, as pointed out by Moriya [5].

The aim of our study was to examine the possibility of obtaining the homogeneous samples with the $C14$ structure for $x < 0.60$. Influence of Ni substitution for Fe on structural and magnetic properties such as hyperfine interaction parameters and the Curie temperatures T_C of $Sc(Fe_{1-x}Ni_x)_2$ compounds also was a subject of the presented studies. Estimation of Fe magnetic moments using the hyperfine coupling constant A has been done.

2. Experimental

Intermetallic compounds of $Sc(Fe_{1-x}Ni_x)_2$ for $x \leq 0.60$ in the polycrystalline form were synthesized by melting appropriate stoichiometric amounts of scandium,

iron and nickel of high purity under quasihydrostatic high pressure of 8 GPa. The metals were placed in the high pressure cell in a NaCl envelope. A toroid-type high pressure chamber designed by Khvostantsev et al. in the Institute for High Pressure Physics at Troitsk was used [6]. The other details of the procedure used in this experiment have been given elsewhere [7]. Phase analysis was carried out by means of X-ray powder diffraction with nickel-filtered Cu K_α radiation. The diffraction patterns were obtained in the range of 30° to 90° (2θ). The Mössbauer spectra of powder samples were recorded using a constant acceleration spectrometer in the range from room temperature to 800 K temperature with a $^{57}Co(Rh)$ source. The Mössbauer spectra were analyzed 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.

The X-ray diffraction (XRD) patterns were fitted by the FULLPROF program for the Rietveld method refinement.

3. Results and discussion

The crystallographic structure of the investigated $Sc(Fe_{1-x}Ni_x)_2$ Laves phases was examined by means of XRD measurements. The obtained diffraction patterns are shown in Fig. 1. The samples with $x = 0$ and 0.10 show the hexagonal $C14$-type structure ($hP12$, space group $P6_3/mmc$). In the $Sc(Fe_{0.80}Ni_{0.20})_2$ compound both the cubic $C15$ and hexagonal $C14$ phases co-exist in the proportion approximately equal to 2:1. For the higher Ni concentration only the $C15$ phase occurs. It appears that using the pressure of 8 GPa does not lead to the $C14$ structure stabilization in the whole concentration range. Only small of the order of 2–3% admixtures of Sc_2O_3 and non-stoichiometric $Sc_{0.92}O$ oxides were identified for $x = 0.40$ and 0.60. In Fig. 2 the lattice parameters a and c for the hexagonal $C14$ phases and a for the cubic $C15$ intermetallics dependence on Ni concentration are presented. For the comparison, the results from [1] for cubic phases prepared under normal pressure are also shown. Both parameters in the samples with the hexagonal structure remain constant. The phases with the cubic structure exhibit the invar--type concentration dependence of the lattice parameter at $0.20 < x < 0.40$, unlike the samples prepared under normal pressure, where a linear decrease in lattice constant a according to the Vegard law has been observed [1]. The equilibrium lattice parameters a for the cubic phases prepared in both ways are practically the same except for $x = 0.20$.

Figure 3 shows the Mössbauer spectra of $Sc(Fe_{1-x}Ni_x)_2$ in the $0.0 \leq x \leq 0.60$ 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
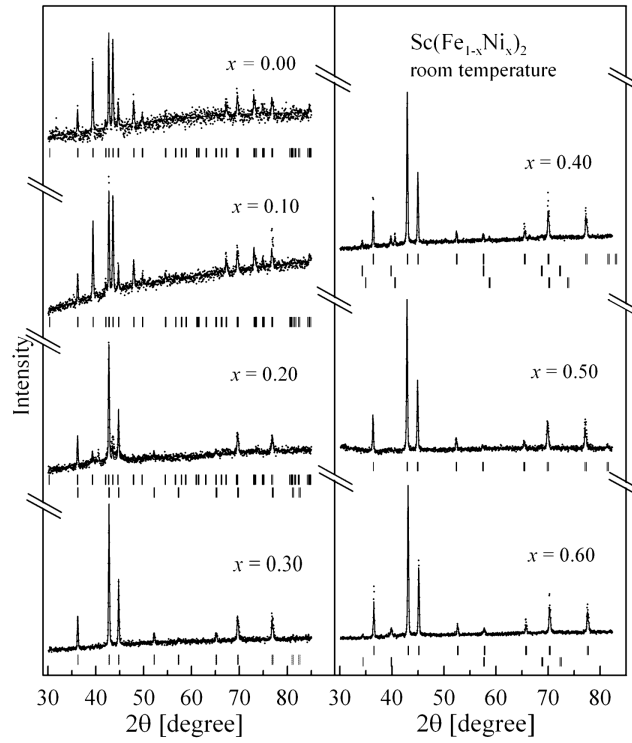
Fig. 1. Recorded (points) and calculated (full line) XRD patterns of $Sc(Fe_{1-x}Ni_x)_2$ for $0 \le x \le 0.60$.

