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Linear and non-linear magnetic response of potentially re-entrant Fe–Zr glasses

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Abstract. Detailed measurements are presented of the field and temperature dependent AC susceptibility of a number of FeZr metallic glasses. By following the behaviour of the 'cross-over' line, the presence of a paramagnetic to ferromagnetic transition below room temperature in this system is confirmed; the asymptotic exponent values characterizing this transition display near Heisenberg-like values (for the index δ, measurements extend to much lower fields than previous studies), although complications arising from anisotropy (most probably spin–orbit coupling) are also revealed. For the first time, the leading term in the non-linear response is shown to display a distinct anomaly at low temperatures. Although not divergent (as in Ising model predictions) the temperature at which this anomaly occurs in the 8 at.% Zr sample agrees with the transverse spin-freezing temperature estimated recently from in-field Mössbauer measurements. While detailed realistic three-dimensional model predictions describing sequential phase transitions in systems with competing exchange interactions are currently unavailable, the present data, nevertheless, support the possibility of a second 're-entrant' transition in this system.

1. Introduction

The magnetic properties of glassy Fe_xZr_{1-x} alloys with $x > 0.85$ have been the focus of much interest and controversy during the past decade [1]. The measured magnetic ordering temperatures T_c of these magnetic glasses is depressed rapidly with increasing Fe concentration to temperatures below room temperature at a rate $dT_c/dx \approx -25$ K/at.% [1, 2]. Furthermore, there have been substantial differences in the nature of the spin ordering attributed to this system in the vicinity of T_c as this latter temperature falls [3–5]. Recent AC susceptibility and magnetization studies [3, 4] have, however, demonstrated conclusively that the *asymptotic* static critical exponents characterizing the transition at T_c are consistent with ferromagnetic ordering, since these measured asymptotic exponents are close in value to those calculated for the isotropic three-dimensional Heisenberg model ($\gamma = 1.386$, $\beta = 0.365$, $\delta = 4.80$) [6]. Nevertheless the effective Kouvel–Fisher susceptibility exponent [7] exhibits a non-monotonic temperature variation above T_c [8] (a feature that appears to be characteristic of many disordered systems), which leads to large apparent values for this exponent if the latter is averaged over data acquired outside the true asymptotic critical region.

In contrast with the behaviour inferred from the asymptotic critical exponents, other measurements have been interpreted as indicating that simple ferromagnetic ordering does not occur at T_c. Specifically it has been argued [1] that the failure of the high-field

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magnetization to saturate indicates a substantial non-collinear spin component below T_c, a suggestion that has received support from small angle neutron scattering (SANS) which revealed a non-divergence in the correlation length $\xi(T)$ at the transition temperature [9]. More recently however, some confusion has been raised over precisely what correlation length is determined by such measurements [4].

The suggestion that Fe_xZr_{1-x} ($x > 0.9$) metallic glasses were not simple ferromagnets was made almost a decade ago [10]; in addition to the transition at T_c the magnetic properties of these glasses in this composition range appears to be further complicated by the possibility of a second magnetic transition at temperatures below T_c. While the appearance of irreversibilities [10] and peaks [11] in the low-field magnetic response, along with a field induced anisotropy [12] and anomalies revealed by Mössbauer [13] and SANS measurements [9, 4] support such a suggestion, the nature of this proposed second transition remains controversial. Opinions vary currently from its being a re-entrant ferromagnetic-spin glass transition [3, 14, 15] to its resulting simply from the effects of a strong temperature-dependent magnetic coercivity [16, 17].

Strong experimental support for the former view has been obtained from recent Mössbauer measurements in the presence of considerable applied fields [2]. These measurements have been interpreted as indicating a steady growth of frozen spin components in a plane perpendicular to the applied field direction (despite the obvious presence of such a field) as the temperature is lowered below some characteristic temperature $T_{xy} < T_c$. The coexistence of longitudinal ferromagnetic ordering (first established at T_c) with transverse spin-glass freezing below T_{xy} has led to comparisons of the proposed phase-diagram for a-FeZr with that predicted for infinite ranged vector models for magnetic systems with competing exchange interactions [18]. However, it should be pointed out that while these recent Mössbauer data provide strong evidence for the presence of transverse spin freezing, they do *not* indicate that this process is spontaneous in the sense associated with a genuine thermodynamic phase transition, as vector models predict [18].

In this paper we present detailed measurements of the AC susceptibility of several a-FeZr samples in varying static biasing fields at temperatures around both potential transitions. These data enable detailed comparisons to be made between the observed magnetic response of these systems and that predicted by an effective field model in which both upper and lower transitions are true thermodynamic transitions (although of different order) [19]. These results and comparisons are discussed below.

2. Experimental details

Alloys of Fe_xZr_{1-x} ($x = 0.89, 0.90, 0.91$ and 0.92) were fabricated at McGill University from 99.99% pure Fe and 99.95% pure Zr by arc-melting under titanium-gettered argon. Amorphous ribbons up to 1 m long, 1–2 mm wide and 10–20 μm thick were produced subsequently by melt spinning under high-purity helium using a copper wheel with a tangential speed of 50 m s^{-1}. Sample quality was verified by differential scanning calorimetry and x-ray diffraction [1, 20]; in particular, since the (110) and (200) α-Fe reflections [21] could not be detected from either surface of the ribbon, crystalline phases (if present there at all) were below the ~1% level of detection characteristic of this technique. Room temperature Mössbauer spectra suggest that this level is actually below 0.1% [22]. Furthermore, similarly produced samples subjected to analysis by electron beam microprobe displayed homogeneity—on a 1 μm scale—within the instrumental

resolution (0.2%) both along and across the sample [20]. In spite of the results of these tests, the abrasion of the ribbon's surface layer to remove *possible* inhomogeneities there was considered. Mechanical abrasion was ruled out on both practical grounds (i.e. the mechanical integrity of ribbons of this thickness) and because it was felt that such a process might result in a significant increase in domain wall pinning (some theories of apparent re-entrant behaviour suggest an origin due to pinning/anisotropy mechanisms). A piece of the 9 at.% Zr sample was etched using in acid solution; however, since this led to an increase in the Curie temperature accompanied by a decrease in the coercivity, it was concluded that the principal effect of such a treatment was to introduce hydrogen, as in FeSc [23], with marked associated changes. Consequently, the in-phase component of the susceptibility of as-spun samples of approximate dimensions $(16 \times 1 \times 0.02)$ mm^3 (with rounded corners) was recorded *continuously* using a phase-locked susceptometer [24] operating at 2.4 kHz with a calculated driving field of 5 μT RMS (applied along the largest specimen dimension). Static biasing fields ($\mu_0 H_a$) between 0 and 0.1 T could be applied using a collinearly mounted solenoid. The sample temperature was measured using a Au + 0.03 at.% Fe versus Chromel P thermocouple screened from the applied field but in good thermal contact with the sample.

