Thermoremanence anomaly in Fe-Zr(B,Cu) Invar metallic glasses: Volume expansion induced ferromagnetism

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We report the existence of a thermally induced sharp increase of thermoremanence around the Curie temperature of Invar-like Fe-Zr(B,Cu) soft magnetic glasses. Neutron-diffraction measurements indicate that a true enhancement of the average local magnetic moment, rather than only a change in the domain structure, occurs. Such enhancement has been tentatively attributed to the increasing volume expansion that takes place beyond the Curie temperature and reinforces ferromagnetism in some low-density clusters.

The origin of the complex magnetic properties of iron-rich metallic glasses containing low concentrations of early transition metals (Zr,Sc,Hf,Y) have attracted considerable interest during more than two decades, giving rise to several controversial microscopic interpretations.[1–4] In particular Fe_xZr_{100-x} amorphous alloys with x above 80 at.% rank among the most extensively studied spin system,[5–10] exhibiting weak itinerant ferromagnetism, low-temperature spin-glass-like behavior and Invar character.

Nowadays it is clear that Invar-like iron-rich Fe_xZr_{100-x}, as well as Fe-Zr(B,Cu),[12] soft magnetic glasses exhibit: (i) a sharp increase of the thermal expansion above the Curie temperature, T_C,[2,3] (ii) a large high-field susceptibility,[5] (iii) a decrease in both the magnetic moment and T_C with increasing x,[9] (iv) a large positive spontaneous volume magnetostriction,[11] (v) a positive shift in T_C with the tensile stress,[12] and a large but negative shift with pressure.[2,3] Moreover, it is well established that, as a consequence of competitive positive and negative interactions, the spontaneous magnetization is low and the effect of the field is to induce local magnetic moment, as pointed out by the high volume magnetostriction at low fields.[11] In addition, due to the sensitivity of the local magnetic moment to the interatomic distances, the spontaneous magnetization is expected to fluctuate with density fluctuations which are always present in amorphous structures. The sign of the magnetic interactions depends on the interatomic distances giving rise to the coexistence of complex magnetic phases and in this way both cluster[13] and frustration[8] microscopic models have been proposed to account for the overall behavior. According to the positive volume magnetostriction experimentally observed,[11] it is accepted that those regions or clusters with lower local density should exhibit the higher local magnetic moment and thus stronger ferromagnetic character. On the other hand, spin-glass-like regions with higher density will surround these ferromagnetic clusters so decreasing the average local magnetic moment.

In this work we present the highlights of a detailed experimental study regarding the thermoremanence behavior in amorphous Fe-Zr(B,Cu) which confirms the appearance of a reversible magnetic transition that occurs around their Curie points. The nature of the transition is elucidated through neutron-diffraction measurements.

Amorphous $Fe_{88}Zr_7B_4Cu$, $Fe_{87.2}Zr_{7.4}B_{4.3}Cu_{1.1}$, $Fe_{90}Zr_7B_3$, and $Fe_{90}Zr_{10}$ were produced in the form of ribbons, with approximate thicknesses of 20 μm, using the melt spinning technique. The amorphous structure of all the samples was checked by x-ray diffraction and Mössbauer spectroscopy. The room-temperature Mössbauer spectra of the samples analyzed confirmed the absence of ferromagnetic bcc-Fe grains, at least in volume fraction above 1%. The thermomagnetic behavior was investigated in a temperature range from 77 to 550 K, using both a Quantum design MPMS super conducting quantum interference device magnetometer and a vibrating sample magnetometer. The magnetic-field values could be set to an accuracy of $\pm 10^{-6}$ T and the temperature to within $\pm 10^{-2}$ K.

Figure 1(a) shows the thermoremanence behavior, corresponding to the sample $Fe_{88}Zr_7B_4Cu$, after cooling in zero-field conditions from room temperature and measuring the magnetic moment on increasing the temperature. On the other hand, Fig. 1(b) shows several thermomagnetic curves obtained when cooling in a field of 100 mT and measuring the magnetic moment on increasing the temperature in zero-field conditions, and with low applied fields of 0.05 and 0.1 mT, respectively.

From the measurements presented in Figs. 1(a) and 1(b), it is clear that a sharp and reversible increase of the macroscopic magnetic moment occurs in amorphous $Fe_{88}Zr_7B_4Cu$, around its Curie point (see below).

