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Static critical phenomena in ball milled $(Fe_{0.74}Cu_{0.26})_{85}Zr_{15}$ amorphous alloy

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Abstract. The magnetic second-order phase transition that occurs at the Curie temperature in ball milled amorphous $(Fe_{0.74}Cu_{0.26})_{85}Zr_{15}$ metallic alloy has been investigated. The critical exponents β, γ and δ, and the Curie temperature were obtained using modified Arrot plots in an iterative manner and embracing the narrow temperature range $|T - T_C|/T_C \approx 0.1$. The values of the resulting critical exponents β, γ and δ are in good agreement with those predicted by the mean field theory, indicating that the exchange interactions are of long-range type. Furthermore, the temperature dependence of the spontaneous magnetization, determined for the exponents calculated, was obtained for a wider temperature range from 5 K to the Curie temperature. The presence of spin-wave excitations contributing to the thermomagnetization process at low temperatures is suggested by the mean field theory approach to the temperature dependence of the spontaneous magnetization. We propose a mictomagnetic low-temperature ground state, which appears to be reached through a thermally activated magnetization process.

1. Introduction

Considerable interest has been devoted during the last two decades to the influence of disorder on the static critical behaviour of spin systems that exhibit a second order phase transition [1–4]. This magnetic transition embraces a paramagnetic phase and an ordered ferromagnetic state and occurs at the Curie temperature (T_C). Moreover, glassy magnetic structures can be produced by rapid quenching, ball milling, sputtering and evaporation techniques. In this way, the magnetic behaviour around T_C of samples with the same composition but produced by each of these methods should be analysed separately since the configuration of the magnetic or structural inhomogeneities in each type of sample could produce different critical phenomena and add further controversy to this difficult research field.

Up to the present date, most of the work reported on the critical phenomena of disordered systems has been performed on samples produced by rapid quenching (for a review see [5]) and only recently some data concerning amorphous thin films has appeared [6]. The critical exponents derived in this recent publication appear different to those predicted by the 3D Heisenberg model, suggesting a possible structural origin of the critical behaviour, which appears worthwhile to pursue. As a result studies of the critical phenomena in amorphous samples produced using different techniques are of increasing interest.

In addition, the magnetic behaviour in amorphous magnetic systems appears to be further complicated by the possibility of a second transition to a disordered magnetic phase at a

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temperature, T_{xy}, below T_C. Evidence of this transition can be found for example in Mössbauer as well as thermomagnetization data [7], although considerable controversy still exists as to whether this latter transition is a true thermodynamic phase transition.

On the other hand, the high-energy ball milling technique offered the possibility of producing high-quality amorphous samples whose critical behaviour appeared unexplored. Our previous studies in ball milled Fe–Cu alloys [8] led us to focus on this system. However up to the present date the production of FeCu based amorphous alloys using high-energy ball milling had been unsuccessful. Nevertheless it appeared well established that rich 3d transition metals could be amorphized by adding small amounts of early transition metals such as Zr, Ti, Y or Hf [9]. In the present work and in order to induce amorphicity in the FeCu system we have added Zr. A nanocrystalline solid solution of the three elements (i.e. Fe, Cu and Zr), with average crystallite sizes below 10 nm, was found for low Zr contents (7 at.%) [10]. Yet an amorphous structure was obtained on increasing the Zr content to around 15 at.%. The aim of the present contribution is to analyse the static critical behaviour around the magnetic phase transition of $(Fe_{0.74}Cu_{0.26})_{85}Zr_{15}$ amorphous alloy produced by high-energy ball milling.

2. Static critical analysis

The temperature dependence of various thermo-dynamical quantities in an ideal magnetic solid near the phase transition temperature (T_C) can be described by a series of power laws which are satisfied for the critical exponents β, γ and δ [11]. The critical exponents β and γ describe the temperature dependence of the spontaneous magnetization, $M_S = M(0, T)$, and the inverse zero-field susceptibility, $\chi_0^{-1} = \chi^{-1}(0, T)$, respectively. On the other hand, the exponent δ determines the field dependence of the magnetization at T_C. The above mentioned power laws can be written as:

$$M_s = \lim_{(H\to 0)} M \propto (-\varepsilon)^\beta \qquad \varepsilon < 0 \tag{1}$$

$$\chi_0^{-1} = \lim_{(H\to 0)} (H/M) \propto (\varepsilon)^\gamma \qquad \varepsilon > 0 \tag{2}$$

$$M \propto H^{1/\delta} \qquad \varepsilon = 0 \tag{3}$$

where $\varepsilon = (T - T_C)/T_C$.

