

Structural and magnetic properties of $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ compounds studied by means of Mössbauer effect and neutron diffraction

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Abstract. The subject of the investigations were quasibinary $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ Laves phases in which structural and magnetic properties depend on replacement of Fe atoms by Cu atoms. Powder X-ray diffraction and neutron diffraction measurements carried out at room temperature revealed that samples were a mixture of two phases: the quasibinary $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ compounds with cubic C15 structure and ScCu_2 with tetragonal structure. ^{57}Fe Mössbauer spectroscopy revealed that the $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ compounds are ferrimagnetic up to an actual concentration $x_{act} < 0.30$. A decreasing of mean values of hyperfine magnetic fields was observed. On the basis of analysis of the neutron diffraction spectra the mean values of Fe magnetic moments were determined, considering the component connected with the quasibinary $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ phases. These moments change from $1.45(29) \mu_B$ in the $\text{Sc}(\text{Fe}_{0.92}\text{Cu}_{0.08})_2$ to $1.18(32) \mu_B$ in $\text{Sc}(\text{Fe}_{0.72}\text{Cu}_{0.28})_2$ phase at 8 K. From the results of independent hyperfine magnetic field on ^{57}Fe probes and magnetic Fe moments measurements, the hyperfine coupling constant in quasibinary ferrimagnetic $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ phases is estimated as equal to $13 \text{ T}/\mu_B$ at room temperature.

Key words: hyperfine fields • Mössbauer effect • neutron diffraction • quasibinary Laves phase

Introduction

The diversity of magnetic phenomena due to $3d$ - $3d$ exchange interactions present in alloys and intermetallic compounds was a matter of interest for a long time [4]. Among the large number of such materials, the binary Laves phases with comparatively simple crystal structure give the possibility of substituting the $3d$ metals with each other or non-magnetic sp elements without changing the crystal structure over a wide range of compositions. This appears to be one of the main advantages of pseudobinary alloy systems compared with binary alloys to investigate the onset of magnetism as a function of alloy composition. For example, it is known that Cu has a very low solubility in metallic Fe of the order of 2 at.% at 600 K [1] and the Cu solubility in Sc not exceeds 0.5% at 865 K [10]. In the quasibinary system Sc-Fe-Cu, where Fe atoms are gradually substituted for Cu atoms, an initial ScFe_2 compound belongs to the Laves phases. It has hexagonal C36 structure (hP24, space group $P6_3/mmc$) and it is a ferromagnet with $T_C = 642 \text{ K}$ [13]. Quasibinary $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ compounds are also the Laves phases, but already a small addition of Cu stabilizes cubic C15 structure in these phases. The sequence of phases in the system ends with the ScCu_2 intermetallic paramagnetic phase having a tetragonal C11_b-type structure [3]. In this ScFe_2 iron atoms occupy three non-equivalent positions: $6g$, $6h$ and $4f$ (Wyckoff notation) and have magnetic moments equal to $1.31(1)$,

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1.78(1) and 1.52(1) μ_B at room temperature (RT), respectively. The mean value of hyperfine magnetic field in this compound is 18.2(2) T [13]. The theoretical calculations of band structure for ScFe_2 with C15 cubic structure give the magnetic moment of Fe atom of 1.56 μ_B and predict the occurrence of antiparallel induced magnetic moments of about 0.52 μ_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 $\mu_{\text{Sc}} = 1.05(5) \mu_B$ [8]. In regular cubic C15 phase (cF24, space group $Fd\bar{3}m$) Fe/Cu atoms occupy only one type of sites, i.e. $16d$ with the point symmetry $3m$ and form regular tetrahedrons ($16d$ positions) connected via their corners. Six Fe and six Sc ($8a$ positions) atoms surround each Fe atom composing its nearest neighbourhood. In ferromagnetic state the investigated compounds belong to the class of materials called itinerant magnets [2, 15]. One of the important characteristics of these materials is that amplitude of the local spin fluctuation varies significantly with temperature, as pointed out by Moriya [6] or with local concentration fluctuations. Formation of magnetic clusters and mictomagnetic behaviour at low temperatures were often observed earlier in the pseudobinary Laves phases [7, 9].

