

# INFLUENCE OF ANNEALING TEMPERATURE ON MAGNETIC MICROSTRUCTURE OF $\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$ ALLOY

Tomáš Kaňuch — Marcel Miglierini \*

Magnetic microstructure of NANOPERM-type  $\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  alloy is studied by  $^{57}\text{Fe}$  Mössbauer spectroscopy in amorphous and nanocrystalline states. The method used provides detailed a view on structural and magnetic changes induced by heat treatment. The latter was performed in the range from 300 to 550 °C for 1 hour. Mössbauer spectra recorded at room temperature and at the temperature of liquid nitrogen were analyzed by the help of distributions of hyperfine fields and quadrupole splitting. The crystalline phase that evolved after annealing at 450 °C represents iron atoms in bcc arrangement. With increasing the temperature of heat treatment above the first crystallisation stage, different amounts of nanocrystallites were obtained reaching up to 40% of the total volume fraction.

**Keywords:** Mössbauer spectroscopy, nanocrystalline alloys, hyperfine fields

## 1 INTRODUCTION

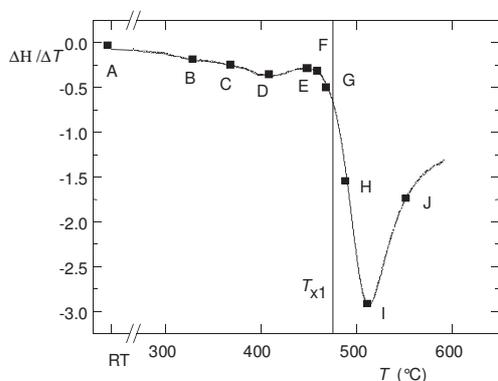
Nanocrystalline materials are interesting for several practical applications, which results from their specific magnetic properties. Generally, the NANOPERM-type alloys have very low energy losses at power frequencies, making them potentially interesting for electrical power distribution transformers. The observed macroscopic characteristics result from the microstructure as well as interactions and arrangement of the compositional atoms. Hence, microscopic methods of analysis should be employed among which Mössbauer spectrometry plays an unmatched role.

The aim of this paper is to study the structure-to-magnetic relationship in a  $\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  alloy and its characteristic dependence upon the annealing temperature, *ie* the amount of nanocrystallites. This particular composition is especially suitable for such studies due to high sensitivity of Mössbauer spectra to structural changes in the vicinity of the magnetic ordering

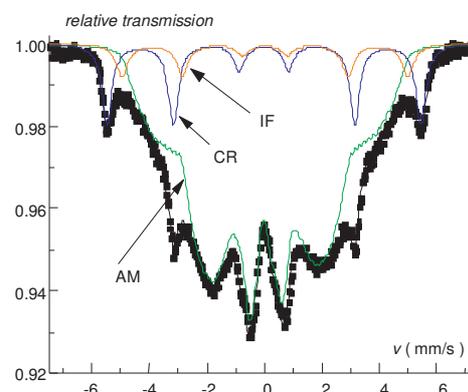
temperature. The latter is close to room temperature ( $T_{\text{Cam}} \approx 310 \text{ K}$  [1]) that allows investigating the interactions between magnetic structures during the crystallization process and below the onset of crystallization. Creation of small crystalline grains with a size of several nanometres that are embedded in a residual amorphous matrix can be easily controlled by the annealing treatment. This allows examining the influence of heat treatment on the magnetic arrangement of both the crystalline and amorphous phases [1, 2].

## 2 EXPERIMENTAL DETAILS

Amorphous ribbons of  $\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  alloy (6 mm wide, 20  $\mu\text{m}$  thick) were prepared by the method of planar-flow casting. Annealing of amorphous precursors was performed in vacuum in the temperature range of 300 – 550 °C for 1 hour. Samples with various amounts of nanocrystallites were thus produced. Temperatures of

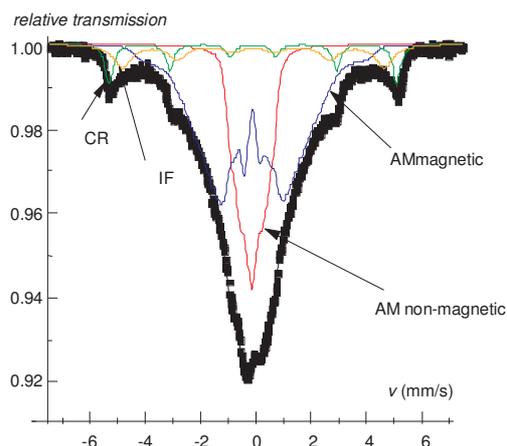


**Fig. 1.** DSC curve with indicated annealing temperatures. The arrow shows the onset of crystallization at  $T_{x1}$ .



**Fig. 2.** Fitting model applied to a low temperature Mössbauer spectrum (sample H annealed at 490 °C — see text).

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**Fig. 3.** Fitting model applied to a room temperature Mössbauer spectrum (sample H annealed at 490 °C — see text).

annealing were chosen according to the results of differential scanning calorimetry (DSC) so that they covered the whole range up to the end of the first crystallization peak. Notation of the samples obtained from heat treatments performed at specific temperatures is shown in Fig. 1.

