The influence of Co and V substitution on structural properties of FINEMET-type alloys

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Abstract. The effect of addition of Co and V on the hyperfine parameters of amorphous as well as nanocrystalline Finemet-type alloys has been studied by means of transmission Mössbauer spectrometry. It was stated that these elements infiltrate into crystalline grains in the course of crystallization, what causes alteration in structure. Different evolution of magnetic hyperfine field is reported in both cases and analyzed. In the series of alloys substituted by vanadium, the substantial paramagnetic component attributed to iron-poor regions in the amorphous remainder was found.

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Introduction

Classical Finemet ($Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$) belongs to the group of nanocrystalline alloys that show excellent magnetic properties owing to coexistence of an amorphous phase and crystallites of nanometer size embedded inside [5, 7, 9, 13, 17]. Such a structure is generated as a result of controlled annealing of the as-quenched material. Nanocrystalline constitution and exchange interactions between grains through the amorphous matrix are the key features determining the special magnetic softness of these alloys. In order to improve excellent magnetic properties of Finemet, addition of various elements is considered – including replacement of iron by other metals, e.g. Cr [4, 11], Al [3, 14, 15, 20], Co [8, 10, 18], V.

In this article, the results of Mössbauer investigations, which were carried out for Finemet-type alloys substituted by cobalt and vanadium are presented. Mössbauer studies of these materials reported up to now are limited to few compositions only [1, 2]. The main subject of our interest was the influence of substitution on hyperfine parameters in the as-quenched and nanocrystalline samples as well as on structure, chemical composition and relative amount of crystalline phase in the annealed alloys.

Experimental

Transmission Mössbauer spectrometry was used to investigate amorphous and nanocrystalline Finemet-type alloys of composition: $(Fe_{1-x}Co_x)_{73.5}Cu_1Nb_3Si_{13.5}B_9$ ($x = 0, 0.1,..., 0.9$), $Fe_{73.5-y}V_yCu_1Nb_3Si_{13.5}B_9$ ($y = 1, 3, 5, 7$) and $Fe_{73.5}V_zCu_1Nb_{3-z}Si_{13.5}B_9$ ($z = 1.5, 3$). Amorphous
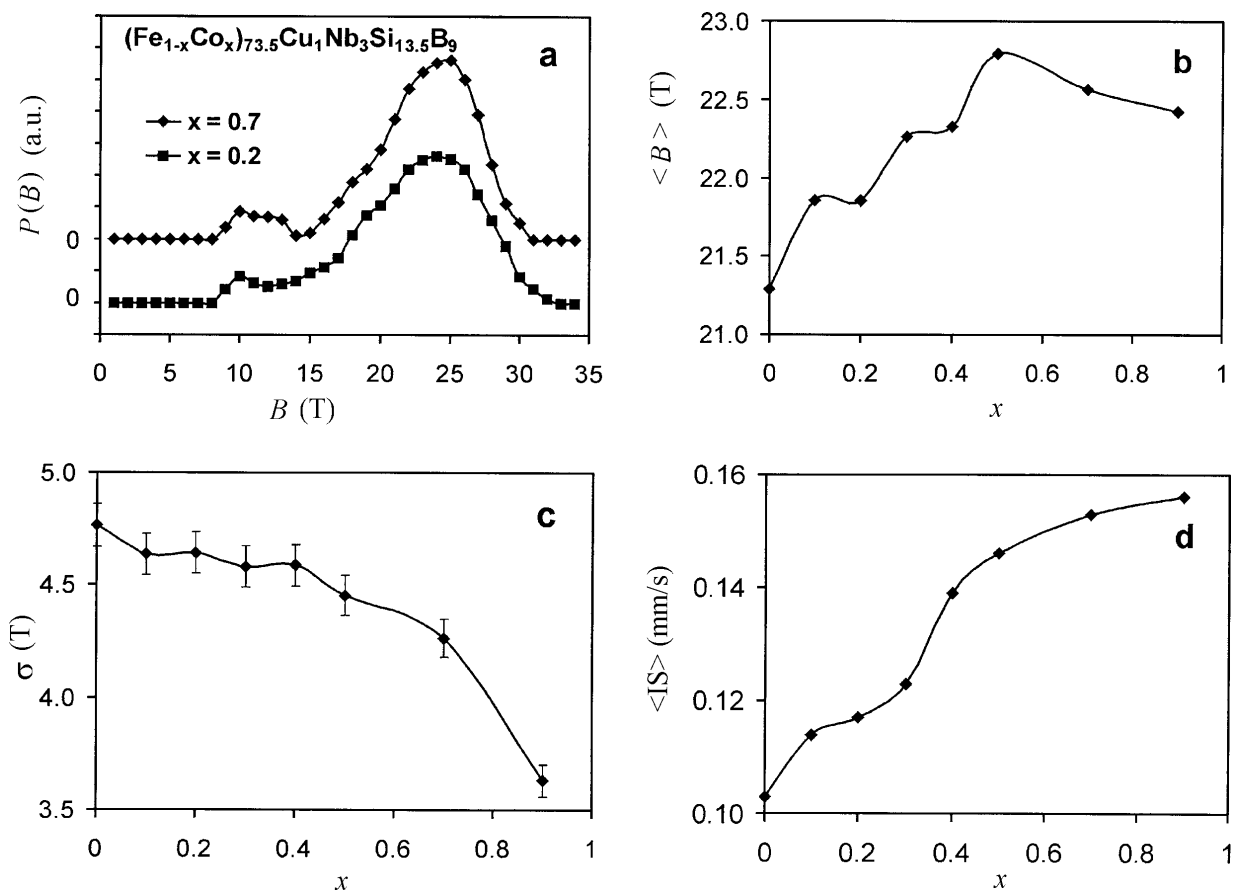
Fig. 1. a – Magnetic hyperfine field distribution derived for as-quenched Finemet substituted by cobalt; b – mean MHF; c – standard deviation of MHF distribution; d – mean isomer shift. Solid line is a guide for eyes.

