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Amorphous Fe–B alloys in B–Fe–Ag multilayers studied by magnetization and Mössbauer measurements

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ABSTRACT

Bulk and local magnetic properties were studied in [1 nm B + 1 nm ^{57}Fe + x nm Ag]$_5$, x = 1, 2, 4, 5 and 10, multilayer samples. Although Ag does not mix with either of the other two elements the magnetic properties of the multilayers are strongly influenced by the Ag thickness below x = 5, whereas no such effect is observed above this value. The Mössbauer measurements indicate a complete amorphization of the thin Fe layers in each sample, as a result of intermixing with the B layers. The variation of the magnetic properties is explained by the variation of the average B concentration of the amorphous Fe–B layers, which depends on the thickness of the Ag barrier layers. The magnetization measurements indicate ferromagnetic behaviour of the ultra-thin amorphous layers with the presence of less than 10% superparamagnetic moments for x = 5 and 10. The average B concentration of the amorphous Fe–B alloy, as estimated from the Fe hyperfine fields, is around 40 at%. It is significantly lower than the 60 at% nominal B concentration, suggesting the presence of an unalloyed B layer, as well. This picture is supported by transmission electron microscopy investigations which reveal two amorphous layers of different B concentration in between the crystalline Ag layers.

1. Introduction

The physical properties of nanometer scale multilayers differ significantly from those expected on the base of averaging over the constituents. The difference is caused partly by the reduced scale (i.e. the increased ratio of the surface atoms with respect to the bulk) and partly by the formation of interface layers. The structure, size and chemical composition of the interface layer is of great importance both from theoretical and practical point of view. They influence several phenomena observed exclusively in nanostructures (giant magnetic resistance, exchange bias, diffusion amorphization, etc.). The diffusion amorphization at the interfaces of Fe–B multilayers was studied in detail by Mössbauer spectroscopy and transmission electron microscopy (TEM) [1] and it was found that the thickness of the bcc-Fe layer was reduced by 2 nm due to the formation of amorphous Fe–B alloys on both (bottom and top, defined by the growth direction) interfaces.

The properties of the interface layers can be different at the top and the bottom of a given layer, depending partly on the surface and interface energies of the constituents, and partly on the experimental parameters determining the surface diffusion (i.e. substrate temperature, surface defects, atomic flux to the surface, etc.) [2]. Recently a new approach called sequence permutation of three building block multilayers [3] was used to study the difference between the top and bottom interface layers of nanometer scale multilayers. These investigations have shown that a more Fe-rich interface alloy is formed at the B/Fe (Fe on top of B) than at the Fe/B (B on top of Fe) interfaces. Besides that the Fe-rich alloys are more interesting from magnetic point of view, the B/Fe/Ag sequenced multi-trilayers have the advantage of a better layer morphology [3] than the Fe/B/Ag sequenced samples. In a recent publication [4] it was found that the Ag layer thickness influences the chemical mixing of Fe and B to some extent and this influence was studied in case of 2 nm B/2 nm Fe/x nm Ag sequenced multi-trilayers. The thickness of the non-alloyed Fe layer and the composition of the amorphous Fe–B interface alloy were shown to change below 5 nm Ag thickness, which was explained by discontinuities of the Ag barrier layer below 5 nm nominal thickness.

The aim of this work is to study the amorphous alloy formed at the B/Fe interface as a function of the Ag layer thickness in 1 nm B/1 nm Fe/x nm Ag multilayers, where the Fe layers are so thin that there remain no unalloyed bcc-Fe layers and all the Fe atoms belong to an amorphous alloy layer.