The form of the function of local density of states near the Fermi level for this class of materials [2] is the reason of the fact that even not large changes in $3d$ electrons number in a common Fe and atoms substituting Fe atoms, $3d$ band may drastically violate stability of magnetic long range order.

The aim of the presented study was to examine the influence of Cu substitution for Fe on structural and magnetic properties of $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ compounds. In particular, the dependence of hyperfine interaction parameters and Fe magnetic moments on concentration x , and changes of T_C in these compounds were the object of our interest.

Experimental details

Intermetallic compounds of $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ for nominal $x \leq 0.90$ in the polycrystalline form were prepared by triple arc melting appropriate stoichiometric amounts of scandium, iron and copper of high purity under an inert argon atmosphere. The ingots were annealed in vacuum at about 1100 K for 72 h to ensure their homogeneity. The crystallographic structures of the samples were examined by means of powder X-ray diffraction with $\text{CuK}\alpha$ radiation. The scans were obtained in the approximate range of 2θ 30° to 96° . The Mössbauer spectra of powder samples were recorded at room temperature using a constant acceleration spectrometer and a $^{57}\text{Co}(\text{Rh})$ source. The obtained spectra were analysed 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 with nominal $x = 0.10, 0.20$ and 0.70 , neutron powder diffraction (ND) measurements were performed with a time-of-flight powder diffractometer in the temperature range from 8 to 800 K. The DN2

time-of-flight diffractometer at the fast pulsed reactor IBR2 in the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research was used. The X-ray and neutron diffraction patterns were refined by the FULLPROF program for Rietveld refinement. A convolution pseudo-Voigt with double exponential function was chosen to generate the line shape of the diffraction peaks. In the final run the following parameters were refined from the XRD and ND data: scale factor, unit cell parameters, positional coordinates of atoms, thermal factors and additionally for ND magnitude and orientation of the Fe and Sc ferrimagnetically ordered magnetic moments. The neutron coherent scattering lengths for Sc, Fe and Al were taken as equal to 12.3 fm, 9.45 fm and 7.72 fm, respectively. In the obtained for $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ neutron diffraction patterns one pair of peaks $\langle 111 \rangle$ and $\langle 101 \rangle$ at $d \approx 4.15 \text{ \AA}$ with a strong dependence of their intensity on temperature was found (see Fig. 6). These peaks come from practically pure magnetic scattering. Nuclear scattering contributions to them from different atoms at different crystallographic sites cancel each other out to a large extent. This fact allows us to determine the magnitude of the Fe and Sc ordered magnetic moments.

Results and discussion

The obtained XRD patterns of the selected samples are shown in Fig. 1. The samples with nominal $x \geq 0.05$ were principally a mixture of two phases: quasibinary $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ phases with cubic C15 structure and tetragonal C11_b ScCu_2 phase. The contribution of the latter phase increases from about 3 to 87% for the samples with nominal $x = 0.10$ and $x = 0.90$, respectively. Small admixtures of Sc_2O_3 and pure Cu inclusions (below 3–5%) were also detected. This result was confirmed by ND measurements for some samples. The neutron diffraction spectra are shown in Fig. 6. The Bragg peaks related to tetragonal phase are considerably broadened. Two factors are responsible for this effect. The former is considerable dispersion of this phase and the latter presumably dominating factor is mechanical strains produced in the grinding of specimens process. The large sensitivity of XRD results to grinding for a similar ScCu_4 phase was reported in [5].

The occurrence of ScCu_2 means that the nominal concentration x_{nom} is not a good parameter to characterize the elemental composition of $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ phases. An estimation of actual concentration x_{act} was done on the basis of data on phase weight contents obtained from XRD and ND patterns. For a comparison, both nominal and actual concentrations are given in all figures and in the table. In the subsequent result discussion and presented dependencies only x_{act} will be used.

For cubic phases $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$, the lattice parameter a dependence on the Cu actual concentration is presented in Fig. 2. The replacement of Fe atoms (covalent radius 0.124 nm) by larger Cu atoms (covalent radius 0.128 nm) in this phase leads to the almost linear slight increase of lattice constant a according to Vegard's law.

