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Mössbauer and AC susceptibility study of structurally modified Fe–Ni–Cr–Mo–Si–B-type metallic glasses

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Abstract. The effect of prolonged heat treatment and neutron irradiation on $Fe_{30}Ni_{40}Cr_8Mo_2Si_5B_{15}$ glassy ribbons has been studied by Mössbauer spectroscopy and AC susceptibility measurements. Mössbauer data were fitted considering the asymmetry of the lines using NORMOS DIST programs. Hyperfine field distributions (HFDs) and quadrupole splittings have been constructed by a histogram method. Data obtained from Mössbauer measurements at liquid-nitrogen temperature indicate a bimodal character of $P(H)$ distributions. Neutron irradiation induces changes in atomic rearrangement towards Cr clustering at the iron sites, causing a fall in the average value of a HFD while heat treatment increases the number of Fe atoms with higher magnetic moments. The analysis of the set of AC susceptibility measurements provides direct evidence of changes in Curie temperature due to the sources of structural modifications discussed.

1. Introduction

Chromium-containing metallic glasses (MGs) attract a good deal of interest at present. Their unusual behaviour is subject to detailed investigation by means of various macroscopic and microscopic methods. Among them Mössbauer spectroscopy plays an important role.

In the case of Fe-based MGs the presence of Cr significantly affects the magnetic moments at the Fe site. Consequently, the Curie temperature T_C is reduced according to the Cr content in the sample (Lin *et al* 1987, Hargraves and Dunlap 1988, Auric *et al* 1989, Serfözö *et al* 1990a). Depending on the latter, the ferromagnetic-to-paramagnetic transition often appears earlier than crystallization, contrary to most Fe-based MGs without Cr (Lin *et al* 1987, Kedves *et al* 1987). Here, Mössbauer spectroscopy seems to be a very useful tool which monitors the nearest surroundings of resonant atoms. The hyperfine parameters of Mössbauer spectra sensitively reflect changes in a local short-range order (SRO). In particular, the hyperfine field distribution (HFD), sometimes also called a $P(H)$ distribution, is of a close interest (see, e.g., Rajaram *et al* 1983, Lin *et al* 1987, Miglierini 1990). It is about one order of magnitude more sensitive to deviations in local environment than are the other hyperfine parameters, e.g. quadrupole splitting distribution $P(QS)$ in the case of the paramagnetic behaviour of MGs (Dunlap *et al* 1988).

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However, much discussion has arisen concerning the shape of the HFD of Cr-containing MGs (Whittle *et al* 1982). Its double-peak (bimodal) character is a point of controversy. Boliang *et al* (1984), Stewart and Whittle (1985) or Whittle *et al* (1986) explain the low-field component of a HFD as a consequence of the diminishing iron magnetic moments due to the presence of non-magnetic Cr atoms, whereas Brand (1987a) finds it to be a possible result of an ambiguous fitting procedure owing to strong line overlapping. In fact, such bimodal distributions are out of the validity region proposed by LeCaër *et al* (1984).

The aim of the present paper is to analyse the influence of prolonged heat treatment and neutron irradiation on the local SRO of amorphous $Fe_{30}Ni_{40}Cr_8Mo_2Si_5B_{15}$. We have chosen this MG because its Curie temperature is close to room temperature. Thus, significant changes in Mössbauer spectra of structurally modified samples may be expected even at room temperature. ^{57}Fe Mössbauer room-temperature and liquid-nitrogen-temperature spectra provide bimodal $P(H)$ distributions. These are analysed and discussed also using additional results of low-field AC susceptibility measurements.

2. Experimental details

Samples (thickness, 27 μm; width, 6 mm) of amorphous $Fe_{30}Ni_{40}Cr_8Mo_2Si_5B_{15}$ ribbon were prepared by the melt-spinning method at the Institute of Physics, Slovak Academy of Sciences, Bratislava. Their amorphicity was checked by x-ray diffraction and Mössbauer spectroscopy.

Three specimens were investigated: sample A, as-received or reference sample; sample B, sample annealed at 573 K in an argon atmosphere for 5×10^3 min; sample C, sample after neutron irradiation in a nuclear pile to a total dose of 5×10^{18} neutrons cm^2 by fast and thermal neutrons with a relative ratio of 12:10. The temperature during irradiation did not exceed 345 K.