samples were manufactured by rapid quenching of the melt and afterwards were subjected to the annealing in vacuum for 1 h at 550°C, which induced partial crystallization. The investigated samples had a form of 0.03–0.06 mm thick and 0.7–3 mm wide ribbons. Mössbauer studies were carried out by means of a conventional spectrometer arranged in vertical geometry. A ^{57}Co(Rh) source of gamma radiation and a drive system working in a constant acceleration mode were employed. In order to evaluate the quadrupole interactions, several measurements were realized for sample placed in a vacuum furnace, at elevated temperature up to 300°C. The numerical analysis of spectra was performed by means of the MOSFIT program basing on the Varret method [16].

Results and discussion

In all cases of the as-quenched samples, Mössbauer spectra were fitted using histogram-like magnetic hyperfine field (MHF) distribution which was linearly correlated with the isomer shift (IS) one, in order to reproduce a slight asymmetry of spectra. Several local picks or swells can be distinguished in the hyperfine field distribution of cobalt-doped amorphous alloys (positioned at about: 10, 20, 24 T – Fig. 1a), reflecting preferential surrounding of iron atoms. Addition of cobalt causes an increase of mean MHF value up to

$x = 0.5$, whereas a slow diminution is observed for the higher cobalt content (Fig. 1b). These results are very similar to those obtained by Borrego *et al.* [2], particularly taking into account somewhat different range of chemical composition of samples. The non-monotonic evolution of mean MHF is not well correlated with decreasing trend of macroscopic magnetization reported by Mazaleyrat *et al.* [8] and Müller *et al.* [10]. As a possible explanation, we suggest strong modification of electronic structure by Co addition or existence of nonmagnetic regions which do not comprise iron and, consequently, are not detected with Mössbauer spectroscopy. The standard deviation σ – the quantity which can be treated as a measure of local disorder in the environment of iron atoms – is a decreasing function of cobalt concentration (Fig. 1c). Simultaneously, the isomer shift reveals a monotonic growth with rising Co addition what evidences the decreasing charge density on the Fe nucleus (Fig. 1d).

Numerical analysis of Mössbauer spectra collected for nanocrystalline Finemet(Co) has been performed with two kinds of components (shown in Fig. 2a,b): a smeared Zeeman sextet with broad MHF distribution is related to the amorphous remainder, whereas a set of five or six sharp sextets corresponds to the (Fe,Co)Si crystalline phase. Sextets denoted as A8,..., A4, that constitute the spectra of cobalt-poor samples, are typical for Fe-Si grains of disordered DO_3 structure in pure Finemet, although they are characterized by a little
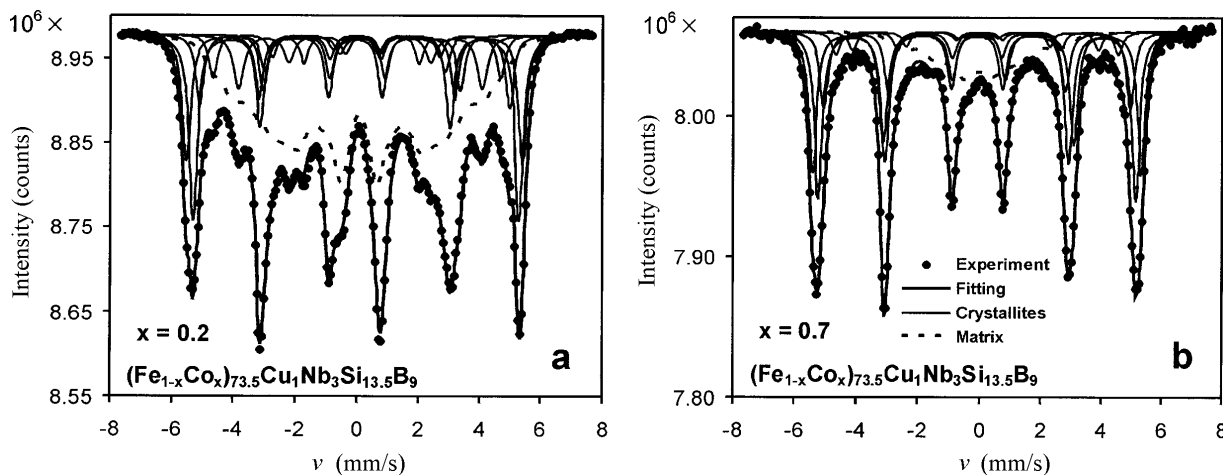
Fig. 2. Mössbauer spectra obtained for selected nanocrystalline Finemet substituted by cobalt. Solid and dashed lines mark the components attributed to the crystalline and amorphous phase, respectively.