Figure 3 shows the room temperature Mössbauer spectra of $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ with x_{act} in the $0.08 \leq x_{\text{act}} \leq 0.35$

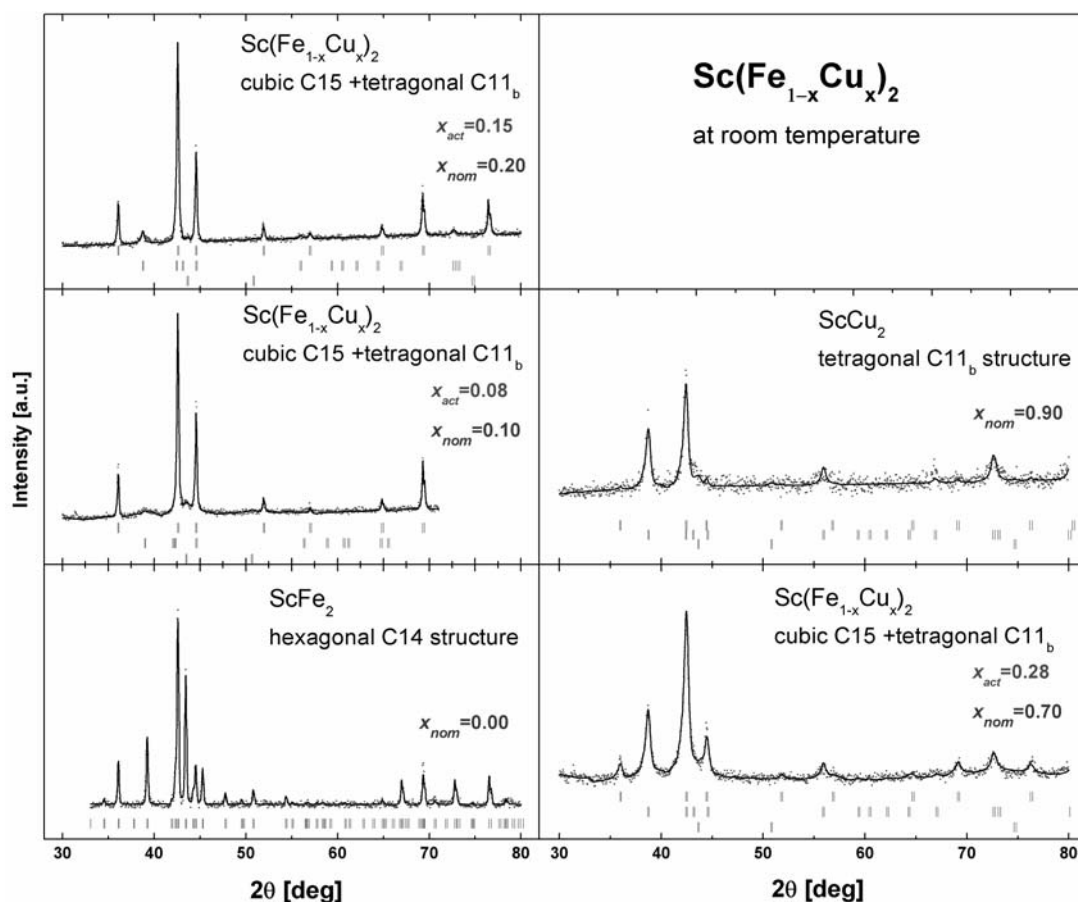


Fig. 1. XRD patterns of $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ for the selected concentrations x .

range. In order to obtain satisfactory fit to the experimental data it was assumed in the first approximation that Cu 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. Only the nearest neighbours (NN) were taken into account because merely replacement of Fe atom in NN has a strong influence and may be registered with a high reliability. Next, an initially accepted from XRD and ND actual concentration was varied with a step 0.005 and calculations of the number and relative intensity of components were repeated. Finally, x_{act} values giving the best fits are accepted as final results. The right panel of Fig. 3 shows the contributions of sextets larger than 5%. All

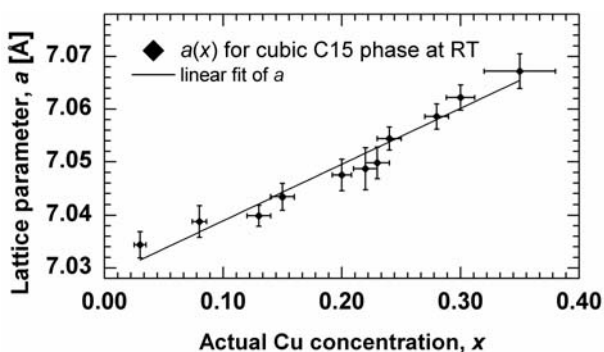


Fig. 2. The lattice parameter a values vs. the actual Cu concentration, x , for quasibinary $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ phases obtained from XRD measurements.