A conventional constant-acceleration Mössbauer spectrometer with a ^{57}Co(Rh) source was used in transmission geometry. The spectra were recorded at room temperature (295 K) and liquid-nitrogen temperature (78 K). Calibration of the apparatus was performed using a 12.5 μm natural iron foil produced by Amersham.

To fit the Mössbauer spectra the NORMOS DIST program developed by Brand (1987b) was applied. $P(H)$ and $P(QS)$ distributions were constructed by a histogram method (DISTRI = 1) from 33 sextets and 20 doublets, respectively; a linewidth of 0.30 mm s^{-1} was assumed. Spectrum asymmetries were covered by introducing a linear increase in the isomer shift (METHOD = 2 and 6, respectively) and by the parameters related to SRO (I_p, H_{1p}, Q_p and H_{2p}) for magnetically split patterns.

The Curie temperature of the samples was determined by the AC susceptibility measurements. The AC low-field susceptibility was obtained in the temperature range from 78 to 370 K. We used a mutual inductance bridge of Hartshorn type with a driving field of 3 A m^{-1} at 15 kHz.

3. Results and discussion

3.1. Mössbauer measurements

Room-temperature Mössbauer spectra of the amorphous $Fe_{30}Ni_{40}Cr_8Mo_2Si_5B_{15}$ are illustrated in figure 1 along with the corresponding distributions. Fully overlapped and

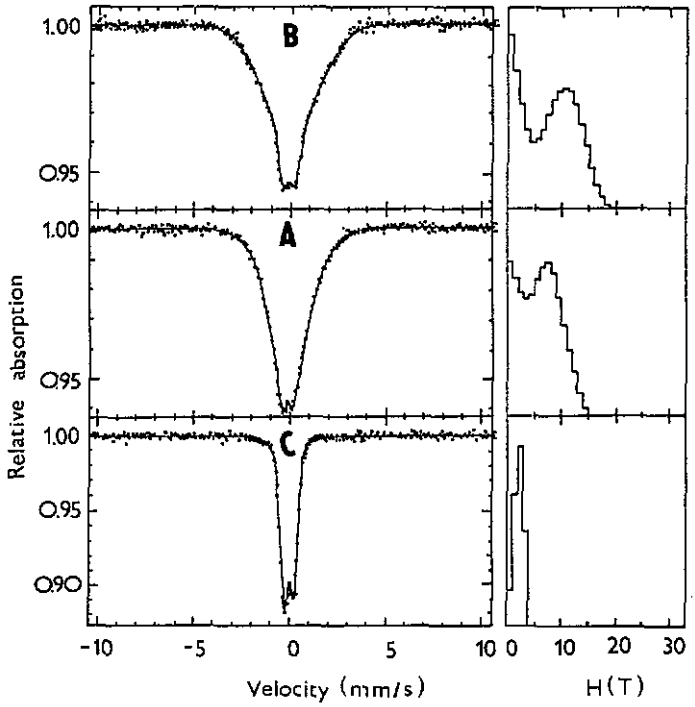

Figure 1. Room-temperature Mössbauer spectra and corresponding HFDs (see text) for amorphous $Fe_{30}Ni_{40}Cr_8Mo_2Si_5B_{15}$: curve A, reference sample A; curve B, sample after an anneal at 573 K for 5×10^3 min (sample B); curve C, sample after neutron irradiation with a total dose of 5×10^{18} neutrons cm^{-2} (sample C).

unresolved patterns, which are expected to be sextets in shape, with very pronounced central parts can be seen for reference sample A and annealed sample B. The latter is somewhat broader, implying that higher field values tend to dominate. On the other hand, the Mössbauer spectrum of the reference sample completely changed its shape after neutron irradiation (figure 1, curve C). No ferromagnetic sextet is presented and only a pure doublet is observed. It should be noted here that the corresponding distribution on the right-hand side of the figure is in fact the quadrupole-splitting distribution $P(QS)$ (Dunlap *et al* 1988).

