Ideal superspin glass behaviour in a random-close-packed ensemble of maghemite nanoparticles

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Abstract. Highly uniform (8 nm) bare maghemite nanoparticles were pressed into a disc with a volume fraction close to the characteristic filling factor of random-close-packed ensembles of spherical particles. We review the ideal superspin glass behaviour exhibited by this material, including an onset of the absorption component of the ac susceptibility at the freezing transition as sharp (in a normalized temperature scale) as those observed in atomic spin glasses, narrow memory dips in the zero-field cooled magnetization, and a spin-glass characteristic field-dependence of the susceptibility. Critical exponents were extracted from static and dynamic scaling analysis.

1. Introduction
Increasing possibilities in the control of nanoparticle (NP) uniformity and spatial arrangement have prompted magnetic studies on super- (or supra-) crystals, ordered 3D arrays of NPs [1]. However, their “super-amorphous” counterparts, the a priori simpler random-close-packed (RCP) ensembles of NPs, have been scarcely approached. Here we demonstrate ideal superspin glass (SSG) behaviour in one such system of bare ferrimagnetic oxide NPs. Compared to previous reports on strongly interacting but less concentrated frozen ferrofluids, granular films and “packed” powders of typically ill-defined filling factor (see references in Ref. 2), the properties of this material are found to be remarkably close to those of conventional atomic spin glasses.

2. Experimental
Highly crystalline, very uniform bare maghemite (γ-Fe₂O₃) NPs were obtained after the complete removal of the oleic acid surfactant (employed in their synthesis) by thermal decomposition [3]. These
bare NPs were compacted under a uniaxial pressure of 0.7 GPa to form a disc. The particles were characterized by transmission electron microscopy (TEM), as well as small (SAXS) and wide (WAXS) angle X-ray scattering. The pressed disc density was measured by the Archimedes’ method. A Quantum Design MPMS magnetometer was employed to characterize the field and temperature dependence of the ac and dc susceptibility after different standard protocols (zero-field-, ZFC, and field-cooling, FC, as well as ZFC protocols with aging stops during the cooling).

3. Results and discussion

The TEM micrograph in Figure 1 shows the high uniformity of the **bare** nanoparticles (2% diameter dispersion), with an average diameter of 8.0 nm, employed to prepare the pressed disc displayed in the inset. The oscillations for $Q$ (scattering vector) > 1 nm$^{-1}$ in the SAXS pattern recorded in a loose powder of oleic-acid coated NPs (right panel in Figure 1) consistently indicate a well-defined NP form factor and, thus, particle diameter, whereas the first peak relates to the random configuration of the particles [3]. The filling factor of the disc (67 %), derived directly from its density and that of the constituent NPs (measured by XRD), is only slightly higher than that of an array of random-close-packed hard spheres (64 %), justifying the name “RCP” for this sample.

![Figure 1. Left: transmission electron micrographs of bare maghemite nanoparticles and a photograph of the random-close-packed sample (RCP), a 6 mm diameter disc prepared with the bare particles. Right: SAXS from oleic-acid coated NPs, fitted as described in Ref. 3. Adapted from Ref. 3.](image)

The RCP sample exhibits FC and ZFC magnetization curves (Figure 2) typical of spin glasses, but with a ZFC peak temperature $T_{\text{peak}} = 145$ K about four times (an unusually high factor) the blocking temperature of the NPs ($T_B = 36$ K) as measured in a dilute reference sample prepared with the same particles coated with thick (17 nm) silica shells [3]. This indicates the presence of particularly strong dipolar interactions in the RCP sample.

The presence of the characteristic chaotic dynamics of the spin-glass state is unequivocally manifested by the so-called “memory effect” [4], also plotted in Fig. 2 (left panel): when the system is zero-field cooled, stops (of 4 hours each) performed at some temperatures below the freezing temperature ($T_g \approx T_{\text{peak}}$), in this case $T_{S1} = 110$ K and $T_{S2} = 70$ K, during the cooling produce dips at the stop temperatures when the magnetization is subsequently recorded upon heating from the base temperature. The memory curve coincides with the reference curve at low temperatures (i.e. the system *rejuvenates*) and it merges with the reference curve at temperatures sufficiently far from the stop temperatures. The very faint memory registered at the lowest stop temperature $T_{S3} = 30$ K ($< T_B$ in the dilute reference sample) reflects the fact that most particles are blocked on the timescale of the experiment, and therefore the system is not observed to age. Both memory dips in Fig. 2 exhibit a 5%
depth and a width at half maximum of $\Delta T \approx 17$ K or, in relative units, $\Delta T/T_g \approx 12\%$. This parameter is smaller than those previously measured in a variety of non-close-packed superspin glasses (see references in Ref. 2). Atomic spin-glasses exhibit still somewhat narrower dips than the RCP sample [5].