Measurements in applied fields of less than 1–2 mT were carried out on a single strip with the above dimensions; however, since the susceptibility is rapidly suppressed by a field (particularly near T_c), measurements at higher fields were made on bundles of such strips (electrically insulated from each other, but in good thermal contact) to increase the sample signal. These strips were cut from various sections of the melt-spun ribbon, and since no change could be detected in the measured susceptibility from single and multiple strips at the indicated fields (within experimental uncertainty, estimated under the above conditions† to be approximately 0.1–0.3%), the magnetic homogeneity of the strips appears to be very good. Effects of aging were also investigated to a limited extent; the zero-field susceptibility was measured before and after the series of measurements in applied fields (an interval of one to three weeks, depending on the sample) and no change in its value at T_c was found (to within the limits set on this temperature—see table 1). This result leads us to state with some confidence that since the present samples were melt spun some two weeks prior to the beginning of the susceptibility measurements reported below, from the same ingots used to prepare amorphous specimens for recent Mössbauer studies [1], comparisons with these latter data are meaningful.

3. Results and discussion

3.1. Background survey

Before presenting the results and their analysis, a review of the model predictions with which they will be compared is appropriate.

The occurrence of magnetic phase transitions in systems with competing exchange interactions has been a subject of extensive recent debate [25]. If these competing

† While relative susceptibility values can be determined with high precision (~1 in 10^5), absolute values can, in general, be in error by up to 5 or even 10%, due primarily to filling factor and demagnetization correction uncertainties. However, in the present experiments by making samples not only with the same dimensions but with dimensions that minimize demagnetizing constraints (see section 3.2), the level of reproducibility indicated can be achieved..

interactions are represented by a Gaussian distribution with first and second moment $\bar{J}_0$ and $\bar{J}$ respectively, then the consensus of current experiments indicates that in systems with $\bar{J}_0 \gg \bar{J}$ a ferromagnetic ground state evolves below a critical temperature $T_c \propto \bar{J}_0$, and in the vicinity of this temperature the entire magnetic response can be expressed in the form of a scaling function [26]

$$\chi(h, t) = t^{-\gamma} F(h/t^{\gamma+\beta}) \tag{1}$$

where $h = g\mu_B H_i/k_B T_c$ and $t = |T - T_c|/T_c$ are the conventional linear scaling fields, while γ, β and $\delta (= 1 + \gamma/\beta$, if the Widom equality holds) are the usual critical exponents. In the opposite limit, $0 \leqq \bar{J}_0 \ll \bar{J}$, a phase transition still occurs at temperature $T_{sg} \propto \bar{J}$, but here the transition is to a ground state with randomly frozen spins, so that the 'spontaneous' magnetization $m = \langle\langle S_i \rangle_T \rangle_J = 0$ while $q = \langle\langle S_i \rangle_T^2 \rangle_J \neq 0$. The order parameter q does not couple to the linear response, so that above T_{sg} the non-linear components of the susceptibility alone follow a scaling behaviour [27, 28],

$$\chi_{NL}(h, t) = \chi(0, t) - \chi(h, t) = t^{\beta'} F\left(\frac{h^2}{t^{\gamma'+\beta'}}\right) \sim + \frac{h^2}{t^{\gamma'}} - \frac{h^4}{t^{2\gamma'+\beta'}} \ldots \tag{2}$$

with $h = g\mu_B H_i/k_B T_{sg}$ and $t = (T - T_{sg})/T_{sg}$. Numerous experiments confirm the predicted divergence in the coefficients of the h^2, h^4 etc. terms in the non-linear response as the temperature approaches T_{sg} from above [27–30]. Furthermore, some experiments [28–30] also support the suggestion that crystalline metallic spin-glasses might belong in the same universality class (independent of the precise details of their exchange bond distribution). However, the situation occurring below T_{sg} is less certain at present. The many [25] (but not unanimous [31]) claims that the replica symmetric solutions of the Sherrington–Kirkpatrick/Ising model spin-glass (or its effective field equivalent) become unstable below T_{sg} have led to the replacement of these solutions by the apparently 'exact' Parisi solution [32]. The latter, however, exhibits no singular behaviour below T_{sg}, in direct contradiction of several experimental investigations. By contrast effective field models are in substantial agreement with experimental observations [27–30], in predicting not only nearly symmetric critical behaviour above and below T_{sg} [33], but also in reproducing the relative range of dominance of various non-linear components in χ_{NL} as a function of temperature, field and bond ratio ($\eta = \bar{J}_0/\bar{J}$) [33], as well as reproducing the measured field dependence of the susceptibility peak amplitude [34, 35] as these peaks move progressively below T_{sg} with increasing field†.

The above remarks are particularly relevant in the context of the present experiments. When the exchange bond ratio is intermediate between the limits discussed above, specifically $1 \leqq \bar{J}_0/\bar{J} < 2$, vector models predict that the paramagnetic to ferromagnetic transition (involving the longitudinal spin components, so that $m_\parallel \neq 0$, $q_\parallel \neq 0$; $m_\perp = 0$, $q_\perp = 0$) at $T_c \propto \bar{J}_0$ is accompanied by at least one further transition at lower temperature (T_{xy}) corresponding to the spin-glass like freezing of transverse spin components (so that $m_\perp = 0$, $q_\perp \neq 0$) [18]. Such a sequence is frequently identified through susceptibility measurements, which display a rapid increase with decreasing temperature as the ferromagnetic phase boundary is approached from above, followed by an intermediate plateau-like regime (which may or may not exhibit a weak temperature dependence, but is not limited by demagnetizing constraints); at still lower temperatures the

† The Parisi solution appears to reproduce the behaviour of the field-cooled magnetization alone. By contrast the reversible response (down to frequencies as low as 10^{-3} Hz) behaves quite differently, following effective field/SK model predictions.

