Cluster spin-glass model for amorphous Fe–Zr alloys near the critical concentration: a magnetization study

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Abstract

The magnetic properties of melt-quenched amorphous Fe$_{100-x}$Zr$_x$ (x = 7–12) alloys were studied in the temperature and magnetic field ranges 15 K < T < 300 K and 0 < H$_{ext}$ < 1.8 T, respectively. Assuming that Fe$_{93}$Zr$_7$ is an assembly of magnetic clusters with a blocking temperature distribution, the magnetization versus magnetic field curves were fitted using Néel's theory for fine particles at several temperatures in order to obtain the evolution of cluster parameters with temperature. The same model is used for Fe$_{92}$Zr$_8$ and Fe$_{98}$Zr$_{12}$ above the Curie temperature ($T_C$). When Néel's theory is modified to account for the interaction between the cluster moments, the experimental data are properly described by this frame. This model can explain both the low-temperature anomalies of susceptibility observed for x = 7–10 and the high-temperature superparamagnetic behaviour which is shown to be a characteristic feature of the whole a-Fe$_{100-x}$Zr$_x$ alloy series. The evolution of magnetic cluster behaviour with temperature and concentration is discussed.

1. Introduction

A proper understanding of the magnetic properties of amorphous Fe$_{100-x}$Zr$_x$ alloys near the critical concentration (x$_c$ = 7) has been a great challenge for more than a decade [1]. Three different types of magnetic behaviour are observed in this alloy series: (i) ferromagnet-like alloys (x = 12) characterized by the Curie temperature $T_C$; (ii) re-entrant spin glasses (RSG, x = 8–10) characterized by two transition temperatures, $T_C$ denoting a transition from paramagnetic (PM) to ferromagnetic (FM) state and $T_f$ from ferromagnetic to spin-glass (SG) state; and (iii) spin glasses (x = 7), where only one transition from paramagnetic to spin-glass state occurs at $T_g$ [1–5]. The Curie temperature $T_C$ decreases with decreasing Zr content, while $T_f$ changes in the opposite way, coinciding with $T_g$ for x = 7. Below $T_f$ or $T_g$, the coercivity increases enormously both with decreasing temperature and with decreasing Zr content at constant temperature (i.e. approaching the critical concentration) [2,4,5]. In addition, time-dependent magnetization (magnetic viscosity) is observed below the spin-glass temperature ($T_f$, $T_g$) suggesting non-equilibrium effects in Fe–Zr glassy alloys, similar to those observed in amorphous Fe–Y [6]. In a-Fe$_{100-x}$Zr$_x$ (7 ≤ x ≤ 12) the magnetization versus magnetic field curve shows no saturation even up to 20 T [2,7]. It is similar to that of a superparamagnetic system for
intermediate fields $0.2 \, T < H_{\text{eng}} < 2 \, T$. The high-field susceptibility ($\chi_{\text{hf}}$) is thus at least one order of magnitude higher than that for amorphous Co–Zr alloys of similar composition [3]. The large $\chi_{\text{hf}}$ value is one of the characteristic features which are generally associated with Invar properties and is observed in many other amorphous [9–11] and crystalline [12] alloy systems as well.

Several models attempt to account for the above-mentioned magnetic properties of Fe–Zr amorphous alloys. The model of Saito et al. [13] assumes that the spin-glass state below $T_f$ is due to the freezing of frustrated spin clusters of antiferromagnetic Fe spins distributed in a ferromagnetic matrix. However, Mössbauer spectra taken in external magnetic fields [14] do not support the existence of antiferromagnetic coupling between Fe spins. Kaul and co-workers [15–18] suggest that amorphous Fe$_{100-x}$Zr$_x$ ($x = 8–10$) alloys consist of a ferromagnetic matrix (infinite cluster) plus finite ferromagnetic clusters separated and magnetically isolated by frustration zones. This picture is supported by bulk magnetic [15] and ferromagnetic resonance (FMR) data [16] and is further strengthened by measuring the effect of isothermal annealing on the magnetic behaviour of amorphous Fe–Zr alloys using FMR technique [17,18]. The existence of a real (collinear) FM matrix in Fe-rich amorphous Fe–Zr alloys is questioned by Ryan and co-workers [2,19] in their ‘wandering-axis ferromagnet’ model in which the spin structure is locally ferromagnetic with small variations in neighbouring spin directions but the local ferromagnetic axis changes direction over distances of the order of 25 Å. According to this model a phase transition to an asperomagnetic state [19] takes place at $T_f$ (transverse spin freezing), similar to that in the theoretical model of Gabay and Toulouse [20]. The basic idea behind the above models is the existence of competing (ferromagnetic and antiferromagnetic) exchange interactions between neighbouring Fe spins caused by fluctuating interatomic distances due to the amorphous structure.

