Critical spin-glass dynamics in a heterogeneous nanogranular system

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The analysis of ac magnetic susceptibility data has shown that mechanically alloyed $Fe_{30}Ag_{40}W_{30}$, a highly heterogeneous nanogranular system, exhibits critical dynamics in its transition to a low-temperature spin-glass-like phase, as proved by the power-law divergence of the relaxation time at $T_g = 19.7$ K, and by the dynamic scaling behavior of the out-of-phase component of the susceptibility. Both analyses yielded a dynamic critical exponent $z\nu = 10.2 \pm 0.9$, confirming the existence of a spin-glass-like phase transition at T_g, which, however, is not accompanied by the usual Mössbauer signature.

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I. INTRODUCTION

This work tackles two recent controversial issues in the area of magnetically glassy materials, chronologically: the possibility of producing spin-glass phases using the bulk technique of mechanical alloying/milling,[1,2] and the existence of a finite-temperature phase transition to a low temperature spin-glass-like (SGL) state in systems of interacting ferromagnetic nanoparticles.[3–5] Mechanical alloyed (MA) materials are produced through repeated welding, severe plastic deformation, fracturing and rewelding of powder particles in a high-energy ball mill.[6] In this complex scenario, not yet satisfactorily modeled,[7] ferromagnetic fine particles may appear in Fe-based alloys as a result of nanoscale compositional inhomogeneity,[7,8] exhibiting sometimes different SGL features.[9] However, a consistent proof of the existence of a true phase transition has remained elusive so far. In this work, we confirm the critical character and characterize the spin-glass-like transition exhibited by a MA nanocrystalline sample with composition $Fe_{30}Ag_{40}W_{30}$ (FWA). The magnetism of this sample has been shown before to be determined by the presence of very fine interacting particles supporting a magnetic moment $\mu \approx 100\mu_B$,[10] i.e., this is a magnetic nanogranular solid.

After much research over the last decade on the influence of dipolar interaction on the dynamics of ensembles of magnetic nanoparticles, it is now generally accepted that a cooperative SGL phase develops at low temperature in dense ensembles of magnetic nanoparticles with a random spatial distribution.[3–5,11] However, the transition from the high temperature superparamagnetic state to such an SGL state does not usually exhibit a critical character:[5,11] so far, it has only been observed in nearly monodisperse ferrofluids,[4,5] and thus it has been proposed that heterogeneities such as dispersion in the particle size distribution would inhibit the critical character of the transition. Yet, the particle size distribution in FWA is very far from monodisperse, as expected from the synthesis method and proved below by Mössbauer spectroscopy. In fact, the results of the Mössbauer study are remarkable on their own, for the phase transition in FWA does not seem to exhibit the customary and well-known Mössbauer fingerprint of spin freezing, namely, the splitting of a high temperature singlet or doublet into a magnetic sextet with a growing hyperfine field (related to the order parameter) upon cooling down below the freezing transition.[12] The puzzle is resolved when put in the context introduced in the above paragraph.

II. EXPERIMENTAL

The sample (FWA) was prepared by mechanical alloying for 75 hours a mixture of elemental powders with the above mentioned composition in a PM4 Retsch planetary ball mill. The Fe enrichment from the milling tools was below 1 at.%. The detailed synthesis conditions can be found in Ref. 9 and a first approach to the nanocrystalline structure of the sample can be seen in Ref. 10. SQUID magnetometry has been used to record ac and dc susceptibility data *vs* temperature and frequency of the ac field. In the relevant temperature interval (5–50 K), temperature control within 2 mK was reached in every point before performing the measurement. The sample was studied by Transmission Mössbauer Spectroscopy at 4.2 K and 300 K. The spectra were analyzed using a Fortran code FFITA developed at the University of Liverpool that includes FCFCORE routines and NAG libraries.