In order to check whether this transition is a general feature in Fe-Zr(B,Cu) amorphous alloys, we have investigated the thermomagnetic behavior in $Fe_{87.2}Zr_{7.4}B_{4.3}Cu_{1.1}$, $Fe_{90}Zr_7B_3$, and $Fe_{90}Zr_{10}$ amorphous alloys. The field-cooled (FC) curves (obtained with an external applied field of 100 mT) and the thermoremanence measurements, performed by

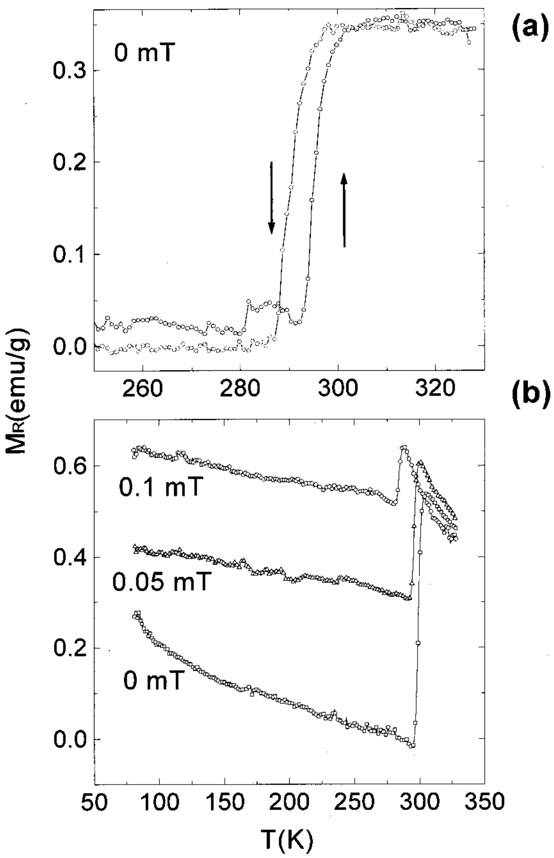

FIG. 1. (a) Thermoremanence behavior of amorphous $Fe_{88}Zr_7B_4Cu$, and (b) thermomagnetic measurements obtained when cooling the sample down in an applied field of 100 mT and measuring with different applied fields. Solid lines are shown as a guide to the eye.

cooling the sample down in zero-field conditions and measuring the magnetic moment with no applied field while increasing the temperature, are plotted in Fig. 2.

The Curie temperatures of the alloys investigated were estimated from the minima of the dM/dT vs T plots,[14] computed from the low-field FC measurements. The results obtained for the alloys: $Fe_{88}Zr_7B_4Cu$ ($T_C = 298$ K), $Fe_{87.2}Zr_{7.4}B_{4.3}Cu_{1.1}$ ($T_C = 314$ K), $Fe_{90}Zr_7B_3$ ($T_C = 248$ K), and $Fe_{90}Zr_{10}$ ($T_C = 219$ K), show good agreement with previously reported data.[9,12] From the present results it can be concluded that a thermally induced reversible magnetic transition occurs for all the samples investigated.

The trends of the temperature dependence of the coercive field corresponding to sample $Fe_{88}Zr_7B_4Cu_3$ are depicted in Fig. 3. A clear increase above the Curie temperature, similar to that observed in the rest of the samples, is exhibited.

An increase of the both remanence and coercive field, has been previously reported in nanocrystalline $Fe_{91}Zr_7B_2$,[15] with crystalline fraction around 50%. Nonetheless our samples are amorphous within the accuracy provided by x-ray and neutron (see below) diffraction as well as Mössbauer spectroscopy. To our knowledge such increase of the coercive field above T_C has not been published in samples with highly diluted impurity phases.

In addition, in amorphous Fe-Zr(B,Cu) alloys a large field-induced volume expansion has been previously reported,[2,3,11] which led us to measure the thermal-expansion

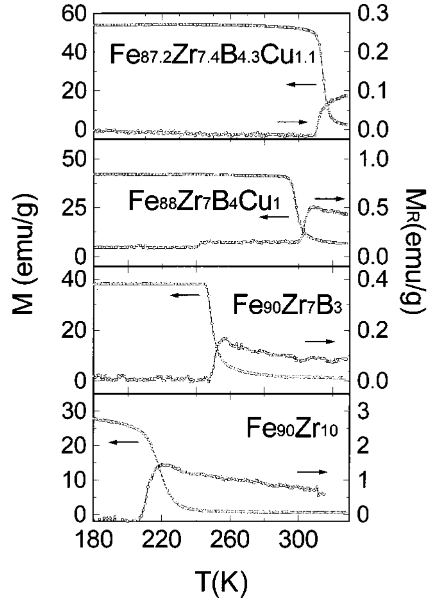

FIG. 2. FC measurements with an applied field of 100 mT (left axis) and thermoremanence curves obtained when cooling the sample down in zero-field conditions and measuring the magnetic moment on increasing the temperature (right axis).