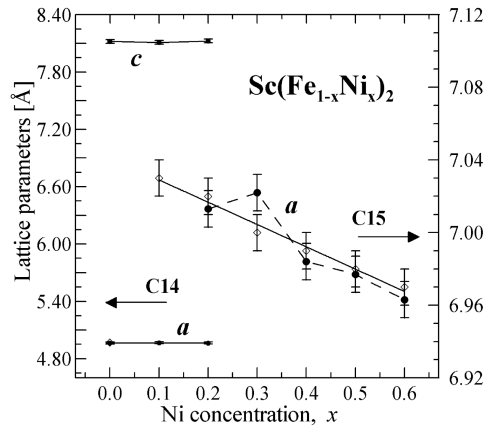Fig. 2. The lattice constant values vs. the Ni concentration x in the cubic $Sc(Fe_{1-x}Ni_x)_2$ phases ($\bullet$ — prepared under pressure of 8 GPa and $\diamond$ — prepared under normal pressure) and in the hexagonal $Sc(Fe_{1-x}Ni_x)_2$ phases derived from the XRD measurements.

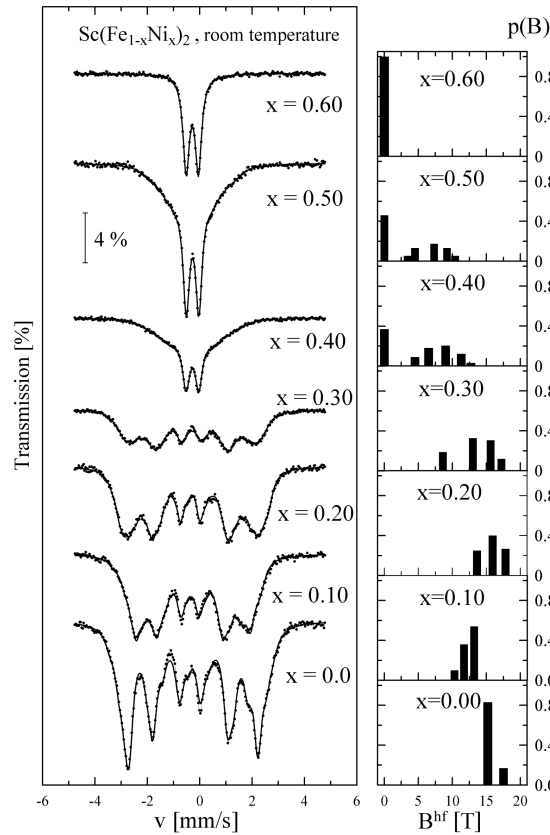Fig. 3. ^{57}Fe Mössbauer spectra of $Sc(Fe_{1-x}Ni_x)_2$ for $0.0 \leq x \leq 0.20$ at room temperature (left) and the hyperfine field discrete distribution accepted from a binomial distribution (right).

of magnetic components in a spectrum related to a given local environment of ^{57}Fe nuclear probe may be estimated on the basis of binomial distribution. The right part of Fig. 3 shows the contributions summed for two crystallographic or magnetic non-equivalent Fe positions larger than 5%. Only the nearest neighbors were taken into account because merely replacement of Fe atom in nearest neighborhood (NN) has strong influence and may be registered with high reliability. Magnetic sextets in the Mössbauer spectra of the samples with $x \leq 0.10$ are asymmetric. This spectrum property is observed if the preferred direction of magnetization is along the hexagonal c axis. A quadrupole splitting (QS) for paramagnetic doublet components of the spectra for the cubic samples with $x \geq 0.40$ at room temperature is equal to 0.48(1) mm/s and its value is preserved for all concentrations. The isomer shifts for these components are practically constant for all concentrations x and equal to –0.19 mm/s at room temperature. In the fitting procedure the quadrupole shifts for all sextets defined as $\varepsilon_Q = QS(3\cos^2\theta - 1)/2$ were not