To examine the samples in the same magnetic state and also for the purpose of quantitative analysis we lowered the temperature down below T_C to 78 K. The observed shape of the liquid-nitrogen-temperature Mössbauer spectra (figure 2) shows that there exists a wide range of hyperfine field values with a noticeable population at low fields. Consequently, the corresponding $P(H)$ distributions depict a bimodal character. It is supposed that the origin of the low-field component in $P(H)$ should be associated with those Fe atoms that are surrounded by a considerable amount of neighbouring Cr atoms. The high-field component is due to those Fe atoms that have primarily Fe, Ni and possibly some Cr as their neighbours (Chien 1979, Lin *et al* 1987).

The calculated values of $P(H)$ parameters and the intensity ratio D_{23} of line 2 to line 3 of the spectrum are collected in table 1. The average value $\langle H \rangle$ of $P(H)$ for the annealed sample B is markedly higher than for the reference sample A. However, a small decrease in $\langle H \rangle$ is observed for the irradiated sample C. The standard deviation

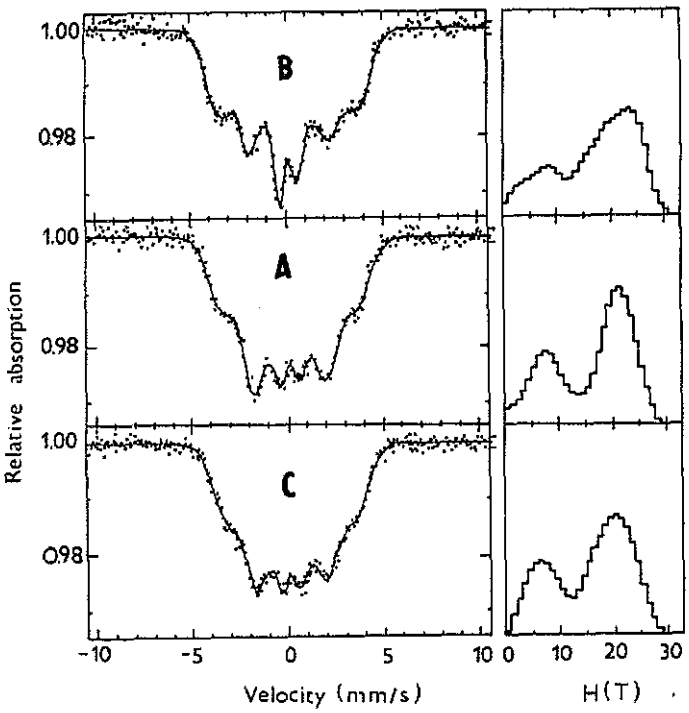

Figure 2. Liquid-nitrogen temperature Mössbauer spectra and corresponding $P(H)$ distributions for amorphous $Fe_{30}Ni_{40}Cr_8Mo_2Si_5B_{15}$: curve A, reference sample A; curve B, sample after an anneal at 573 K for 5×10^3 min (sample B); curve C, sample after neutron irradiation with a total dose of 5×10^{18} neutrons cm^{-2} (sample C).

Table 1. Parameters of the HFDs as derived from room-temperature and liquid-nitrogen-temperature Mössbauer spectra for the $Fe_{30}Ni_{40}Cr_8Mo_2Si_5B_{15}$ MG: $\langle H \rangle$, average value; ΔH, standard deviation; D_{23}, intensity ratio of line 2 to line 3 of the spectra. The numbers enclosed in parentheses show the error in the last digit.

	Room temperature			Liquid-nitrogen temperature		
Sample	$\langle H \rangle$ (T)	ΔH (T)	D_{23}	$\langle H \rangle$ (T)	ΔH (T)	D_{23}
B, annealed	7.1(3)	4.8(7)	1.8(2)	16.8(2)	7.5(1)	1.7(2)
A, reference	5.5(4)	3.6(13)	2.8(4)	15.7(2)	7.2(2)	3.7(4)
C, irradiated	0.53(2)[a]	0.26(4)[a]	—	15.1(2)	7.0(2)	2.9(3)

[a] Values for a quadrupole-splitting distribution where $\langle QS \rangle$ (mm s^{-1}) and ΔQS (mm s^{-1}) should be substituted for $\langle H \rangle$ (T) and ΔH (T), respectively.

