LETTER TO THE EDITOR

Inter-grain coupling in nanocrystalline soft magnets

T Kemény†, J Balogh†, I Farkas‡, D Kaptás†, L F Kiss†, T Pusztai†‡,
L Tóth§ and I Vincze†‡

† Research Institute for Solid State Physics, H-1525 Budapest, POB 49, Hungary
‡ Department of Solid State Physics, Eötvös University, Budapest, Hungary
§ Research Institute for Technical Physics of the Hungarian Academy of Sciences, Budapest, Hungary

Abstract. The magnetic coupling between nanosize ferromagnetic *bcc* crystalline grains embedded in a residual amorphous matrix was studied by ^{57}Fe Mössbauer spectroscopy in nanocrystalline Fe–Zr–B–Cu alloys studied above the Curie temperature of the amorphous phase. It is shown that the ferromagnetic coupling is mediated via an about two atomic layer thick interface region between the nanocrystallites.

The study of the coupling between ferromagnetic layers via nonmagnetic spacer layers has both scientific and technological importance. The discovery of the giant magnetoresistance [1] has opened the way to applications in magnetic devices such as magnetoresistive heads and sensors. From indirect (i.e. magnetization) studies the coupling was found [2] to depend in an oscillatory way on the layer thickness of the spacer. Recently very good soft magnetic materials with high initial magnetic permeability and low coercivity have been found [3] consisting of nanosize ferromagnetic granulates embedded in an amorphous matrix. Their excellent magnetic properties are explained by the assumption of a similar mechanism. The nanocrystalline Fe–Cu–Nb–Si–B (i.e. FINEMET) and Fe–Zr–B–Cu alloys [3, 4] belong to this class of materials. These nanocrystalline alloys are prepared by partial crystallization of amorphous ribbons resulting in nanosize crystalline *bcc* precipitates in a residual amorphous matrix. The very good soft magnetic properties of these alloys are often attributed [3, 5] to the exchange interactions mediated by the intergranular amorphous matrix between the adjacent dispersed ferromagnetic grains. This hypothesis would involve two consequences: an enhancement and a considerable smearing out of the Curie temperature of the amorphous interphase [5]. In the following these interactions will be studied by a local probe, i.e. by ^{57}Fe Mössbauer spectroscopy in nanocrystalline Fe–Zr–B–Cu alloys.

These chemically and magnetically heterogeneous systems have been extensively studied by Mössbauer spectroscopy [6–9]. The majority of the measurements were performed at room (or lower) temperatures and the results are controversial concerning the structure of the nanocrystalline *bcc* phase and the interfacial zones. This is not surprising, since even in binary alloys the interpretation of the spectra of ultrafine grained materials prepared by ball-milling is far from simple [10]. The comparison of the spectra of bulk and nanophase *f cc* alloys gives an upper limit of approximately 0.5 nm for the average grain-boundary widths [11]. The present work is aimed at investigating the magnetic coupling of granular materials composed of nanograins with different compositions and atomic structures.

The nanocrystalline samples (ncFe$_{86}$Zr$_7$B$_6$Cu$_1$ and ncFe$_{90}$Zr$_7$B$_2$Cu$_1$) studied were produced by a one hour heat treatment (at 625 °C and 650 °C, respectively) of the
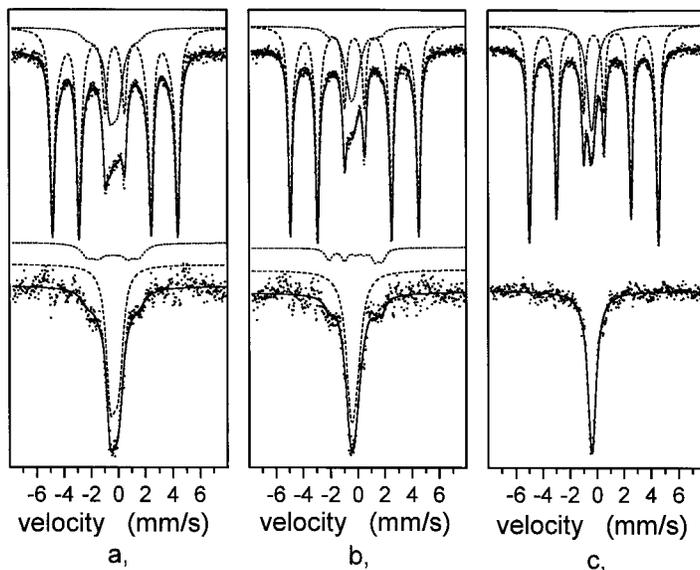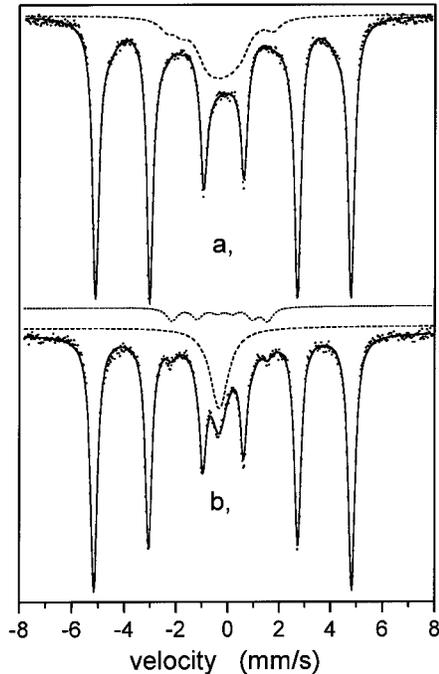
Figure 1. Mössbauer spectra of $ncFe_{84}Zr_7B_6Cu_1$ and $ncFe_{90}Zr_7B_2Cu_1$ taken above T_c^a at $T = 650$ K in the as-formed nanocrystalline state (a and b, respectively) and for $ncFe_{90}Zr_7B_2Cu_1$ after the 900 K annealing (c). The full lines are the fitted curves, their nanocrystalline component and their residual part are marked with the broken and dotted lines, respectively. In the lower half of the figure the residual spectra obtained after the subtraction of the nanocrystalline components are shown and in the as received states the components attributed to the residual amorphous phase (broken line) and to the boundary region (dotted line) are also shown.

