Memory effect and super-spin-glass ordering in an aggregated nanoparticle sample

Olivier Cador, Fabien Grasset, H. Haneda, Jean Etourneau

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Abstract :
A system consisting of aggregated nonstoichiometric zinc ferrite nanoparticles has been studied using AC and DC magnetization measurements. A superparamagnetic–super-spin-glass phase transition at T_g has been identified. The relaxation time diverges at T_g and the nonlinear susceptibility shows an abrupt increase. The critical behavior vanishes when the nanoparticles are not in close contact. The observation of the *memory effect* identical to that which has been already discovered in canonical spin-glass supports the existence of a true thermodynamic transition in agglomerated magnetic nanoparticles.

There has been an increasing number of publications focusing on the magnetic properties of nanoparticle systems in the last few decades [1]. One of the most fascinating problems that researchers have focused on recently is the possible appearance of interparticle long-range magnetic ordering at low temperatures when the interactions between nanoparticles are sufficiently strong. Because of the size distribution of the particles and the randomness inherent to these systems, fingerprints of a possible superparamagnetic–super-spin-glass phase transition, in agreement with canonical spin-glasses, have been pursued and found: (i) the critical slowing down of the relaxation time τ on approaching the transition temperature T_g [2, 3 and 4]; (ii) the divergence of the nonlinear susceptibility χ_{nl} at T_g [5, 6 and 7]; (iii) the magnetic aging in the ordered phase [4, 8, 9 and 10]. So far, most of the investigations have been performed on nanoparticles dispersed in a diamagnetic matrix, which can be a solid or a liquid. The magnetic fluids offer great advantages because the interactions between the particles can be tuned by changing nanoparticle concentration. But the main drawback is that the possibility of forming aggregates in the fluid can never be completely discounted. In aggregated nanoparticle samples this is not a problem and, furthermore, the interactions between the particles are stronger making them suitable for observation of collective behaviors. Consequently, Dormann et al. [4] found that in aggregated samples the low-temperature regime is close to that of a canonical *spin-glass*. However, they did not put in evidence the critical divergence of the nonlinear susceptibility on approaching the transition temperature.

Lately, the spectacular *memory effect* has been found in concentrated ferrofluids [10 and 11]. In a typical memory experiment the sample is cooled in zero external magnetic field. At a given temperature, T_w, the cooling process is halted for a certain time, t_w, then the cooling is resumed. After cooling the AC magnetic response is measured during the warming up of the sample. An infinitesimal cusp appears at T_w when T_w is lower than the blocking temperature, T_B, of the particles [11]. This cusp does not exist when the cooling process is not halted. The *memory effect* had been previously reported below the freezing temperature, T_g, in some spin-glasses [12]. This phenomenon can also be seen as a thermally hidden magnetic inscription. Indeed, at the lowest temperatures (far below T_w), the magnetization is strictly identical if the cooling has been paused or not. In other words, the system has memorized information but the reading is possible only at temperatures in the vicinity at which the information has been stored.

In this paper it is shown that the relaxation time of a sample of aggregated nanoparticles of nonstoichiometric zinc ferrite exhibits a critical slowing down and that the nonlinear susceptibility increases strongly on approaching T_g. In addition, it was found that the sample does show the *memory effect*. These observations support the presence of interactions between the nanoparticles, which may be of dipolar origin and/or exchange. The synthesis and the physical characterizations of these nanoparticles are

described elsewhere [13]. From the observations of 50 nanoparticles it has been concluded that their size is between 4 and 6 nm. The nonstoichiometry associated with the partial inversion of the occupancy of the octahedral and tetrahedral sites by the Fe(III) gives ferrimagnetism to the particles. The saturation magnetization is equal to 64 emu g^{-1}. The magnetization measurements were carried out with a Quantum Design MPMS2 SQUID magnetometer equipped with the low-field option which gives remnant field lower than 50 mOe. The DC measurements were performed with the reciprocating sample option (RSO). In ZFC mode the instrument was paused for 2 min at each temperature before recording the data. AC measurements were performed with the AC driving field amplitude equal to 3 Oe and a frequency range of 0.1–1000 Hz.