modified MHF values (Fig. 3a). These sextets are attributed to iron atoms having 8,..., 4 (respectively) Fe atoms as nearest neighbours (sextet A8 incorporate two structurally in-equivalent positions of iron atoms in DO_3 lattice which differ in chemical composition in their second coordination shell). For $x > 0.2$, an additional sextet of value over 33 T arises – called D – which represents iron atoms with 8 magnetic near neighbours among which several atoms of cobalt are present. The existence of such a component in Mössbauer spectra evidences infiltration of cobalt atoms into nano-crystalline grains. The hyperfine field of sextets: D, A8 and A7 increases slightly up to $x = 0.5$ and drops slowly for higher Co concentration. This effect is probably caused by alteration of chemical order in the second coordination zone as well as by changes in the spin density and interatomic distances.

As it is shown in Fig. 3b, mean MHF of the whole sample and that of the discrete component strongly grow with rising Co content right to $x = 0.7$. This substantial increase cannot be explained in terms of evolution of MHF of individual sextets (which is rather slow), but it is simply a consequence of their intensity

alteration. The relative content of the particular subspectra can be evaluated from the area limited by the corresponding lines or groups of lines. Above $x = 0.2$ the rapid increase of contribution of the Zeeman sextets being characterized by the highest MHF values is observed (i.e. D+A8+A7, Fig. 4a). Since both the kind of structure and silicon concentration inside the crystalline phase determine the proportion between components [6, 12], the observed changes indicate modification of grain constitution; we suppose that disordered DO_3 structure of Fe-Si crystallites (of a dozen or so atomic percents of Si), which occurs in pure Finemet, is replaced by b.c.c. (Fe,Co)Si solid solution comprising about 5 at.% silicon. The enrichment of crystallites in magnetic elements is accompanied by diminution of the amorphous matrix in Fe and Co compared with the nominal content of initial as-quenched ribbon. This is reflected by the strong drop of the mean value of MHF related to the amorphous remainder, which is observed for nanocrystalline samples rich in cobalt, i.e. for $x > 0.4$.

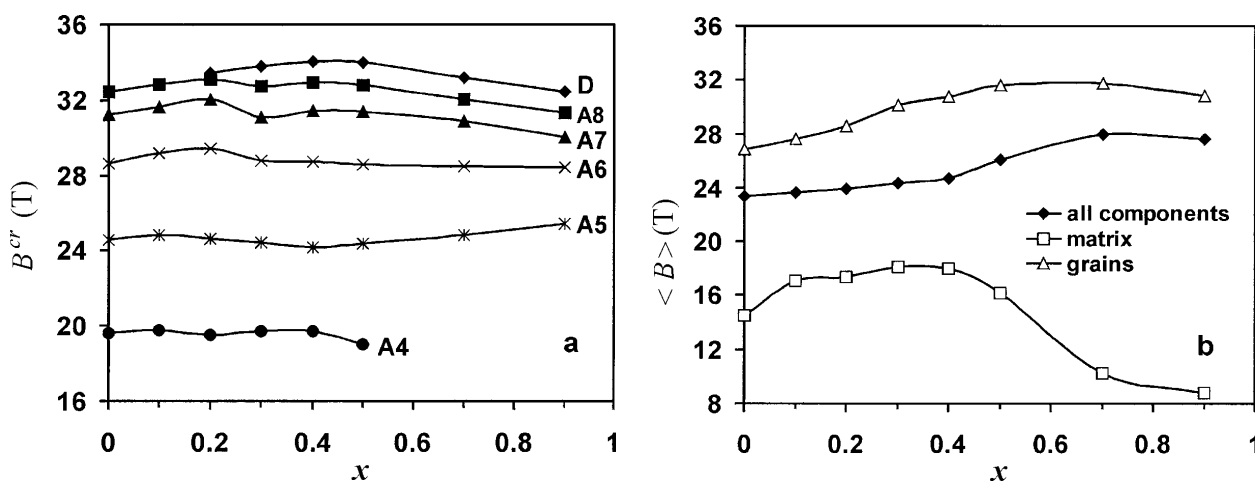In order to evaluate iron concentration in grains, we make the assumption of the homogeneous distribu-