On the other hand, there are models which claim that the anomalous low-temperature magnetic behaviour of Fe-rich amorphous Fe–Zr alloys has nothing to do with spin freezing. Read et al. [4] attribute the abrupt increase in coercivity below $T_f$ to domain wall pinning by antiferromagnetic Fe clusters dispersed in a FM matrix. In this model the transition at $T_f$ is simply caused by the breakdown of the kink point relation ($\chi_{\text{int}} = M / H_{\text{int}} \gg 1 / D$, where $D$ is the demagnetization factor of the sample and $H_{\text{int}}$ is the internal magnetic field) due to the rapid decrease in $\chi_{\text{int}}$ with decreasing temperature. In this picture, $T_f$ depends on $D$ (i.e. the sample geometry) and consequently it does not reflect a real physical transition. Beck and Kronmüller [5] suggest that the anomalous low-temperature properties of Fe-rich amorphous Fe–Zr alloys are determined by increasing local magnetic anisotropy energies of a normal ferromagnet with decreasing temperature. The physical origin of such a temperature dependence of the anisotropy is, however, not clear.

The resemblance of the magnetic properties of fine particles [21] to those of classical spin glasses has led to the assumption of a granular magnetic structure (magnetic clusters) in spin glasses. The assumption of a distribution for the cluster size has been demonstrated to reproduce the spin-glass behaviour in classical spin glasses [22]. Real fine-particle systems differ in many ways from the suppositions of Néel’s classical theory for fine particles [21] (i.e. single and temperature-independent cluster size, absence of cluster anisotropy, temperature-independent saturation magnetization of the clusters, no interaction between cluster moments). Nevertheless, their magnetization versus magnetic field curves at different temperatures can be transformed into universal curves showing the superparamagnetic behaviour of these systems (see details in Section 3). Similar behaviour is thus expected also in spin-glass systems, including amorphous Fe–Zr alloys.

In order to study the effect of magnetic clusters on the magnetic behaviour of Fe-rich Fe$_{100-x}$Zr$_x$ amorphous alloys, we focused our attention mainly on the alloy at the critical concentration ($x_c = 7$) where no ferromagnetic matrix is expected to occur. Measurements were also made on samples near the critical concentration ($x = 8$, 9, 10 and 12) where the alloys approach FM-like behaviour with increasing $x$. It suggests
that the magnetic anomalies, which are also observed for \( x = 7 \), do not arise from the FM matrix (infinite cluster) but from what we suppose to be finite magnetic clusters. Two types of bulk magnetic measurements were performed. First, the low-field magnetization \( (H_{\text{ext}} = 10 \, \text{Oe}) \) was measured as a function of temperature \( (15 \, \text{K} < T < 300 \, \text{K}) \) both after zero-field cooling and after cooling in \( H_{\text{cool}} = 10 \, \text{Oe} \) external field (‘field cooling’). Second, the magnetization versus external magnetic field \( (0 < H_{\text{ext}} < 1.8 \, \text{T}) \) was recorded at several selected temperatures. The magnetic data of a-Fe\(_{100-x}\)Zr\(_{x}\) below \( T_g \) \((x = 7) \) or \( T_i \) \((x = 8) \) and above \( T_g \) or \( T_i \) \((x = 8 \) and 12) are described in terms of a model according to which the material consists of an assembly of interacting magnetic clusters. The model is based on Néel’s theory for fine particles [21] assuming a blocking-temperature (i.e. cluster size) distribution for the clusters and treating their interactions in an approximate way (see details in Section 3).