2. Experimental

A multilayer series of 5 nm Ag/[1 nm B/1 nm ^{57}Fe/x nm Ag]$_5$/50 nm Ag/100 nm B, with x = 1, 2, 4, 5 and 10, were prepared over Si substrate by thermal evaporation in vacuum with a base pressure of 10^{-7} Pa onto Si(1 1 1) wafers at room temper-

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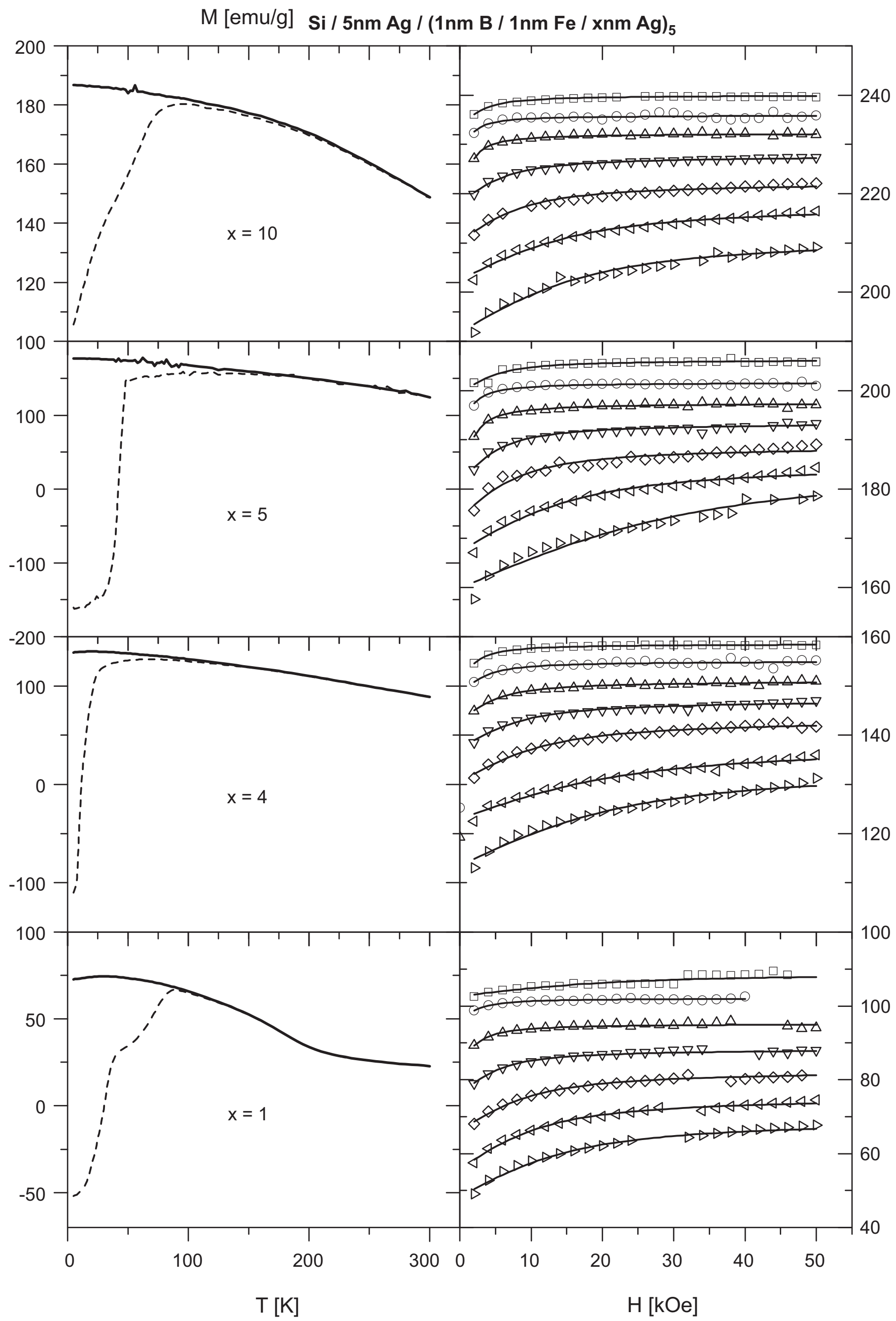