fixed. The obtained values were smaller than 0.02 mm/s and had both positive and negative signs according to the symmetry of local environment of Fe sites. This result suggests that for all ^{57}Fe probes located at 16d sites the angle θ between the direction of hyperfine magnetic field (HMF) and the local principal axis of the electric field gradient (EFG) tensor is approximately equal to 54.7° and the mean quadrupole shift value 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 of Ni atoms for Fe atoms in NN of ^{57}Fe probe in the pseudobinary cubic samples 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 the investigated compounds.
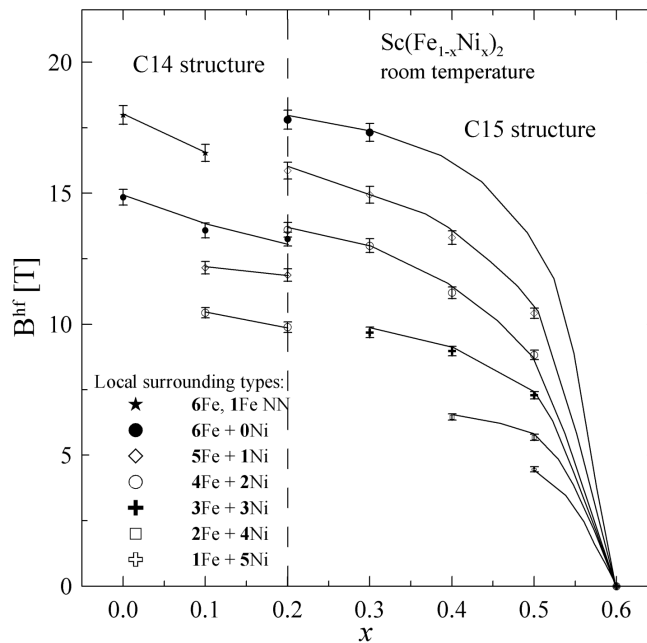

Fig. 4. The concentration dependences of the ^{57}Fe hyperfine magnetic fields on Fe sites for individual types of local surroundings at room temperature. For the $C14$ phase values averaged over two crystallographically and magnetically non-equivalent Fe sites were accepted.

The results obtained for the hyperfine magnetic fields for local surroundings with a different number of Ni atoms are collected in Fig. 4. For the $C14$ phase values averaged over two non-equivalent positions are given. From these dependences the critical concentration at RT for the existence of long-range magnetic order may be estimated as $x_c \approx 0.60$. Replacement of 1 Fe atom by Ni atom in the first sphere

of coordination causes the decrease in the hyperfine magnetic field by the values changing from about 1.5 T to 3 T. In the hexagonal $ScFe_2$ sample the Fe sites with the high hyperfine magnetic fields of about 17.5 T and the contribution of about 17% to the total spectrum were detected. A possible explanation is following. In the local surroundings of some Fe nuclear probes there appear additional Fe atoms at Sc sites. It seems that making use of high pressure in the sample preparation process promotes such an occupation of crystal sites. Additionally, it follows from the Mössbauer investigations of influence of deviations from stoichiometry in the $TiFe_2$ Laves phases that Fe atom located in the antisite position increases ^{57}Fe hyperfine magnetic field on the average by approximately 1.6 T [8]. Interstitial positions of Fe atoms are rather excluded because in the whole range of concentration x the widths of XRD diffraction peaks remain unbroadened. The Mössbauer measurements in the temperature range from room temperature to those above the Curie points T_C of the individual samples have been also performed. For the illustration of these studies, the spectra for $Sc(Fe_{0.60}Ni_{0.40})_2$ recorded at different temperatures are shown in Fig. 5 together with those of the sample with the same composition prepared under normal pressure. From the comparison of the spectra for both ways of the preparation, it is clear that T_C for the sample obtained under the high pressure is considerably lower than that for the latter way of preparation. This is a surprising result in the light of very well, both experimentally and theoretically confirmed fact that all magnetic properties and particularly Curie temperatures of pseudobinary Laves phases are very sensitive to lattice parameter changes. As mentioned above, these parameters in the investigated samples are the same.

The spectra in Figs. 3 and 5 exhibit one more feature characteristic of $Sc(Fe_{1-x}Ni_x)_2$. At room temperature for the samples with $0.40 \leq x \leq 0.60$ the paramagnetic doublet appears with the intensity increasing with the increase in 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 a 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 behavior at low temperatures was observed earlier in analogical pseudobinary phases many times [9, 10].

The thermal evolutions of the mean ^{57}Fe magnetic hyperfine field B_m^{hf} derived from the numerical analysis are shown in Fig. 6 together with the Brillouin curves fitted to the experimental points. Extrapolation of this curve to the zero field value allows determining of the Curie temperatures.