III. RESULTS AND DISCUSSION

As it was reported in the above cited preliminary paper,[10] our nanogranular sample exhibits some magnetic properties clearly reminiscent of spin-glass behavior, like a strong thermoirreversibility between the field cooled (FC) and zero-field cooled (ZFC) magnetization at temperatures below the maximum in the latter curve at $T_{max} \approx 20.4$ K, and the flattening out of the FC magnetization at low temperatures (see the inset in the upper panel of Fig. 1). In this work, the possible critical character of the transition signaled by T_{max} is investigated by studying the temperature and frequency dependence of the dynamic susceptibility, which displayed a cusp at $T_f(\omega)$ slightly larger than T_{max} (ω is the frequency of the ac field). Both the in-phase and out-of-phase components of the susceptibility are shown in Fig. 1 for the relevant temperature interval, although a larger temperature range is used in the inset of panel (b) in order to give more perspec-

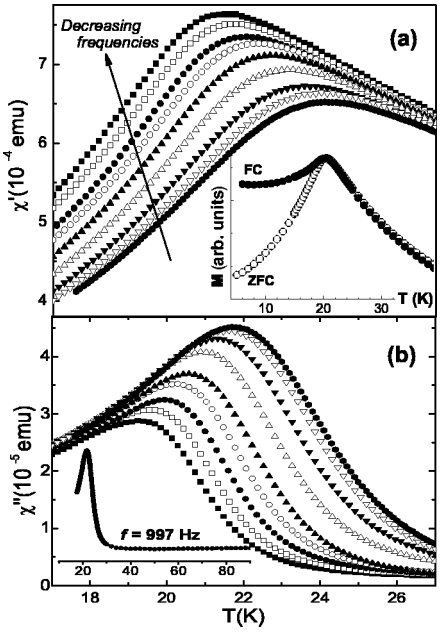

FIG. 1. In-phase (a) and out of phase (b) components of the ac susceptibility as a function of temperature and frequency of the ac field (H=1 Oe). The nine frequencies were chosen to scan logarithmically the available range (0.1–1000 Hz). A plot with a larger temperature scale is included as an inset in panel (b). The inset in panel (a) shows the field cooled (FC) and zero-field cooled (ZFC) magnetization measured in a dc magnetic field H=5 Oe.

tive on the sharpness of the peak and make clear the absence of any other features at higher temperatures. The shape of the absorption component evolves from a sudden onset at low frequencies (as in spin-glasses) to a more Lorentzian-like aspect at high frequencies (as in certain dense nanoparticle systems,[5] including some mechanical alloyed samples[9]). All the frequency-dependent features in these curves are very similar to those found in canonical spin-glasses, such as the variation of the peak's height and position, $T_f(\omega)$, whose rightwards shift yields a frequency-sensitivity parameter $p=\Delta T_f/(T_f \log_{10}\omega)=0.03$, only slightly larger than those exhibited by canonical spin-glasses.[12] This parameter is a rather simple approach to quantify the degree of interaction between magnetic moments.

The existence of a true phase transition can be tested using ac susceptibility data as that presented in Fig. 1 by two different well-established analyses: (i) the fit of the spin relaxation time $\tau(T)$, relating the peaks in $\chi'(T;\omega)$ to the situation where the characteristic relaxation time of the system τ equals the observation time $t_m=1/\omega$, to a power law divergence of the type

$$\tau=\omega^{-1}=\tau^*\varepsilon^{-z\nu}, \tag{1}$$

where $\varepsilon=(T_f/T_g-1)$ is the reduced temperature, T_g is the static freezing transition temperature, ν is the exponent describing the divergence of the correlation length ξ, and z the exponent involved in the *dynamic scaling hypothesis* ($\tau\sim\xi^z$), which is valid only for T close to T_g, justifying our choice of temperature range; and (ii) the full dynamic scaling relation, for instance, for the absorption component of the ac

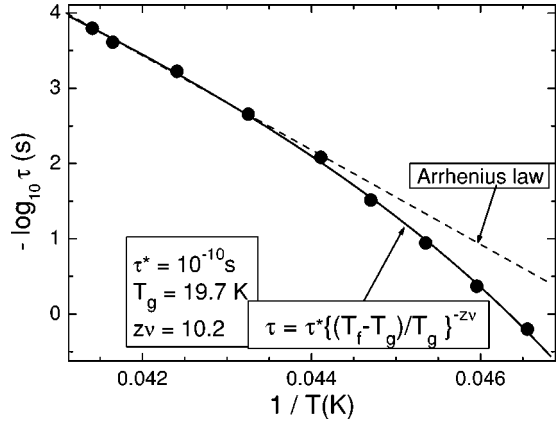

FIG. 2. Shift of the χ' maxima fitted by the critical slowing down law [Eq. (1)]. The dashed line is included to emphasize the deviation of the data from the Arrhenius law.

susceptibility, theoretically predicted from the mentioned hypothesis in conjunction with linear response:[13]

$$\chi''(T,\omega)=\varepsilon^{\beta}F(\omega\varepsilon^{-z\nu}), \tag{2}$$

where β is the critical exponent defining how the order parameter q approaches zero, with a mean field value $\beta=1$. The asymptotic behavior of $F(x)$ for large values of x is $F(x)\propto x^{\beta/z\nu}$.