Fig. 1. Magnetization vs. temperature in low field (10 Oe, left side) and magnetization vs. applied magnetic field (right side), at temperatures from 5 to 300 K (in 50 K steps from top to bottom) for [1 nm B/1 nm Fe/*x* nm Ag]$_5$ multilayers with different Ag thicknesses, *x*. Dashed and thick lines denote zero field and field cooling, respectively. The magnetization vs. field curves were fitted by a sum of a constant and a Langevin function. Limited significance should only be given to the nominal [emu/g] figures due to the relatively large errors of the sample mass, as discussed in the text.

ature. Ag and B were evaporated from Cu cold crucibles by electron guns while ^{57}Fe was evaporated from a heated W boat. The layer thickness was measured by a quartz oscillator. The last two layers were applied to prevent the samples from oxidation and also to increase the overall thickness in order to make them easily removable from the substrate. The magnetization of the as received samples were measured with a Quantum Design MPMS-5S SQUID magnetometer whereas the ^{57}Fe transmission Mössbauer measurements were performed on samples removed from the substrate applying a 50 mCi ^{57}Co–Rh source in a standard constant acceleration spectrometer. The Fe hyperfine field (HF) distributions were evaluated according to the Hesse–Rübartsch method [5]. The structure of the samples was studied in cross-sectional view using transmission electron microscopy (TEM). The cross-sectional specimens were prepared by mechanical polishing and argon ion beam milling at low energies (<1 keV) in order to minimize the ion beam damage. The specimens were studied using a FEI Tecnai G2 microscope at 200 kV.

3. Results

Fig. 1 shows the results of the magnetization measurements vs. temperature (left side) and vs. applied magnetic field (right side) for the $x = 1, 4, 5$, and 10 multilayer samples. Dashed and thick lines denote the magnetization measured during warming the sample in $H = 10$ Oe after cooling it in zero field (ZFC) and after cooling it in $H = 10$ Oe (FC), respectively. The bifurcations of the ZFC and FC curves hint at the presence of superparamagnetic clusters. The saturation magnetizations have a considerable increase with increasing *x*, however the absolute values have a 10–20% uncertainty due to the relatively large errors in measuring the few nm thickness of the

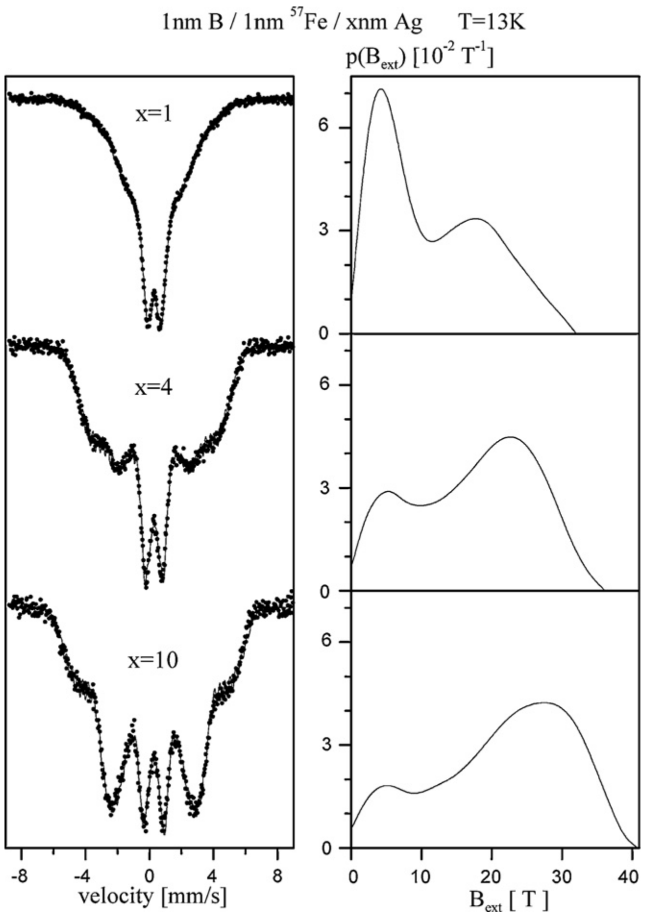

Fig. 2. Mössbauer spectra vs. Ag thickness measured at $T = 13$ K for [1 nm B/1 nm Fe/x nm Ag]$_5$ multilayers with $x = 1$, 4 and 10, together with the corresponding hyperfine field distributions.