Fig. 3. Hyperfine parameters derived for nanocrystalline $(Fe_{1-x}Co_x)_{73.5}Cu_1Nb_3Si_{13.5}B_9$ vs. the cobalt content: a – magnetic hyperfine field of particular sextets attributed to the crystallites; b – mean MHF over the whole sample and over individual phases (amorphous matrix and crystalline grains).
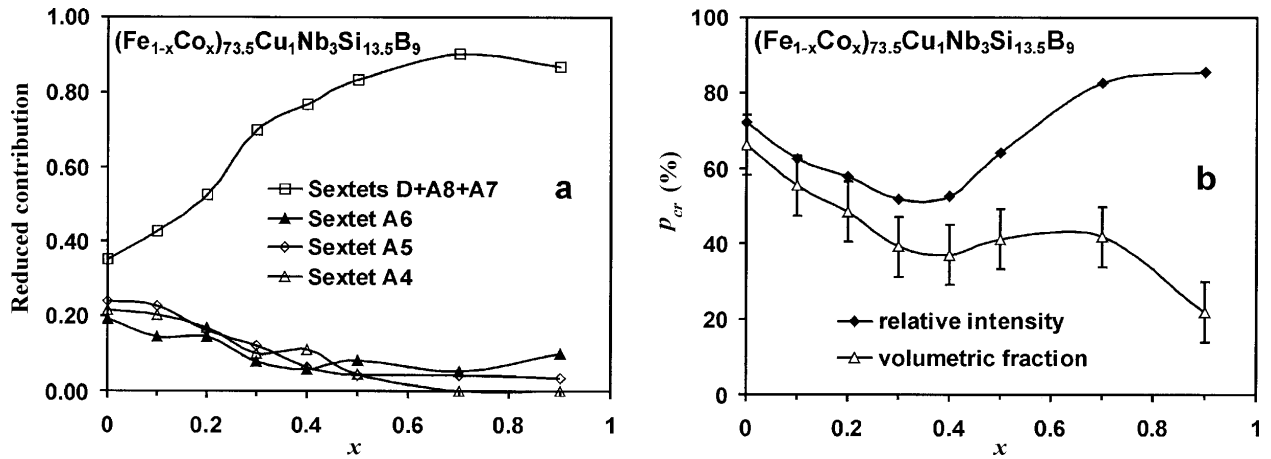
Fig. 4. Evolution of proportions between subspectra: a – reduced contribution of individual sextets to the component attributed to crystalline phase; b – total contribution of "crystalline" components in proportion to the whole spectrum and volumetric fraction of the crystalline phase in the annealed Co-substituted Finemet.

tion of cobalt in the whole sample. Such a result was reported by Borrego *et al.* [1, 2] on the basis of structural and Mössbauer investigations of Finemet substituted by cobalt and also by Zhang *et al.* [19] for alloys of similar composition. Analysing relative intensities of particular subspectra as well as using simple relations representing the balance of elements in the nanocrystalline alloys, the volumetric fraction of crystalline phase and iron content in grains was derived. It was found that iron concentration in crystallites changes from 80 at.% for $x = 0$ to

about 30 at.% for $x = 0.9$. Moreover, it was stated that cobalt substitution of Finemet has a noticeable influence on the crystallization process. The volumetric fraction of crystalline phase is a decreasing function of Co concentration (a slight minimum, observed for x equal to about 0.3÷0.4, can be omitted in the limit of uncertainty, Fig. 4b).