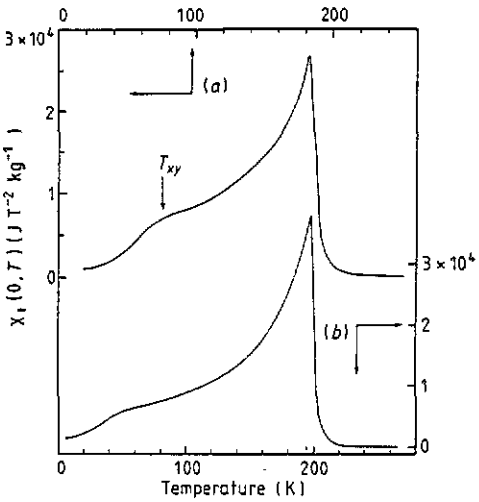

Figure 1. The true, in-phase component of the zero field susceptibility $\chi_t(0, T)$ in J T^{-2}kg^{-1}) (corrected for demagnetizing and background effects) plotted against temperature for (*a*) the Fe–8 at.% Zr sample, (*b*) the Fe–9 at.% Zr sample. T_{xy} marks the transverse spin-freezing temperature derived from Mössbauer data [2].

susceptibility exhibits an abrupt decrease, a feature which is often identified with entry into the transverse spin-glass state. Such a sequence has been observed in FeZr in the composition range studied here [3, 11, 36]. While specific predictions—based on equation (1)—exist and have been utilized in investigating the upper transition at T_c in detail, the behaviour expected near the lower 're-entrant' transition is not well established at present. As in the direct paramagnetic spin glass transition, replica symmetry is broken at T_{xy}, and while no Parisi-like solution exists for this ground state in vector models, it is, nevertheless, a widely held belief that the replica symmetric solutions are again unstable below the lower transition line. This belief persists in spite of the inability of current broken-symmetry models to reproduce the double-peaked structure observed in the temperature-dependent reversible response of a number of re-entrant systems measured in fixed biasing fields. This feature *is* present in effective field models, which can mimic measurements which show that these two peaks are driven apart in temperature and suppressed in amplitude (the upper peak amplitude more rapidly than the lower one) as the applied field increases [19]. In particular effective field Ising models predict a divergence in the non-linear susceptibility as T_{xy} is approached *from below* in re-entrant systems, this divergence being similar to the one occurring at a direct paramagnetic spin glass transition as T_{sg} is approached *from above* [19, 33]. These effective field model predictions are by far the most successful in reproducing many of the features measured recently [37] in the archetypal crystalline re-entrant system (PdFe)Mn, and consequently they form the basis of the analysis carried out below.

3.2. Zero field susceptibility: general features

Figures 1(*a*) and 1(*b*) reproduce the in-phase component of the zero-field susceptibility of the 8 and 9 at.% Zr samples as a function of temperature. These data represent the 'true' susceptibility of these systems, i.e.,

$$\chi_t(H_i, T) = \frac{\partial M}{\partial H_i} = \frac{\chi_m(H_a, T)}{1 - N\chi_m(H_a, T)} \tag{3}$$

in which $\chi_m(H_a, T) = \partial M/\partial H_a$ is the measured susceptibility, H_i the internal and H_a the

applied field, related by $H_i = H_a - NM$. These zero-field measurements were carried out on a single strip of material (with rounded corners) with previously specified dimensions. The demagnetizing factor N for each sample was estimated by approximating it by an ellipsoid with principal axes equal to the sample dimensions and evaluating the corresponding elliptic integral [38]. While such a procedure sets an upper limit on N [39, 40] of $\approx 0.023 \times 10^{-4}$ (when $\chi_m(H_a, T)$ is the susceptibility per unit mass), the correction for demagnetizing effects through equation (3) does not exceed 9% at any temperature for any sample studied here.

The zero-field susceptibility curves in figures 1(*a*) and 1(*b*) exhibit features which have previously been identified as signifying re-entrant behaviour associated with sequential transitions. On cooling, the zero-field AC susceptibility $\chi_t(0, T)$ increases rapidly with decreasing temperature as the Curie temperature T_c is approached from above, $\chi_t(0, T)$ passes through a maximum (the Hopkinson peak) just below T_c, and then falls rapidly towards a plateau region; the latter terminate at a diffuse knee (at T_D), below which the susceptibility falls again. With increasing Zr content, T_c moves upward and T_D downward, while $\chi_t(0, T_D)$ falls. On the basis of these features the regions $T > T_c$, $T_c > T > T_D$ and $T_D > T$ have been respectively designated previously as 'paramagnetic', 'ferromagnetic' and 're-entrant spin-glass'.

Direct comparisons between the present data and those reported previously on samples of comparable nominal composition are difficult for a variety of reasons. Measured susceptibilities χ_m (rather than true susceptibilities χ_t) have been presented as a function of temperature either in units of the inverse demagnetizing factor N^{-1} but with insufficient information supplied to calculate N [3], or in arbitrary units on samples of specified dimensions [41]. In the former [3] it is then unclear whether the apparent divergence in the true susceptibility χ_t is an artifact of using a sample with too large a demagnetizing factor (as demonstrated recently for NiMn [42]), while in the latter case [41] the inference is made that the measured susceptibility actually exceeds the limit set by demagnetizing constraints just below T_c. A divergent, true susceptibility is *not* observed in the current measurements. Notwithstanding such uncertainties, the temperatures of both the Hopkinson peak and the low temperature knee (identified in [3] as the temperature below which the measured susceptibility falls from its demagnetization limited plateau) are in reasonable agreement between different studies on nominally comparably concentrated samples. Furthermore such agreement holds despite the use of AC driving fields of considerably different amplitude (0.5 μT in [3] and [41] compared to 5 μT here, for which differing driving frequencies do not appear to be significant [3, 41]) provided this amplitude is not too large. Driving fields above 10 μT can distort the zero field response significantly by progressively depressing the temperature at which the Hopkinson peak occurs [11]; indeed at 0.4 mT the measured susceptibility just below T_c becomes nearly an order of magnitude *less* than that near T_D [36], although whether this is accomplished via a suppression of the response near T_c or an enhancement near T_D is unclear (the susceptibility being presented in arbitrary units).