layers. The magnetization vs. fields curves were fitted by the sum of a field-independent ferromagnetic component and a Langevin part describing the behaviour of superparamagnetic clusters: $M(H, T) = M_0 + nm\,\mathrm{L}(mH/k_BT)$ where $\mathrm{L}(x) = \coth(x) - 1/x$ is the Langevin function, M_0 is a constant (saturation magnetization of the ferromagnetic component), n and m are the density and magnetic moment of the superparamagnetic clusters and k_B is Boltzmann's constant. The values of the obtained cluster moments lie between 500 and 700 μ_B and are only weakly temperature dependent above the temperatures of the bifurcation point. For $x = 1$ the inflection point observed in the low-field magnetization vs. temperature curve indicates the Curie point of a ferromagnetic phase. In the other cases the Curie temperature is higher than 300 K.

Fig. 2 shows the Ag thickness dependence of the Mössbauer spectra measured at $T = 13$ K for selected multilayers, together with the respective HF distributions. All the spectra were best fitted by close to 3:4:1:1:4:3 intensity ratios of the lines of the magnetic sextets, indicating in-plane magnetic moments. Sharp lines characteristic to bcc-Fe cannot be found in any of the spectra, although for $x = 10$ the HF distribution stretches above the 33 T value characteristic to bcc-Fe. These components are attributed to Fe atoms being at the amorphous Fe–B/Ag interface and having Ag neighbors, as well. Note that the thicker the Ag layer, the higher the value of the corresponding average hyperfine field.

The Mössbauer spectra and the corresponding HF distributions of the samples with 5 and 10 nm thick Ag layers measured at 4.2 K and room temperature are compared in detail in Fig. 3. It is observed that the spectra are very similar at both temperatures for the two samples, i.e. above 5 nm the increase of the Ag layer thickness does not influence either the Fe–B mixing or the magnetic coupling between the layers. The 4.2 K HF distributions are broader than those of melt quenched [6] and evaporated [7] amorphous alloys covering the whole range from 0 to 40 T and exhibiting two well separated peaks. The broad HF distribution signifies a broad distribution of the local neighborhoods, which probably origins from the large number of interface atoms in the thin amorphous layers. As explained above the components above 30 T may originate from the Fe–B/Ag interface. Since the 1:1 layer thickness ratio corresponds to the nonmagnetic $Fe_{40}B_{60}$ alloy composition, the predominance of the magnetic components in the spectra indicates that a significant amount of the B atoms remains segregated from the amorphous alloy layer. Therefore, the less than 2 nm thick amorphous Fe–B layers should be bordered by B and Ag layers at the bottom and top sides, respectively. The low field peak can be associated to Fe atoms at the B/Fe–B interface which have more B neighbors than those Fe atoms which are inside the amorphous Fe–B layer. Note that the 4.2 K spectra reveal that 5–10% of the Fe atoms are in a phase with a high hyperfine field (around 47 T), pointing to the presence of a superparamagnetic oxide phase. At elevated temperatures the ratio of the low field peak of the HF distribution increases and the position of the high field peak of the HF distribution shifts to lower values, as it can be seen in Fig. 3 for the 300 K spectra. The increase of the intensity of the low field peak with the increase of temperature can be equally attributed to the presence of superparamagnetic components or ferromagnetic components with Curie temperature below 300 K. According to studies on Fe–B amorphous thin films [8,9] the Curie temperature of the Fe–B phases is below 300 K in the 40–45% B concentration range.