The Mössbauer spectra collected for as-quenched samples of Finemet substituted by vanadium have the form typical of amorphous alloys. The distributions of
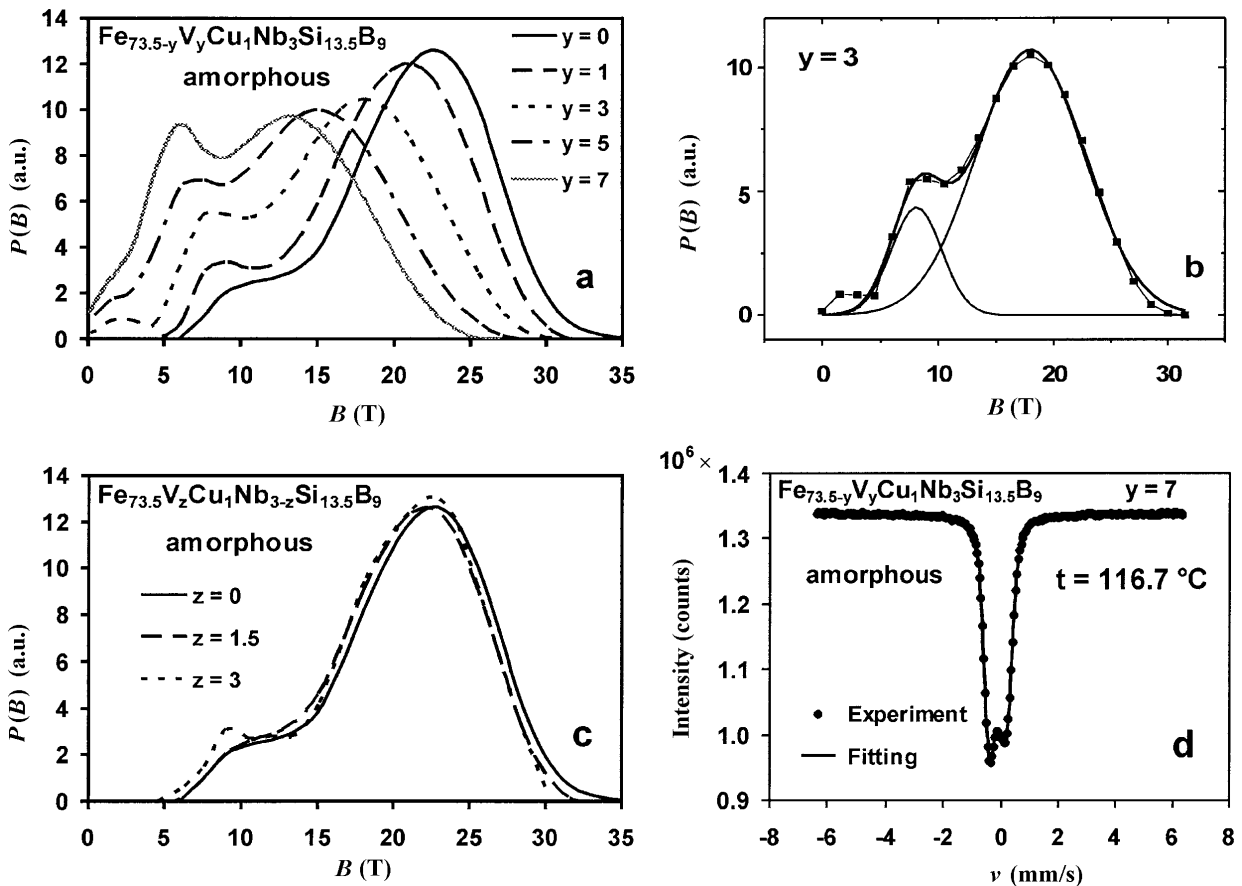

Fig. 5. a, b, c – Magnetic hyperfine field distribution derived for as-quenched Finemet substituted by vanadium (from RT spectra); d – spectrum collected above the Curie temperature.
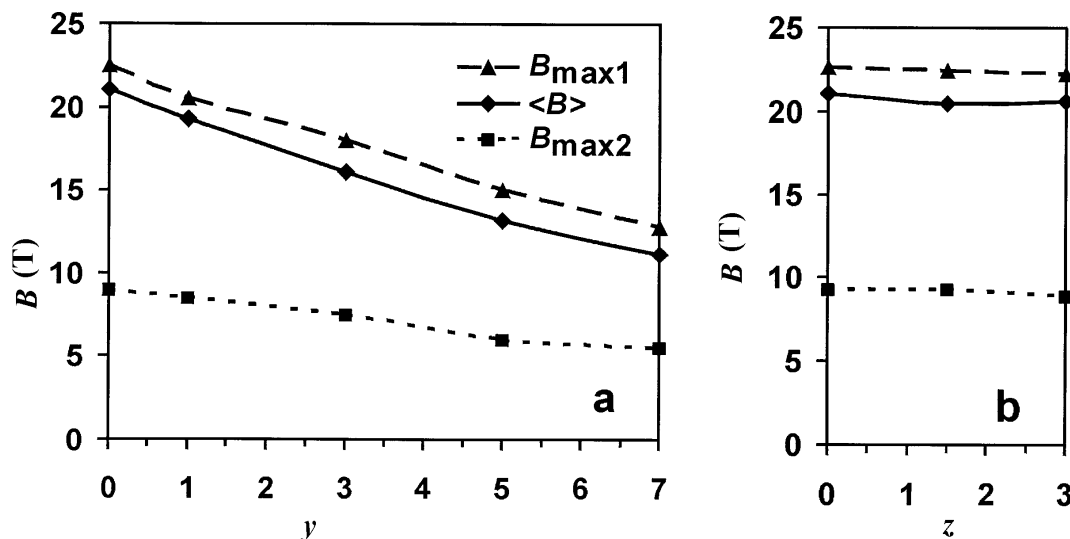
Fig. 6. Mean magnetic hyperfine field $<B>$, and the values corresponding to the first (B_{max2}) and the last (B_{max1}) picks in the hyperfine distribution, derived for as-quenched $Fe_{73.5-y}V_yCu_1Nb_3Si_{13.5}B_9$ (a) and $Fe_{73.5}V_zCu_1Nb_{3-z}Si_{13.5}B_9$ (b) alloys.