2. Experimental

The magnetization was measured by a Foner-type vibrating sample magnetometer with a sensitivity of \( 10^{-4} \, \text{emu} \) in an electromagnet with magnetic fields up to 1.8 T. The temperature of the sample was varied using a continuous-flow He cryostat. The samples were produced by melt-spinning in ribbon form of cross section \( 1 \, \text{mm} \times 12 \, \mu\text{m} \) and their amorphous state was checked by X-ray diffraction and Mössbauer spectroscopy. 10–15 ribbon pieces each 4 mm length with a total mass of about 2.5 mg were glued together by water-glass (sodium silicate). The magnetic field during the measurements was directed in plane and along the length of the ribbons.

3. Results and discussion

Fig. 1 displays the low-field magnetization at \( H_{\text{ext}} = 10 \, \text{Oe} \) as a function of temperature for \( x = 7 \) and 8 after cooling (from room temperature) in zero field (ZFC) and in \( H_{\text{ext}} = 10 \, \text{Oe} \) (FC). Fe\(_{93}\)Zr\(_7\) and Fe\(_{92}\)Zr\(_8\) show typical spin-glass-like (with a cusp at \( T_g \)) and re-entrant spin-glass (RSG) behaviour (with transition temperatures \( T_f \) defined in Fig. 1 and Curie temperature \( T_C \)), respectively, in accordance with literature data [1–5]. Similar RSG behaviour of the \( M-T \) curves is found for \( x = 9 \) and 10 and only a seemingly normal ferromagnetic behaviour is observed for Fe\(_{98}\)Zr\(_{12}\). The \( T_g \), \( T_i \) and \( T_C \) values are summarized in Table 1 for the studied amorphous Fe-Zr alloys. (The values of \( T_g \) and \( T_i \) are slightly field dependent; Table 1 contains \( T_g \) and \( T_i \) values measured at \( H_{\text{ext}} = 10 \, \text{Oe} \).)

Based upon Fig. 1 and considerations made by Beck [23] the internal susceptibility \( (\chi_{\text{int}} = M/H_{\text{int}}) \) must be of the same order of magnitude as the external susceptibility \( (\chi_{\text{ext}} = M/H_{\text{ext}}) \) in

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the Fe-rich a-Fe_{100-x}Zr_x alloys near the critical concentration \(x = 8, 9, 10\) and 12) and \(\chi_{\text{ext}}\) is not demagnetization-controlled as in a real ferromagnet. This suggests that these alloys are not conventional ferromagnets even in the temperature range \(T_f < T < T_C\). Moreover, it also follows that \(\chi_{\text{int}} = \chi_{\text{ext}}\) for susceptibility values smaller than \(\chi_{\text{ext}} = 0.4-0.5\) emu/g Oe, i.e. for the whole \(M-T\) curve of Fe_{93}Zr_7 and for temperatures \(T < T_f\) and \(T > T_C\) in the case of the other compositions.

The magnetization as a function of external magnetic field is shown in Figs. 2(a)–2(c) for \(x = 7, 8\) and 12 at several selected temperatures. It agrees with previous experimental results [1–5].

3.1. The model of non-interacting cluster moments

On cooling, the magnetic moment of a cluster is thermally trapped by the magnetic anisotropy at a temperature (called the blocking temperature, \(T_B\)) above which the assembly of the clusters shows superparamagnetic behaviour [21]. The blocking temperature is given by \(T_B = KV/25k\), where \(K\) and \(V\) are the uniaxial anisotropy constant and the volume of the clusters, respectively [21,24], \(k\) denotes the Boltzmann constant, and the numerical factor of 25 is obtained in the case

![Fig. 2. Magnetization \(M\) versus external magnetic field \(H_{\text{ext}}\) for \(x = 7\) (a), 8 (b) and 12 (c) of the a-Fe_{100-x}Zr_x alloy series at selected temperatures as denoted at each curve.](image)

![Fig. 3. Assumed normalized blocking temperature distribution function \(f(T_B)\) for Fe_{93}Zr_7 (solid line) and Fe_{92}Zr_8 (broken line).](image)
of static measurements \((\nu = 10^{-2} \text{1/s, where } \nu \text{ is frequency})\) using a Larmor frequency of \(\nu_0 = 10^9 \text{ Hz}\) [25].

In order to account for the observed susceptibility–temperature relation shown in Fig. 1, a distribution in cluster volume (and hence in blocking temperature \(f(T_B)\)) is assumed. The steep susceptibility increase with increasing temperature below \(T_g\) or \(T_f\) on the ZFC curves is interpreted as the gradual disappearance of cluster blocking at their individual \(T_B\)'s according to the distribution function \(f(T_B)\).