amorphous ribbons prepared by melt spinning in protective atmosphere. The second stage of crystallization starts at about 1000 K under dynamic heating. The present treatment was chosen since it results in the maximum initial permeability. The nanocrystalline state of the alloys was checked by x-ray diffraction and transmission electron microscopy (TEM) studies. These confirmed the formation of 10–15 nm large ferromagnetic *bcc* grains. The soft magnetic properties were monitored during the nanocrystallization [12] and were in good agreement with literature data [13].

The Mössbauer measurements were performed between 4.2 and 900 K using a conventional constant acceleration spectrometer with a 50 mCi $^{57}CoRh$ source at room temperature.

Mössbauer spectra of $ncFe_{84}Zr_7B_6Cu_1$ and $ncFe_{90}Zr_7B_2Cu_1$ measured at 650 K are shown in figures 1(a), (b) and 2(a), respectively. The spectra shown in figure 1(a) and (b) are taken well above the Curie temperature of the residual amorphous matrix, T_c^a. Three features can be well distinguished in the spectra: an asymmetric narrow sextet attributed to the *bcc* nanocrystals, a central paramagnetic component belonging to the residual amorphous phase and a small magnetically split component with a low hyperfine field which will be shown to originate from the interfacial layer.

The Mössbauer parameters (isomer shift, IS_m and hyperfine field, B_m) of the strongest narrow sextet which will be referred as the main line are similar to those of pure *bcc* Fe but B_m decreases somewhat faster with increasing temperature than the hyperfine field of pure *bcc* Fe. The main line has a shoulder on the low-field side which is quite broad and its hyperfine field, B_s follows closely the temperature dependence of B_m in a broad

Figure 2. Mössbauer spectra of ncFe$_{90}$Zr$_7$B$_2$Cu$_1$ taken below T_c^a at $T = 550$ K in the as-formed nanocrystalline state (a) and after the 900 K annealing (b). The full lines are the fitted curves, in (a) the residual part beside the nanocrystalline components is marked with a broken line; in (b) the components attributed to the residual amorphous phase (broken line) and to the crystallized boundary region (dotted line) are shown.

temperature range [12]. Since the same shoulder structure and temperature behaviour is observed in the melt-quenched microcrystalline Fe–Zr solid solution [12], we suppose that the nanocrystalline *bcc* Fe phase contains about 2 at.% Zr and a limited amount of B dissolved in the *bcc* structure. Magnetic measurements also indicate that the Curie temperature of the nanocrystalline phase is lower than that of pure *bcc* Fe [14]. In this Fe-rich nanocrystalline solid solution, B_m is the hyperfine field of Fe atoms with no Zr or B nearest and next nearest neighbours, while B_s is the average hyperfine field of Fe atoms with at least one impurity neighbour in the first two co-ordination shells. At higher temperatures the amplitude and the linewidth of the shoulder contribution is gradually reduced and its hyperfine field B_s approaches that of the main line, $B_m(T)$. The process starts above ≈ 650 K and is not completely finished even after two days treatment at 900 K. The observed effects are due to the relatively long measuring times (1–2 days at each temperature) which induce irreversible changes; rearrangement and diffusion of the impurities causes the approach of $B_s(T)$ to $B_m(T)$.

