

The influence of Al doping on microstructure and hyperfine interactions in FINEMET

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Abstract Structure and hyperfine interactions of amorphous and nanocrystalline FINEMET were investigated by means of Mössbauer spectrometry. It was found that substitution of x iron atoms with aluminum ones causes changes in the properties of both amorphous and nanocrystalline alloys as well as in the structure of individual phases. The reduction of hyperfine magnetic field caused by atom substitution is a non-linear function of x , unlike the linear dependence expected because of dilution. Temperature studies reveal a double magnetic phase transition at 250°C and 330°C as well as point to the variety of phases in the examined material.

Key words Mössbauer spectroscopy • FINEMET • nanocrystalline alloys • Al-doped FINEMET

Introduction

Multicomponent alloys based on iron called FINEMET, NANOPERM or HIPTERM are an important group of systems being soft magnetic materials [4, 5, 8]. They have excellent magnetic properties both in the amorphous phase and in the nanocrystalline state that can be obtained by controlled annealing of the amorphous precursor. This causes partial crystallization and formation of fine crystalline grains embedded in the amorphous remainder. Since 1988 when Yoshizawa *et al.* [11] has discovered FINEMET, a number of studies have been reported concerned with nanocrystalline alloys based on Fe, Si and B. A small admixture of other elements can significantly modify the microstructure and magnetic properties of the alloy. Good results were achieved when replacing a certain number of iron atoms in classical FINEMET by aluminum, which improved such characteristics as magnetization, mean magnetic moment, saturation magnetostriction and coercivity [6, 9, 12, 13].

In this paper, systematic Mössbauer investigations of Al-doped FINEMET are presented, which are complementary to previous magnetic, microscopic as well as diffraction studies [6, 12, 13]. The main goals of our work are: to study the influence of Al substitution on the microstructures and hyperfine interactions in the as-quenched and nanocrystalline samples, to determine chemical composition, the structure and relative amount of grains in nanocrystalline samples and to study temperature evolution of hyperfine parameters.

Experimental

Conventional Mössbauer spectrometry was used to investigate amorphous and nanocrystalline $\text{Fe}_{73.5-x}\text{Al}_x\text{Nb}_3\text{Cu}_1\text{Si}_{13.5}\text{B}_9$

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alloys. Two series of samples were prepared basing on 30 μm thick and 5 mm wide ribbons obtained by the rapid quenching method and containing $x = 0, 1, 2, 3, 5, 7$ at.% of aluminum (called below Al0, Al1, Al2, Al3, Al5, Al7, respectively). In each series, the as-quenched samples were subjected to isothermal heat treatment at 490°C or 550°C for 1 h in a vacuum furnace. Mössbauer studies were carried out in the temperature range 20°C–400°C by means of a transmission spectrometer arranged in vertical geometry. A $^{57}\text{Co}(\text{Rh})$ source of gamma radiation and a drive system working in a constant acceleration mode were employed. The numerical analysis of spectra was performed by means of the MOSFIT program basing on the Varret method [10].

The transmission electron microscopy and diffraction outcomes revealed that nearly all as-quenched alloys were fully amorphous, while the annealed samples show nanocrystalline structure with grain sizes almost independent of aluminum content. For more details we refer the reader to [6, 12].

Results and discussion

Mössbauer spectra of the as-quenched samples have the form of broad sextets characteristic of systems with continuous distribution of hyperfine field. A typical Mössbauer spectrum of the annealed alloys is shown in Fig. 1. In contrast to the spectra of the as-quenched samples, it contains discrete subspectra. Several components can be distinguished: a set of sharp sextets originating from the crystalline phase and corresponding to Fe atom sites with 8, 7, 6, 5 and 4 Fe neighbors in the first coordination zone (called below D+A8, A7, A6, A5, A4, respectively, according to the iron positions in DO_3 -type structure), a smeared sextet attributed to the amorphous matrix and a paramagnetic doublet. In most spectra, the best fit was obtained by the use of four Zeeman sextets, numbered below I–IV, to reproduce the “crystalline” part, but in some of them five (for $x = 0$) or three sextets (for $x = 5, 7$) give better results. The reason of the differences is the evolution of the crystalline phase with Al content as well as the fact that it is not possible to make a reliable