ΔH is higher after the heat treatment. Values of D_{23} decreased both after the irradiation and after the heat treatment.

In order to interpret the observed changes in the investigation parameters the possible annealing and neutron irradiation effects on the local SRO around the Fe atoms must be taken into consideration (Morito and Egami 1983, Hargraves and Dunlap 1988,

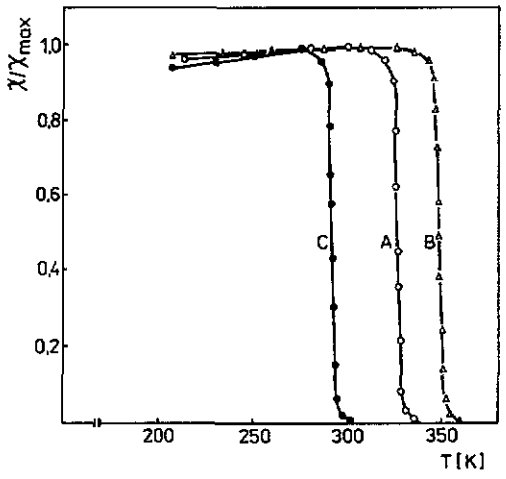

Figure 3. Relative AC magnetic susceptibility χ/χ_{max} versus temperature for amorphous $Fe_{30}Ni_{40}Cr_8Mo_2Si_5B_{15}$: curve A, O, reference sample A; curve B, △, sample after an anneal at 573 K for 5×10^3 min (sample B); curve C, ●, sample after neutron irradiation with a total dose of 5×10^{18} neutrons cm^{-2} (sample C).

Dunlap *et al* 1988). At elevated temperatures, individual atoms become more mobile within the amorphous structure and occupy energetically more favourable sites. The shift of the $P(H)$ peaks towards higher values is then assumed to be due to the possibilities for Ni atoms to occupy more and more Fe nearest-neighbour sites which, consequently, leads to the displacement of Cr and Fe from these sites (Chandra *et al* 1986). The opposite changes in the investigated parameters after neutron irradiation suggest the character of atomic arrangement to be less advantageous from an energetic point of view. We assume that clustering of Cr atoms causes the shift of the $P(H)$ to the left and also increases the low-field tail.

The influence of neutron irradiation on the magnetic structure can be demonstrated by the decrease in the intensity ratio D_{23} (see table 1). Since D_{23} reveals the relative orientation between γ-rays and the magnetic moment, information about the orientation of the net magnetic moment can be obtained. The decrease in D_{23} indicates the tendency of the moment to turn out of the ribbon plane. We suppose that in sample C this behaviour is due to spin reorientation around the stress centres as a result of mixing of atoms after the irradiation (Kuzmann and Spirov 1986, Serfözö *et al* 1990b). Although bulk Mössbauer experiments revealed no crystalline phases in the irradiated sample, a contribution from the partially crystallized surface layers to the discussed effect cannot be unambiguously ruled out (Hayashi *et al* 1989). The observed decrease in D_{23} for sample B can also be ascribed to surface crystallization owing to the prolonged heat treatment (Gupta *et al* 1990).

3.2. Low-field AC susceptibility measurements

The influence of annealing- and neutron-irradiation-induced structural modifications on the temperature variations in the low-field AC magnetic susceptibility χ of amorphous $Fe_{30}Ni_{40}Cr_8Mo_2Si_5B_{15}$ is demonstrated in figure 3. The values of the Curie temperature were taken as the points of inflection at the ferromagnetic transitions. We have obtained ordering temperatures of 327 K, 348 K and 292 K for the reference (as-received) sample A, annealed sample B and irradiated sample C, respectively.

The observed changes in T_C may be associated with some deviations in topological and chemical SRO around the magnetic atoms. The possible mechanism responsible for

the above-mentioned changes is the increase in the population of preferred Fe–Ni pairs with respect to the unpreferred Fe–Cr pairs in the annealed sample B. The opposite is true for the irradiated sample C, where the population of Fe–Cr pairs seems to dominate that of Fe–Ni pairs (Morito and Egami 1983, Škorvánek *et al* 1988).