Figure 2 shows the $\tau(T)$ data extracted from the frequency dependence of T_f. This kind of plot is linear for thermally activated processes [described by the Arrhenius law: $\tau=\tau_0\exp(KV/k_BT)$], as indicated by the dotted line. However, the data deviates clearly from linearity at low temperatures, and is well fitted to the critical slowing down law [Eq. (1)] with the values $\tau^*\approx 10^{-10}$ s, $T_g=(19.7\pm0.2)$ K, and $z\nu=10.2\pm0.9$. All these values are physically meaningful. In particular, and remarkably, the result for the exponent $z\nu$ agrees very well with those reported in different dense nanoparticle systems, such as frozen ferrofluids[5,14,15] and discontinuous multilayers,[16] even though the size of the magnetic moments considered here is significantly smaller. The value obtained for the individual superspin relaxation time τ^*, which obeys the Arrhenius–Néel law but can be considered constant in the narrow temperature interval studied,[5] is roughly midway between the fluctuation time of an atomic spin and that found in the above referred nanoparticle systems. This is consistent with the ultrafine size ($\mu\approx 100\mu_B$) of the moments present in FWA.

Yet, even a fit with reasonable values to the power law divergence of the relaxation time might not be conclusive on its own as to the existence of a finite-temperature phase transition: for instance, Hansen *et al.* have recently studied a 5% vol. concentrated ferrofluid whose relaxation time, according to such a fit, seemed to diverge with $z\nu=10.8\pm1$; however, no data collapse could be found using the full scaling relation (equation 2), a non-critical dynamics being concluded for this system.[5] In FWA, the parameter values obtained from the critical slowing down law, together with $\beta=0.8\pm0.1$, led to the best data collapse that could be achieved (see Fig. 3), thus confirming unmistakably the critical character of the

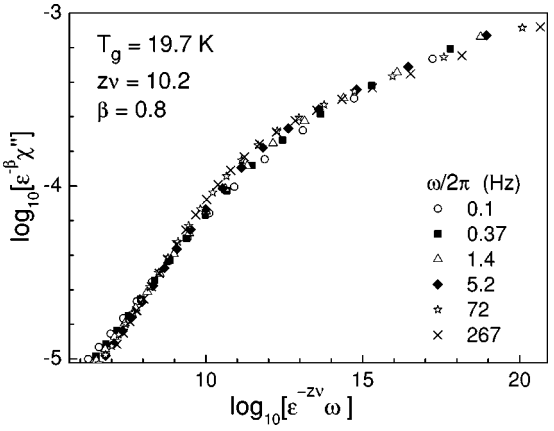

FIG. 3. Dynamical scaling analysis of $\chi''(T,\omega)$ data for $T>T_g$ according to Eq. (2). The best data collapse was obtained for the indicated parameter values (the value of the static freezing temperature T_g was taken from the fit in Fig. 3).

SGL phase transition under study. Moreover, the value for $\beta/z\nu \approx 0.076$ extracted from the asymptotic behavior of the scaling function $F(x)$ for large values of the argument is consistent with the derived values of β and $z\nu$. The result obtained for β lies in the middle of the rather large typical range of values reported for RKKY spin-glasses,[12,13] and it is slightly smaller than those found in the above mentioned dipolar spin glasses (where $\beta \approx 1.0$).

Once the critical character of the transition was confirmed, a Mössbauer study was performed in order to explore its structural origin. Figure 4 presents the Mössbauer spectra taken at room temperature and at 4.2 K. In a first visual inspection, and after proving the existence of a clear SGL phase transition at $T_g = 19.7$ K, the apparent clear absence of a magnetic component in the 4.2 K spectrum is striking. A possible scenario where the magnetic sextet would be obscured by a larger nonmagnetic component is a system where