One further comparison that can be made is with recent Mössbauer measurements which were interpreted as indicating transverse spin-freezing at $T_{xy} = 76 \pm 3$ K which, as shown in figure 1(*a*), is quite close to the diffuse knee (at T_D) as measured on a sample taken from the same batch.

3.3. The ferromagnetic transition

While the ferromagnetic nature of the upper transition in potentially re-entrant FeZr has been demonstrated previously [3, 4, 8], it is nevertheless important to confirm that

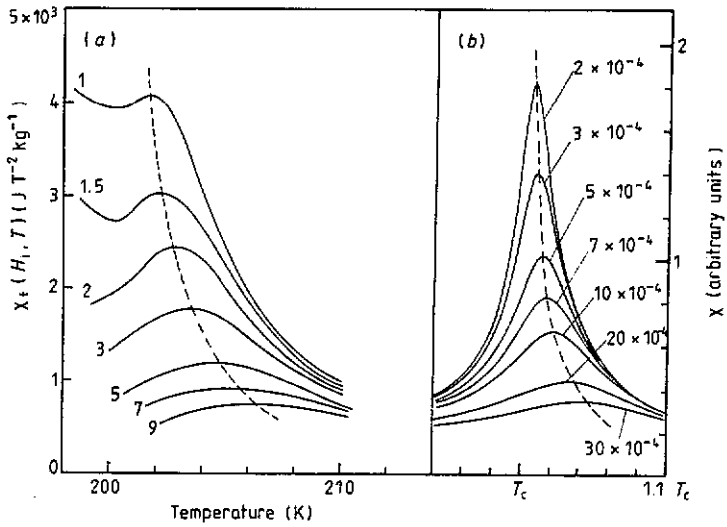

Figure 2. (*a*) The true susceptibility $\chi_t(H_i, T)$ (in J T^{-2} kg^{-1}) of the 9 at.% Zr specimen plotted as a function of temperature in the vicinity of the Curie temperature; various static biasing fields $\mu_0 H_i$ (in mT) are indicated alongside the appropriate curve. The broken curve represents the cross-over line. (*b*) The corresponding susceptibility (in arbitrary units) calculated from an effective field model [43] using $\eta = 1.1$ for various reduced fields h (see text) shown against each curve.

it occurs in the samples examined in the current study. Furthermore, the present measurements exploit an unconventional approach by following the field dependence of a cross-over line above T_c; specifically, this enables estimates for the exponent δ to be obtained from much lower field data than those reported previously, while also revealing the presence of spin–orbit induced anisotropy.

Figure 2(*a*) reproduces a representative set of measurements of $\chi_t(H_a, T)$ taken in constant applied field H_a ('isokaps') as a function of temperature in the vicinity of the ferromagnetic ordering temperature T_c (i.e. just above the Hopkinson peak). The application of an external field results in the suppression of the Hopkinson maximum, thus facilitating the observation of true critical peaks. These latter peaks can be seen to be decreased in amplitude while their location (at temperature T_m) moves upward as the field increases. This behaviour is in agreement with the static scaling law—equation (1)—which predicts the occurrence of a cross-over line *above* T_c (a line evident in figure 2, along which $(\partial\chi/\partial T)_H = 0$) which moves upwards with increasing field according to [43–45]

$$t_m = (T_m - T_c)/T_c \propto H_i^{(\gamma+\beta)^{-1}} \tag{4}$$

with the decreasing magnitude of the peak susceptibility $\chi_t(H_i, T_m)$ being governed by

$$\chi_t(H_i, T_m) \propto H_i^{(1/\delta)-1}. \tag{5}$$

The power law relationships contained in equations (4) and (5) have been verified not only by calculations based on specific models [46, 47] (figure 2(*b*) shows model-generated data for comparison) but also by experiments on a number of systems (see, for example, [48]) in which they have also been used to extract estimates for the critical temperature

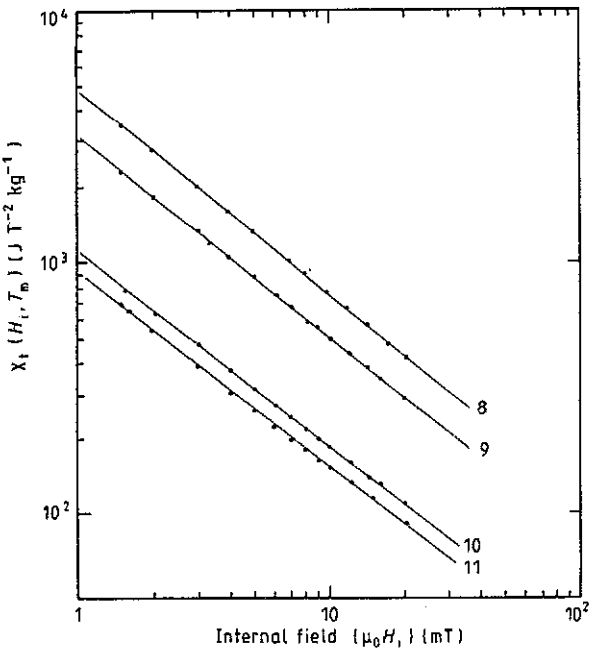

Figure 3. The peak susceptibility $\chi_t(H_i, T_m)$ (in J T^{-2} kg^{-1}) (i.e. measured along the cross-over line) plotted on a double logarithmic scale against the internal field $\mu_0 H_i$ (in mT). The slopes of these lines yield the δ-values shown in table 1. The atomic percentage of Zr is marked against each line; the vertical scale applies to the 8 at.% Zr specimen, as the other lines have been shifted (for clarity). The appropriate intercepts (in J T^{-2} kg^{-1}) at $\mu_0 H_i = 1$ mT are: 0.41×10^3 (9 at.%), 0.33×10^3 (10 at.%) and 0.31×10^3 (11 at.%).