Fig. 4 shows the bright-field TEM micrograph of the [1 nm B/1 nm Fe/5 nm Ag]$_5$ multilayer. The 5 nm thick Ag layer has polycrystalline microstructure and forms a continuous layer well separating the Fe and the B layers that are located below and above it, respectively. The bright-contrast amorphous layer on top of the Ag layers is the unalloyed (or low Fe content) B layer. As a result of intermixing of Fe and B, an amorphous Fe-rich layer is formed

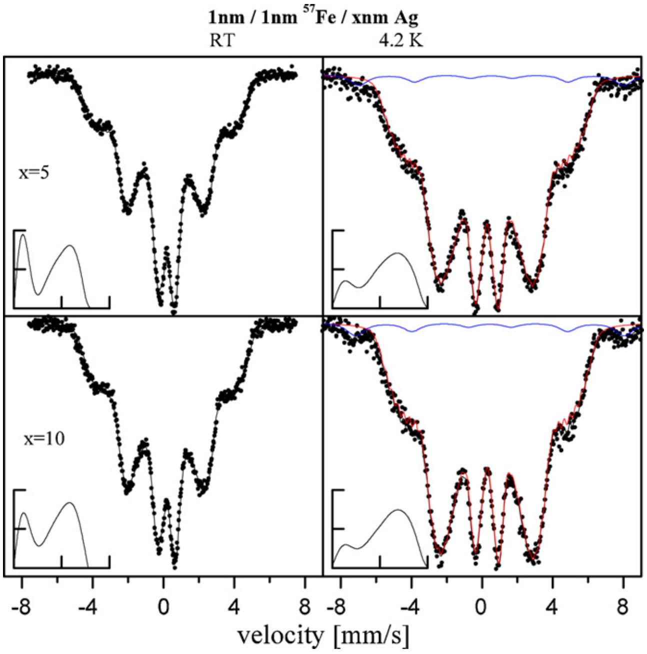

Fig. 3. Mössbauer spectra at $T = 4.2$ K and room temperature of the [1 nm B/1 nm Fe/x nm Ag]$_5$ multilayers for $x = 5$ and 10 and the fitted hyperfine field distributions. The hyperfine field distributions are shown in the 0–40 T and 0–0.06 x–y ranges. (At 4.2 K a separate sextet due to an oxide phase is also fitted.)

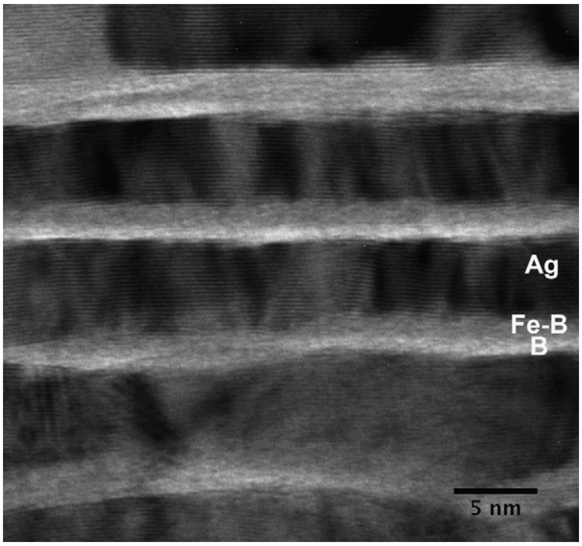

Fig. 4. Bright field TEM image of the [1 nm B/1 nm Fe/10 nm Ag]$_5$ multilayer. The amorphous B, amorphous Fe–B and crystalline Ag layers are marked.

on top of the B layer. Crystalline phase other than fcc-Ag is not indicated by the diffraction pattern (not shown here).