observed magnetic sextets are slightly asymmetric. In a regular cubic C15 phase Fe/Cu atoms occupy only one type of sites, i.e. $16d$ with the point symmetry $3-m$ and create a lattice of regular tetrahedrons ($16d$ positions) connected via their corners. However, there are two magnetically non-equivalent types of Fe positions in this structure for which an easy magnetization axis $\langle 111 \rangle$ makes the angles θ of 70° (site type I) or 0° (site type II) with the principal axis of the electric field gradient. A population ratio of these sites is equal to 3:1, respectively. In such a case two different mean quadrupole shifts $\varepsilon_Q = QS(3\cos^2\theta - 1)/2$ for the sextet components occur what gives a ratio of $\varepsilon_{Q,I}$ and $\varepsilon_{Q,II}$ values $-1:3$ [12]. Such situation is valid for all investigated quasibinary phases. It means that the direction of the easy magnetization axis is not changed when Fe atoms are replaced with Cu atoms. In the performed fitting procedure the population of sites and quadrupole shift values ratios for all sextets has been fixed. In contrary to the case of other quasibinary phases (containing Al, Ni or Co) [7, 9, 14] there is no paramagnetic component in the Mössbauer spectra of $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ for x_{act} up to about 0.35 (nominal 0.90). It proves that paramagnetic clusters related to spin fluctuations caused by local concentration fluctuations do not occur in the investigated samples.

In Figure 4 the mean value of hyperfine magnetic field averaged with suitable statistical weights of individual magnetic components related to specific local surroundings of ^{57}Fe nuclear probes is presented as a function of x_{act} . This dependence has a linear character with different slopes in two concentration ranges. The point of deflection occurs at $x_{act} \approx 0.20$.

The Mössbauer spectrum of the sample with nominal $x_{nom} = 0.90$ contains only a set of paramagnetic doublets (Fig. 3). Without hyperfine magnetic interaction sites I and II are fully equivalent from the point of view of hyperfine interactions. The best fit was obtained for the number and relative contribution of doublets accepted from binominal distribution for $x_{act} \approx 0.35$. Thus, the theoretical pattern was built up from altogether five

subspectra with relative intensities larger than 5%. Additionally, in the fitting procedure it was assumed that both isomer shift, IS, and quadrupole splitting, QS, depend upon the number of Cu near neighbours in a linear way. Values of QS changes from 0.46(8) mm/s for the 6Fe/0Cu surrounding to 0.3(1) mm/s for the 2Fe/4Cu one. There is a lack of a doublet with much higher QS expected for ^{57}Fe probes at Cu site $4e$ with