Experimentally, $M(H, T)$ and $\chi^{-1}(H, T)$ can be measured, but it is not possible to obtain directly the values of these parameters for $H = 0$, and extrapolation methods are needed. To determine the exponents β and γ, the raw thermomagnetization data were first converted into magnetization isotherms. When this was achieved, we applied modified Arrot plots [5], based on the Arrot–Noakes equation of state [12, 13], given by

$$\left(\frac{H}{M}\right)^{1/\gamma} = \frac{(T - T_C)}{T_1} + \left(\frac{M}{M_1}\right)^{1/\beta} \tag{4}$$

where T_1 and M_1 are material dependent parameters.

Linear extrapolation of the high-field straight-line portions of the isotherms in these plots yields intercepts on the $(M)^{1/\beta}$ and $(H/M)^{1/\gamma}$ axes. These intercepts provide a precise measure of the spontaneous magnetization at zero field (intercepts with the $(M)^{1/\beta}$ axes) and the inverse zero-field susceptibility (intercepts with the $(H/M)^{1/\gamma}$ axes), respectively. Both these set of values were then fitted to equations (1) and (2) within the narrow temperature range $|T - T_C|/T_C \approx 0.1$ [5], and β, γ and T_C determined. Using this first set of exponents, modified Arrot plots were computed and a new set of intercepts obtained. In order to compute accurate values of β, γ and T_C we have developed a self-consistent iterative procedure [14] until two successive iterations leave the functions M_s and χ_0^{-1}, and hence β, γ and T_C, unaltered.

Other authors claimed that this procedure provides a typical error of ± 0.02 [5] in the exponents determined.

3. Sample preparation; composition and structure

Powders of nominal composition $(Fe_{0.7}Cu_{0.3})_{85}Zr_{15}$ (at.%) were prepared by high-energy ball milling using Fe and Cu powders and Zr cutting files [10]. The milling was performed in a planetary mill with hardened stainless-steel vials and 10 mm stainless-steel balls in a ball-to-powder weight ratio of 15:1. To avoid oxidation during the milling process, the vials were sealed under an argon atmosphere prior to the milling. The composition of the powder was checked by energy dispersive x-ray analysis (EDX). From the composition determined, $(Fe_{0.74}Cu_{0.26})_{85}Zr_{15}$ (at.%), it can be inferred that the Fe content is slightly higher than that corresponding to the nominal composition, perhaps due to the contamination induced by the milling process. No traces of Cr and Ni were found in the EDX measurements.

In order to investigate the structure of the as milled sample, x-ray diffraction measurements were obtained using Co Kα radiation in the θ–2θ mode. Additionally room temperature Mössbauer spectroscopy was performed using a ^{57}Co source embedded in an Rh matrix. The Mössbauer spectra was obtained in an standard transmission geometry using a conventional constant acceleration spectrometer with a triangular modulation of the source. The fitting of the Mössbauer spectra was performed using the model proposed by Billiard and Chamberod [15].

The x-ray diffraction pattern of the sample investigated, clearly showing a broad halo characteristic of amorphous systems, is depicted in figure 1. A characteristic particle size of about 20 Å was deduced from this x-ray diffraction pattern, confirming the absence of a crystalline phase (see also [16] and references cited therein).