4. Conclusions

The combined use of Mössbauer spectroscopy and AC susceptibility measurements has given complementary results in elucidating some of the factors which govern the magnetic structure of the $Fe_{30}Ni_{40}Cr_8Mo_2Si_5B_{15}$ MGs.

The Mössbauer spectra of reference, annealed and neutron-irradiated samples have been recorded both at room temperature and liquid–nitrogen temperature. They have been fitted under the assumptions of Brand's model and double-peak HFDs have been obtained. The only exception is the room-temperature Mössbauer spectrum of the neutron-irradiated sample. It is created by a pure paramagnetic doublet and that is why a quadrupole-splitting distribution should be considered. However, lowering the temperature of the experiment below T_C enabled us to study $P(H)$ distributions in all cases.

From the average field values obtained, together with the qualitative analysis of the HFDs as well as the results of the AC susceptibility measurements we conclude that

(i) the number of iron atoms with higher magnetic moments increases after prolonged heat treatment,

(ii) irradiation of the glass by neutrons leads to a rearrangement of the atoms towards clustering of Cr in the vicinity of iron atoms, implying a fall in the average HFD value, and

(iii) both these sources of structural modifications influence the Curie temperature in opposite ways.

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References

Auric P, Greneche J M, deBouvier O and Rameau J J 1989 *J. Magn. Magn. Mater.* **82** 243–8
Boliang Yu, Coey J M D, Olivier M and Ström-Olsen J O 1984 *J. Appl. Phys.* **55** 1748–50
Brand R A 1987a *Nucl. Instrum. Methods* B **28** 398–416
—— 1987b *NORMOS Programs, Internal Report* Angewandte Physik, Universität, Duisburg
Chandra G, Rajaram G, Prasad S, Srinivas V, Shringi S N and Krishnan R 1986 *Hyperfine Interact.* **27** 305–8
Chien C L 1979 *Phys. Rev.* B **19** 81–6
Dunlap R A, Lawther D W, Hargraves P and Sinclair P 1988 *J. Phys. F: Met. Phys.* **18** 2479–86

Gupta A, Habibi S, Lal S and Principi G 1990 *Hyperfine Interact.* **55** 967–72
Hargraves P and Dunlap R A 1988 *J. Magn. Magn. Mater.* **75** 378–82
Hayashi N, Toriyama T, Sakamoto I and Hisatake K 1989 *J. Phys.: Condens. Matter* **1** 3849–58
Kedves F J, Hordós M, Potocký L, Kisdi-Koszó E and Kováč J 1987 *Phys. Status Solidi* a **103** 273–80
Kuzmann E and Spirov I N 1986 *Hyperfine Interact.* **29** 1175–8
LeCaër G, Dubois J M, Fischer H, Gonser U and Wagner H G 1984 *Nucl. Instrum. Methods* B **5** 25–33
Lin S T, Jang L Y and Chiang D P 1987 *J. Phys. F: Met. Phys.* **17** 1231–42
Miglierini M 1990 *J. Mater. Sci. Lett.* **9** 497–9
Morito N and Egami T 1983 *IEEE Trans. Magn.* **MAG-19** 1901–3
Rajaram G, Prasad S, Chandra G, Shringi S N and Krishnan R 1983 *Phys. Lett.* **98A** 57–9
Serfözö G, Kisdi-Koszó E, Slawska-Waniewska A, Potocký L, Joneliunas S and Baran M 1990a *Phys. Status Solidi* a **118** 307–10
Serfözö G, Kiss L F, Daróczi Cs S, Kisdi-Koszó E, Vértesy G and Slawska-Waniewska A 1990b *IEEE Trans. Magn.* **MAG-26** 1418–20
Škorvánek I, Idzikowski B, Zentko A and Mosiniewicz-Szablewska E 1988 *Phys. Status Solidi* a **108** 747–51
Stewart A M and Whittle G L 1985 *Rapidly Quenched Metals (Würtzburg)* ed S Steeb and H Warlimont (Amsterdam: Elsevier) pp 553–6
Whittle G L, Campbell S J and Stewart A M 1982 *Phys. Status Solidi* a **71** 245–51
Whittle G L, Stewart A M and Kaiser A B 1986 *Phys. Status Solidi* a **97** 199–211