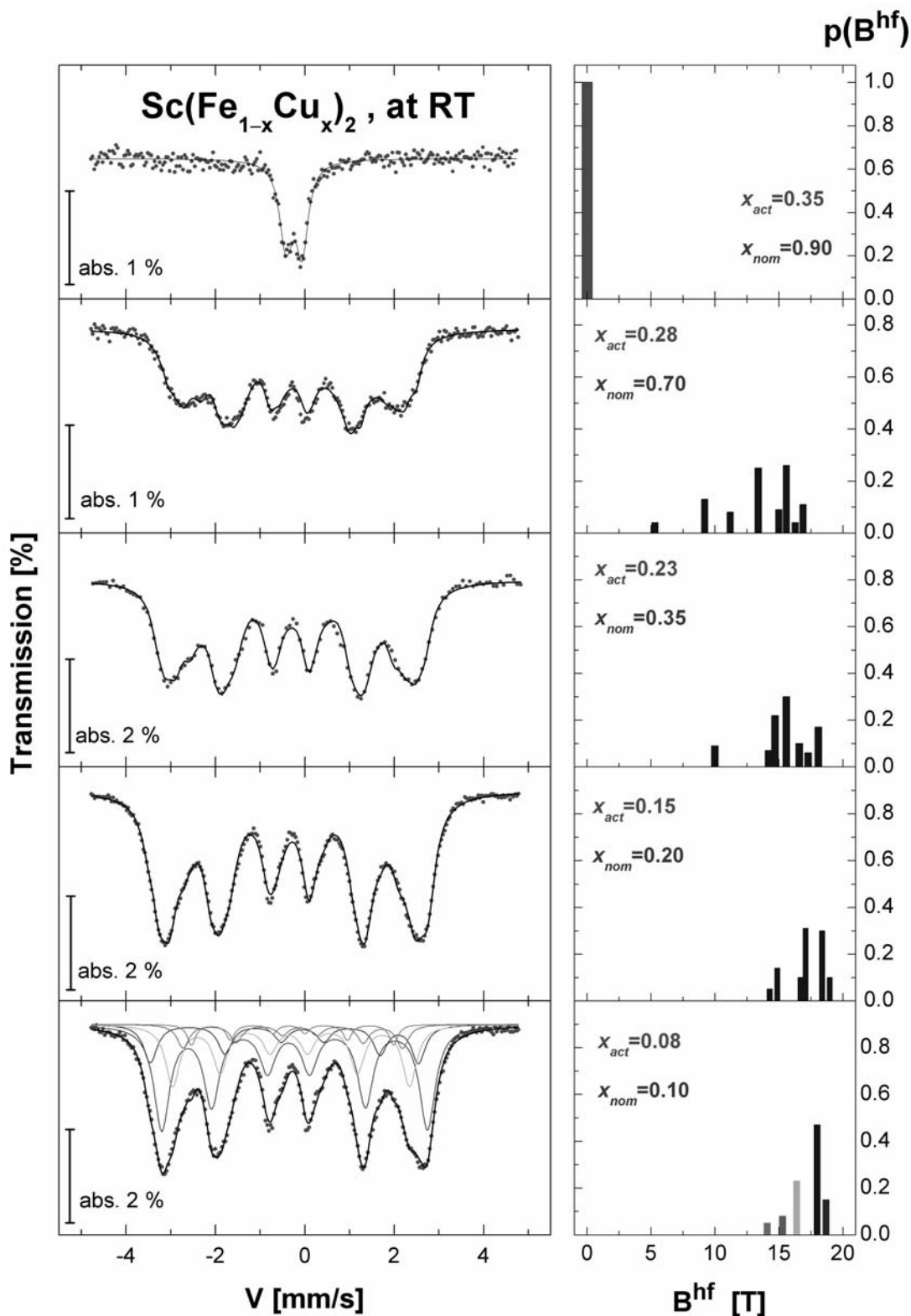


Fig. 3. The ^{57}Fe Mössbauer spectra of $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ at RT (left) and the hyperfine field discrete distribution accepted from a binominal distribution (right).

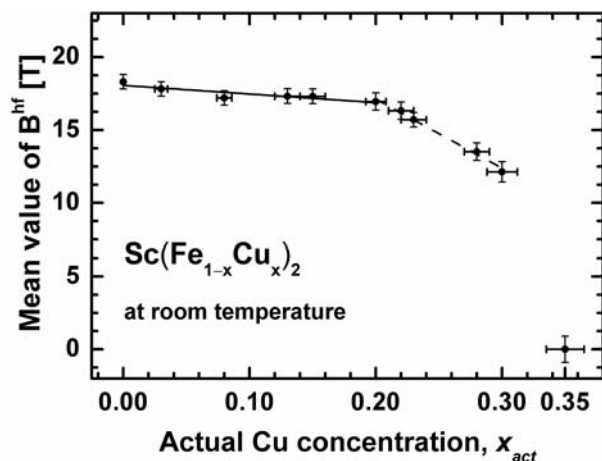


Fig. 4. The concentration dependence of the mean ^{57}Fe hyperfine magnetic field at RT.