After subtraction of the nanocrystalline contributions (B_m and B_s) the remaining spectrum is shown in the lower half of figures 1(a) and (b), respectively. It consists of a broad central line and a broad sextet with a small hyperfine field (≈ 12 T). Below the Curie temperature of the residual amorphous phase only a broad structure characterized by a hyperfine field distribution was observed, as shown in figure 2(a). The Curie temperature of the residual amorphous matrix ($T_c^a = 430$ and 567 K [15] for ncFe$_{86}$Zr$_7$B$_6$Cu$_1$ and
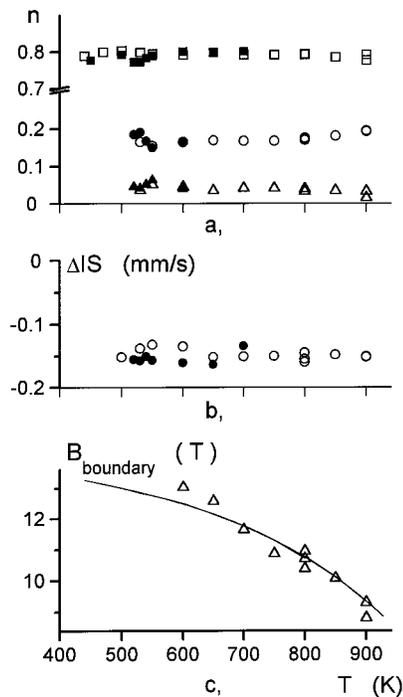
Figure 3. Temperature dependence of the Mössbauer parameters of $nc\text{Fe}_{90}\text{Zr}_7\text{B}_2\text{Cu}_1$ in the as-formed nanocrystalline state (empty symbols) and after the 900 K annealing (full symbols). The relative amount of Fe atoms in the nanocrystalline *bcc* phase (squares), in the residual amorphous phase (circles), in the boundary region (empty triangle) and after its crystallization (full triangles) are shown in (a). $\Delta IS = IS_m - IS_{am}$, the difference between the isomer shifts of the main nanocrystalline line (IS_m) and the residual amorphous phase (IS_{am}), is shown in (b). The temperature dependence of the hyperfine field of the boundary region, $B_{boundary}$ is shown to follow that of the main nanocrystalline component B_m (continuous line) in (c). The results of three independent measurements at 800 K show the typical statistical and systematical errors of the evaluation.

$nc\text{Fe}_{90}\text{Zr}_7\text{B}_2\text{Cu}_1$, respectively) was determined from the B_a^3 versus T plot, where B_a is its average hyperfine field. Around these temperatures no unusual behaviour can be found in the soft magnetic properties (initial permeability, coercivity) [16]. In contrast to the findings of Randrianantoandro *et al* [17] for Cr containing FINEMET alloys, anomalous behaviour is not observed [15] at this temperature in the hyperfine parameters of the *bcc* phase. Detailed data will be given for $nc\text{Fe}_{90}\text{Zr}_7\text{B}_2\text{Cu}_1$. Figure 3(a) shows that above T_c^a the relative amount of Fe atoms contributing to the broadened central line and to the nanocrystalline phase remains temperature independent. The large fraction of the *bcc* nanocrystals corresponds to a very close packing; the nanocrystalline spheres practically touch each other. $\Delta IS = IS_m - IS_{am}$, the difference between the isomer shift of the main nanocrystalline line (IS_m) and this central line (IS_{am}), is shown in figure 3(b). The large negative value of ΔIS (about -0.15 mm s^{-1}) reflects Zr-rich environments and supports the conclusion that the broadened central line above T_c^a belongs to the paramagnetic residual amorphous phase.

The third characteristic feature of the spectra in figures 1(a) and (b) is the appearance of a weak broad sextet with small hyperfine field. This component could not be
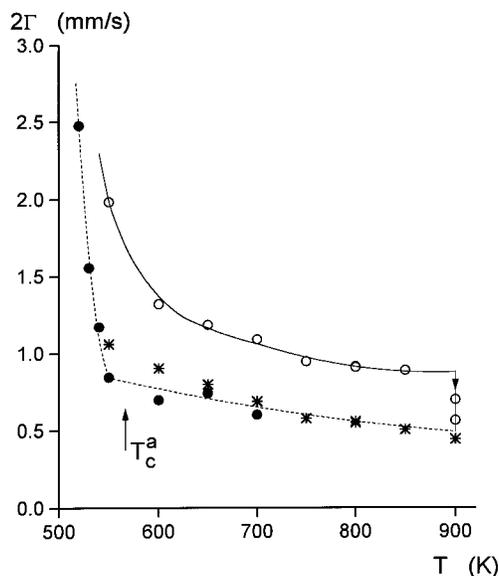
Figure 4. Temperature dependence of the linewidth of the residual amorphous phase in the as-formed state (open circles) and after the 900 K annealing (full circles). The stars correspond to the linewidth in the as-formed state obtained after the removal of the broadening due to the inner field of the magnetic domains, see text. The continuous and dotted lines are guides to the eye.

