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Tensile stress dependence of the Curie temperature and hyperfine field in Fe-Zr-B-(Cu) amorphous alloys

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FeZrB(Cu) metallic glasses present the same Invar (like) properties as the pure FeZr ones, in particular a large dependence of the Curie temperature on pressure. Magnetic and Mössbauer measurements show a decrease of the Invar character as the boron concentration increases, with a linear relationship between the change of Curie temperature per unit stress and the reciprocal of the Curie temperature itself. The influence of boron is shown to greatly enhance the weak itinerant ferromagnetism of FeZr glasses leading to stronger ferromagnetic behavior. [S0163-1829(96)09229-6]

INTRODUCTION

FeZr glasses have attracted large interest in the past years[1–5] as a very peculiar magnetic system displaying reentrant spin-glass behavior and Invar character. The theoretical explanation of such effects is still controversial and very abundant literature is still appearing on this subject, trying to elucidate the opposite ''cluster''[6] or ''frustration''[7] models. From an experimental point of view some facts are clearly established: the Curie temperature T_C increases as the Zr content (up to about 25 at. % Zr for which $T_C \approx 268$ K), but the spin-glass T_{sg} temperature decreases, vanishing at about 11 at. % Zr. On the other hand, the Curie temperature shows a large dependence on hydrostatic pressure, which is always negative (reaching about -60 K/GPa).[4,8] This dependence is larger in low Zr containing glasses, showing the same trend as the spin-glass behavior.

A recent study on FeZrB glasses[9] shows that the effect of boron is to increase the Curie temperature of the alloys reaching easily room temperature. The iron magnetic moment also increases with boron but the general evolution of the magnetization with temperature remains almost unchanged. Mössbauer spectra are also very similar in glasses with and without boron. This can indicate that the same mechanisms should be present in FeZr and FeZrB glasses. Furthermore, a new group of nanocrystalline magnets produced by crystallization of the amorphous state has increased the interest in FeZrB(Cu) glasses, as the latter are precursors of such nanocrystalline materials.[10]

The main aim of the study undertaken and reported here is to show the existence of a large influence of the simple tensile stress on the Curie temperature of the FeZrB amorphous alloys, having T_C near room temperature. The ribbon geometry of the samples, and the outstanding elastic properties of the metallic glasses makes them an ideal system for applying large tensile stresses, giving rise to strains in the range of 1–2 %, with perfect elastic recovery. Under the influence of such stresses they are expected to display a large shift in the Curie temperature, associated with the Invar behavior. The study has been completed with Mössbauer spectroscopy to show that the microscopic effects of the stresses are in agreement with the macroscopic observations and to get insight into the possible origin of the effect. FeZrB(Cu) metallic glasses, with the Curie temperature close to the room temperature are specially suited for such study. A preliminary study of the influence of the tensile stress on T_C by means of magnetic measurement under Joule heating has been reported in Ref. 11.

EXPERIMENTAL RESULTS

FeZrB(Cu) amorphous ribbons have been obtained by means of the melt spinning method under controlled atmosphere. The composition and some characteristic properties are summarized in Table I. Typical dimensions of their cross section were 2 mm wide and 20 μm thick. They were shown to be amorphous by x-ray diffraction and Mössbauer spectroscopy. The Curie temperature and other magnetic properties were determined by means of a superconducting quantum interference device magnetometer and conventional induction measurements. The latter was also used in magnetic measurements under stress, and a small furnace allowed to change the temperature. Stress could be applied also to the samples during the Mössbauer spectra recording, at room temperature, by means of a cantilever system loaded by a weight.

Figure 1 shows the evolution of the magnetization of the sample $Fe_{87}Cu_1Zr_6B_6$ (measured in a field of about 2500 A/m) as a function of the applied stress for different tempera-

TABLE I. Curie temperatures, its change under stress and average hyperfine fields at 291 K (18 °C) for the three studied compositions.

	T_C (K)	$dT_C/d\sigma$ (K/GPa)	$\langle B_{HF}\rangle$ (T)
$(Fe_{0.92}Zr_{0.08})_{96}B_4$	283 ± 2	19 ± 1	a
$Fe_{87}Zr_6Cu_1B_6$	300 ± 2	14 ± 1	4.3 ± 0.2
$Fe_{80}Zr_{10}B_{10}$	355 ± 2	3 ± 1	12.2 ± 0.4

[a] Paramagnetic at RT.