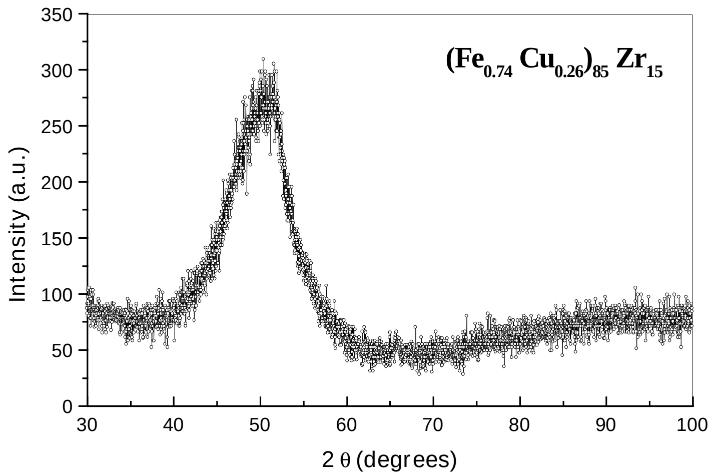

Figure 1. X-ray spectrum corresponding to the as-milled $(Fe_{0.74}Cu_{0.26})_{85}Zr_{15}$ alloy.

The room temperature Mössbauer spectra (see figure 2) corresponding to the sample analysed consists of a single line characterized by a high value of the full width at half maximum, FWHM, of 0.9 mm s^{-1}, confirming the amorphous nature of the sample. In addition, it should be remarked that no traces of ferromagnetic bcc-Fe are resolved. Consequently, the spectrum was fitted by assuming a distribution of Fe environments, in the same sense as the density fluctuation model predicts for Fe-rich Fe_xZr_{100-x} amorphous alloys [17].

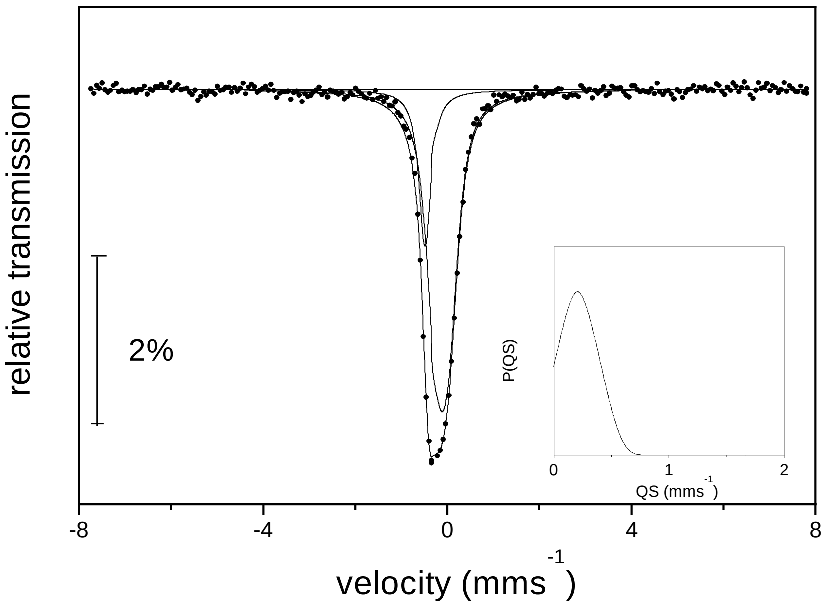

Figure 2. Room temperature Mössbauer spectrum corresponding to the $(Fe_{0.74}Cu_{0.26})_{85}Zr_{15}$ amorphous alloy. The inset shows the quadrupole distribution function used to fit the spectrum.

This spectrum was fitted to both a distribution of quadrupole splittings $P(\mathrm{QS})$ and a distribution of hyperfine fields, $P(B_{hf})$.

The quadrupole splitting distribution, $P(\mathrm{QS})$, shows a typical bell shape like with no distinct structure. This distribution suggests that the amorphous structure of the sample is a homogeneous one.

On the other hand, the high value of FWHM suggests that the origin of the spectrum is an overlapping of the six lines corresponding to a Zeeman sextet with a low value of the hyperfine field. The fitting to a distribution of hyperfine field yields $\langle B_{hf}\rangle = 4$ T and this low value suggests the proximity of the Curie temperature (as deduced below from magnetic measurements). Overall the above presented measurements guarantee that the sample analysed exhibits an amorphous structure, in the same context as those reported for metallic glasses produced by melt spinning or sputtering [5, 6].