magnetic hyperfine field derived for the first series ($Fe_{73.5-y}V_yCu_1Nb_3Si_{13.5}B_9$) take on a bimodal shape with growing low-field component when increasing concentration of vanadium (Fig. 5a,b,c). It should be noticed that low-field maximum observed in the MHF distribution of amorphous alloys is sometimes interpreted as an artefact of the fitting procedure; especially when quadrupole interaction is strong, so FOPT (first order perturbation theory) approximation is not a correct approach. In our case the lower value of the pick position, about 5 T, corresponds to the energy which is considerably larger (about thrice) than the quadrupole interaction derived from spectra collected at elevated temperature – in the paramagnetic state (Fig. 5d). Therefore, FOPT approximation can be used and the maxima in the distribution can be attributed to distinctly different, preferred local environments of iron atoms. One of them is analogous as in classical Finemet; the second is clearly related to iron-poor surrounding. Positions of these two maxima in the distribution as well as mean hyperfine field shift almost linearly with y towards lower values, which is shown in Fig. 6a. In contrast, only slight changes are observed in the case of

the second series, where z vanadium atoms nominally replace the niobium ones (Fig. 6b). A similar tendency is visible in the evolution of isomer shift. This allows to conclude that the most crucial changes result from the diminution of iron content. We suppose that atoms of vanadium are localized in different surrounding, dependently on iron concentration; in iron-rich Finemet they take positions rather distant from iron atoms, therefore they do not influence considerably the hyperfine parameters.

In Mössbauer spectra collected for nanocrystalline Finemet(V), besides magnetically splitted subspectra corresponding to the amorphous matrix and to the nanocrystalline grains, one can distinguish a paramagnetic component (Fig. 7a,b). In order to reproduce this component and obtain a satisfactory fit it is necessary to use a quasi-continuous quadrupole splitting distribution, what proves that the paramagnetic phase is located inside the amorphous matrix. In the first series of nanocrystalline samples a mean value of hyperfine field (averaged over all phases of nanocrystalline samples) drops clearly with vanadium concentration, whereas in the second one it changes much slower (Fig. 8a,b). The
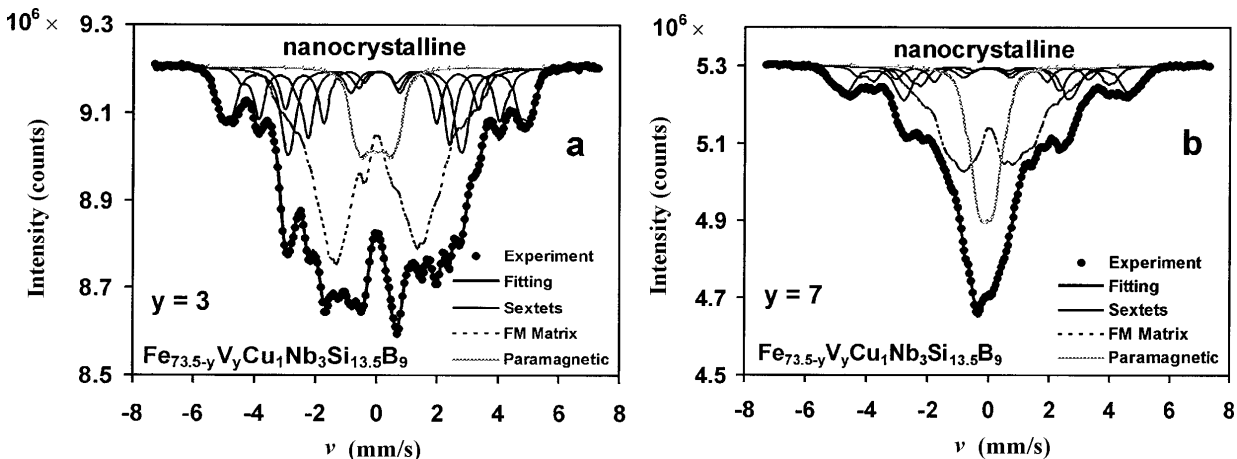

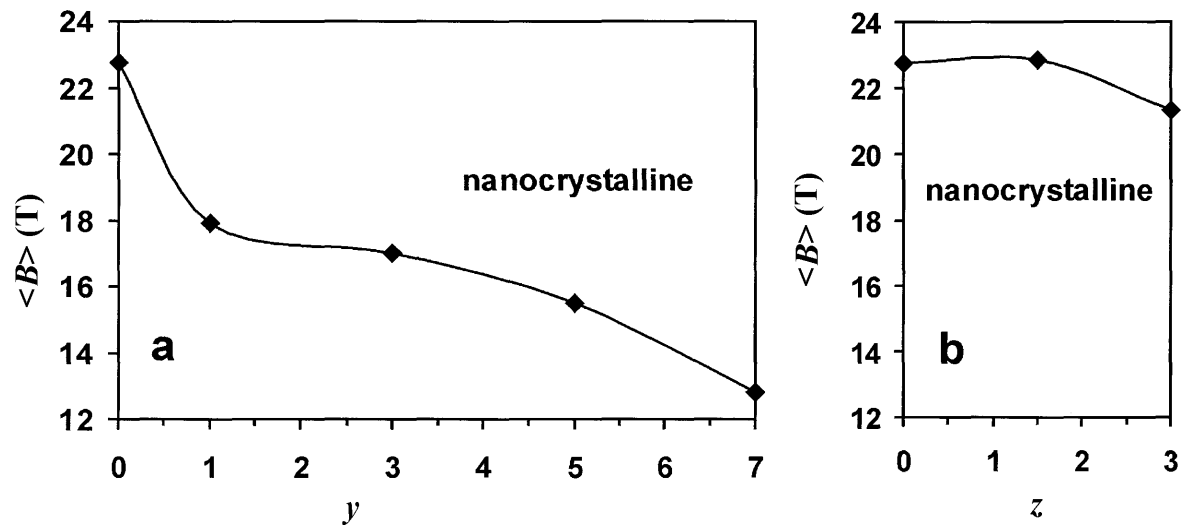**Fig. 7.** Spectra collected for nanocrystalline Finemet substituted by vanadium.