4. Discussion

According to Figs. 2 and 3 the variation of the Ag layer thickness have a drastic effect on the hyperfine fields of the [1 nm B/1 nm Fe/x nm Ag]$_5$ multilayers below 5 nm and have no effect above. However, the saturation magnetization values, M_0 deduced from the M–H curves of Fig. 1 for $x = 5$ and 10 do not agree with each other in absolute values. The difference can be due to deviations of the effective thicknesses of the individual layers from the nominal ones. One atomic layer error over 10 layers in course of the thickness measurements could explain the observed 10% difference of M_0. To circumvent this problem the magnetization values measured in 5 T at different temperatures were normalized with respect to the 5 K value and are shown in Fig. 5 for the whole multilayer series. The temperature dependence of the normalized magnetization is significantly different for the samples up to 5 nm Ag thickness and remains invariable above this thickness, i.e. the normalized magnetization data are in line with the Mössbauer data.

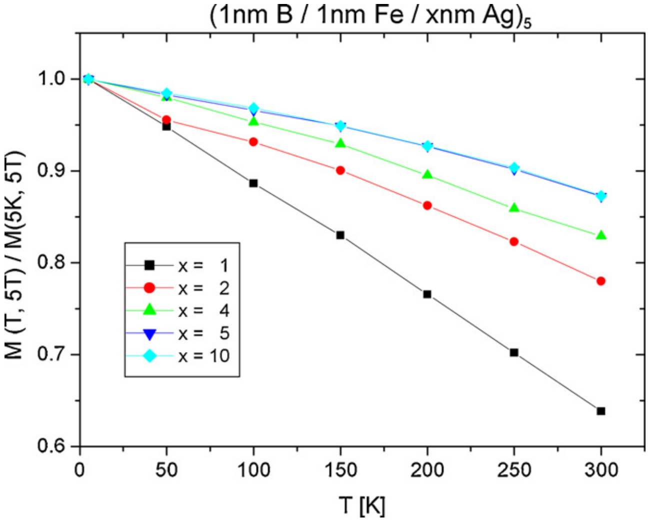

Fig. 5. Normalized magnetization vs. temperature curves of the [1 nm B/1 nm Fe/x nm Ag]$_5$ multilayers calculated from the data measured in 5 T magnetic field.

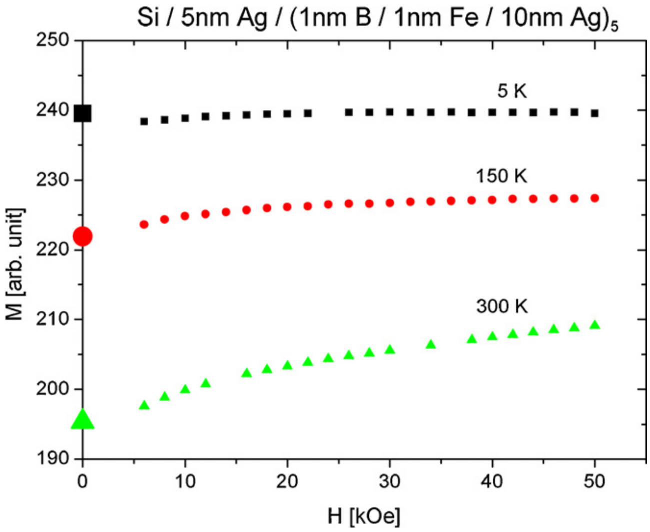

Fig. 6. Magnetization vs. applied magnetic field for the [1 nm B/1 nm Fe/10 nm Ag]$_5$ multilayer, together with the hypothetic magnetization values at zero field, as derived from the temperature dependence of the position of the high-field-peak of the hyperfine distribution.