4. Critical behaviour and discussion

In order to infer the critical behaviour around T_C, magnetic measurements in fields up to 5.5 T and at temperatures from 5 K to 350 K were performed using a Quantum Design MPMS SQUID magnetometer. The sample was introduced in a cylindrical shaped capsule, the demagnetizing field was estimated from shape considerations and corrections were made. A rough estimation of the Curie temperature of the sample investigated, deduced from kink-point calculations [18], yielded a value of 330 K.

The raw thermomagnetization data obtained for the sample investigated (not all the data are plotted for the sake of clarity) are shown in figure 3. Only the high-field data (see [5] for details), which were converted into magnetization isotherms, were used to perform the analytical procedure described in section 2.

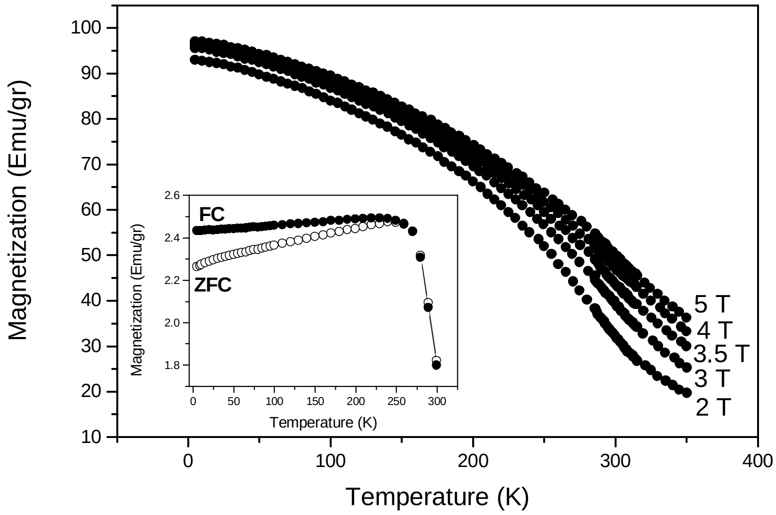

Figure 3. Thermomagnetization measurements with applied fields of 2 T, 3 T, 3.5 T, 4 T and 5 T, for the as-milled $(Fe_{0.74}Cu_{0.26})_{85}Zr_{15}$ amorphous alloy. The inset shows the ZFC/FC measurement of this sample with an applied field of 10 mT. Solid lines are shown as a guide to the eye.

The inset in figure 3 shows the ZFC/FC measurements performed with an applied field of 10 mT. This low-field thermomagnetization measurement is shown as an example of the irreversibility that occurs between the ZFC (open circles) and FC (full circles) curves at a temperature $T_{xy} \approx 250$ K. As mentioned previously this temperature is generally regarded as the transition temperature to a disordered magnetic phase [7]. In our case the value of this splitting temperature decreases on increasing the applied magnetic field until, for a sufficiently high field around 100 mT, the ZFC and FC curves coincide within the whole low-temperature range. In addition the first magnetization curves, obtained from hysteresis loop measurements, fail to saturate with fields as high as 5.5 T. On the other hand, the present alloy exhibited non-negligible values of the coercive field around T_{xy}, which disregards the possibility of ascribing this temperature to a superparamagnetic blocking temperature. With all the above mentioned features, the low-temperature magnetic state of the present sample can be tentatively regarded as a micromagnetic structure [9], in which ferromagnetic order coexists with cluster spin-glass order in the low-temperature range.

The experimental thermomagnetization data was measured using a temperature step of 1 K for temperatures between 275 K and 325 K and with a step of 5 K for the rest of the range. A portion of the final modified Arrot plots, obtained from the iterative procedure described in section 2, is shown in figure 4. Due to the extremely large number of isotherms, only a small portion of the modified Arrot plots is shown in figure 4. The data are well fitted to straight lines for fields higher that 3 T. The line that crosses the origin in the modified Arrot plots corresponds to the isotherm measured at the value of the Curie temperature. The value of δ (determined as the inverse of the slope of $\ln M - \ln H$ plots using the isotherm measured at the exact value of T_C) is 3.15.

Figure 5 shows the final curves corresponding to the spontaneous magnetization, M_s, and the inverse zero-field susceptibility, χ_0^{-1}, obtained from the intercepts on the $(M)^{1/\beta}$ and $(H/M)^{1/\gamma}$ axes of figure 4.

