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Christian Binek

*University of Nebraska-Lincoln*, [cbinek@unl.edu](mailto:cbinek@unl.edu)

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# Superspin glass behavior of interacting ferromagnetic nanoparticles in discontinuous magnetic multilayers

O. Petracic, W. Kleemann\* and Ch. Binek

*Laboratorium für Angewandte Physik, Gerhard-Mercator-Universität,  
47048 Duisburg, Germany*

G. N. Kakazei, Yu. G. Pogorelov and J. B. Sousa

*IFIMUP, Departamento de Fisica, Universidade de Porto, 4169-007 Porto, Portugal*

S. Cardoso and P. P. Freitas

*INESC, Rua Alves Redol 9-1, 1000, Lisbon, Portugal*

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## Abstract

Discontinuous magnetic multilayers  $[\text{Co}_{80}\text{Fe}_{20}(t)/\text{Al}_2\text{O}_3(3\text{nm})]_{10}$  with  $t = 0.9$  and  $1.0\text{nm}$  are studied by SQUID magnetometry and *ac* susceptibility. Owing to dipolar interaction the superparamagnetic cluster systems undergo collective glass-like freezing upon cooling. While both samples exhibit very similar glass temperatures  $T_g \approx 45$  K and critical exponents  $z\mathbf{n} \approx 10$  and  $\mathbf{g} \approx 1.4$  as obtained from the temperature dependencies of the relaxation time,  $\tau$ , and the nonlinear susceptibility,  $\mathbf{c}_3$ , dynamical scaling reveals different critical exponents,  $\mathbf{b}(0.9\text{nm}) \approx 1.0$  and  $\mathbf{b}(1.0\text{nm}) \approx 0.6$ , respectively.

**Keywords:** Multilayers, *ac* susceptibility, superparamagnetism, dipolar interactions, spin glass behavior

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\* Corresponding author: Fax : ++49-203-1965, email: wolfgang@kleemann.uni-duisburg.de

## INTRODUCTION

The magnetic behavior of ensembles of small ferromagnetic particles has found considerable interest during the past 50 years (Néel, 1949; Brown, 1963; Djurberg *et al.*, 1997; Dormann *et al.*, 1997). Most investigations have been focused onto single-domain particles on a nanoscale. They are usually randomly distributed in a diamagnetic metallic or insulating matrix and possess randomly oriented anisotropy axes. In the absence of interactions the dynamics of such a superparamagnetic (*SPM*) system is governed by the magnetic relaxation time of the particles with volume  $V$  at a given temperature,  $T$ ,

$$\mathbf{t} = \mathbf{t}_0 \exp(KV / k_B T), \quad (1)$$

where  $K$  and  $\mathbf{t}_0$  are the anisotropy constant and the inverse attempt frequency, respectively (Néel, 1949; Brown, 1963). In the case of a monodisperse ensemble the real and the imaginary part of the complex *ac* susceptibility,  $\mathbf{c} = \mathbf{c}' - i\mathbf{c}''$ , become analytical functions of the *ac* frequency,  $f$ , and temperature (Andersson *et al.*, 1997).  $\mathbf{c}'(T)$  and  $\mathbf{c}''(T)$  exhibit peaks at temperatures  $T_m$  and  $T^*$ , respectively.  $T_m$  asymptotically approaches zero with decreasing  $f$  and paramagnetic Curie-type static susceptibility is achieved as  $f \rightarrow 0$ .

This is different in the presence of interactions between the *superspins*, e.g. of RKKY- or dipolar origin. Although conflicting models have been discussed (Dormann *et al.*, 1999b), both experimentally (Djurberg *et al.*, 1997; Jonsson *et al.*, 1998) and theoretically (Andersson *et al.*, 1997) much evidence was found for various systems that a *superspin glass* (*SSG*) phase may exist below a well-defined glass temperature,  $T_g$ . The dynamics of the system then follows a critical scaling law of the form (Ogielski, 1985)

$$\mathbf{t} = \mathbf{t}_0 (T / T_g - 1)^{-\mathbf{n}} \quad (2)$$

in the ergodic regime at  $T > T_g$ . While  $\mathbf{n}$  is the critical exponent of the correlation length,  $\mathbf{x} \propto (T/T_g - 1)^{-\mathbf{n}}$ , the exponent  $z$  relates the relaxation time to the correlation length,  $\mathbf{t} \propto \mathbf{x}^z$ . The

relaxation time  $t$  usually refers to the peak temperature,  $T_m$ , of the  $ac$  susceptibility, where  $t = 1/2\pi f$  is connected with the  $ac$  frequency  $f$  of the experiment (Dormann *et al.*, 1999a).