The magnetic field \((H_{\text{int}} = H_{\text{ext}} \equiv H)\) and temperature dependence of the magnetization \(M(H, T)\) are given for high fields, i.e. for \(mH \gg kT\) \((m\) is the magnetic moment of a cluster), similar to Ref. [23, as

\[
M(H, T) = M_s \int_0^T f(T_B) L \left( \frac{m(T_B) H}{kT} \right) \, dT_B
\]

\[
+ M_s \int_T^\infty f(T_B) \, dT_B + \chi_{\text{hf}} H,
\]

where \(L(a) = \coth a - 1/a\) denotes the Langevin function, \(f(T_B)\) is the distribution of the blocking temperatures satisfying \(\int_0^T f(T_B) \, dT_B = 1\), \(m(T_B) = M_s V(T_B) = 50kT_B/H_A\) is the magnetic moment of a cluster with the anisotropy field \(H_A = 2K/M_s\), and \(M_s\) is the saturation magnetization. The first term in (1) describes the superparamagnetic behaviour of the clusters whose blocking temperatures are lower than the actual temperature \(T\). The second term gives the magnetization of the blocked clusters whose \(T_B\)'s are higher than \(T\) and whose moments are aligned along a field high enough to overcome the anisotropy field of the clusters. The third term in (1) accounts for the rather large high-field susceptibility \(\chi_{\text{hf}}\) observed in these alloys (Figs. 2a–c). The factors giving rise to \(\chi_{\text{hf}}\), which cannot be overcome even by a field as high as 20 T [2,7], may not cause the low-temperature anomalies of amorphous Fe–Zr alloys which cease to exist in fields as low as a few hundred Oe [1–5].

In terms of the model described above the initial susceptibility \((H \to 0)\) can be expressed as

\[
\chi(T) = \int_0^T f(T_B) \frac{C(T_B)}{T} \, dT_B + \chi_{\text{hf}}, \tag{2}
\]

where \(C(T_B) = n(T_B)m^2(T_B)/3k = M_s m(T_B)/3k\) is the Curie constant, with \(n(T_B)\) denoting the number of clusters per gram. The first term in (2) gives the contribution to the susceptibility of the free (superparamagnetic) clusters whose \(T_B\)'s are below \(T\), the actual temperature. The contribution of the blocked clusters to \(\chi(T)\) can be neglected [22].

In order to determine the parameters by fitting, some assumptions about \(f(T_B)\) should be made. Theoretically, \(f(T_B)\) can be derived from (2) as

\[
f(T_B) = \frac{\frac{d}{dT_B} (T_B \chi) / \lim_{T_B \to \infty} (T_B \chi),}{\text{but because of the } T\text{-dependent Curie constant and the large scattering of data points for Fe}_{93-Zr}_{7}, \text{a quantitative result for } f(T_B) \text{ could not be obtained. An additional problem arises in calculating } f(T_B) \text{ of Fe}_{92-Zr}_{8}, \text{ by the simultaneous presence of a ferromagnetic fraction in the alloy. Therefore, inspired by the linearly increasing } \frac{d}{dT} (T \chi) \text{ functions below } T = 90 \text{ and } 60 \text{ K for Fe}_{93-Zr}_{7} \text{ and Fe}_{92-Zr}_{8}, \text{ respectively, we suggest blocking temperature distribution functions } f(T_B) \text{ as shown in Fig. 3 for these two alloys. The temperatures at which } f(T_B) \text{ attains its maximum, are chosen in the vicinity of } T_g \text{ for Fe}_{93-Zr}_{7}, \text{ and } T_f \text{ for Fe}_{92-Zr}_{8}. \text{ The maximum blocking temperature } T_B^{\text{max}}, \text{ above which } f(T_B) \text{ is zero, is taken to be } T_B^{\text{max}} = 120 \text{ K for Fe}_{92-Zr}_{8}, \text{ because Mössbauer results on the same alloy show clear paramagnetic behaviour above 115 K [26]. Such an estimation is not possible for Fe}_{92-Zr}_{8}, \text{ because of the ferromagnetic fraction present in this alloy, therefore in this case } T_B^{\text{max}} \text{ is chosen to be } T_B^{\text{max}} = 80 \text{ K (by analogy to Fe}_{93-Zr}_{7}. \text{ Slight changes in } f(T_B) \text{ have no significant effect on the results.}