identified by measurements below T_c^a since it strongly overlaps with the amorphous subspectra. Approximately 4% of the Fe atoms contribute to this feature and this amount is temperature independent up to 900 K within the considerable statistical and systematical errors (figure 3(a)). The hyperfine field corresponding to this component is denoted by $B_{boundary}$ and it is plotted as a function of temperature in figure 3(c). $B_{boundary}(T)$ follows closely the temperature dependence of the B_m nanocrystalline component. The value of $B_{boundary}$ extrapolated to 0 K using the temperature dependence of $B_m(T)$ is about 13 T, i.e. the magnetic moment of these Fe atoms is about 1 μ_B which means Zr-rich iron environments. This is also supported by its negative isomer shift with respect to the main line. The characteristic size of the nanocrystallites is about 10–15 nm, thus on the basis of its intensity the $B_{boundary}$ component corresponds to Fe atoms which form about two atomic layers on the boundary of the nanocrystalline grains and are directly exchange coupled to the ferromagnetic nanocrystallites.

The width of the broadened central line corresponding to the paramagnetic residual amorphous phase (figure 4) shows temperature dependent broadening which is attributed to an about 1.5–2 T internal magnetic field originating from the large ferromagnetic domains. A similar value of internal magnetic field was found in an *nc*FeSiBNbCu alloy by the small angle neutron scattering (SANS) technique [18]. This paramagnetic line of the amorphous phase significantly narrowed for prolonged measurement at 900 K (which means ≈2 days annealing). This narrowing is accompanied by other remarkable changes in the Mössbauer spectrum as shown for $T = 650$ K in figure 1(c). The B_s and the $B_{boundary}$ components have practically disappeared, while the intensity of the B_m component has increased. In this annealed state a new magnetically split component appeared as shown for $T = 550$ K in figure 2(b). The relative amount of Fe atoms in the nanocrystalline grains and in the residual

amorphous phase remained unchanged, the intensity of the new crystalline component is identical with that of the former $B_{boundary}$ component (figure 3(a)). The Curie temperature of the new crystalline phase is between 600 and 650 K. The composition of the residual amorphous phase has not changed due to this annealing process as the value of ΔIS is unchanged (figure 3(b)). On the other hand, although the temperature of the paramagnetic–ferromagnetic transition of the amorphous phase has not changed significantly, it has become sharper and the linewidth of the residual amorphous phase narrower as shown in figure 4. The narrowing of the linewidth might be explained by the absence of the internal magnetic fields, which would also explain the sharper transition. The possible cancelling of the magnetic stray fields of the ferromagnetic domains indicates a change in the domain structure which needs further investigations.

These results are supported by the x-ray and TEM data. According to the x-ray data the average grain size has increased less than 30–35% after the 900 K annealing. The appearance of a small amount of new crystalline phase was also confirmed. It was identified as Fe_3Zr [19] on the base of the TEM measurements.

In the present work a formerly not identified component was found by Mössbauer measurements above the Curie temperature of the residual amorphous phase. On the basis of its atomic fraction it is supposed to form an approximately two atomic layer thick interface of substantial Zr content on the surface of the *bcc* nanocrystalline grains. The dense packed ferromagnetic nanocrystallites are magnetically coupled via this interface layer which is manifested in the temperature dependence of its hyperfine field. Annealing below the crystallization temperature of the residual amorphous phase results in the rejection of Zr (and B) from the nanocrystalline grains and in the crystallization of this interface region. The characteristic properties (isomer shift, hyperfine field, Curie temperature) of the amorphous phase do not change and the grain size remains in the nanocrystalline range during the anneal. In the paramagnetic temperature range only the effect of the stray magnetic fields (less than 2 T) was observed in the residual amorphous phase. No evidence was found for the magnetic coupling through the amorphous phase as the corresponding polarizing effect is definitely not observed in the Mössbauer spectra. This way the good soft magnetic properties should be connected to the interfacial layer and the deterioration of these properties is due to the transformation of this layer into a small amount of hard magnetic phase ($Fe_3Zr/B/$) and due to the consequent change in the domain structure.

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