The frequency dependence of the in-phase AC susceptibility χ′ is represented in Fig. 1. In the superparamagnetic model the maximum of χ′ at T_{max} corresponds to the average blocking temperature of the sample. This point is not clear however, and it might be the maximum of χ″ that could be used [14]. When the particles interact, authors use different criteria to extract the characteristic relaxation time [15]. Calculations based on the Néel–Brown model describe the variation of T_{max} with the frequency of the oscillating driving field [1]. This model developed first for noninteracting particles remains quantitatively valid in the case of weakly interacting particles [1 and 16]. If the interactions are too strong a dynamic scaling analysis of the data is more appropriate. This has been shown in concentrated ferrofluids and aggregates of nanoparticles [2, 3 and 4]. The characteristic relaxation time varies with temperature according to $\tau=\tau_*(T/T_g-1)^{-zv}$, where T_g is the transition temperature, $z\nu$ the critical exponent and τ_* is related to the relaxation time of individual particles. The freezing temperature T_f at a given frequency $f=1/\tau$ is taken at the maximum of χ′. The fitting procedure with Eq. (1) is in good agreement with the experimental data (see inset of Fig. 1) with the values $\tau_*=6\times10^{-10}$ s, $z\nu=8.4$ and $T_g=31.5$ K. In systems of nanoparticles, values of $z\nu$ between 6.9 and 11 have been reported [2, 3, 4, 17 and 18], which are similar to those found in spin-glasses [19]. Attempts to fit the data with the Néel–Brown model gave poor agreements with unrealistic values, especially from the microscopic relaxation time τ_0 which is of the order of 10^{-25} s. The strictest criterion to identify a spin-glass is the divergence of the nonlinear susceptibility at T_g. The magnetization can be written as follows:

$$\frac{M}{H} = \chi_0 - a_3(T)\chi_0^3 H^2 + a_5(T)\chi_0^5 H^4 + \cdots.$$

where the a_i's reflect the nonlinear behavior. In spin-glasses the coefficient a_3 diverges at T_g with $a_3 \propto (T_g/(T-T_g))^{\gamma}$, while for a paramagnet, it is temperature independent and derives from the Taylor expansion of the Brillouin function. One of the simplest ways to probe the nonlinear coefficients is to record the zero-field-cooled magnetization (ZFCM) at several fields and to compare the M/H curves (see Fig. 2). It can be seen that the ratios M/H are superimposed except around T_g which, according to Eq. (2), means that the nonlinear terms are insignificant away from T_g but significant near T_g. In order to show the thermal variation of the a_i's the thermal variation of $(M-\chi_0 H)/(\chi_0 H)^3$ for H=5 and 10 Oe, with $\chi_0=M/H$ recorded at 1 Oe,[1] has been plotted in the inset of Fig. 2. According to Eq. (2) we can write

$$\frac{M-\chi_0 H}{(\chi_0 H)^3} = -a_3(T) + a_5(T)(\chi_0 H)^2 + \cdots.$$

Both curves show an abrupt negative peak near T_g. The nonlinear coefficient a_3 is close to zero at temperatures higher than 40 K and increases abruptly below 40 K. The results resemble those which have been observed in the genuine spin-glass Ag (11 at% Mn) [20. P. Jönsson, T. Jonsson, J.L. García-Palacios and P. Svedlindh. *J. Magn. Magn. Mater.* **222** (2000), p. 219.and suggest a phase transition at T_g, though the divergence is much less accentuated. The difference between the 5 and 10 Oe curves is difficult to elucidate. It is possible to argue from an experimental point of view that the initial susceptibility