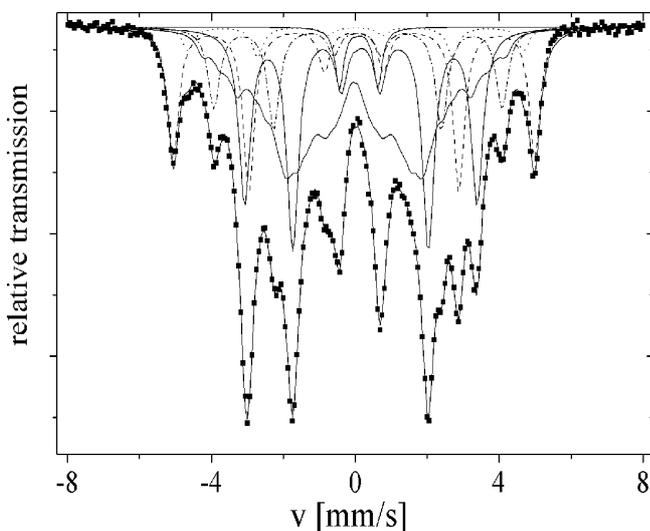


Fig. 1. Spectrum of sample Al3, annealed at 490°C.

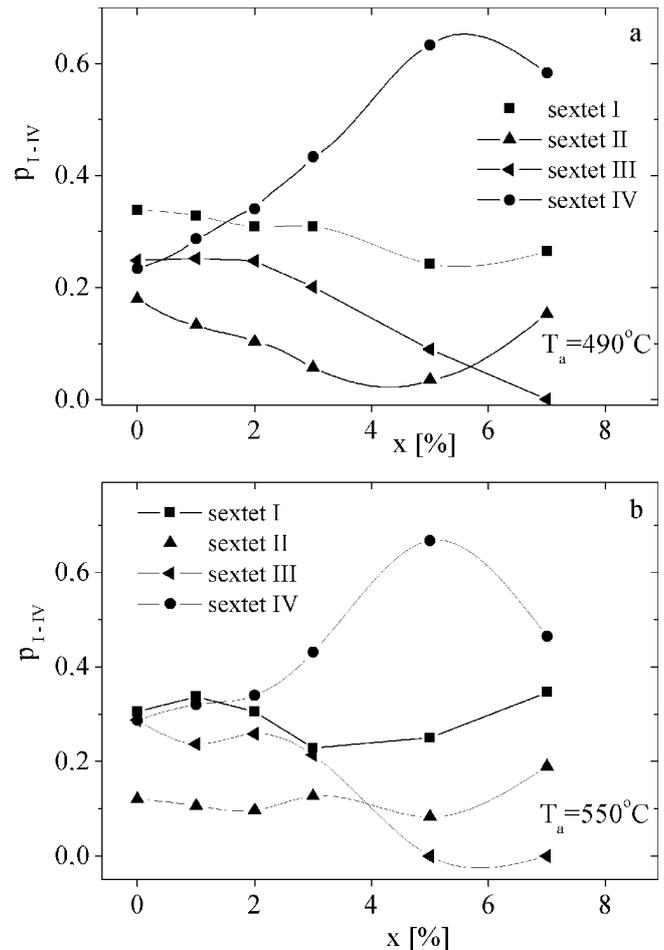


Fig. 2. Relative contribution of individual sextets p_i ($\sum p_i = 1$) vs. aluminum content for samples annealed at: a – 490°C, b – 550°C.

decomposition of A7, A8 and D subspectra. Comparing the hyperfine field of the well resolved sextet IV to the values characteristic of bcc Fe-Si crystalline alloys [3, 7], we can evaluate the silicon content in the crystalline phase: it increases from 18% at $x = 0$ to 23% at $x = 5$. As the admixture of aluminum modifies the hyperfine field, thus the above values must be treated as approximate and refer rather to the total Si + Al content.