$^{57}\text{Fe}$  Mössbauer spectra were obtained in transmission geometry using a  $^{57}\text{Co}(\text{Rh})$  source and a spectrometer working with constant acceleration at room and low (77 K) temperatures. Calibration was performed with  $\alpha\text{-Fe}$  and isomer shifts are given relative to the room temperature Mössbauer spectrum of  $\alpha\text{-Fe}$ . Hyperfine parameters of the spectra were refined using the NORMOS fitting software [3].

### 3 FITTING MODEL

Iron based nanocrystalline materials prepared by annealing from amorphous precursors contain well-developed crystalline grains that are embedded in the remaining amorphous phase. Consequently, the corresponding Mössbauer spectra consist of sharp absorption lines superimposed upon a broadened spectral component as seen in Fig. 2. The former belong to the crystalline phase whereas the latter are assigned to the amorphous residuum. As seen from Fig. 2, the inner parts of the outermost sharp lines are broadened which indicates the presence of another component. It can be ascribed to regions between the crystalline grains and the amorphous matrix. We shall denote these atoms as belonging to the so-called interface phase. From the structural point of view, the interface atoms are located on the surface of nanocrystals. Due to symmetry breaking their Mössbauer lines indicate distribution of hyperfine parameters.

The fitting model chosen should represent this physical concept of the structural arrangement as well as interactions between particular components. Distributions of hyperfine fields  $P(B)$  were employed to reconstruct the amorphous (AM) phase. The interface (IF) and crystalline (CR) phases were reconstructed by single sextets.

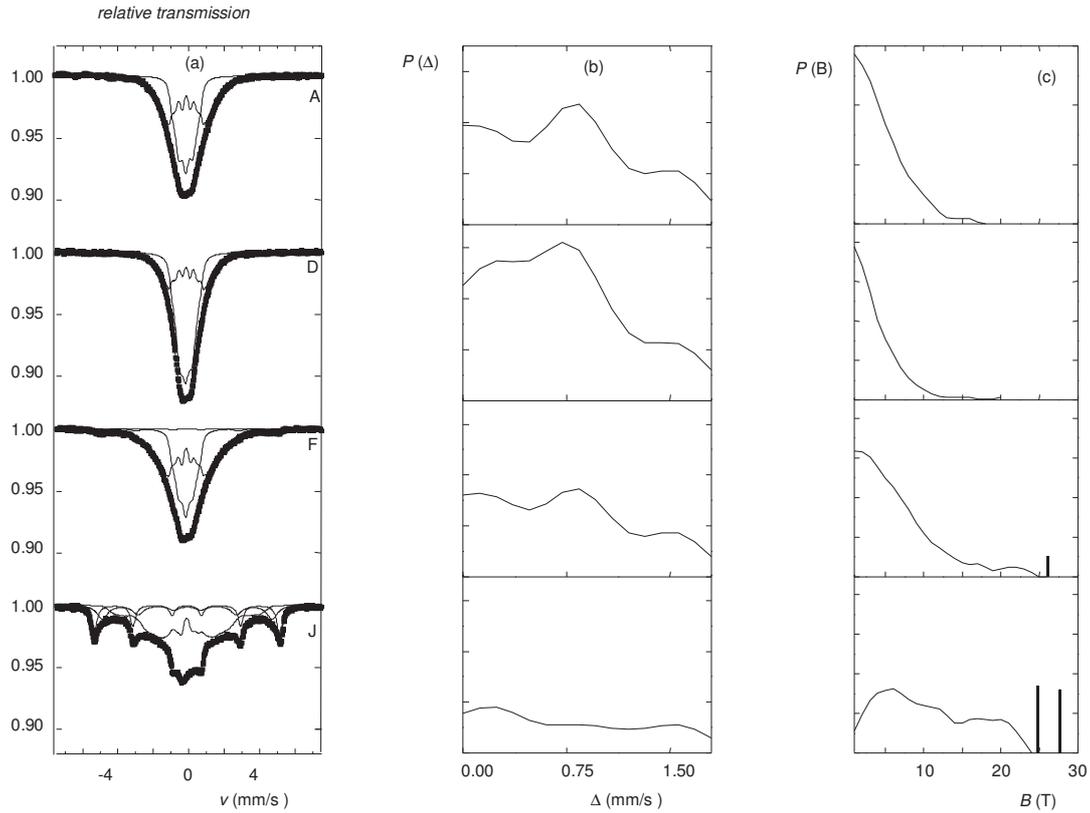
IF was modelled by a discrete subspectrum of broadened Lorentzian lines accounting for the disordered nature of IF atoms. The typical example of a low temperature (77 K) Mössbauer spectrum of the nanocrystalline  $\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  alloy in Fig. 2 shows the particular spectral components.