Expressions (1) and (2) can be fitted simultaneously to the measured \(M(H)\) and \(\chi(T)\) curve, with the use of \(f(T_B)\) depicted in Fig. 3 and by varying the three fitting parameters \(M_s, H_A\) and \(\chi_{\text{hf}}\). Derived quantities from the fitting parameters are (i) the average magnetic moment of the free (superparamagnetic) clusters \(m_s\), (ii) the average number of Fe spins in a cluster \(N\), and (iii)
the average number of clusters per gram $\bar{n}$. Since $\text{Fe}_{88}\text{Zr}_{12}$ shows no re-entrant spin-glass temperature, no $f(T_B)$ can be postulated for it. In this case the second term is zero in (1) and the first term is replaced by $M_s \cdot L(\bar{m}_s H/kT)$ without averaging over $f(T_B)$ in the whole temperature range. Similar changes have to be considered in (2). Thus in case of $\text{Fe}_{88}\text{Zr}_{12}$, $\bar{m}_s$ takes the role of $H_A$ as one of the fitting parameters. The fitting procedure can only be made if $\chi_{\text{int}}(T)$ is known, which (as previously discussed) is the case for $\text{Fe}_{93}\text{Zr}_7$ over the whole temperature range investigated and for the other amorphous Fe–Zr alloys at temperatures $T < T_f$ and $T > T_C$. $\bar{N}$ is found to be about 22 000 and 32 000 below $T_g$ or $T_f$ for $\text{Fe}_{93}\text{Zr}_7$ and $\text{Fe}_{92}\text{Zr}_8$, respectively, and decreases rapidly with temperature above $T_C$ for all the three alloys. $\chi_{\text{hf}}$ ranges between 0.9 and $1.3 \times 10^{-3}$ emu/g Oe for all the fits, while $H_A$ assumes values of several thousand Oe for $\text{Fe}_{93}\text{Zr}_7$ and $\text{Fe}_{92}\text{Zr}_8$. The fit is not sensitive for two of the parameters, $M_s$ and $\chi_{\text{hf}}$, meaning that large variation of $H_A (\bar{m}_s)$ has little effect on them and similar values could be obtained for $M_s$.

Fig. 4. Universal function $[M(H) - \chi_{\text{hf}} H]/M_s^*$ versus $a = \bar{m}_s H/kT$ for $\text{Fe}_{93}\text{Zr}_7$, at $T = 121$ K (×), 141 K (+) and 162 K (○) (a); for $\text{Fe}_{92}\text{Zr}_8$ at $T = 184$ K (×) and 200 K (+) (b) and for $\text{Fe}_{88}\text{Zr}_{12}$ at $T = 259$ K (×) and 267 K (+) (c), together with the theoretical curves $M'/M_s$ versus $a = \bar{m}_s H/kT$ for fine particles with interaction for interaction parameters $b = \bar{m}_s H/kT = 1, 1.5, 2$ and 2.5, and the Langevin function of the interaction-free model.
and $\chi_{hf}$ by simply drawing a straight line to the high-field portion of the $M(H)$ curves. The fit is rather poor for intermediate magnetic fields between 0.1 and 1.5 T. We show later that it can be significantly improved by taking into account the interactions between the cluster moments.

For an assembly of superparamagnetic particles without interaction, $M$ versus $H/T$ is a universal function which is independent of temperature and particle anisotropy [27]. The $M$ versus $H/T$ curves should also be corrected for the variation of $M$, with $T$ [28] and for the magnetization contribution originating from $\chi_{hf}$. The corrected data $(M(H) - \chi_{hf}H)/M_s$ versus $M_s H/T$ for all the alloys investigated approach a universal curve for $T > T_g$ and $T_C$, where all the magnetic clusters rotate freely. These quasi-universal curves allow us to determine $\bar{m}_s$ and $\bar{N}$ independently from the previous fitting procedure (using only the two insensitive parameters, $M_s$ and $\chi_{hf}$). According to Néel's model for superparamagnetic particles [29] $(M - \chi_{hf}H)/M_s$ for relatively high fields ($mH \gg kT$) can be approximated as

$$\frac{M - \chi_{hf}H}{M_s} = 1 - \frac{\bar{N}kT}{M_s H}. \quad (3)$$

$\bar{N}$ and $\bar{m}_s$ thus calculated from the high-field portion of the $M(H)$ curve are much smaller and have much smoother temperature dependences (above $T_g$ or $T_f$) than those previously determined essentially from a low-field fitting to the susceptibility.