T_c and the exponents γ, β and δ. Such peaks have been observed previously in FeZr [11], but this is the first occasion on which they have been subjected to critical analysis.

3.3.1. The exponent δ. The advantage of using equation (5) to evaluate the exponent δ rather than measurements taken along the critical isotherm ($T \equiv T_c$; $t \equiv 0$) is that it does not rely in any way on the choice for T_c. Its use might, however, suffer a possible drawback, also common to data acquired along the critical isotherm, in that it assumes that the measured response is completely dominated by that component arising from critical fluctuations; this assumption is discussed below.

Figure 3 shows double logarithmic plots of the susceptibility at the peak taken from figure 2 (corrected for both demagnetizing effects and background signals) against the internal field H_i. The latter was estimated numerically from

$$H_i = H_a - N\int_0^{H_i} \chi_t \, dH_i = H_a - N\int_0^{H_a} \chi_m \, dH_a \qquad (6)$$

using trapezoidal rule integration of experimental data. This figure confirms that the power-law prediction—equation (5)—is obeyed over the field range shown ($\mu_0 H_a$ = 1.5–15 mT) with a unique slope (and hence δ value) in the four samples examined (with the possible exception of the 11 at.% Zr specimen); the corresponding δ values are listed in table 1. Several aspects of these data warrant comment.

(i) The tabulated δ values are in excellent agreement with those reported previously from measurements along the critical isotherm on a number of samples with comparable composition (reviewed in [4]); they are also close to the value of $\delta = 4.80$ predicted for the isotropic 3D Heisenberg model [6]. It should be emphasized, however, that exponent values should be estimated, where possible, from asymptotic low field or low (reduced)

Table 1. Summary of parameters deduced from the AC susceptibility data on **FeZr**.

Sample (at.% Zr)	T_c(K)	δ	$(\gamma+\beta)$†	Coercive field $\mu_0 H_c$ (mT)‡		
				77 K	4.2 K	1.6 K
8	181.9 ± 0.5	5.15 ± 0.1	1.75	0.2	>10	>10
9	200.2 ± 0.5	4.85 ± 0.15	1.75	0.05	5	7
10	237.3 ± 0.5	4.55 ± 0.15	1.75	0.2	2	3
11	247.0 ± 0.5	4.5 ± 0.15	1.75	0.2	1	1.5

† As discussed in the text, these data are *consistent* with Heisenberg model values ($\gamma = 1.386, \beta = 0.365$).

‡ Estimated from the splitting in the 'butterfly' loops, following cycling to ±40 mT; estimated uncertainty ~10%.

temperature data, a point which has been stressed recently for the susceptibility exponent γ in particular [3, 8, 49]. In this respect the present estimates should be the most reliable since they were obtained not only from data acquired at much lower fields (1.5–15 mT) than those used previously (15 mT–2.2 T, or higher, see [4] for example), but they are also independent of the choice for T_c (which can also influence estimates for this exponent [4]).

(ii) While the data on **FeZr** presented in figure 3 extend to much lower fields than previous studies of this system†, the resolution of these critical peaks still requires fields in excess of 1.5 mT, which is an order of magnitude larger than those needed to resolve similar structure in magnetically soft materials, such as **Pd**Mn [43, 50] and (**Pd**Fe)Mn [37]. These latter systems represent examples of materials with a relatively low net moment in which the regular or non-critical contribution to the measured response (due to coherent rotation and/or domain wall motion) can be driven to saturation in low applied fields (often approaching the demagnetizing field). Under these conditions the Hopkinson peak is shifted downward in temperature and is suppressed in amplitude, thus enabling the emerging critical peak structure to be resolved. That such structure is not evident below 1.5 mT in **FeZr** provides indirect evidence for an anisotropy mechanism which prevents technical saturation from being attained at low fields. Indeed, the differences between the measured response and model predictions evident *below* the cross-over line in figures 2(*a*) and 2(*b*) is a direct indication of the effects of the non-saturated regular contribution. Furthermore, the recent report of a non-vanishing spontaneous resistive anisotropy (SRA) in **FeZr** below T_c [51] strongly suggests that this anisotropy arises from spin–orbit coupling.

As a corollary it should be stated that the present estimates *may* thus still not represent the true *asymptotic* value for $\delta(h \rightarrow 0)$ in spite of the low field nature of the present measurements.

(iii) The *possibility* that the 11 at.% Zr sample displays an effective exponent which increases as the internal field decreases (the data on this specimen display *slight* curvature just beyond the limits of experimental uncertainty) could be explained in two ways. Effective δ^* values which decrease with increasing field have been reported for a number

† δ values near 5 result in a very rapid decrease in $\chi_t(H_a, T_m)$ with increasing field, so that susceptibility peak amplitudes in fields ($\mu_0 H_a$) beyond about 20 mT are too diffuse to measure with certainty in the present susceptometer.

of systems in which the exchange bond distribution fluctuates about a non-zero mean [48]. Such behaviour is predicted by model calculations [47] for systems in which the ratio $\eta = \bar{J}_0/\bar{J}$ of the first to second moment of this distribution is not infinite; furthermore, while the asymptotic δ value in this model remains unchanged, the effective exponent exhibits a progressively more marked reduction with increasing field as the ratio η declines towards unity and the limit of stability of the ferromagnetic ground state is approached. If this were the case in FeZr, not only would its influence more likely be seen at lower rather than higher Zr concentration (judging by the proposed phase diagram [1, 2]), but one might also expect its effects to be revealed by measurements at higher fields [4]; neither expectation agrees with experimental observations. The second, more plausible, explanation is based on spin–orbit effects; the latter could result in a significant, *non-critical* low field contribution to the response which would produce an apparent enhancement of such data.