Fig. 8. Mean magnetic hyperfine field, calculated for nanocrystalline $Fe_{73.5-y}V_yCu_1Nb_3Si_{13.5}B_9$ (a) and $Fe_{73.5}V_zCu_1Nb_{3-z}Si_{13.5}B_9$ alloys (b).
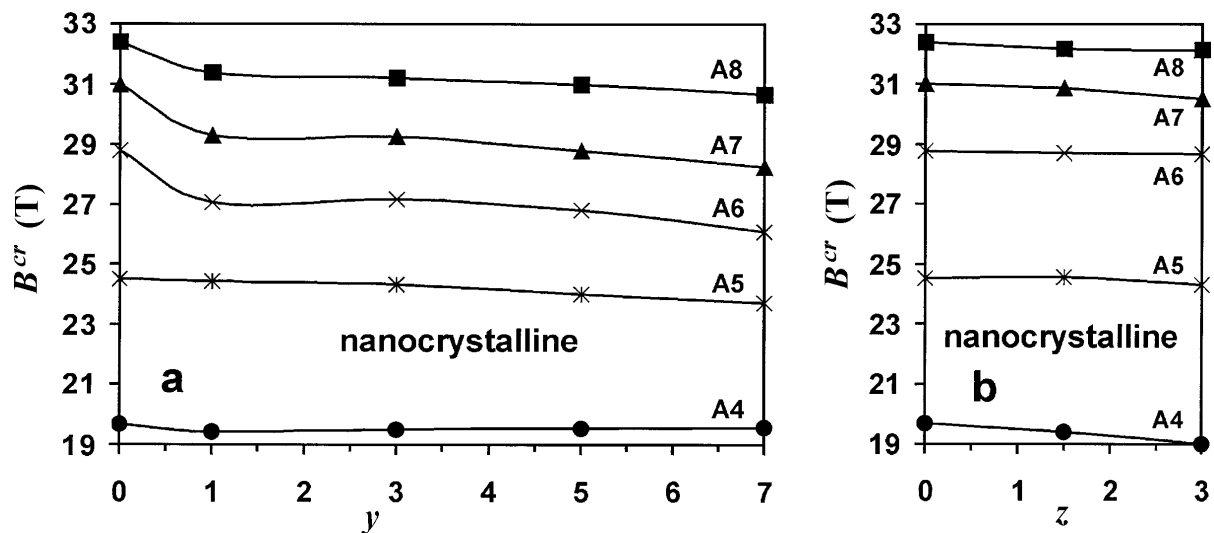

Fig. 9. Magnetic hyperfine field of individual sextets attributed to crystallites (derived for nanocrystalline Finemet substituted by vanadium).
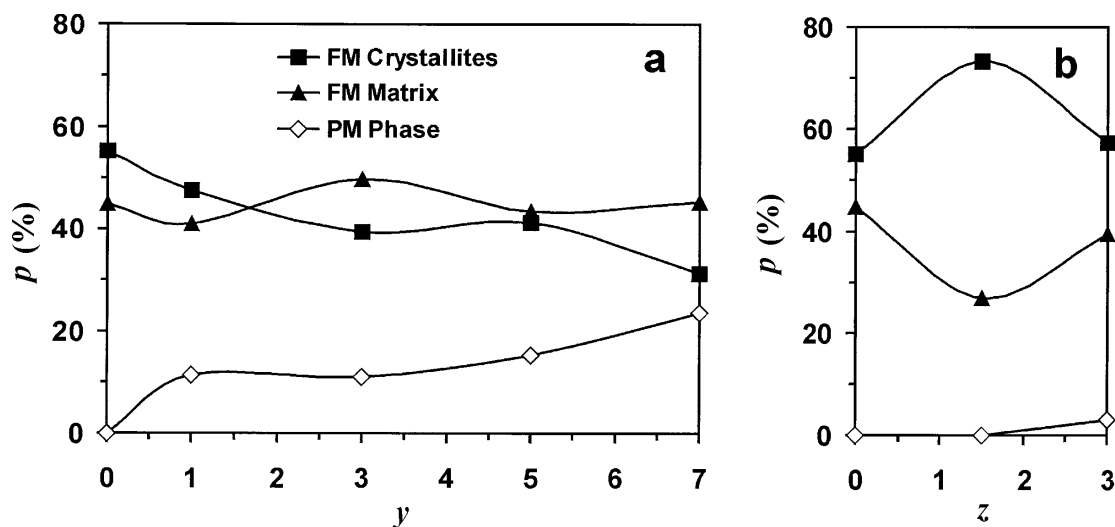