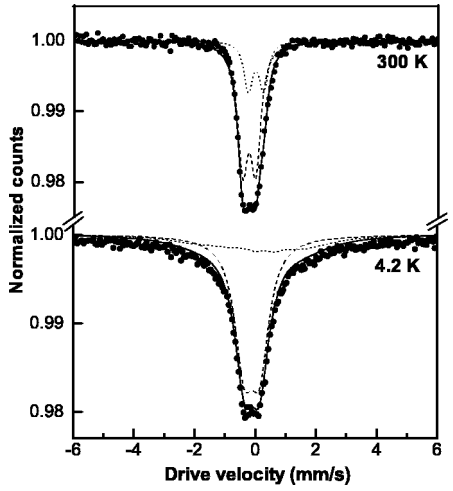

FIG. 4. Mössbauer spectra at temperatures well above ($T = 300$ K) and below ($T = 4.2$ K) the spin-glass phase transition ($T_g = 19.7$ K). The spectrum at 300 K is fitted with two doublets, the less intense one is substituted by an unresolved magnetic component in the low temperature spectrum.

only a minority of spins freeze at low temperature, while the rest remain paramagnetic. However, there is no reason why this should happen in a homogeneous material. Thus, the absence of a clear magnetic component in the low temperature Mössbauer spectrum is an indication of heterogeneous microstructure. In spite of being a minority, the spins freezing at low temperature determine, as shown in the first figures, the magnetic static and dynamical responses. This enhanced low-field susceptibility of the minority spins can only be understood, once again, if they are grouped in ferromagnetic nanoparticles. Furthermore, in order to remain hidden effectively by the matrix component, the magnetic sextet should be unresolved (due to a large distribution of hyperfine fields). The 4.2 K spectrum differs from the RT one only in a certain broadening of the adsorption peak. Structural transformations can be discarded. In principle, this relatively small effect could be related to simple paramagnetic relaxation, but following the model proposed in the above discussion—and previous experience in structurally similar systems—[17] we have fitted both spectra with two components accounting for the magnetic nanoparticles and the paramagnetic matrix where they are embedded. The former contribution is superparamagnetic at RT, and, in the 4.2 K spectrum, is accounted for using a magnetic sextet with very wide peaks (in fact, there is not any resolved structure). The model is consistent from the Mössbauer viewpoint, for the area of the *nanoparticle component* turned out to be the same, within one percent, in both spectra: $\sim 25\%$. This is in rough agreement with the percentage of sample Fe taking part in the particle phase deduced from the measured saturation magnetization (not shown) assuming that the particles contain pure Fe with its bulk magnetic moment (14%). In fact, the discrepancy between the two values has the right sign, for it can be explained by simply dropping the above hypothesis and taking a reduced atomic moment for the Fe atoms ($\mu = 1.2\mu_B$), as it is the case in nanoparticles with compositions deviating from pure Fe.[17] The very wide range of hyperfine fields present in the magnetic component is most probably caused by composition fluctuations, which, together with variations in the size of the magnetic regions, result in a wide distribution of magnetic moments. The mean hyperfine field of the magnetic splitting (MHF = 120 kOe) is significantly lower than in α-Fe, reinforcing the idea that the Fe in the nanoparticles—although in a concentration high enough to support a spontaneous magnetic moment of about 100 μ_B—is also alloyed with W and Ag.

The main conclusion of this structural investigation is that the origin of the observed spin-glass behavior is to be found in the presence of fine magnetic particles, with a broad particle distribution, comprising about 25% of the Fe atoms in the sample. It must be pointed out that these Fe-richer nanosized regions are not due to insufficient milling, they are characteristic of the stationary state (dynamical equilibrium) achieved after milling for long enough powders with an Fe concentration around 30% at. or higher, as proved by the quasiuniversal magnetic behavior reported for a variety of Fe-based mechanically alloyed materials.[9] Even before the low temperature characterization, the measurement of the loss in magnetic moment (at $H = 15$ kOe) with the milling

time, down to 1.3% of its initial value after 75 hours, allowed us to confidently state that the sample had essentially achieved the stationary state. Delcroix *et al.* have also found ultrafine magnetic particles in the stationary state of mechanically alloyed $Fe_{30}Cr_{70}$.[18,19] The moments estimated from Langevin fits for these particles ($\mu \approx 150\ \mu_B$) and for those present in FWA are remarkably similar, however, these authors observed blocking processes taking place in a very broad temperature interval. In mechanically alloyed $Fe_{30}Al_{49}Cu_{21}$, favorable contrast condition—the Fe-rich regions were crystalline and the matrix surrounding them amorphous—allowed to directly image the magnetic particles using high resolution TEM.[20] Our interpretation for the structural origin of the magnetism exhibited by FWA is supported by the conclusions of two recent articles dealing with the generic issue of nanoscale compositional heterogeneity in alloys obtained by nonequilibrium methods. He *et al.* reported that supersaturated solid solutions—a frequent product in the mechanical alloying of metal powders—exhibit decomposition features on the scale of 1 nm, usually overlooked by conventional diffraction methods.[21] More specifically, molecular simulations of binary alloys under extrinsic forcing have shown that complex segregated structures may evolve even in the absence of thermally activated diffusion.[7]