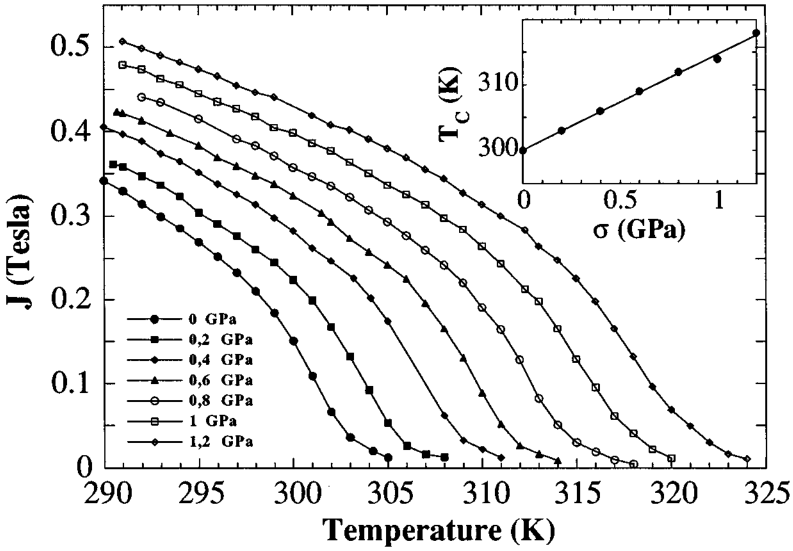

FIG. 1. Thermal evolution of the magnetic polarization, J, at 2.5 kA/m, as a function of the tensile stress applied to a metallic glass of composition $Fe_{87}Cu_1Zr_6B_6$. The inset shows the linear change in Curie temperature produced by the tensile stress. All the changes are perfectly reversible as the stress never reaches the elastic limit.

tures. A large shift of the Curie point is evident. The latter has been defined as the inflection point of the magnetization curve, and increases about 15 K/GPa in this sample (see the inset of Fig. 1).

Mössbauer spectra of this sample have been taken at a single temperature of 291 K (18 °C) under different loads. Fitting of the spectra has been performed by means of a computer program, developed by Brand, Lauer, and Herlach,[12] which allows a distribution of hyperfine fields (B_{HF}) and a relationship of the hyperfine field with distributions of isomer shift and/or quadrupole splitting (QS). Owing to the nearness of the Curie temperature, the quadrupole splitting can not be considered as a first-order perturbation of the magnetic splitting and second-order terms were taken into account.[13] Average hyperfine field increases as a function of the applied tensile stress, see Fig. 2, and follows the increase of the magnetization at the same temperature, both being linear with the stress and having a relationship close to 15 T/μ_B, as expected in these compounds.[7] This result rules out any possible artifact of the magnetic measurements related to the induction of magnetoelastic anisotropies or other domain effects of the tensile stress. The width of the distribution also increases with the stress, developing long tails for high fields, thus increasing the asymmetry of the distribution. On the other hand, the values of the isomer shift and QS do not change even at the largest applied stress, within the experimental uncertainty.

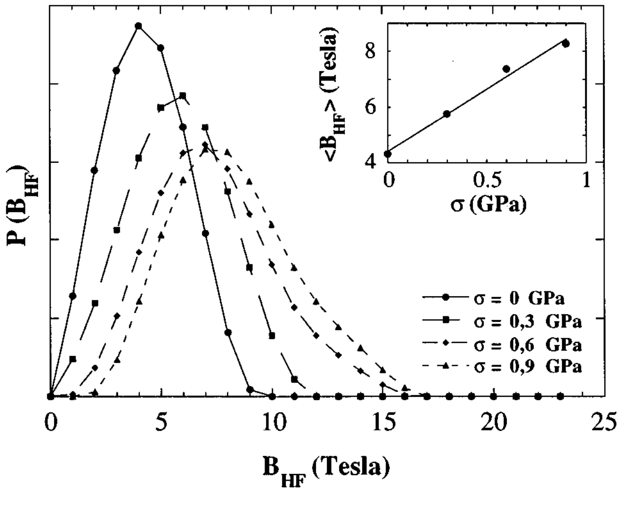

FIG. 2. Changes in the hyperfine field distributions, $P(B_{HF})$, of the $Fe_{87}Cu_1Zr_6B_6$ sample for different applied stresses. Broadening of the distribution as a function of the tensile stress is evident. The inset shows the linear increase of the average field $\langle B_{HF} \rangle$ as a function of the stress.