In room temperature Mössbauer spectra, AM was refined using two distributions — that of hyperfine magnetic fields  $P(B)$  and of quadrupole splitting  $P(\Delta)$  when simultaneous presence of magnetic and non-magnetic regions, respectively, was encountered in a particular sample. This is observed at sufficiently high temperatures (room temperature for this particular sample) when a certain fraction of resonant atoms of AM is already in paramagnetic state. The fitting model accounts for the presence of non-magnetic regions within the amorphous rest by introducing the second distribution of quadrupole splitting. The nanocrystalline  $\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  alloy is only weakly magnetic at room temperature. Thus, the resulting Mössbauer spectrum in Fig. 3 exhibits electric quadrupole interactions demonstrated by a broad asymmetric doublet. Magnetic regions in the amorphous rest with low values of hyperfine magnetic fields are fitted using a distribution of sextets as in the previous case of spectra measured at low temperature.

### 4 RESULTS AND DISCUSSION

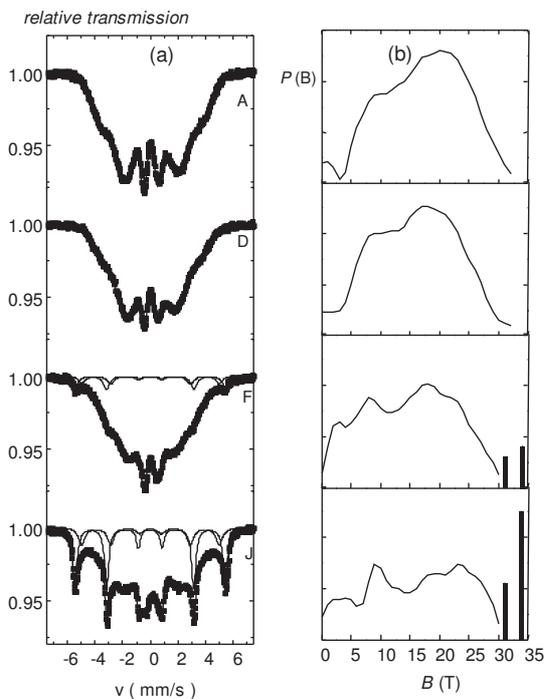
Figure 4 shows typical examples of room temperature (RT) Mössbauer spectra of the  $\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  alloy annealed at temperatures below and above the crystallization point. Corresponding distributions of quadrupole splitting  $P(\Delta)$  and hyperfine magnetic fields  $P(B)$  are depicted on the right-hand panel. Microstructure of specimens A–D (specimens' labels are shown in Fig. 1) contains disordered Fe atoms of an amorphous matrix. Mössbauer spectra exhibit both electric quadrupole and magnetic dipole hyperfine interactions that are characteristic for resonant atoms in the vicinity of the magnetic phase transition. The relative fraction of magnetic ( $A_{\text{BHF}}$ ) and paramagnetic ( $A_{\text{QUA}}$ ) atoms ranges from 51 to 35% and from 49 to 65%, respectively. Magnetic and non-magnetic atoms are homogeneously distributed in the still amorphous matrix. At low temperatures (77 K), one distribution of hyperfine fields was used to refine the AM part of Mössbauer spectra, which are shown in Fig. 5.

Spectral parameters belonging to the amorphous residual phase, namely the average hyperfine field  $\langle B_{\text{AM}} \rangle$ , average quadrupole splitting of the non-magnetic part  $\langle \Delta \rangle$ , and isomer shift  $\langle \delta \rangle$  are plotted as a function of the annealing temperature  $T_a$  in Fig. 6. A systematic decrease in the average values of  $\langle \Delta \rangle$  and  $\langle B_{\text{AM}} \rangle$  at room temperature up to sample C (370 °C) is caused by structural rearrangement of atoms in the amorphous matrix due to moderate thermal treatment well below the onset of crystallization as indicated also by a decline of the DSC curve in Fig. 1. Iron atoms tend to occupy energetically more favourable sites, which lead to changes in the short-range



**Fig. 4.** Room temperature Mössbauer spectra of  $\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  alloy (a) with  $P(\Delta)$  (b), and  $P(B)$  (c) distributions corresponding to non-magnetic and magnetic AM phase, respectively.