The T_C dependence on concentration is given in Fig. 7. The determined T_C is related to the ferromagnetic matrix. Critical temperatures for magnetic clusters
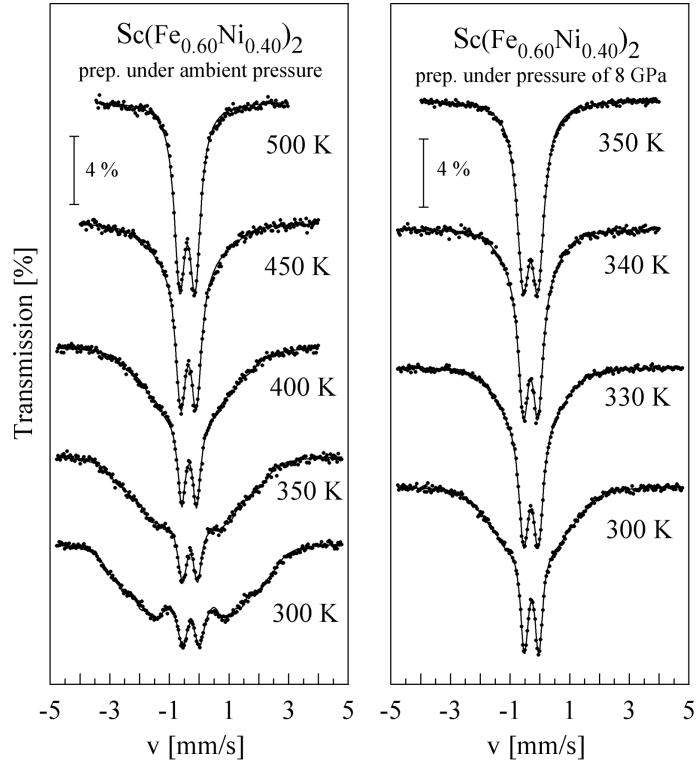
Fig. 5. ^{57}Fe Mössbauer spectra of the Sc(Fe$_{0.60}$Ni$_{0.40}$) compounds prepared under the pressure of 8 GPa (right part) and under normal pressure (left part) measured at various temperatures.

are lower and they may lie in a very wide range of temperatures. The concentration dependence of T_C for the Sc(Fe$_{1-x}$Ni$_x$)$_2$ system with the cubic $C15$ structure prepared under the high pressure differs significantly from the analogous system produced at normal pressure. The former dependence is strongly nonlinear and indicates considerably lower values of T_C than the latter one. The differences are particularly large for the last two samples and reach about 130 K and 80 K, respectively. Such behavior must result from the changes in the electronic structure of the investigated materials caused by using high pressure during initial ingredients melting.

In Table the results for hyperfine magnetic fields and isomer shifts measurements at room temperature and magnetic moments of Fe atoms estimated using the hyperfine coupling constant $A = 12$ T/μ_B determined from the Mössbauer spectroscopy (MS) and neutron diffraction measurements [1] are collected. For ScFe$_2$ the obtained values of μ_{Fe}(6h) $= 1.3(3)\mu_B$ and μ_{Fe}(2a) $= 1.2(3)\mu_B$ are near to those determined by means of NMR method: $1.49\mu_B$ and $1.44\mu_B$, respectively [3]. The obtained values of isomer shifts at room temperature, in the range of
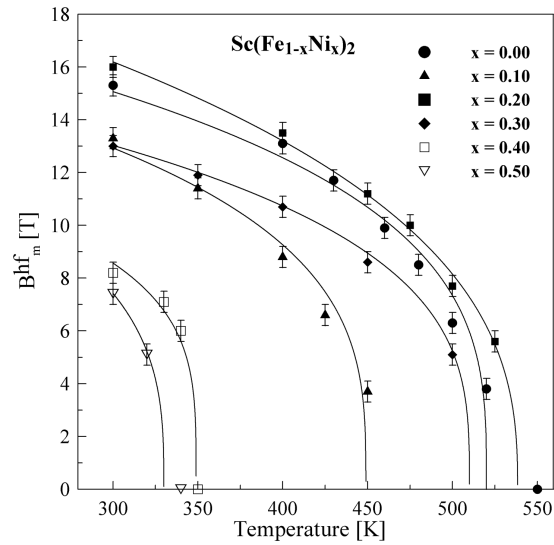
Fig. 6. Temperature dependence of the magnetic hyperfine fields derived from the computer fits to the ^{57}Fe Mössbauer spectra obtained for the $Sc(Fe_{1-x}Ni_x)_2$ compounds prepared under the pressure of 8 GPa. The continuous line represents the least-squares fit of the Brillouin function.
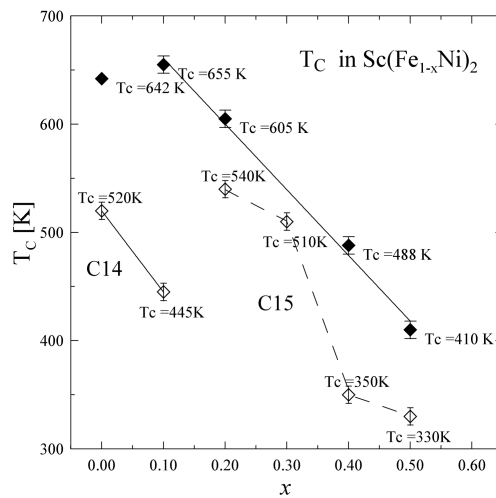