coefficient as a function of the temperature (see Fig. 4). These measurements were obtained by means of an strain gauge cemented to the ribbon and placed parallel to its axis. It is manifest, from the data shown in Fig. 4, that as expected,[2,3] there is a sharp increase of the thermal-expansion coefficient in amorphous $Fe_{88}Zr_7B_4Cu$ for temperatures above T_C.

The increase of thermoremanence, shown in Figs. 1 and 2, as well as the increase of the coercive field, Fig. 3, might be related with the existence of an impurity phase with higher Curie temperature (for instance an amount below 1% weight of α-Fe) which would not be detected by Mössbauer measurements. In this case the softer amorphous phase should produce a magnetic shielding of the remanence associated with the harder impurity phase. At the Curie temperature of the amorphous matrix the magnetic shielding would disappear and the remanence of the grains should merge macro-

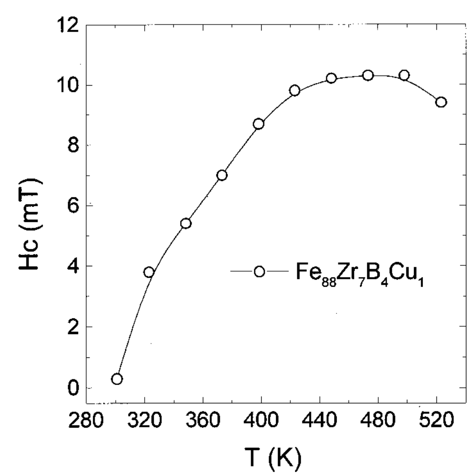

FIG. 3. Thermal dependence of coercive field corresponding to amorphous $Fe_{88}Zr_7B_4Cu$. Solid line is shown as a guide to the eye.

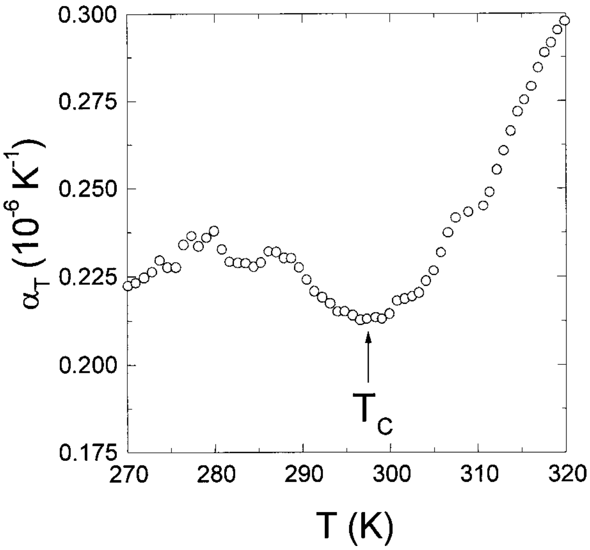

FIG. 4. Temperature dependence of the thermal-expansion coefficient in amorphous $Fe_{88}Zr_7B_4Cu$.

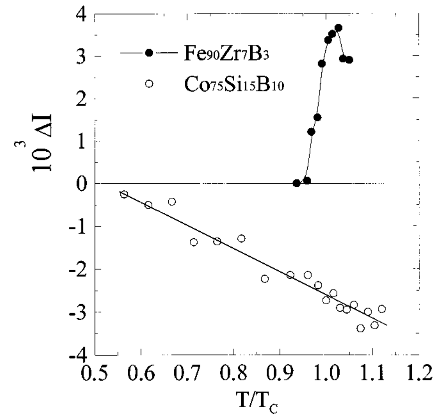

FIG. 5. Integrated intensity, obtained from neutron-diffraction measurements, plotted versus the reduced temperature, T/T_C, corresponding to $Fe_{90}Zr_7B_3$ (solid circles) and $Co_{75}Si_{15}B_{10}$ (open circles) amorphous alloys. Solid lines are shown as a guide to the eye.

scopically. Therefore, the increment of thermoremanence should be due to an increase of the technical magnetization rather than to an increment of the local ferromagnetic order. In order to elucidate this possibility it is necessary to use an experimental technique sensitive to the average local magnetic moment. Thus, we have carried out neutron-diffraction experiments at the DIB diffractometer of the ILL in Grenoble (France). If the origin of thermoremanence anomaly were only the existence of an impurity phase the magnetic contribution below T_C would consist in two components, one due to the amorphous phase and another originated from the impurity phase, which should remain above T_C. Hence, the magnetic contribution to the neutron-diffraction intensity would either decrease at the Curie temperature of the matrix or remain constant, if the contribution of the amorphous matrix to the diffracted intensity were negligible below T_C.