Another crucial test of collective glassy freezing relies on the criticality of the nonlinear susceptibility,  $c_3$ , as defined by the expansion of the magnetization  $M$  with respect to a weak magnetic field  $H$  (Djurberg *et al.*, 1997),

$$M = c_1 H - c_3 H^3 + O(H^5). \quad (3)$$

A power law

$$c_3 = c_3^0 (T/T_g - 1)^{-g} \quad (4)$$

with a critical exponent  $g \geq 1$  is expected to hold close to  $T_g$  in the ergodic *SPM* regime.

Finally, dynamic critical scaling can be used to test the universality of the system. The imaginary part of the susceptibility,  $c''(\omega, T)$ , measured at various frequencies  $\omega$  is expected to yield a data collapse onto a single function  $H(\omega, t)$  according to (Gunnarsson *et al.*, 1988)

$$c'' / c_{eq} = (T/T_g - 1)^b H(\omega, t), \quad T > T_g, \quad (5)$$

where  $b$  is the order parameter exponent and  $c_{eq}$  denotes the equilibrium susceptibility in the limit  $\omega \rightarrow 0$ .

In the present paper the magnetic behavior of discontinuous multilayers (*DMIMs*)  $[\text{Co}_{80}\text{Fe}_{20}(t)/\text{Al}_2\text{O}_3(3 \text{ nm})]_{10}$  with  $t = 0.9$  and  $1.0 \text{ nm}$  is investigated. In these systems the CoFe layers are known to form isolated quasi-spherical ferromagnetic (*FM*) nanoclusters embedded in the alumina matrix (Kakazei *et al.*, 1999). It will be shown that generic *SSG* behavior emerges at low temperatures,  $T < 60 \text{ K}$ , despite the fairly wide size distribution as determined by high resolution electron microscopy, e.g.  $\langle 2r \rangle \approx 3 \text{ nm}$  and  $s = 2.7$  for  $t = 1.3 \text{ nm}$  (Kakazei *et al.*, 2000). Previously it has been shown that *superferromagnetism* occurs for slightly higher CoFe thickness but still below site percolation for  $1.4 \leq t < 1.8 \text{ nm}$  at room temperature (Kakazei *et al.*, 2000) and for  $1.1 \leq t \leq 1.3 \text{ nm}$  below room temperature (Kleemann *et al.*, 2000a, b).

Under these conditions magnetic percolation takes place in a particularly dense fraction of the nanocluster system, while another, more dilute one still undergoes *SSG* freezing.

## EXPERIMENT

*DMIM* systems of the structure  $[\text{Co}_{80}\text{Fe}_{20}(t)/\text{Al}_2\text{O}_3(3\text{nm})]_{10}$  are prepared on a glass substrate covered by a  $\text{Al}_2\text{O}_3(3\text{nm})$  buffer layer by ion-beam sputtering (Kakazei *et al.*, 1999). The thickness of the alumina layers were kept fixed.

The measurements were performed by use of a commercial Superconducting Quantum Interference Device (*SQUID*) magnetometer (*MPMS-5S*, Quantum Design). The *ac* susceptibility was measured by applying a small oscillating field with amplitude  $m_0 H_{ac} = 0.05\text{mT}$  in zero external field and frequencies  $0.01\text{Hz} \leq f \leq 1\text{ Hz}$ . The real and the imaginary parts,  $\chi'$  and  $\chi''$  respectively, are extracted as in- and out-of-phase components of the time-dependent magnetization response, respectively.

For nonlinear susceptibility studies the magnetization curves  $M$  vs.  $H$  were recorded after zero-field cooling (*ZFC*) from  $T = 300\text{K}$  at temperatures  $55 \leq T \leq 65\text{K}$  in fields  $-5 \leq m_0 H \leq 5\text{mT}$  with  $0.01\text{mT}$  resolution. In order to warrant thermal equilibrium, the critical slowing down has been overcome by isothermal waiting times between data points,  $t_w = 100$  and  $500\text{s}$  at  $T > 60\text{K}$  and  $\leq 60\text{K}$ , respectively.

## RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the real and imaginary part of  $\chi$  for seven different *ac* frequencies,  $f = 0.01 - 1\text{ Hz}$  obtained on both samples,  $t = 0.9$  (a) and  $1.0\text{ nm}$  (b) in virtually zero-field ( $|m_0 H| < 0.02\text{ mT}$ ) after zero-field cooling (*ZFC*) from  $T = 200\text{ K}$ . It is seen

that the peaks of both  $\chi''$  and  $\chi'$  shift gently towards lower  $T$  on decreasing the frequency  $f$ , while the  $\chi'$  curves peak on the low- $T$  branches of the corresponding  $\chi''$  curves as expected for spin glass-like systems (Djurberg *et al.*, 1997).  $T_m(f)$  values are extracted from the interpolated peak positions of  $\chi''(T)$ . Fig. 2 shows double-logarithmic plots of  $t = (2\pi f)^{-1}$  versus the reduced temperature  $T_m/T_g - 1$  for both samples together with best-fitted power laws, Eq. (2) (solid lines). The fits are seen to be satisfactory with essentially the same slopes, i.e. equal critical exponents  $z\nu$ . The following sets of data are obtained by best-fit procedures:  $T_g = (45.6 \pm 4.6)\text{K}$ ,  $t_0 = (2.8 \pm 1.3) \cdot 10^{-7}\text{s}$ ,  $z\nu = 10.2 \pm 4.6$  for  $t = 0.9$  nm and  $T_g = (47.1 \pm 5.3)\text{K}$ ,  $t_0 = (6.7 \pm 1.4) \cdot 10^{-7}\text{s}$ ,  $z\nu = 10.0 \pm 3.6$  for  $t = 1.0$  nm. Similar results, albeit with shorter  $t_0$  values, were obtained on  $\text{FeC}$  and  $\text{g-Fe}_2\text{O}_3$  nanoparticle systems (Djurberg *et al.*, 1997; Dormann *et al.*, 1999b). While the value of  $z\nu$  agrees with that predicted for 3D spin glasses (Gunnarsson *et al.*, 1988), the large "spin-flip" time  $t_0$  accounts for the cluster nature of the "superspins" (Djurberg *et al.*, 1997; Pfannes *et al.*, 2000).

Interestingly, the glass temperature  $T_g$  decreases but little as the  $\text{CoFe}$  layers become thinner. This agrees with observations on spin glass-like dilute  $FM$  systems (Fischer and Hertz, 1991; Mydosh, 1993).  $T_g$  is virtually independent of the concentration below a critical concentration,  $x_c$ , as soon as the average interaction  $\langle J \rangle$  becomes smaller than the width  $dJ$  of its distribution. Since  $T_g \approx dJ/k_B$ , one does not expect important changes upon decreasing the average interspin distance, although  $\langle J \rangle$  is further decreased. Similarly, when assuming heterogeneous nucleation in our  $DMIM$ s (Kakazei *et al.*, 1999) and thus virtually constant particle density, the clearance between nearest-neighbor particles is enhanced at decreasing  $t$ . Hence,  $\langle J \rangle$  will decrease, while  $dJ$  remains virtually unaffected.

Nonlinear susceptibility studies corroborate the above conjectured  $SSG$  nature of the  $DMIM$  system with  $t = 1.0\text{nm}$ . To this end magnetization curves  $M$  vs.  $H$  were recorded after ZFC from  $T = 300\text{K}$  at temperatures  $55 \leq T \leq 65\text{K}$  in fields  $-5 \leq m_0 H \leq 5\text{mT}$  with  $0.01\text{mT}$