The magnetic dynamics of the sample was studied by ac susceptibility. The freezing transition is signalled by a cusp in the temperature dependence of the in-phase component $\chi'$ (see Ref. 2) and a sudden onset in the out-of-phase component $\chi''$ [2]. The right panel in Figure 2 compares this unusually abrupt onset of the absorption component with data from previous reports of superspin glasses as well as from a model atomic spin glass. Not only the RCP sample improves the sharpness of the transition observed in previous quality particle systems, it also becomes remarkably close to the behaviour observed in model atomic spin glasses.

Figure 2. Left: thermal dependence of the magnetization (measured in an applied field of 5 Oe) and memory effect after a triple-stop (of 4 hours each at the indicated temperatures) during cooling. Right: normalized comparison of the absorption component in the RCP system with previous reports of SSGs (a = Ref. 6, b = Ref. 7, c = Ref. 8) and with a model atomic spin glass (sg = Ref. 9). Adapted from Ref. 2.

The critical character of the glass transition was further tested with both dynamic and static scaling analyses, and the corresponding critical exponents were extracted (see Refs. 2 and 10). The peak in $\chi(T)$, as well as the ZFC maximum in Figure 2, reflect the system’s optimum response to the driving field when its characteristic relaxation time, $\tau$, equals the experiment observation time $t_m=1/\omega$. Thus, the temperature dependence of this relaxation time can be found from the shift of the $\chi'(T)$ peak temperature with increasing frequency $\omega$ of the driving ac field. This $\tau(T)$ data was successfully fitted to the critical slowing down power law $\tau = \tau_0 \exp(-\varepsilon/\omega)$, where $\varepsilon = (T/T_g - 1)$ is the reduced temperature and the prefactor $\tau_0 = \tau_0 \exp(KV/k_BT)$ is the temperature dependent Néel-Brown relaxation time of the individual particles (which does not introduce any new fitting parameters, since the NP anisotropy barrier $KV$ and attempt time $\tau_0$ were previously determined using the above mentioned reference dilute sample [2]), yielding $T_g = 140.1(4)$ K and a critical exponent $zv = 9.5(2)$, in good agreement with values of $zv$ reported in long-range SGs as well as in some SSGs [8].

The ac susceptibility was found to be very sensitive to superposed dc-fields, as is usually observed in superspin glasses [10]. Recording the ac-susceptibility as a function of dc magnetic field above $T_g$ can be used to extract the non-linear susceptibility of the system and check whether the system undergoes a true spin-glass phase transition. The magnetization $M$ in a spin glass can be
expressed as $M = \chi_1 H + \chi_3 H^3 + \chi_5 H^5 + \ldots$, where $\chi_1$ is the linear susceptibility and the higher order terms represent the non-linear susceptibility defined as $\chi_n(H) = \chi_1 - M/H^n$. In a spin glass all the non-linear coefficients, like, e.g., $\chi_3$, diverge at $T_g$ [10]. The non-linear susceptibility can be conveniently extracted from ac susceptibility data as a function of superposed dc fields, since above $T_g$ (where $\chi'' = 0$ and, thus, $\chi = \chi'$ and $\chi_n = \chi_n'$) the dc field dependence of the nonlinear susceptibility is given by $\chi_n(H) = \chi'_n(H) - \chi'(H = 0) - \chi'(H)$. It can be shown that for small dc fields (but still much larger than the ac driving field) $\chi'_n \propto -3\chi_3 H^2$ [10]. Fitting the low field region of the so-obtained $\chi_n(H;T)$ data to such expression, we can extract $\chi_3^*$, the lowest order term of $\chi_n^*$, at each of the measured temperatures (see Ref. 10). At any phase transition $\chi_3(T)$ is expected to diverge with the reduced temperature $\varepsilon = (T - T_g)/T_g$ as $\chi_3 \propto \varepsilon^{-\gamma}$ [10,11]. This is the case indeed for the data extracted for the RCP sample, where $\chi_3(T)$ indeed diverges at $T_g = 140$ K with an associated critical exponent $\gamma = 2.5(5)$. This confirms the occurrence of the spin glass phase transition suggested by the dynamical scaling analysis described above. Further scaling analysis of the complete $\chi_n(T,H)$ data suggests a magnetization exponent $\beta = 0.2(1)$ [10,11]. Within the uncertainties observed in the literature, the values obtained for $\gamma$ and $\beta$ appear closer to those associated with atomic spin glasses than to those reported for superspin glasses.

Finally, it has been shown that interparticle superexchange interactions between the NPs in the RCP sample play a minor role compared to classical dipolar interactions in establishing the collective, superspin-glass state (see Ref. 3). This result was concluded in a comparison of the ZFC peak temperatures (and aging behaviour) in a series of five samples comprising identical maghemite particles in different concentrations, where the concentration was accurately controlled by means of silica shells of different thickness. We found that the freezing temperature of the most concentrated samples in the series (those with $0 \leq$ shell thickness $< 3$ nm), where the ZFC memory effect was also observed, vary in direct proportionality with the volume fraction of the maghemite cores and therefore with the strength of dipolar interactions [3].

Summarizing, we have prepared and characterized what could be considered a benchmark superspin glass, where the optimization of NP uniformity, spatial randomness and strength of dipolar interactions (interparticle exchange has been proven to be negligible) leads to archetypal spin glass behavior.

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