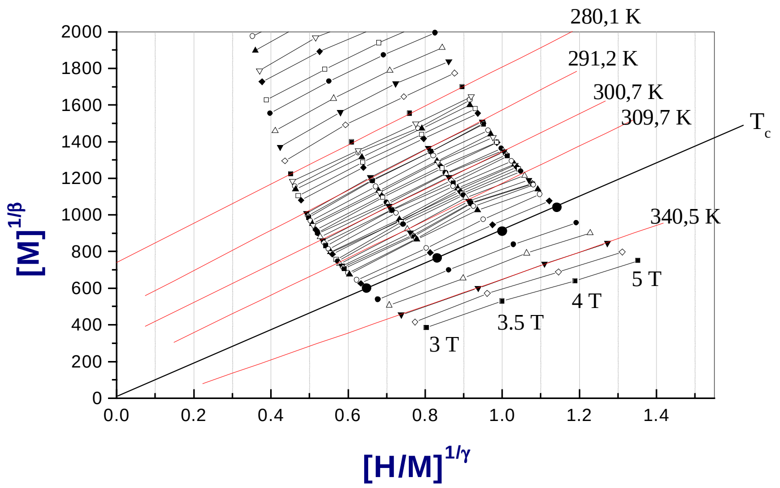

Figure 4. Modified Arrot plots corresponding to the as-milled $(Fe_{0.74}Cu_{0.26})_{85}Zr_{15}$ amorphous alloy.

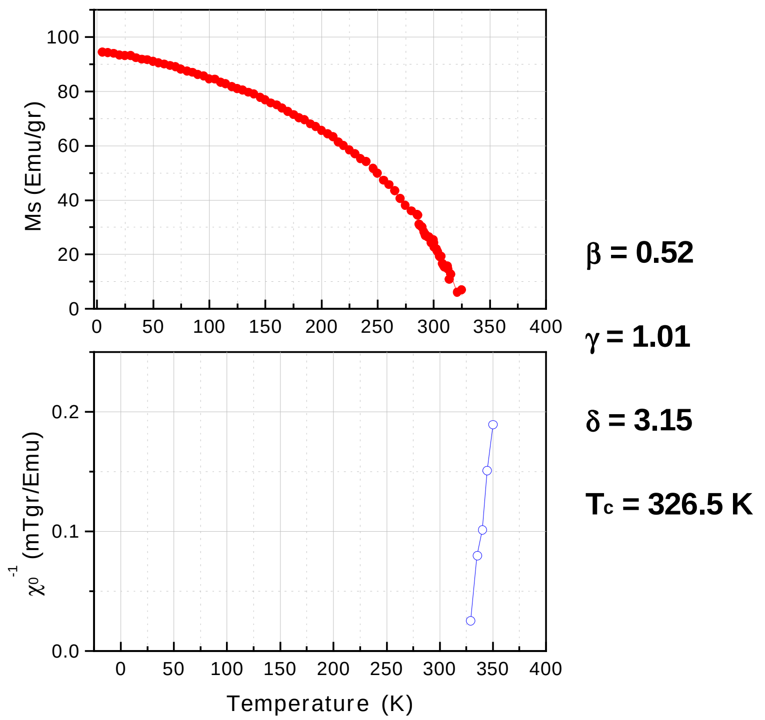

Figure 5. Spontaneous magnetization, M_s, inverse zero-field susceptibility χ_0^{-1} and the values of the critical exponents deduced for the as-milled $(Fe_{0.74}Cu_{0.26})_{85}Zr_{15}$ amorphous alloy.

The evolutions of the values of β, γ and T_C obtained for different numbers of iterations are shown in figure 6.