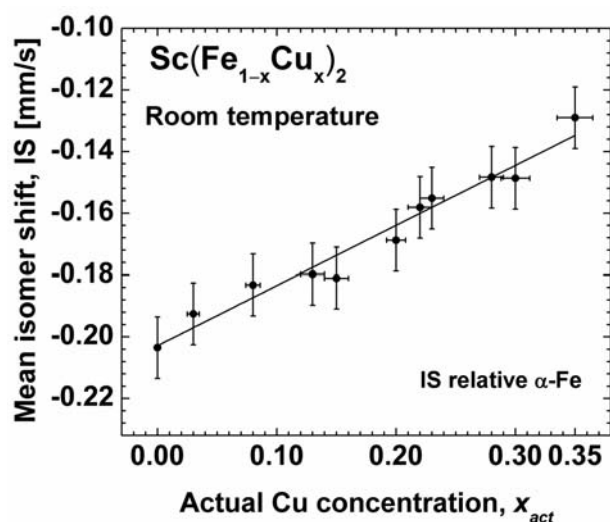


Fig. 5. Mean isomer shift dependence on actual Cu concentration x_{act} .

tetragonal point symmetry $4/mmm$ in the ScCu_2 phase in the paramagnetic phase spectrum.

In Figure 5 the mean isomer shift (IS) in dependence on actual concentration is given. IS increases almost linearly from about $-0.20(1)$ mm/s for ScFe_2 up to $-0.13(2)$ mm/s for the paramagnetic sample at room temperature with nominal $x_{nom} = 0.90$. If the calibration of the observed isomer shifts in term of total s -electron density given in the paper [11] is used, from IS change it can be derived that the replacement of 1 Fe atom by 1 Cu atom reduces the average s -electrons charge at the nuclear ^{57}Fe site by about 0.24 electrons/(a.u.) $^{-3}$.

The ND spectra for $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ recorded for three different x_{act} concentrations are shown in Fig. 6. For each sample, ND measurements in a wide range of temperature from 8 K to about 800 K have been performed but not presented here. On the basis of these measurements, the mean Fe magnetic moments and their temperature dependences were determined. From the Brillouin curve fittings to the experimental data, the Curie temperatures T_C were estimated. The values of T_C for pure ScFe_2 and three quasibinary samples as a function of x_{act} are shown in Fig. 7. The Curie temperature monotonically decreases from 650(8) K for $x = 0.00$ [13] to 450(10) K for $x_{act} = 0.28$.

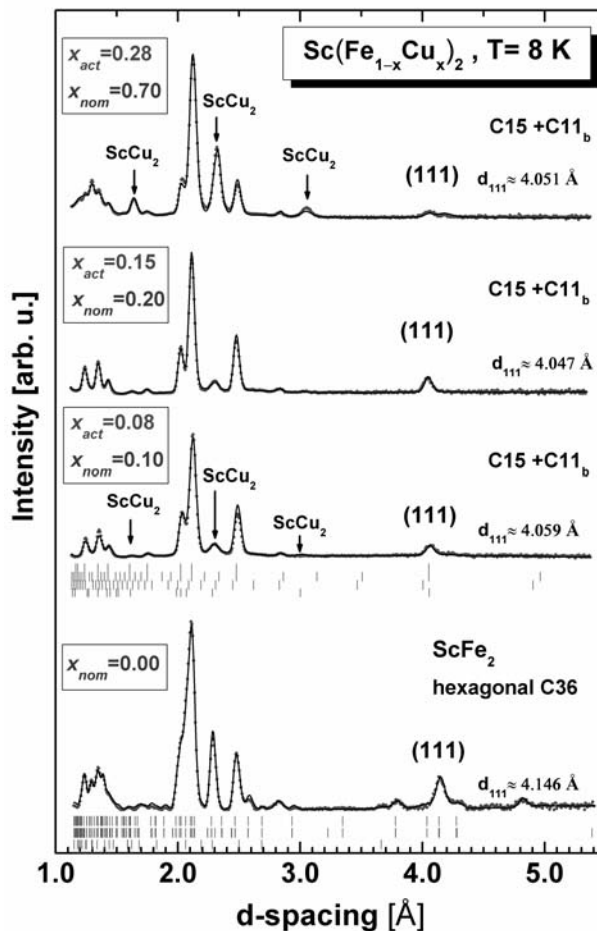


Fig. 6. Neutron diffraction patterns of $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ for actual $x_{act} = 0.08, 0.15$ and 0.28 at 10 K. The points represent experimental data, the full lines show calculated pattern. The short vertical marks below the diffraction pattern for $x_{act} = 0.08$ indicate the calculated nuclear Bragg peak positions (the upmost row) and the magnetic ones (lower row) for quasibinary phase. The third and the fourth row show the nuclear Bragg peaks position for Sc_2O_3 and ScCu_2 , respectively. Three main peaks for ScCu_2 phase with tetragonal C11_b structure not overlapping with cubic C15 structure peaks are denoted by vertical arrows labelled by ScCu_2 caption.