In the crystalline Fe-Si (Al) systems at room temperature two kinds of atom arrangement are reported in this composition range: Fe(Si, Al) solid solution and more or less ordered DO_3 structure [3]. In order to distinguish between them, the relative intensity of the individual sextets are analyzed and presented in Figs. 2a and 2b. Strong evolution of the IVth sextet intensity with Al content is visible: it increases and peaks at $x = 5$. At the same time sextets II+III decrease, therefore for $x = 5, 7$ two components are predominant: sextet IV attributed to A4 position and sextet I attributed to the D+A8 one. The ratio of their intensities is very close to 2:1 (for both samples with $x = 5$), the value characteristic of the ordered DO_3 structure – in disordered solid solution the probability of occupation of A4 position does not exceed several percent at any Si content up to 25%. This indicates that in the proximity of $x = 5$ a transition proceeds from the disordered Fe-Si-Al DO_3 -type structure of crystalline phase to the almost ordered DO_3 one. This effect is not so distinct for $x = 7$; in

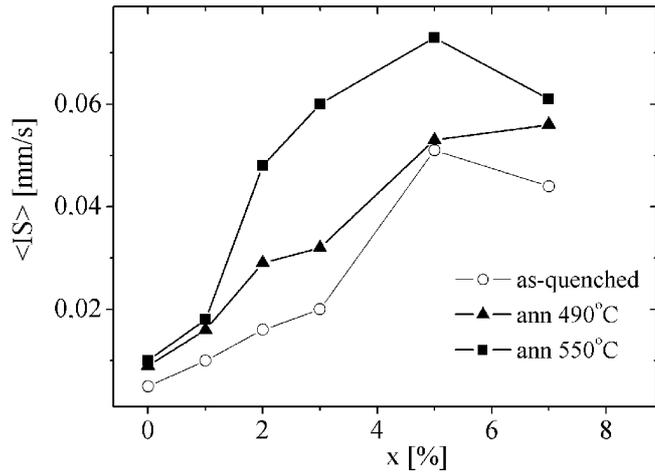


Fig. 3. Mean isomer shift (relatively to iron) of $\text{Fe}_{73.5-x}\text{Al}_x\text{Nb}_3\text{Cu}_1\text{Si}_{13.5}\text{B}_9$ alloys.

this case probably the proportion of Si + Al atoms to Fe atoms inside the grains is larger than 1:3, which is the value optimal for forming the ordered DO_3 structure.

Both in the as-quenched samples and in the annealed ones the mean isomer shift increases with the content of aluminum (Fig. 3) indicating a decrease of electron density at the Mössbauer nuclei. At the same time, the hyperfine field decreases slightly for $x < 3$ and more distinctly for $x > 3$ (Fig. 4) unlike the linear dependence expected because of dilution. The results suggest that some strengthening of the hyperfine interactions proceeds in the former content range, whereas the influence of dilution dominates in the latter one. Such an effect was reported earlier on the basis of results of magnetic measurements [13]. As seen in Figs. 4, 5a, 5b, the reduction of the mean hyperfine field is caused mainly by changes in the amorphous matrix although some evolution of individual sharp sextets is observed, too. These results suggest that aluminum atoms are situated both in amorphous and crystalline regions of the nanocrystalline alloys. Therefore the chemical composition of the crystalline as well as amorphous phase does not differ significantly. Assuming that the f -factor is similar for individual phases, the relative content of them

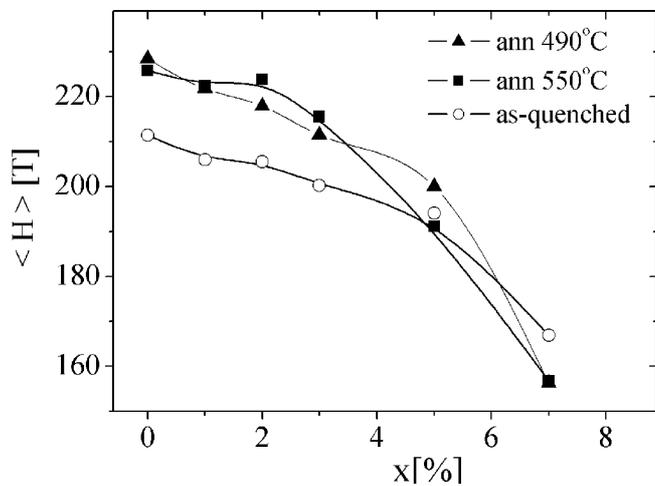


Fig. 4. Mean hyperfine field of $\text{Fe}_{73.5-x}\text{Al}_x\text{Nb}_3\text{Cu}_1\text{Si}_{13.5}\text{B}_9$ alloys.