3.3.2. The critical temperature T_c, and the exponents γ and β. In a number of soft ferromagnetic materials, it has been possible to examine the predictions of equation (4) in detail using double logarithmic plots of t_m against H_i and thus obtain reliable estimates for T_c, γ and β [37, 50]. For FeZr the presence of spin–orbit coupling complicates such an analysis through its influence on the field-dependence of the Hopkinson maximum; not only does such coupling obscure the emerging critical peak at low field (which curtails the field range over which double log plots can be implemented), but it also introduces increasing uncertainty in the critical peak temperature T_m through peak broadening effects† (such uncertainty is quite marked on a logarithmic scale as $t_m \rightarrow 0$ ($T_m \rightarrow T_c$)). These restrictions preclude a direct evaluation of β and γ from the field dependence of the cross-over line (although γ can still be evaluated separately from the zero-field susceptibility), and simply admit a demonstration (figure 4) that these data are *consistent* with exponent values close to those predicted for the isotropic 3D Heisenberg model [6]. A similar situation was reported recently for PdNi [50] in which the Ni impurity is known to carry an orbital moment.

Despite such complications, T_c values can be estimated with reasonable precision from such data, and these are also listed in table 1; they are close to several previous estimates obtained using conventional approaches on specimens of comparable nominal composition.

3.3.3. The effective susceptibility exponent $\gamma^*(T)$. The susceptibility exponent γ is most often estimated—once T_c has been identified—from double logarithmic plots of $\chi_i(0, T)$ against t. In disordered systems in general, and in FeZr in particular, it is well documented [8, 44, 49] that the true asymptotic susceptibility exponent value can only be established from data acquired close to T_c. Furthermore, the effective Kouvel–Fisher exponent [7]

$$\gamma^*(T) = \frac{d \ln(\chi_i(0, t))}{d \ln(t)} \qquad (7)$$

is known to display a characteristic maximum above T_c. Figure 5, which typifies current data, confirms that this same general behaviour is also present in the samples used here.

† The presence of anisotropy associated with spin–orbit coupling results in a less rapid suppression of the Hopkinson maximum with increasing field. This causes the temperature derivative of the response to reverse quite rapidly just below T_m, consequently the associated critical peaks appear rather broad as can be seen by comparing figures 2(*a*) and 2(*b*).

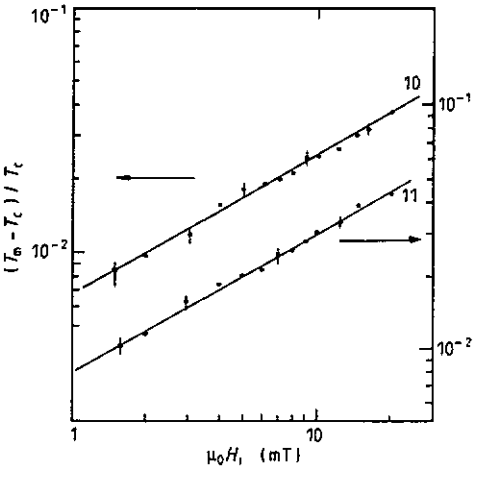

Figure 4. Plots of the temperature of the cross-over line (in reduced units) against the internal field $\mu_0 H_i$ (in mT) on a double logarithmic scale for the 10 and 11 at.% Zr specimens. The lines drawn have a slope corresponding to $\gamma + \beta = 1.75$.

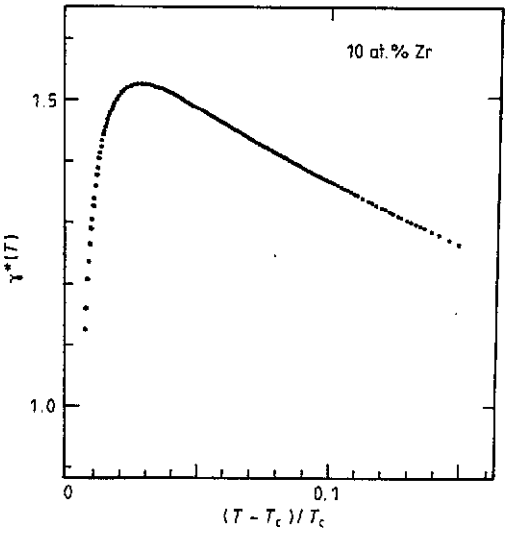

Figure 5. The effective Kouvel–Fisher susceptibility exponent $\gamma^*(T)$ plotted against the reduced temperature for the 10 at.% Zr alloy.

However, one important difference in the present data is that $\gamma^*(T)$ approaches the isotropic 3D Heisenberg model value near $t \approx 10^{-2}$; below this temperature $\gamma^*(T)$ appears to fall to lower values. This is a direct consequence of the behaviour discussed in section 3.2; the failure of the measured response to approach the demagnetization limit means that $\gamma^*(T)$ must fall to very low values sufficiently close to T_c. In the present system this is attributed to anisotropy effects (which prevent the true susceptibility from diverging) associated with spin–orbit coupling; these effects become evident here due to the use of samples with very small demagnetizing factors, as demonstrated recently for crystalline systems with orbital components in the moment [48].

In summary, it has been demonstrated that the higher temperature transition in potentially re-entrant **FeZr** is a ferromagnetic one, being characterized by asymptotic exponent values consistent with theoretical predictions for the isotropic 3D Heisenberg model, although complicating effects associated with an anisotropy (most probably spin–orbit coupling) are evident.

3.4. The lower candidate transition

Following the discussion of section 3.1, a detailed investigation of the field dependence of the susceptibility as a function of temperature has been carried out, as summarized in figure 6. This figure demonstrates that there is no second (or third) peak in $\chi_t(H, T)$ in the vicinity of T_D as found in **AuFe** [52] and **NiMn** [42] and also reported for this system at larger driving fields [11]. From such data the coefficient of the leading† non-linear

† Symmetry considerations dictate this is an H^2 term in the supposed spin-glass phase, but in the intermediate ferromagnetic phase the presence of a spontaneous magnetization breaks this symmetry [19]. This is discussed further in section 3.5.