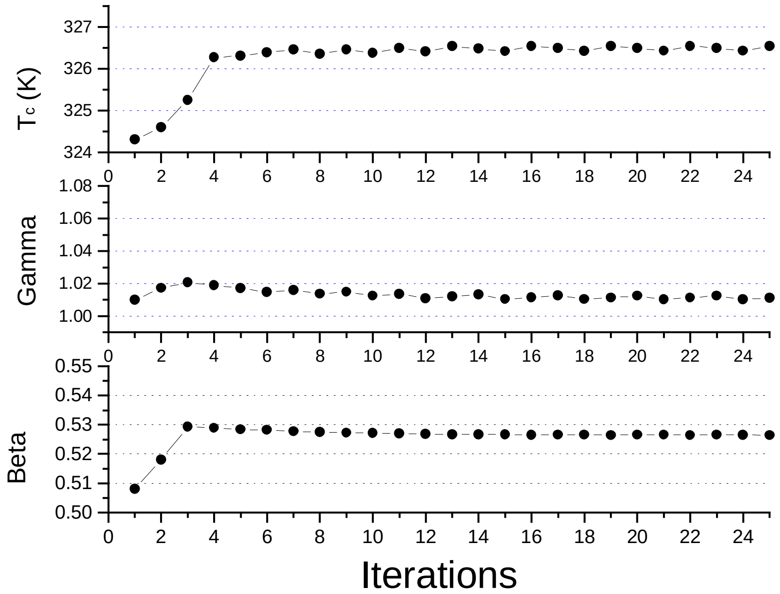

Figure 6. Values of β, γ and T_C obtained for different numbers of iterations.

The values obtained for β (0.52) and γ (1.01) are in good agreement with the values of these parameters predicted by the mean field theory ($\beta = 0.50$ and $\gamma = 1.0$) [19]. However it is generally accepted [5] that disordered ferromagnets exhibit critical exponents close to those predicted by the 3D Heisenberg model ($\beta = 0.365$ and $\gamma = 1.387$).

Using a renormalization group analysis [20] for the critical exponents of systems with long-range exchange interactions of the form $J(r) \approx 1/r^{d+\sigma}$ (where d is the dimension of the system and σ a measure of the interaction range) it has been concluded that the mean field theory exponents are only reached for the long-range order limit ($\sigma > \frac{1}{2}$).

Moreover the critical exponents in crystalline magnetic solids such as Ni appear to obey static equations [5], such as $\delta = 1 + \gamma/\beta$. However in amorphous metallic structures the spatial fluctuations of exchange integrals produce deviations in the M_s function [21] which could lead to anomalous static critical phenomena [22]. There is a slight variation between the experimentally obtained value of δ, 3.15, and that computed using the above mentioned static equation, 2.94.

The deviations in M_s, due to the amorphous magnetic structure of the $(Fe_{0.74}Cu_{0.26})_{85}Zr_{15}$ amorphous alloy sample, can be analysed using the Handrich theory [23], which provides an approach to the temperature dependence of the spontaneous magnetization using the mean field theory. Using this approach the reduced magnetization, $M_s(T)/M_s(0)$, can be written in terms of the reduced temperature, T/T_C, as

$$\frac{M_s(T)}{M_s(0)} = \frac{1}{2}\{B_J[z(1+\Delta)] + B_J[z(1-\Delta)]\} \tag{5}$$

where B_J are Brillouin functions,

$$z = \left(\frac{3S}{S+1}\right)(T_C/T)\frac{M_s(T)}{M_s(0)} \tag{6}$$

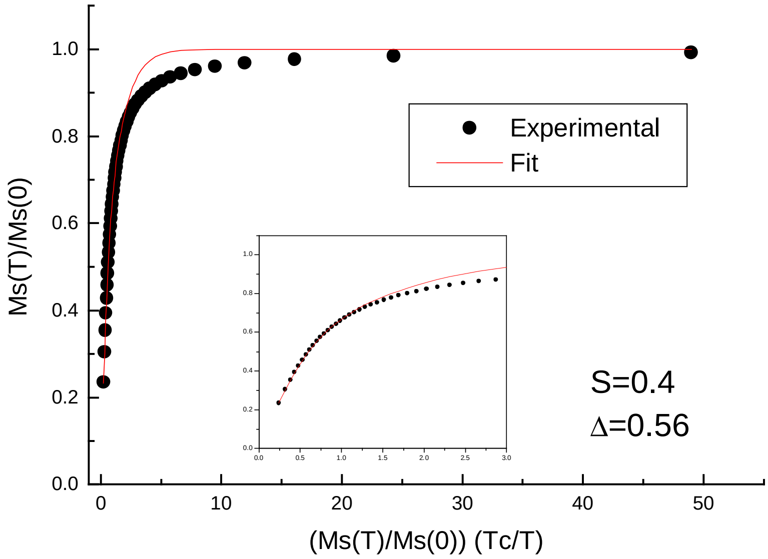

Figure 7. $M_s(T)/M_s(0)$–$M_s(T)T_C/M_s(0)T$ plot corresponding to the sample investigated. The solid line corresponds to the fitting, by the least squares method, to equation (5). The values of S and Δ corresponding to the fitted curve are also given. The inset shows the agreement obtained in the fittings for the high-temperature range.