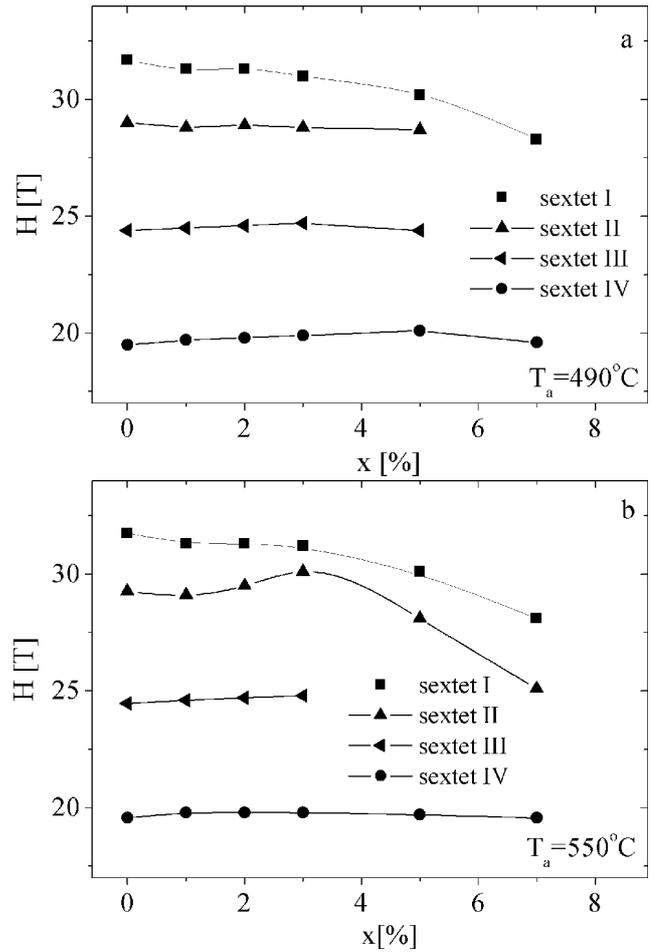


Fig. 5. Compositional dependence of hyperfine field of sextets I-IV corresponding Fe atoms in positions D+A7+A8, A6, A5, A4 - $\text{Fe}_{73.5-x}\text{Al}_x\text{Nb}_3\text{Cu}_1\text{Si}_{13.5}\text{B}_9$ alloys annealed at: a - 490°C, b - 550°C.

can be evaluated. The outcomes are presented in Fig. 6. It is easily seen that the results obtained for samples belonging to both series are very near. When the Al content increases, the amount of continuous contribution attributed to the amorphous matrix decreases slightly up to $x = 5$ whereas

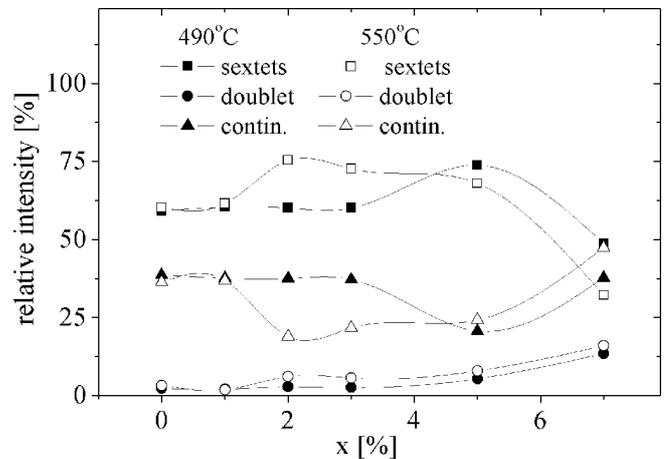


Fig. 6. The relative content of: the discrete component (sextets), the pattern with the continuous hyperfine field distribution, the central doublet.

for $x = 7$ a strong increase of this component is observed. A similar behavior of the paramagnetic component represented by the doublet is found. The discrete ferromagnetic contribution peaks at about $x = 3-5$ and then drops.

Searching for the origin of the paramagnetic component we have to consider two possible explanations: (i) superparamagnetic effects connected with very small grains; (ii) existence of iron atoms which are isolated from ferromagnetic interactions. The former hypothesis is rather unfounded because no visible changes of grain sizes with increasing x were observed, while the paramagnetic component is clearly larger in the spectra of samples with the higher percentage of aluminum. Moreover, the exchange interactions between crystallites through the magnetically ordered amorphous matrix are expected at room temperature that prevail temperature relaxations. We suppose that the paramagnetic component originates from isolated Fe atoms or small groups of Fe atoms in the aluminum-rich regions inside the grains. This is confirmed by the fact that the increase of doublet is associated with the augmentation of width of Mössbauer lines, which testifies the growing disorder inside the grains.