Fig. 7. The variation of the Curie temperature T_C values with Ni concentration determined by extrapolation of the Brillouin curve to the zero fields for the samples prepared under pressure of 8 GPa (◇) and synthesized under normal pressure (◆).

accuracy, are independent of the Ni concentration x. An expected decrease in an absolute value of isomer shift because of the larger electronegativity of nickel (1.8 in the Pauling scale) in comparison with iron (1.6) is probably compensated by

^{57}Fe hyperfine magnetic fields and Fe magnetic moments estimated using a hyperfine coupling constant $A = 12(1)$ T/μ_B for Sc(Fe$_{1-x}$Ni$_x$)$_2$ and the mean values of isomer shifts (IS) in relation to α-Fe at room temperature.

	C14 structure				C15 structure		
x	Site	B_{hf} [T]	μ_{Fe} [μ_B]	IS [mm/s]	x	B^{hf} [T]	μ_{Fe} [μ_B]	IS [mm/s]
0.00	6h	15.3(2)	1.28(27)	−0.22(1)	0.20	16.0(2)	1.33(28)	−0.21(1)
	2a	14.7(2)	1.23(25)	−0.19(1)				
0.10	6h	12.6(2)	1.05(21)	− 0.21(1)	0.30	13.9(2)	1.16(27)	−0.20(1)
	2a	12.1(2)	1.014(20)	−0.20(1)				
0.20	6h	11.7(2)	0.98(20)	−0.21(1)	0.40	8.8(2)	0.73(24)	−0.20(1)
	2a	11.3(2)	0.94(19)	−0.19(1)				
					0.50	7.1(2)	0.59(23)	−0.19(1)

a weaker shielding of inner $3s$ Fe electrons by the $3d$ Fe electrons. The shielding becomes weaker along with a decrease in the degree of Fe $3d$ states localization caused by an increase in the width of the $3d$ Fe/Ni band.

4. Conclusions

The concentration dependence of the hyperfine magnetic fields in the Sc(Fe$_{1-x}$Ni$_x$)$_2$ series and the decrease in Fe magnetic moments may be qualitatively explained by the increase in $3d$ band occupation. Each atom of nickel introduces approximately 2.2 of $3d$ electrons more than iron atom. An occurrence of Fe sites with high hyperfine magnetic fields in ScFe$_2$ may suggest coexistence of Fe atoms in two different high-spin and low-spin states in analogy to a situation in the ordered alloy Fe$_{0.75}$Ni$_{0.25}$ [11]. Alternative explanation is an influence of the presence of additional Fe atoms located at Sc sites (4f) in local surroundings of some Fe sites. Fe atoms in 4f positions have 12 Fe atoms in its nearest neighbor but a distance to them is equal to about 0.291 nm in comparison with Fe–Fe distances for 6h (2a) sites (0.232 nm). The transition from the ferromagnetic state to the paramagnetic one in the investigated Sc(Fe$_{1-x}$Ni$_x$)$_2$ compounds takes place over a large temperature range. It is a consequence of the occurrence of clusters coming from the short-range magnetic order. With the 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. The high pressure applied in the preparation of the samples seems to be an essential factor promoting the cluster formation and the magnetic order instability. The form of the function of local density of states near the Fermi level [2] in ScFe$_2$ makes stability of magnetic long-range order very sensitive to even not large changes of the $3d$

electrons number in a common Fe and Ni $3d$ band. It should be also remembered that in such type of compounds the amplitude of local spin fluctuations varies significantly with temperature and it seems that simultaneously they are strongly dependent on local defects. The defects like antisite occupation of Sc (8a) by Ni or Fe atoms cannot be detected in the XRD investigations due to similar Z of all three elements.

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