Fig. 10. Relative content of iron atoms in crystallites, ferromagnetic matrix and in the paramagnetic phase (obtained for $Fe_{73.5-y}V_yCu_1Nb_3Si_{13.5}B_9$ and $Fe_{73.5}V_zCu_1Nb_{3-z}Si_{13.5}B_9$).

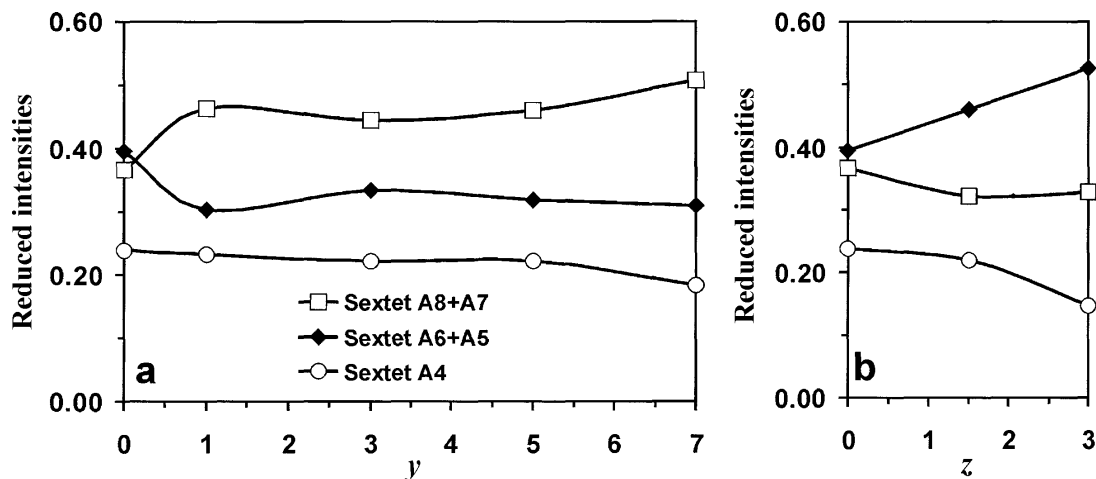**Fig. 11.** Reduced intensities of the components attributed to crystalline phase (obtained for $Fe_{73.5-y}V_yCu_1Nb_3Si_{13.5}B_9$ and $Fe_{73.5}V_zCu_1Nb_{3-z}Si_{13.5}B_9$ alloys). Total contribution of all sextets has been normalized to 1.

analogous behaviour can be observed in the evolution of hyperfine fields of sextets corresponding to the nanocrystalline phase (mainly for sextets A8, A7 and A6 – Fig. 9a,b). Thus one can state that vanadium atoms enter into the grains in the case of the first series. The smaller concentration of iron in these alloys seems to be the key feature which facilitates penetration of vanadium into crystallites. This effect is much slimmer when substituting niobium by vanadium, providing constant iron percentage. It should be underlined that the diminution of mean hyperfine field cannot be explained only in terms of weakening magnetism of nanocrystalline and amorphous constituents but it arises mainly due to the growing contribution of paramagnetic phase observed in both series of samples with increasing percentage of vanadium (Fig. 10a,b). The analysis of proportions between intensities of sextets attributed to the crystalline phase exhibit the growth of sextets A8+A7 as well as decline of intensities of sextets A6+A5 and A4 (Fig. 11a,b). This effect suggests possible alteration of grain structure comparing with classical Finemet.

Conclusions

Substitution of Fe atoms by Co in Finemet results in non-monotonic compositional evolution of magnetic hyperfine field in as-quenched and annealed samples; for $x = 0.5$ the maximal value of MHF is observed. Addition of this element causes alteration of disordered DO_3-type structure of the Fe-Si grains, occurred in classical nanocrystalline Finemet, into b.c.c. (Fe,Co)Si solid solution of low Si concentration. The crystalline phase is rich in iron, in contrast to the amorphous remainder. Replacement of Fe atoms by V ones in nominal composition of Finemet causes diminution of hyperfine magnetic field both in amorphous and nanocrystalline samples. It also induces the creation of paramagnetic phase attributed to iron-poor regions in the amorphous remainder. Substitution of Nb by V atoms modifies hyperfine parameters to less extent. Reduction of iron in the composition of the initial

sample favors infiltration of Co and V into grains in the course of crystallization.

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