Similar trend of the HF data was observed in case of thicker Fe and B layers [1,4] and was explained by discontinuities of the Ag layer below 5 nm thickness. Since Ag does not mix with Fe and B, it acts as a barrier layer for the diffusion of B atoms deposited on top of it. In case of thicker Fe layers, discontinuities of the Ag barrier layer allowed the formation of a Fe/B interface and through diffusion amorphization reduced the thickness of the Fe layer below it. The average composition of the amorphous layers also changed because of the varying weight of Fe/B and B/Fe interfaces formed at the two sides of the Fe layers. In the present case the role of the Ag layers is similar, but the layer formation is somewhat different. First, in accordance with previous results [1,4] the whole 1 nm Fe layer is intermixed with the bottom B layer, as it is obvious from Fig. 3. Second, B atoms entering through discontinuities of the Ag layers on the top does not mix with a Fe layer but with a preexisting amorphous layer and increase the B content of the amorphous alloy layer. This way the amorphous layers formed are more homogeneous and better approach the nominal composition than in case of the thicker Fe layers. For the same reason, in the present case the B content of the amorphous alloy is the highest when the Ag thickness is the smallest. Note that the B content of the Fe–B interface layer is high enough for $x = 1$ to shift the Curie temperature of a large magnetic fraction below room temperature as seen from the temperature dependence of the low field magnetization in Fig. 1. Increasing the thickness of the Ag layer, the Fe–B interface region will become more and more Fe-rich because an increasing portion of the Ag layers will be continuous.

From magnetic point of view the $x = 5$ and 10 samples are the most interesting ones. As it was deduced from the HF distributions of Fig. 3 and also indicated by the TEM results shown in Fig. 4, in these samples a less than 2 nm thick amorphous Fe–B layer is sandwiched in between amorphous B and crystalline Ag layers. Surprisingly, the ultra-thin amorphous Fe–B layer is predominantly ferromagnetic, as it is revealed both by the magnetization and the Mössbauer measurements of Figs. 1 and 3, respectively. The intensity of the low field (paramagnetic) peak of the HF distribution is temperature dependent, which can be explained by the observed small amount of superparamagnetic oxide phase and some possible low Curie point fractions of the amorphous Fe–B layer. The intensity of this peak at 4.2 K can be well explained by the presence of a B/Fe–B interface. The high field peak of the HF distribution shifts to higher values as the temperature is lowered. This component can be directly related to the ferromagnetic part of the magnetization vs. field curves. This is shown for the $x = 10$ sample in Fig. 6 where the field dependence of the magnetization is plotted for selected temperatures, together with some hypothetic magnetization values at zero field calculated from the temperature dependence of the high-field-peak positions of the HF distributions: $M_{\mathrm{calculated}}(T) = M(5\mathrm{K})B_{\mathrm{hf}}^{\max}(T)/B_{\mathrm{hf}}^{\max}(5\mathrm{K})$. As seen in Fig. 6 the calculated values seem to be natural extrapolations of the magnetization vs. field curves to zero field.

Besides the ferromagnetic component, a superparamagnetic part of relatively small ratio (around 10% for $x = 10$) was necessary to describe the field dependence of the magnetization (Fig. 1). According to the Mössbauer measurements it is attributed to some kind of oxide phase which incorporates 5–10% of the Fe atoms (see Fig. 3). This would also explain the finding that the cluster moments are rather similar for the whole multilayer series (500–700 μ_B).

5. Conclusions

Formation of amorphous Fe–B layers was observed in the [1 nm B + 1 nm ^{57}Fe + x nm Ag]$_5$ ($1 \le x \le 10$) multilayer series. Below 5 nm thickness the Ag layer was found to affect strongly the magnetic properties of the amorphous Fe–B layers. It is explained by the variation of the B concentration of the amorphous alloy layers. The Ag layers act as diffusion barriers in between an underlying intermixed Fe–B layer and an overlying B layer. At about 5 nm thickness a complete diffusion barrier is built up as the Ag layers become continuous and the further increase of their thickness does not influence the magnetic properties. In this latter range the average Fe concentration of the amorphous Fe–B layer is around 60 at% and the ultra-thin layers, sandwiched in between amorphous B and crystalline Ag, show good ferromagnetic properties.

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