### 3.2. Interaction between cluster moments

In the mean-field approximation $H$ is replaced by $H + \lambda M'(H)$, where $M'(H) = M(H) - \chi_{hf}H$ and $\lambda$ is the molecular field constant, so we get from (2) for $H \to 0$ (when $L(a) \to a/3$):

$$M(H) = M_s \left[ \frac{\bar{m}_s(H + \lambda M')}{3kT} \right] + \chi_{hf}H. \quad (4)$$

Expressing $\bar{m}_s$ in terms of the measured susceptibility $\chi = M/H_s$, we obtain:

$$\bar{m}_s = \frac{\bar{m}_s^0}{1 + \lambda(\chi - \chi_{hf})}, \quad (5)$$

where $\bar{m}_s^0 = \frac{3kT(\chi - \chi_{hf})}{M_s}$ is the magnetic moment without interaction ($\lambda = 0$). Note that $m_s$ and $\lambda$ cannot be unambiguously determined from the measured $\chi$ (i.e. if only low-field data are used).

For higher fields we have to solve the following two equations:

$$\frac{M'}{M_s} = \frac{kT}{\bar{m}_s \lambda M_s} \left( a' - \frac{\bar{m}_s H}{kT} \right), \quad (6)$$

$$\frac{M'/M_s}{L(a')} = \frac{m_s \lambda}{kT} \approx a, \quad (7)$$

where $a' = \bar{m}_s(H + \lambda M')/kT$. The $m_s H/kT \equiv a$ and $m_s \lambda m_s/kT \equiv b$ are dimensionless parameters for the magnetic field and the interaction, respectively. Figs. 4(a)-(c) show among others the theoretical $M'/M_s$ versus $a$ curves for several $b$ parameters, together with the Langevin function of the non-interacting case. The introduction of an interaction has a relatively high effect on the initial susceptibility but the congruency of the curves is only slightly affected at higher fields.

Supposing that the apparent large average magnetic moments ($\bar{m}_s^0$) obtained from the first, low-field fitting are the consequence of the neglected interaction and using their more realistic values ($\bar{m}_s$) from the second, high-field fitting, the molecular field constant $\lambda$ can be calculated according to (5). The dimensionless interaction parameter $b$ can be readily obtained from $\lambda$ by definition.

Knowing the cluster parameters above $T_g$ or $T_C$, the measured $M(H)$ curves can be transformed into dimensionless master curves, $(M - \chi_{hf}H)/M_s$ versus $a = \bar{m}_s H/kT$. However, $M_s$ determined in the first fitting procedure was systematically underestimated by several percent because artificially large moments had to be used in the argument of the Langevin function to fit the susceptibility. (The larger the moment, the more rapidly the Langevin function saturates.) Correcting $M_s$ for this effect ($M_s^*$) in $(M - \chi_{hf}H)/M_s$ and leaving $a$ unchanged, we get the master curves shown in Figs. 4(a)-(c) for Fe$_{92}$Zr$_7$, Fe$_{92}$Zr$_8$ and Fe$_{88}$Zr$_{12}$, respectively. For comparison, the theoretical $M'$ versus $a$ curves for several values of the parameter $b$ are also drawn. The quantities derived from the fitting parame-
ters would be only slightly (and systematically) modified by this correction, therefore the original values will be used in the discussion. The measured curves with calculated interaction parameters \( b \) between 1.7 and 2.7 lie in the stripe of the corresponding theoretical curves. The congruency of the measured curves with the theoretical ones for interacting fine particles is striking and indicates that the Fe-rich Fe\(_{100-x}\)Zr\(_x\) amorphous alloys show superparamagnetic behaviour above the spin-glass temperature \( T_g \) (\( x = 7 \)) and the Curie temperature \( T_C \) (\( x = 8-12 \)). The only discrepancy at the shoulder of the curves (\( a = 2-6 \)) may be attributed to the fact that the distribution of the moments was not taken into account in the calculation of the theoretical curves.