The experiments described for this sample are difficult to repeat for other compositions as they have their Curie temperatures either lower than room temperature, or too high to see any appreciable change in the magnetization curves or Mössbauer spectra at room temperature. We succeed, however, in preparing a sample, $(Fe_{0.92}Zr_{0.08})_{96}B_4$, with T_C below but very near room temperature (RT). The large effect of the tensile stress can be directly observed on the magnetization curve. Figure 3 shows the parallel appearance of the hysteresis loop and the broadening of the Mössbauer spectra at 291 K (18 °C) when the applied stress reaches 0.6 GPa. Although the spectra at the onset of ferromagnetism does not allow any accurate fit for determining the distribution of B_{HF}, one can observe that part of the Fe atoms remain almost in the paramagnetic state, as the doublet corresponding to the QS has not changed. By measuring the evolution of the magnetization as a function of stress, for temperatures between 289 (16 °C) and 295 K (22 °C), we could deduce a dependence of T_C with the stress of about 20 K/GPa, clearly larger than the one obtained for the former sample.

The third sample studied $(Fe_{80}Zr_{10}B_{10})$ does not show any magnetization changes at room temperature and only very subtle ones when approaching to the Curie temperature. From magnetic measurements we determined a maximum change in T_C of about 3–4 K/GPa of applied tensile stress.

DISCUSSION

The increase of T_C with the stress can be explained in terms of a corresponding decrease of T_C with the hydrostatic

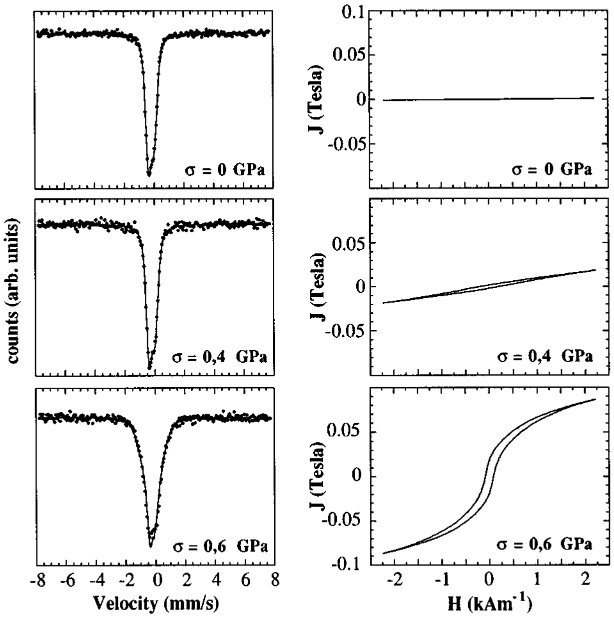

FIG. 3. Effect of the stress on the Mössbauer spectra and magnetization of the room-temperature paramagnetic alloy $(Fe_{0.92}Zr_{0.08})_{96}B_4$. The onset of ferromagnetism is clear for $\sigma=0.6$ GPa, where the hysteresis loop and the magnetic splitting of the spectra appear. Under lower tensile stresses, no changes can be observed in the spectra, showing the small influence on the alloys structure.

pressure, as reported a long time ago for the binary FeZr amorphous alloys. As is well known, the application of a tensile stress σ results in an increase of the volume of the sample given by[14]

$$\frac{\Delta V}{V}=\frac{\sigma}{E}(1-2\nu),$$

which is one third of the decrease of volume produced by the application of the same hydrostatic pressure p:

$$\frac{\Delta V}{V}=-\frac{p}{K}=-\frac{3p}{E}(1-2\nu).$$

Here E and K are the Young's modulus and bulk modulus, respectively, and ν is the Poisson's ratio. If the observed dependence of T_C with tensile stress is translated to a dependence with hydrostatic pressure we obtain values of about -10, -45, and -60 K/GPa which are of the same order as those found in binary FeZr glasses, which are properly described by the itinerant weak ferromagnetism model.[15] This dependence is lower for the alloys containing more zirconium and/or boron, but the dependence with composition can be translated to a relationship with the value of the Curie temperature of the alloy. As deduced from the very simple Wohlfarth's model[16] of itinerant weak ferromagnetism for Invar alloys, we should expect a linear relationship of $\Delta T_C/\Delta p$ with the reciprocal of T_C itself, crossing through zero near the origin. Such dependence is depicted in Fig. 4 showing a slope of -7×10^4 K^2/GPa which is almost an order of magnitude larger than in FeNiZr amorphous alloys (about -10^4 K^2/GPa) and even much larger than in FeNi crystalline alloys (-2×10^4 K^2/GPa).[8] Moreover, the extrapolation of the linear fit crosses the $1/T_C$ axes far from the origin (≈0.0027 K^{-1}). These results indicate that the addition of boron greatly enhances the itinerant weak ferromagnetism that describes the behavior of FeZr alloys. Therefore, collective excitations cannot be excluded to explain the origin of T_C in FeZrB alloys, which are not more weak ferromagnets. The large slope of dT_C/dp vs $1/T_C$ reflects the transition from a weak ferromagnetic behavior in pure FeZr to a strong ferromagnetic behavior in FeZrB. The value of dT_C/dp expected for strong itinerant ferromagnets or localized ferromagnets is small and positive.[16]