In order to make sure of this hypothesis, the temperature of Mössbauer measurements for sample Al7 annealed at 550°C were performed. The other reason of our special interest in this alloy is that we want to confirm and supplement the results of magnetic investigations reported

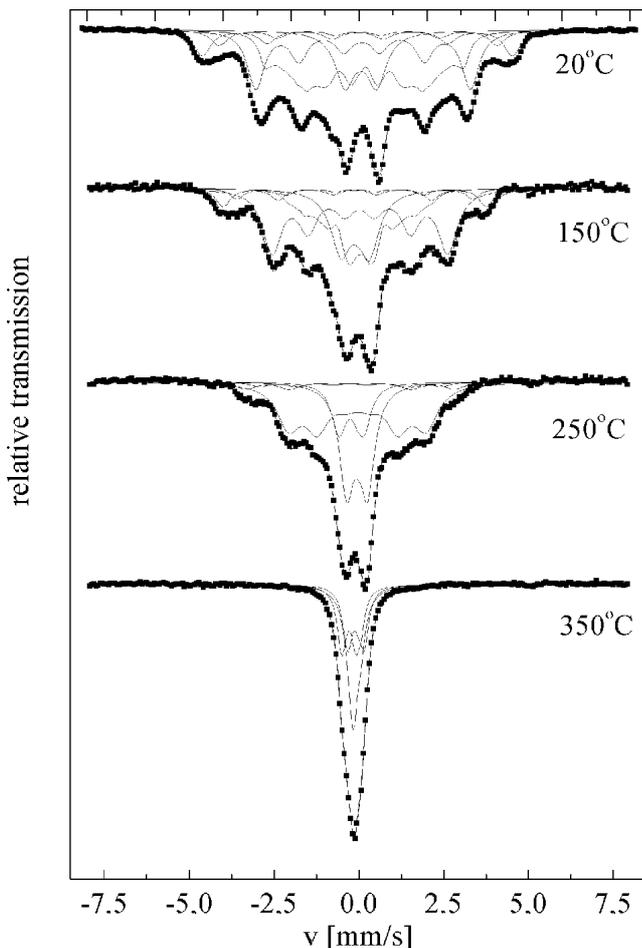


Fig. 7. Temperature evolution of Mössbauer spectra collected for $\text{Fe}_{66.5}\text{Al}_7\text{Nb}_3\text{Cu}_1\text{Si}_{13.5}\text{B}_9$ alloy annealed at 550°C.

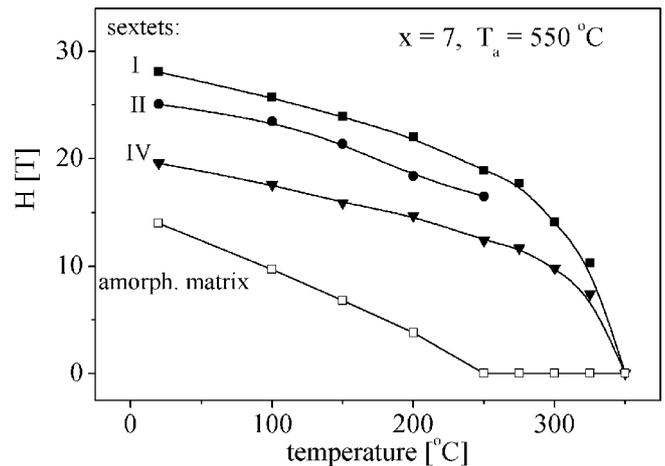


Fig. 8. Temperature dependence of magnetic hyperfine field ($\text{Fe}_{66.5}\text{Al}_7\text{Nb}_3\text{Cu}_1\text{Si}_{13.5}\text{B}_9$ alloy annealed at 550°C).