The values of the integrated neutron diffracted intensity, corresponding to the broad $S(Q)$ amorphous halo of the $Fe_{90}Zr_7B_3$, alloy measured at different temperatures, surprisingly increase around the Curie temperature of the sample, as depicted in Fig. 5.

To be sure that this anomalous behavior is not an artifact, data corresponding to another amorphous ferromagnetic alloy ($Co_{75}Si_{15}B_{10}$), which does not exhibit the same volume sensitivity for the spontaneous magnetization, is also presented for comparison. In this case the total diffracted intensity decreases at T_C indicating the disappearance of the magnetic contribution. Although some structural (nuclear) component cannot be discarded in the Fe-Zr-B neutron-diffraction pattern, the significant increase of the magnetic signal in the vicinity of T_C is clearly anomalous.

The increase of the diffraction intensity presented in Fig. 5 indicates that the corresponding sharp increase of thermoremanence at T_C, shown in Figs. 1 and 2, is due to a true enhancement of the average local magnetic moment. Although the presence of some impurities cannot be ruled out, such impurities could only account for an increase of the technical magnetization and never for the enhancement of the intrinsic magnetic moment inferred from the results shown in Fig. 5.

Once the nature of the transition has been elucidated, some microscopic considerations regarding the possible origin of the enhancement of the average local magnetic moment are outlined. The overall behavior can be well understood by considering the increase of the volume expansion coefficient that occurs at, and above, T_C. As summarized in the introduction, low-density clusters with enhanced ferromagnetic order are present and coexist with regions exhibiting spin-glass-like magnetic behavior. Below T_C the magnetic signal of the neutron-diffraction pattern reflects the contribution of both spin-glass-like regions and ferromagnetic clusters. Therefore, the increase of the diffracted intensity at T_C points out an increase of the average magnetic moment of the clusters. Thus, the results presented in this work suggest that at the Curie temperature of the alloy, the ferromagnetic clusters expand, so reinforcing their ferromagnetic character. This effect would account for the sharp increase of thermoremanence as well as for the thermal dependence of the magnetic contribution given by the integrated neutron-diffraction intensity. Moreover, the steep enlargement of the coercive field shown in Fig. 3 reinforces the idea of density fluctuations provided that only the lower density pockets are ferromagnetic. In addition, the high values of the coercive field indicate that the average size of these pockets should be below the single-domain size. It appears difficult to ascribe the increase of the coercivity to the diminution of exchange coupling between particles, provided that it occurs far beyond T_C.

In our case, it appears more reasonable to invoke an increase of the volume of the ferromagnetic particles above T_C to account for the thermal dependence of the coercivity. As the temperature rises, the volume of these low-density pockets expands in such a way that the anisotropy energy of the single-domain particle increases faster than the thermal energy.

A volume expansion in itinerant ferromagnets enhances the ferromagnetic tendency.[16] According to the Stoner criterion $[IN(E_F)>1]$, the tendency to ferromagnetism in itinerant systems is proportional to the product of a measure of the exchange interactions I and the density of states $N(E_F)$. Furthermore, in metallic systems where the main contribution to the exchange is the intratomic one, the exchange interactions do not depend on the interatomic distances. However, a structural expansion will decrease the bandwidth, increasing the density of states (for details see Ref. 16). Below T_C the thermal volume expansion is counterbalanced by the volume reduction due to the decrease of the magnetic moment. On the other hand, above T_C this later contribution vanishes and the volume expansion promotes the increase of the magnetic ordering reported here.

In summary, we have shown that in the absence of an external magnetic field, Fe-Zr(B,Cu) itinerant ferromagnets exhibit a sharp reversible magnetic transition for temperatures around their Curie temperatures. This transition corresponds to an increase of the average magnetic moment and cannot be attributed to the contribution of any impurity phase. The effect has been tentatively explained as being due to a volume expansion that occurs in these alloys above T_C, in some low-density patches. Furthermore, the experimental results reported here seem to confirm the existence of low-density stronger ferromagnetic clusters in the amorphous structure.

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