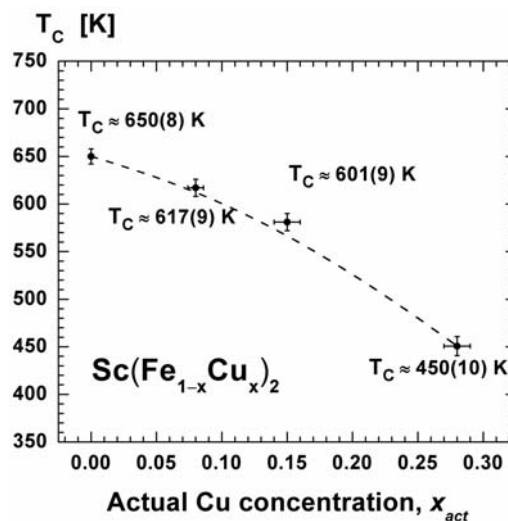


Fig. 7. The variation of the Curie temperature T_C values in $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ series determined by extrapolation of the Brillouin curve fitted to mean Fe magnetic moments temperature dependences. The dashed line is a guide for eyes.

Table 1. ^{57}Fe mean hyperfine magnetic fields, B_{hf} , Fe magnetic moments, μ_{Fe} , and hyperfine coupling constants, A , for $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ determined at room temperature. Actual x_{act} estimated from XRD, ND and MS data

Nominal x_{nom}	Actual x_{act}	B_{hf} (T)	μ_{Fe} (16d) (μ_{B})	A (T/ μ_{B})
0.10	0.080(6)	17.2(6)	1.30(20)	13.2(2.5)
0.20	0.15(1)	17.0(6)	1.26(15)	13.5(2.1)
0.70	0.28(1)	13.5(8)	1.15(19)	11.7(2.6)

In Table 1 the results for magnetic moments of Fe atoms and mean hyperfine magnetic fields measurements at room temperature are collected. Due to the fact that these moments and fields for the $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ Laves phases with $x_{\text{act}} = 0.08, 0.15$ and 0.28 were determined by two independent methods, i.e. MS and ND, it was possible to estimate a hyperfine coupling constant A . The obtained value of about $13 \text{ T}/\mu_{\text{B}}$ is near to that for analogous phases with Ni and Al [14].

Conclusions

It was not possible to obtain the single-phase quasibinary $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ Laves phases by the conventional arc melting method. With increasing Cu content in Sc-Fe-Cu system, a segregation of phases occurred. However, a relatively high actual concentration (up to $0.35(3) \text{ at.}\%$) of Cu dissolved in the intermetallic ScFe_2 Laves phase was achieved.

The concentration dependence of the mean hyperfine magnetic fields in $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ and the decrease of Fe magnetic moments may be qualitatively explained by the increase of $3d$ band occupation. Each atom of Cu introduces approximately 2.8 of $3d$ electrons [15] more than iron atom and then the difference in occupation spin up and down states decreases.

At some critical concentration ($x_{\text{nom}} \approx 0.90$ what corresponds to $x_{\text{act}} \approx 0.35$), cubic C15 quasibinary phase becomes paramagnetic at room temperature. In contrary to the results for analogous samples where Fe atoms were replaced with Ni, Co or Al atoms [7, 9, 14] in the $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ system, the paramagnetic cluster formation related to local concentration fluctuations is not observed.

Defects like antisite occupation of Sc ($8a$) by Cu atom eventually occurring in the quasibinary phases cannot be detected in our diffraction investigations due to a similar atomic number of all three elements and also very similar 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_{act} the diffraction peaks related to quasibinary $\text{Sc}(\text{Fe}_{1-x}\text{Cu}_x)_2$ phases remain unbroader. Next, relatively large widths of diffraction lines of ScCu_2 compound suggest the occurrence of this phase in the form of very small grains dispersed over the whole two-phase sample.

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