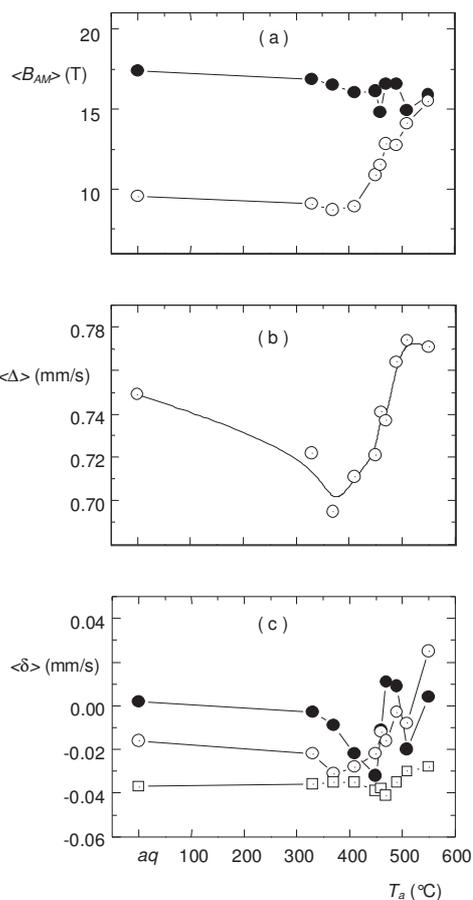
order immediately reflected by the respective spectral parameters.



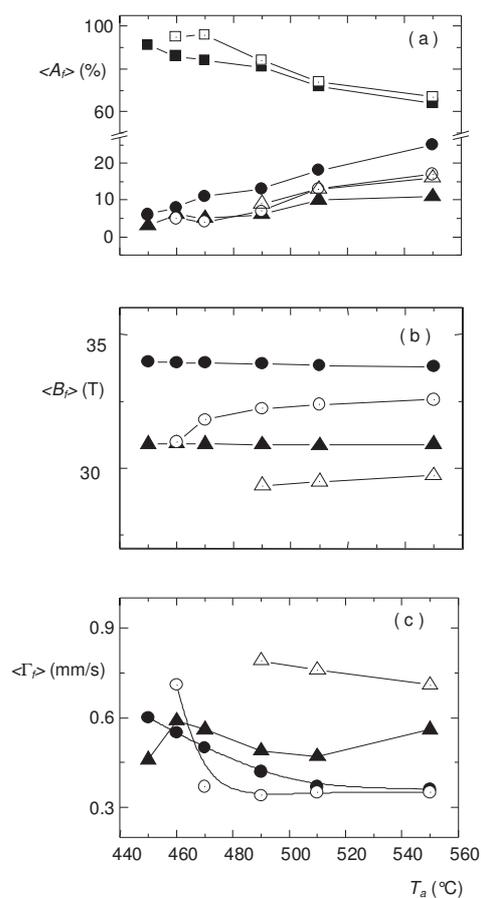
**Fig. 5.** Low temperature (77 K) Mössbauer spectra of  $\text{Fe}_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$  alloy (a) with  $P(B)$  distributions (b) of the AM phase. Vertical lines in (b) correspond to hyperfine fields of the IF and CR phases.

An increase in  $\langle \Delta \rangle$  and  $\langle B_{AM} \rangle$  identified at room temperature for sample D and beyond correlates with the progressive occurrence of nanocrystallites. As the amount of CR rises, the ferromagnetic exchange interactions between the grains are mediated also through the surrounding amorphous residual matrix [4, 5]. Consequently, the average hyperfine field of the latter increases as demonstrated in Fig. 6a. Non-magnetic regions inside AM are also affected giving rise to an increase in  $\langle \Delta \rangle$ , too (Fig. 6b). It is noteworthy that the above mentioned influence of ferromagnetic bcc Fe grains on the remaining amorphous phase can be observed only at room temperature which is close to the Curie point of the original amorphous precursor ( $T_{C_{am}} \approx 310$  K).