Fig. 5 shows the temperature and concentration dependence of the interaction parameters \( \lambda \) and \( b \) for Fe\(_{92}\)Zr\(_7\), Fe\(_{92}\)Zr\(_8\) and Fe\(_{88}\)Zr\(_{12}\) above their critical temperatures (\( T_g \) or \( T_C \)). \( b \), i.e. the ratio of the interaction energy to the thermal one, is the real measure of the interaction between the cluster moments (rather than \( \lambda \)). It decreases with temperature and increases slightly with concentration. The latter is consistent with the experimental fact that the magnetic properties of the Fe-rich Fe\(_{100-x}\)Zr\(_x\) amorphous alloy system approach to those of a normal ferromagnet as \( x \) increases from \( x = 7 \) to 12.

The molecular field constant \( \lambda \) increases with temperature for all the three alloys. A similar dependence of \( \lambda \) on \( T \) was obtained by Beck [23] based on fitting the \( M-H \) curves of crystalline Au\(_{82}\)Fe\(_{18}\) at different temperatures. Those curves can also be described by assuming that the alloy consists of finite superparamagnetic clusters. Mössbauer studies on Fe\(_{90}\)Zr\(_{10}\) [30] and resistance fluctuation experiments in CuMn [31] also support the observed \( \lambda-T \) dependence.

The temperature and concentration dependence of the average number \( \bar{N} \) of Fe spins in a cluster is shown in Fig. 6 for the three alloys above \( T_g \) or \( T_C \). \( \bar{N} \) is either practically constant (Fe\(_{92}\)Zr\(_7\)) or decreases with temperature (the other two alloys). The increase in \( \bar{N} \) upon lowering the temperature can be associated with at least two mechanisms: (i) clusters polarize the spins in their vicinity, aided also by the slow increase in \( M_s \), and (ii) the coalescence of two or more small clusters into a big one. The large static moments found even about 60 K (Fe\(_{92}\)Zr\(_7\)), 25 K (Fe\(_{92}\)Zr\(_8\)) or 10 K (Fe\(_{88}\)Zr\(_{12}\)) above the respective critical temperatures (\( T_g \) or \( T_C \)) can be regarded as anomalous compared to the magnetic behaviour of normal ferromagnets near \( T_C \) (e.g. Ni [32]). Dynamic spin clustering is thought to
cause similar anomalies in this case but in a much narrower temperature range above $T_C$ \[ \varepsilon = (T - T_C)/T_C \leq 0.04 \]. The increase in $\bar{N}$ with composition reflects the compositional increase of the interaction mentioned above. Mössbauer results on the same samples [26] confirm the existence of finite magnetic clusters, yielding a cluster size of approximately 2000 Fe atoms in Fe$_{38}$Zr$_7$ above $T_g$, which is similar to that found for $\bar{N}$ in this work.

4. Conclusions

It has been shown that melt-quenched amorphous Fe$_{100-x}$Zr$_x$ ($x = 7, 8, 9, 10 \text{ and } 12$) alloys contain finite magnetic clusters of increasing average size with Zr content $x$. These clusters are shown to be responsible for the superparamagnetic behaviour of the alloys observed above the spin-glass transition temperature $T_g$ ($x = 7$) or the Curie temperature $T_C$ ($x = 8, 9, 10 \text{ and } 12$) and also for the low-temperature anomalies of the dc susceptibility observed below $T_g$ ($x = 7$) or the re-entrant spin-glass transition temperature $T_f$ ($x = 8, 9 \text{ and } 10$). The interpretation is based on Néel's theory for fine particles with a distribution of blocking temperatures by taking into account the interaction between the cluster moments. The measured $M(H)$ curves for three alloys ($x = 7, 8 \text{ and } 12$) were transformed into universal master curves and were shown to fit to the theoretical curves of the model. The temperature and concentration dependences of the cluster parameters correspond well to the results of other measurements.

Although this description uses a significant number of parameters, there is a well established feature of the experimental results: the magnetic properties of Fe$_{100-x}$Zr$_x$ (and of other widely different spin-glass alloys) are very similar to those of fine particles. It implies that a kind of granular magnetic structure (a not yet understood, perhaps fractal magnetic structure) is present which is not taken into account by the presently accepted theories. This fact might have far-reaching consequences and should initiate new approaches.

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References

[27] see Ref. [24], p. 411.
[28] see Ref. [25], p. 480.
[29] see Ref. [25], p. 479.