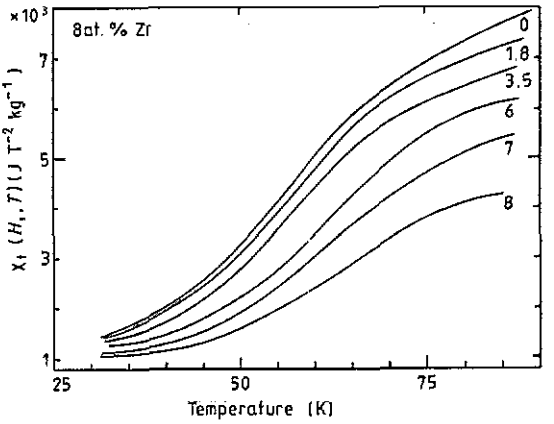

Figure 6. The true susceptibility $\chi_t(H_i, T)$ (in J T^{-2} kg^{-1}) for the 8 at.% Zr sample plotted against temperature in the vicinity of the re-entrant transition temperature; the various static biasing fields $\mu_0 H_a$ (in mT) are displayed against the appropriate curve.

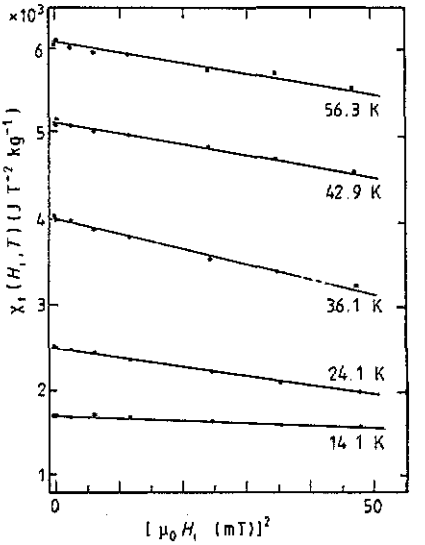

Figure 7. The true susceptibility $\chi_t(H_i, T)$ (in J T^{-2} kg^{-1}) of the 9 at.% Zr sample plotted against the square of the internal field $\mu_0 H_i$ (in mT) at various fixed temperatures (shown against each line); the initial slopes of these lines yield $a_2(T)$.

term ($a_2(T)$) in the response is found by plotting the susceptibility against H^2 at a number of temperatures, as shown in figure 7.

Figure 8 summarizes the temperature dependence of $a_2(T)$ in the 8 and 9 at.% samples on which detailed studies were carried out. This figure enables the following points to be made.

(i) In both samples a non-divergent anomaly in the temperature dependent amplitude of this leading non-linear term is evident at low temperature.

(ii) While the temperature at which $a_2(T)$ peaks is more clearly defined in the 9 at.% sample, in the 8 at.% specimen this maximum at 70 ± 10 K agrees well with the recent Mössbauer determination of $T_{xy} = 76 \pm 3$ K. There is, of course, considerable experimental uncertainty associated with both sets of measurements, but these features are sufficiently consistent not to be dismissed as simply fortuitous. In this respect, it would be particularly interesting to compare the temperature of 36 ± 3 K for the maximum in $a_2(T)$ for the 9 at.% sample with careful Mössbauer measurements in a field. Current estimates for T_{xy} at this composition occur at higher temperatures [1], but these might be revised downward, as at 8 at.% [1, 2].

(iii) The observed anomaly in $a_2(T)$, though distinct, is clearly not divergent and hence is rather weaker than Ising model predictions. Divergent non-linear anomalies provide the principal support for characterizing the direct paramagnetic–spin glass transition as critical [27, 28, 30]. Here, however, the dynamic nature† of the measurements may impose limitations in addition to the complications associated with transverse

† Estimates as large as 11 for $z\nu$ in spin-glasses [53] indicate that finite frequency measurements are affected to a much higher degree by the effects of critical slowing down in them, compared with ferromagnets.

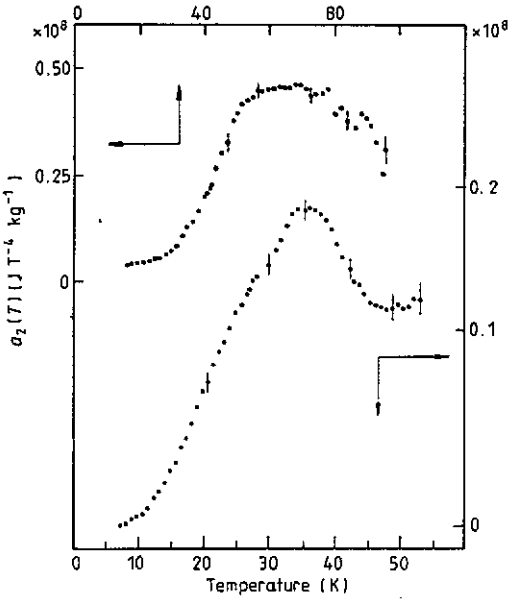

Figure 8. The coefficient $a_2(T)$ (in J T^{-4} kg^{-1}) of the H^2 term in the susceptibility (deduced from plots similar to those shown in figure 7) plotted against temperature (in K) for 8 at.% Zr (upper data) and 9 at.% Zr (lower data).

spin freezing which might couple only weakly to the longitudinal response [54] (a feature which is not considered by Ising models).

(iv) Despite the absence of a further peak in the vicinity of T_D predicted by Ising models, it is, nevertheless, possible to compare the magnitude of the field dependent susceptibility at T_D, $\chi_t(H, T_D)$, with that measured in the same field H at the ferromagnetic peak ($\chi_t(H, T_m)$—at the cross-over line). As can be seen from data in figures 2(*a*), 3, 6 and 7, $\chi_t(H, T_D) > \chi_t(H, T_m)$, in agreement with model predictions [19].

In summary, these experimental data display several features which are consistent with the presence of a second phase transition in this system. However, it must be reiterated that until predictions based on realistic three-dimensional models are available such features cannot be regarded as definitive.