According to the DSC curve in Fig. 1, crystallization starts at  $T_{x1} = 475$  °C. Consequently, one expects an amorphous structure after annealing below  $T_{x1}$  and appearance of crystallites when the samples are heat treated above this temperature. Indeed, Mössbauer spectra with some volume fraction of nanocrystallites as for example spectra F and J in Figs. 4 and 5 consist of Lorentzian sextets representing the crystalline phase of bcc-Fe superimposed on a broadened element of the amorphous rest. It is noteworthy that from the Mössbauer effect data the onset of crystallization is revealed already at 450 °C (sample E) as indicated by the measurement at low temperature. On the other hand, at room temperature we can identify the presence of the crystalline phase only at 460 °C (sam-



**Fig. 6.** Average hyperfine field  $\langle B_{AM} \rangle$  (a), quadrupole splitting  $\langle \Delta \rangle$  (b), and isomer shift  $\langle \delta \rangle$  (c) of the amorphous residual phase plotted against temperature of annealing  $T_a$  as derived from room (open symbols — circles: magnetic part, squares — non-magnetic part) and low (77 K) temperature (solid symbols) Mössbauer spectra of Fe<sub>76</sub>Mo<sub>8</sub>Cu<sub>1</sub>B<sub>15</sub> alloy.



**Fig. 7.** Relative area  $A_f$  (a), hyperfine field  $B_f$  (b), and line width  $\Gamma_f$  (c) of spectral components  $f = AM$  (squares), CR (circles), and IF (triangles) plotted against the temperature of annealing  $T_a$  as derived from room (open symbols) and low (77 K) temperature (solid symbols) Mössbauer spectra of Fe<sub>76</sub>Mo<sub>8</sub>Cu<sub>1</sub>B<sub>15</sub> nanocrystalline alloy.

ple F) and distinguishable interface phase appears only in the 490 °C annealed sample (H). This fact can be explained by the temperature dependence of the recoil free fraction reinforced by very small amounts of nanograins in samples E and F.

Quantitative features comprising relative area  $A_f$ , hyperfine field  $B_f$ , and line width  $\Gamma_f$  of spectral components  $f = AM$ , CR, and IF are plotted in Fig. 7 for the nanocrystalline samples E to J. At low temperature of measurement, the ferromagnetic order of the residual amorphous phase is well established and, as a result, hyperfine fields of CR and IF are well defined, too (Fig. 7b). Small fluctuations in magnetic moments that appear at low annealing temperatures, *ie* when the amount of nanograins is very low, are demonstrated by an increased line width reaching about 0.6 mm/s. As the contribution of CR grows, the line width  $\Gamma_{CR}$  gradually decreases to about 0.35 mm/s (Fig. 7c). At room temperature, fluctuations in the position of magnetic moments associated with nanograins are more pronounced. This behaviour is depicted by high  $\Gamma_{CR}$  and low  $B_{CR}$  for

sample F with a very low amount of nanograins. This is actually a limit at which it is possible to resolve the presence of CR phase in the nanocrystalline alloy. For sample E ( $T_a = 450$  °C) this was possible only by measurement at liquid nitrogen temperature. Spectral signal from the CR phase is smeared out completely at room temperature. Systematic vanishing of fluctuations of magnetic moments with a rising contents of nanograins (increasing  $T_a$ ) is observed by continuing growth of BCR at room temperature (Fig. 7b).

## 5 CONCLUSION

Amorphous Fe<sub>76</sub>Mo<sub>8</sub>Cu<sub>1</sub>B<sub>15</sub> alloy is characterized by the magnetic ordering temperature of about 310 K and the temperature of the onset of crystallization of 475 °C. The latter was determined by means of DSC. Mössbauer effect measurements, however, suggest that crystallization starts already at 450 °C. All specimens annealed up to the temperature of the onset of crystallization show at

room temperature a homogenized magnetic microstructure with almost the same relative contents of magnetic and non-magnetic regions in the amorphous matrix. Nevertheless, structural rearrangement of the constituent atoms takes place up to 410 °C.

Beyond the onset of crystallization, the volume of non-magnetic atoms decreases as well as the relative volume fraction of atoms in the amorphous matrix. During the process of crystallization, iron atoms form bcc nanograins. Consequently, regions with new chemical and topological order emerge in the residual amorphous matrix depleted in iron. In addition, atoms of the amorphous remainder located between nanocrystalline grains are influenced by ferromagnetic exchange coupling between them. Consequently, hyperfine magnetic fields of these atoms are increased in spite of a decreased amount of Fe in the amorphous rest. During the first crystallization, nanocrystallites grow mostly in number. Their size is not significantly affected as documented by transmission electron microscopy [1]. From the point of view of magnetic microstructure, significant fluctuation of magnetic moments is observed especially in samples that contain small amounts of nanograins.

#### Acknowledgement

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