and

$$\Delta = \left\{ \frac{\langle \Delta J^2 \rangle}{\langle J^2 \rangle} \right\}^{1/2} \tag{7}$$

is the root mean square of the deviation from an average exchange integral between two nearest-neighbour spins and ranges from 0 (crystalline ferromagnet) to unity. Figure 7 shows an $M_s(T)/M_s(0)$–$M_s(T)T_C/M_s(0)T$ plot corresponding to the sample investigated. The data used for this plot had a temperature step of 5 K and were fitted by the least squares method to equation (5).

The fit to the theoretic model described above, within the whole temperature range investigated, appears not very accurate, perhaps due to the considerable simplifications introduced in the model [23]. Nonetheless the obtained values can be discussed qualitatively. In this way, most models [24] agree that the value of Δ separating the mictomagnetic and the canonical spin-glass-like behaviour is around 0.7. The value of this parameter obtained for the sample analysed is 0.56. Therefore the values of the exchange fluctuations for this sample can be ascribed as borderline to spin-glass-like behaviour, as expected for a low temperature weak mictomagnetic structure [9, 25]. On the other hand the value obtained for the atomic magnetic moment, S, appears to be lower than that expected for bcc-Fe ($S \approx 1$). This reduction of the magnetic moment appears to be inherent to the alloy nature of the present sample.

Another interesting result of the present fitting is that the calculated data and the theoretical curve are not in good agreement at low temperatures. This effect may not be ascribed to the low-temperature transition since the experimental spontaneous magnetization was obtained using high-field data and the presence of this transition is only observed up to 100 mT. Thus the present results suggests that there is a considerable contribution of spin-wave excitations to the thermomagnetization process at low temperatures as concluded earlier in sputtered Fe_xZr_{100-x} amorphous alloys [26].

Furthermore, recent investigations [27] suggest that T_{xy} can be regarded as a phase transition, in the sense associated with a genuine thermodynamic phase transition, as the vector model predicts [28]. However as mentioned before the value of this temperature decreases when increasing the applied magnetic field and eventually disappears for a sufficiently high field (see also [29]). Nevertheless it appears that, scaling the equation of state [26] to the temperature at which the splitting occurs, one could obtain the critical exponents corresponding to the spin-glass-like transition. In our case, there is no splitting in the scaling plots around T_{xy}. Hence, according to our results, T_{xy} can be tentatively regarded as a continuous spin-freezing temperature and not a true thermodynamic phase transition. Thus the low-temperature mictomagnetic state appears to be achieved through a thermally activated magnetization process. These conclusions have been recently supported by a work performed by Kaul and Srinath [30], in which a detailed analysis of both static and dynamic thermal cycling modes in Fe rich Fe_xZr_{100-x} amorphous alloys clearly demonstrated that T_{xy} is not a true thermodynamic phase transition.

In conclusion the critical behaviour of the ball milled $(Fe_{0.74}Cu_{0.26})_{85}Zr_{15}$ amorphous structure can be ascribed as arising from the spatial fluctuations of the exchange integrals, associated with density fluctuations that appear in amorphous metallic glasses [5, 17]. The critical exponents obtained, using the method described in section 2, are $\beta = 0.52$ and $\gamma = 1.01$, in good agreement with those deduced using the mean field theory ($\beta = 0.50$ and $\gamma = 1.0$). This implies in turn that the exchange interactions are of long-range type. The presence of spin-wave excitations contributing to the thermomagnetization process at low temperatures is suggested by the mean field theory approach to the temperature dependence of the saturation magnetization. In view of the present results and those reported recently by Kaul and Srinath [29], we propose a mictomagnetic low-temperature ground state which appears to be reached through a thermally activated magnetization process.

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