in [12]. The thermomagnetic curves taken in external magnetic field of 2 mT and 10 mT revealed a two-phase material, with two Curie temperatures: one around 300°C, the other around 390°C. The lower Curie temperature was attributed to the amorphous phase, the higher one was interpreted as being associated with the crystalline grains, although it is much lower than the Curie temperature of Fe_3Si phase. However, the transitions are not visible on the high field curves (0.24 T and 0.5 T). Selected Mössbauer spectra are shown in Fig. 7. When the temperature increases, the smeared pattern attributed to the amorphous matrix progressively converges to the centre of spectrum up to $T_C^{\text{am}} \approx 250^\circ\text{C}$, where the magnetic phase transition proceeds manifested itself as a collapse of the broad sextet to a doublet. Afterwards, the discrete pattern originating from nanocrystallites also collapses and at temperature beyond $T_C^{\text{cr}} \approx 330^\circ\text{C}$ the crystalline phase becomes paramagnetic. This behavior is well illustrated in Fig. 8 which presents the temperature dependence of the magnetic hyperfine field. The curve representing the residual matrix is very flat that results from a strong heterogeneity of this regions of the investigated material. The Curie temperatures derived by Mössbauer spectroscopy are smaller than those obtained from thermomagnetic curves (this is an important topic but it exceeds the scope of this paper) however, the results are qualitatively similar. Both in the case of the crystallites and amorphous matrix the values of Curie temperature are considerably reduced with respect to the classical FINEMET. The reason is the presence of a significant amount of aluminum and, probably, temperature relaxations of spin direction occurring at elevated temperature.

It is worth analyzing the relative contribution of the components attributed to different phases in dependence of the temperature (Fig. 9). While the percentage of the paramagnetic component (doublet) only slightly increases, other components vary in greater measure. It seems that the observed changes cannot be explained by measuring errors. One ought to pay special attention to the decrease of the smeared component attributed to the amorphous matrix. It points to the necessity of modifying the previous interpretation. The smeared sextet comprises probably, at least in part, also the contribution originating from grain boundaries and interface regions. Because of complexity of Mössbauer spectra this contribution cannot be well

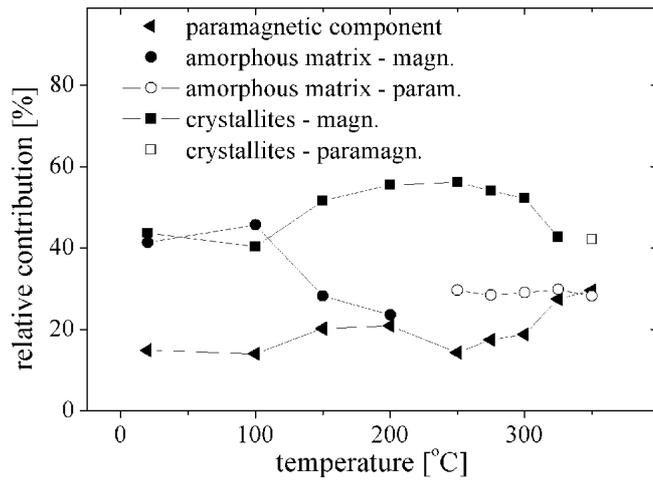


Fig. 9. Relative contribution of individual components of the Mössbauer spectra as a function of temperature ($\text{Fe}_{66.5}\text{Al}_7\text{Nb}_3\text{Cu}_1\text{Si}_{13.5}\text{B}_9$ alloy annealed at 550°C).

distinguished from the crystalline and the amorphous ones. Moreover, the additional difficulty in distinguishing of the phases is that the interactions between the grains and the matrix as well as the grain boundaries cause the smearing of magnetic transition of the amorphous remainder. Such an effect was observed for instance in nanocrystalline NANOPERM alloys [1, 2] in which the crystallites have a simple structure facilitating Mössbauer investigations.

Conclusions

The presented results reveal the presence of two-phase microstructure in the investigated alloys. It was stated that aluminum atoms are placed both in crystallites and in the amorphous matrix causing changes in the mean hyperfine field of the as-quenched as well as the annealed samples. For $x < 3$, the reduction of the hyperfine field is distinctly smaller than expected on account of dilution. In the proximity of $x = 5$, a transition proceeds from disordered Fe-Si-Al DO_3 -type structure of crystalline phase to the almost ordered DO_3 one. The presence of the paramagnetic component arises from the growing disorder in atomic arrangement. Temperature studies reveal double magnetic phase transition at 250°C and 330°C and prove the variety of phases present in the examined material.

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