3.5. The intermediate phase ($T_D \leqq T \leqq T_c$) and the coercivity

The suggestion that this second transition is just an artifact of measuring techniques which fail to correct appropriately for demagnetizing effects in the presence of a rapidly declining initial susceptibility (resulting from an exponentially increasing low-temperature coercivity), has been made on several occasions [16, 17]. However, as is made clear in sections 3.2 and 3.3.1, careful corrections for demagnetizing effects have been attempted; furthermore, due to the choice of sample geometry which minimizes such constraints, the corresponding corrections near T_D amount to no more than a few percent.

It is certainly true though that coercivity effects are present in the FeZr system below T_c. The influence of the latter and of the predicted 'symmetry breaking' due to the presence of a non-vanishing spontaneous magnetization in the intermediate† phase

† In Ising models the spontaneous magnetization vanishes at $T_D(T_{xy})$ and so the leading non-linear term in the response is $a_2(T)H^2$. For 3D models in which $m_\parallel \neq 0$, $q_\perp \neq 0$ below T_c, but $q_\perp \neq 0$ below T_{xy}, the restoration of this symmetry below T_{xy} is not obvious, although it *is* supported by the experimental data (see figure 7).

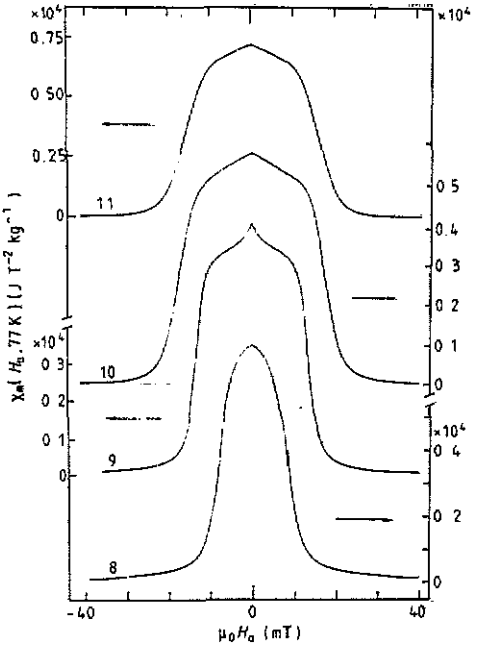

Figure 9. The measured susceptibility $\chi_m(H_a, 77\ \mathrm{K})$ (in $\mathrm{J\,T^{-2}\,kg^{-1}}$) at 77 K plotted against the applied field $\mu_0 H_a$ (in mT); the Zr composition is marked against the corresponding data.

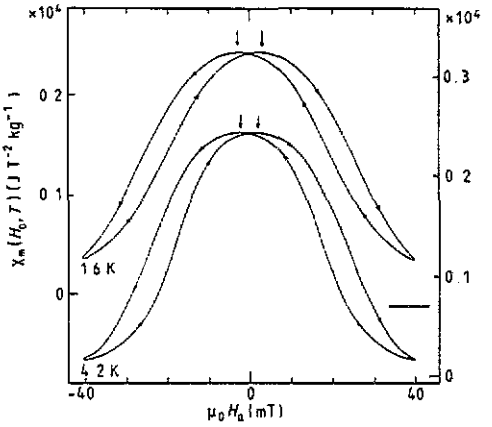

Figure 10. The measured susceptibility $\chi_m(H_a, T)$ (in $\mathrm{J\,T^{-2}\,kg^{-1}}$) for the 10 at.% Zr specimen plotted against the applied field $\mu_0 H_a$ (in mT) at 4.2 K and 1.6 K. The vertical arrows indicate the maxima in $\chi_m(H_a, T)$ (deduced from plots on an enlarged scale) from which the coercive field H_c is estimated.

($T_D \leqq T \leqq T_c$) has been investigated by measuring $\chi_m(H, T)$ as the field is swept at various fixed temperatures. The results of sweeps to ± 40 mT at 77 K for the four samples investigated are shown in figure 9 (the slight hysteresis present, discussed below, has been suppressed for clarity). These data indicate that in the 8 at.% sample the initial (low field) susceptibility is compatible with an H^2 variation as might be anticipated since the sweep was performed at or just below T_{xy}. In the 10 and 11 at.% specimens the initial field dependence is approximately linear, in agreement with Ising model predictions for the intermediate phase with a symmetry breaking spontaneous magnetization [19]. By contrast in the 9 at.% alloy the initial field dependence resembles some *inverse* power of the field. The latter is not predicted by any model, although similar behaviour has been observed recently in NiMn [42, 55]; it might, however, originate from some unusual low field process involving domain wall motion. Indeed, the possible influence of the latter on the behaviour on any of these samples in the intermediate phase ($T_{xy} \leqq T \leqq T_c$) is not well catalogued.

Figure 10 reproduces (on an enlarged scale) the very low field behaviour observed during field sweeps; these so-called 'butterfly loops' [39] enable the coercive field to be estimated directly from the separation evident between the two maxima. As reported previously for FeZr samples of comparable composition [1, 17] the coercivity in all the specimens investigated increases with decreasing temperature and with decreasing Zr concentration; however, it should be emphasized that even at 77 K the coercivity is at

least an order of magnitude larger than the AC driving field of 5 μT. It is consequently very unlikely that the anomalies observed near the proposed T_{xy} (and below 77 K) can be linked to such a mechanism.

4. Summary and conclusions

Measurements of the field and temperature dependent AC susceptibility of a number of FeZr glasses confirm the presence of a paramagnetic to ferromagnetic transition at higher temperatures, with near Heisenberg-like exponents. Some complications due to the presence of anisotropy (most likely spin–orbit coupling) are also revealed.

At lower temperatures the leading term in the non-linear response is shown to exhibit a distinct (though clearly not divergent) anomaly: the temperature at which the latter occurs (70 ± 10 K) is in good agreement with a recent Mössbauer determination of the temperature ($T_{xy} \approx 76 \pm 3$ K) at which transverse spin freezing occurs (in the 8 at.% Zr sample). These susceptibility data thus support the possibility of a second 're-entrant' transition in this system.

Acknowledgments

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