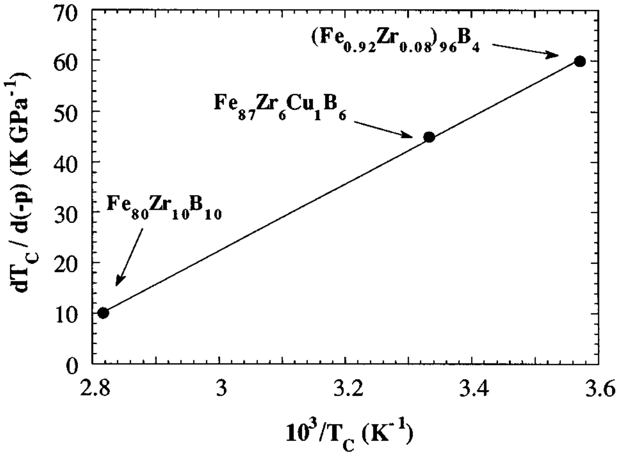

FIG. 4. Pressure dependence of the Curie temperature as a function of the reciprocal of the Curie temperature itself.

The suggested origin for the changes in the Curie temperature under pressure is the change of antiferromagnetic to ferromagnetic interactions between the Fe atoms as the distance between them changes slightly around a critical one of about 2.54 Å.[17] Another alternative for explaining the Invar behavior involves a change from low to high spin, or a moment instability, of the $3d$ metal as a function of the interatomic distance.[18] The change of magnetic moment of Fe is unlikely to occur in our case, as the reduced magnetization curves remain unchanged as a function of the stress, or interatomic distance, and the changes in T_C should directly come from modifications of the exchange strength. This behavior reinforces our previous assumption which excludes weak ferromagnetic behavior.

In tensile stress experiments longitudinal bond length increases whereas transversal ones are shortened, so giving rise to a large spread of the interactions experienced by each Fe atom, a fact perhaps reflected in the broadening of the hyperfine field distribution shown in Fig. 3. However, the overall shift to higher fields of $P(B_{HF})$ with stress indicates that the spread of exchange interactions is not likely to explain the $P(B_{HF})$ behavior, because one should expect a reduction of B_{HF} at the low B_{HF} edge and an increase at the high B_{HF} edge. Under hydrostatic pressure, on the other hand, all bond lengths are shortened, and a different behavior of B_{HF} should be expected. However, Bouzabata, Ingalls, and Rao on FeNiCr alloys[19] show a very similar behavior as that found here, $\langle B_{HF}\rangle$ decrease together with a narrowing of the distribution. This indicates that the effect of the changes in bond length on each atom is averaged over the different neighbors and the changes on the width of $P(B_{\mathrm{HF}})$ reflect the existence of inhomogeneities or fluctuations in the alloys. We cannot conclude from this study, however, whether the inhomogeneity is of a local type or it involves the existence of clusters of different magnetic properties. Spatially sensitive experiments, like small angle neutron scattering,[20] are probably the only way to elucidate this point.

As a conclusion, we can summarize the observation of a large effect of the applied tensile stress on the Curie temperature of FeZrB glasses. An isothermal transition from paramagnetic to ferromagnetic states can be observed in some compositions. The hyperfine-field distribution, revealed by Mössbauer spectroscopy, follows the same trend on average, but displays a broadening which can be related to inhomogeneities of the alloys.

The effect of boron in Fe, on the other hand, is greater than that of Zr for reinforcing the ferromagnetism in these alloys, both in Curie temperatures and Fe magnetic moment.[9] This effect cannot be related to a larger volume effect of the boron atoms since they are smaller than the Zr ones, but to a larger electronic transfer to the $3d$ band of Fe. Such transfer increases the itinerant exchange between Fe atoms and the density of states at the Fermi level and then the magnetic moment, destroying the weak ferromagnetic behavior of FeZr amorphous alloys. On the other hand, the effect of stress has been shown to reinforce the effect of the exchange, probably through an increase in the density of states at the Fermi level, because the direct exchange is believed to be always positive and to decrease as the interatomic distance increases.[21]

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