Following intense investigation over the last decade, mainly on dense frozen ferrofluids, it has been recently suggested that the main reason for the lack of a finite-temperature transition in samples exhibiting low temperature glassy dynamics is linked to ''*mixing of collective and single-particle relaxation effects*,'' originating from a broad particle size distribution or from comparably weak interparticle interactions.[5] In broad distributions, it has been hinted that *early* blocked particles (large moments) may act as random fields in the system, which could impede a thermodynamic phase transition.[22] However, the complexity of the physics involved in the synthesis method employed here, mechanical alloying, provides a straightforward argument against the possibility of having a narrow, or *monodisperse*, particle size distribution in FWA; nonetheless, its largely heterogeneous nature has been confirmed in the above Mössbauer study. Thus, mechanically alloyed FWA constitutes a first example of a widely polydisperse ensemble of particle moments exhibiting critical dynamics. Two observations help to reconcile this finding with the previously mentioned research. First, FWA is a metallic nanogranular system, whereas all the investigations cited above were carried out on insulating superspin glasses (particles dispersed in either a frozen oil/alcohol[4,5,14,15] or in some insulating compound such as Al_2O_3);[16] a metallic matrix would allow the RKKY exchange interaction to play a role. Second, the size of the magnetic moments considered here ($\mu \approx 100\mu_B$) is between one and two orders of magnitude smaller than the size of the nanoparticles involved in the *superspin glasses* reported so far. The magnetic moment of the particles present in FWA is precisely, according to some recent calculations, the crossover size for the dominance of RKKY over dipolar interactions in metallic granular systems.[23,24] However, it must be considered as well that the presence of impurity atoms of the magnetic species in the metallic matrix, as expected in FWA, enhances significantly the RKKY exchange between the nanoparticles, as has been shown recently by López *et al.* in granular CuCo, whose magnetic properties moved from the spin glass to the superparamagnetic scenario as the regions of the matrix surrounding the Co particles were depleted of atoms of Co.[25] The relevance of these factors, interparticle RKKY-like exchange and ultrafine particle size, to compensate the lack of homogeneity in order to maintain the critical character of the transition must be further explored both experimentally and theoretically, but it appears logical that stronger interparticle interactions should counterbalance a higher degree of heterogeneity in the magnetic moment distribution. Dipolar and RKKY-like interactions effectively sum together to increase the freezing temperature since both are able to provide frustration in a system of randomly distributed spins, the former due to its anisotropic character, the latter because of its oscillatory nature. Besides, the combined action of the two types of interactions might well go beyond a simple addition, for instance, in enhanced dipolar interactions between RKKY-coupled clusters. In any case, the predominant interaction is thought to be the commented indirect exchange, for previous estimations in this type of systems yielded dipolar ordering temperatures too low to explain the glass transition.[17] From the results reported here, it is clear that the energy associated with the RKKY-based interactions between the relatively small magnetic moments in FWA is well above single-particle anisotropy barriers.

Concerning the older controversy on the nature of spin-glass-like phenomena in mechanically alloyed materials, either attributed to a ''*true* spin-glass phase transition'' [1] or to the blocking of superparamagnetic particles,[2] the results presented here reconcile to a certain extent both views: there is a glass transition, but it reflects the collective freezing of magnetic nanoparticles, not of atomic spins.

IV. CONCLUSIONS

In short, the results presented here demonstrate that it is possible to achieve a *critical* transition to a low temperature superspin glass in a rather *polydisperse* particle system (mechanically alloyed $Fe_{30}W_{40}Ag_{30}$) when the random interparticle interaction is significantly stronger than in dipolar systems, causing the glass transition to occur at temperatures where the average individual particle time τ^* is still shorter than nanoseconds. This is in contrast to frozen ferrofluids, where the comparably weak dipolar interaction leads to a spin glass transition when the individual particle relaxation time has reached the order of microseconds, allowing only a *monodisperse* particle distribution to undergo a true critical transition.

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