χ_0 is, obviously, field independent. However, at 1 Oe the nonlinear terms might already contribute significantly near T_g. This might induce a small error on χ_0 and consequently on the ratios $(M-\chi_0 H)/(\chi_0 H)^3$. Measurements in extremely low fields, which were not reachable with the apparatus used, would be required to extract the true χ_0 vs. T curve. However, this uncertainty is not responsible for the observed gap between the two curves because it affects both measurements. Other terms in Eq. (3), for example a_5, might significantly contribute to $(M-\chi_0 H)/(\chi_0 H)^3$. No attempt was made to fit the data with the exponent law $a_3 \propto (T_g/(T-T_g))^\gamma$ because of this field dependence. One of the problems dealing with systems in which the particles interact is the distinction between collective and individual behaviors. Pileni et al. [21] have recently reported unusual magnetic properties of nonstoichiometric zinc ferrite nanoparticles dispersed in PVA. The ZFCM–FCM (field-cooled magnetization) curves show unexpected nonlinear response at a low field (H<10 Oe), also centered on the maximum of the ZFCM, but over a wide temperature range. In our case we have determined (not represented) that a ferrofluid containing our particles does not present such a low-field effect, so intrinsic phenomena can be ruled out. The nonlinearity of the particles themselves appears at a field higher than 50 Oe. In order to get more information on the glassy phase the presence of the *memory effect* was probed. To do so a slightly different strategy from Jönsson et al. [11] was employed. Indeed the ZFCM curves were measured with a stop and without a stop (called reference) during the cooling process. The measurements were performed under 1 Oe with and without a halt, t_w=3600 s, at T_w=15 K. The two curves are shown in Fig. 3. The reference ZFCM shows a cusp at T_{max}=31.5 K. Below T_g, $ZFCM_{ref}$ increases steadily without any apparent change of regime. The halted and the reference ZFCM curves do superimpose for all temperature other than around T_w. The $ZFCM_{halted}$ shows a dip centered on T_w. The difference curve $ZFCM_{ref}$–$ZFCM_{halted}$ is shown in the inset of Fig. 3. The maximum lies exactly at T_w. It seems that the effect is more pronounced in this sample than in the ferrofluid studied by Jönsson et al. [11]. It can be noted that the *memory effect* vanishes when the particles are dispersed in a liquid. It is also worth mentioning that a ferrofluid containing the zinc-ferrite nanoparticles does not show any abrupt increase of the nonlinear susceptibility as well as the critical behavior of the relaxation time. The occurrence of a true magnetic phase transition in magnetic particle systems has been the subject of debate in recent times. What has been established previously is that when the interactions between the particles are strong enough the low-temperature regime is close to that of a canonical spin-glass. Most of the investigations have been performed on ferrofluids in which the magnetic interactions between the particles are dipolar. In agglomerated systems the juxtaposition of the particles may switch on exchange interactions between the atoms at the surface. To our knowledge the problem of the exchange interaction between nanoparticles in compacted systems has not been intensely investigated, neither from the theoretical nor the experimental point of view [22]. This very interesting problem has to be tackled in order to figure out whether exchange interactions between particles can or cannot lead to a spin-glass state. To summarize, the superparamagnetic–super-spin-glass phase transition at T_g in a sample of aggregated nonstoichiometric zinc ferrite nanoparticles has been identified. The relaxation time diverges and the nonlinear susceptibility increases abruptly at T_g almost in perfect agreement with the laws of the ‘classical’ paramagnetic–spin-glass phase transition. These critical behaviors vanish when the interactions between the particles are cut (when the particles are dispersed in a diamagnetic medium). The observation of the *memory effect* identical to canonical spin-glass supports the existence of a true thermodynamic transition in agglomerated magnetic nanoparticles.

Acknowledgements :

Two of the authors (O.C. and F.G.) want to thank the Japan Science and Technology Exchange Center (JISTEC) for the

financial support of their postdoctoral fellowships. The authors sincerely thank Dr. Charles Baker for language improvements.

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Fig. 1. The temperature dependence of the real part of the AC susceptibility measured at various frequencies of the oscillating magnetic field. Inset: analysis of the critical slowing down of the relaxation time (see text).

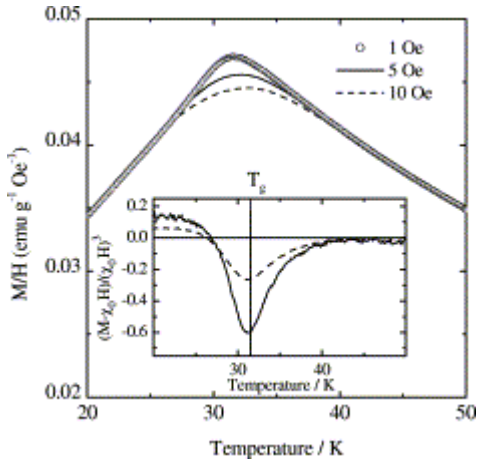

Fig. 2. The temperature dependence of *M*/*H* recorded at different DC magnetic fields and in zero-field-cooled modes. Inset: temperature dependence of the nonlinear terms in Eq. (2).

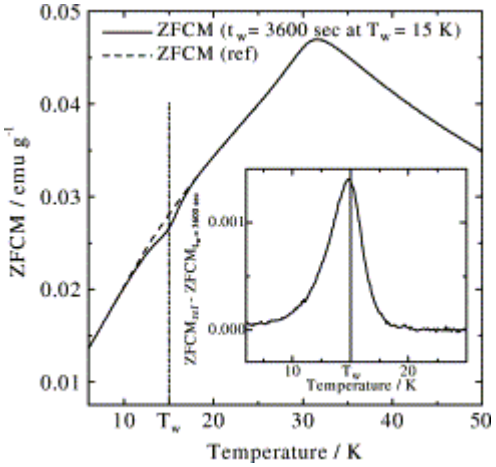

Fig. 3. The temperature dependences of the ZFCM recorded at 1 Oe with and without a stop of 1 h at T_w during the cooling process. We have plotted the difference between the two curves in the inset.