resolution. Isothermal waiting times between data points,  $t_w = 100$  and  $500$ s at  $T > 60$ K and  $\leq 60$ K, respectively, were employed. The data were fitted to a polynomial,  $M = c_1 H - c_3 H^3 + c_5 H^5$ , where  $c_3$  is expected to diverge at  $T_g$  in case of a collective spin-glass-like phase transition (Gunnarsson *et al.*, 1988). The results are plotted in Fig. 2b together with a best-fitted power law,  $c_3 = c_3^0 (T/T_g - 1)^{-g}$  revealing  $T_g = (50.7 \pm 2.3)$ K,  $g = 1.36 \pm 0.53$  and  $c_3^0 = (2.5 \pm 1.3) \cdot 10^{-9} \text{ (m/A)}^2$ . Within errors  $T_g$  agrees with the value obtained from dynamic scaling (see above). The critical exponent  $g \approx 1.4$  is smaller than that observed on spin glasses,  $g \approx 4$  (Gunnarsson *et al.*, 1991). This seems to hint either at proximity to mean-field behavior,  $g = 1$  (Fischer and Hertz, 1991; Mydosh, 1993) owing to the long-range nature of the dipolar interaction, or at spurious blocking processes of large particles within the relatively broad log-normal particle size distribution in our samples (Kakazei *et al.*, 2000).

Dynamic scaling analysis of  $c''(\mathbf{w}, T)$  is shown in Figure 3 for  $t = 0.9$  (a) and  $1.0$  nm (b). Here the data from Figure 1 are best-fitted to Eq. (5) when plotting  $(T/T_g - 1)^{-b} c'' / c_{eq}$  versus  $\mathbf{w}(T/T_g - 1)^{-z\mathbf{n}}$ . The function  $c_{eq}(T)$  is approximated by a Curie-Weiss hyperbola,  $c'(f = 0.01\text{Hz}, T) = c_0 / (T - T_0)$ , best-fitted to the respective low- $f$  data within the range  $60 < T < 90$ K, while trial values of  $z\mathbf{n}$  and  $T_g$  are chosen to be close to the above dynamic power law fits. It is seen that data sets are reasonably collapsing in both cases when choosing consistent parameter sets,  $T_g = 44$ K,  $z\mathbf{n} = 10.0$ ,  $\mathbf{b} = 1.0$  for  $t = 0.9$  nm and  $T_g = 46$ K,  $z\mathbf{n} = 10.0$ ,  $\mathbf{b} = 0.6$  for  $t = 1.0$  nm, respectively. Obviously quite different values of the order parameter exponent  $\mathbf{b}$  emerge in parallel to remarkably different shapes of the scaling functions  $H(\mathbf{w}, t)$ . While  $\mathbf{b} = 1.0$  for  $t = 0.9$  nm complies with observations on SSG systems like  $\text{Fe}_{0.88}\text{C}_{0.22}$  (Jönsson *et al.*, 2000), the low value  $\mathbf{b}(1.0 \text{ nm}) = 0.6$  reminds of that found in the Ising spin glass  $\text{Fe}_{0.5}\text{Mn}_{0.5}\text{TiO}_3$ ,  $\mathbf{b} = 0.45$  (Gunnarsson *et al.*, 1988). However, this agreement is probably fortuitous. Owing to the unusual non-monotonic shape of  $H(\mathbf{w}, t)$  we rather believe that a

crossover situation is encountered for the  $t = 1.0$  nm sample, which is close to exhibit superferromagnetism (Kleemann *et al.*, 2000b). Very likely a subsection of nanoparticles within the broad distribution of particle sizes is close to ferromagnetic percolation (Kleemann *et al.*, 2000b). This gives rise to an extra contribution to the loss function  $\mathbf{c}''(\mathbf{w}, T)$ , which is assumed to be at the origin of the unusual peak structure discovered in  $H(\mathbf{w}, t)$ . Hence, we claim that only the more diluted sample,  $t = 0.9$  nm, might represent a generic *SSG* system, whose critical exponent  $\mathbf{b} \approx 1.0$  agrees with results on related systems (Jönsson *et al.*, 2000).

It should be stressed, however, that apart from these subtle differences both of our systems dominantly exhibit *SSG* freezing as evidenced by the virtually identical parameters  $T_g$  and  $z\mathbf{n}$ . In this context one might consider another useful criterion, which clearly evidences the collective freezing process. It is well-known that the decrease of the gap between logarithmically equally spaced susceptibility curves with decreasing frequency (Fig. 1) can be characterized by specific values of the modulus  $k = (1/T_f)(\Delta T_f / \Delta \log \mathbf{w})$  (Sandlund *et al.*, 1989). When setting the freezing temperatures  $T_f \approx T_m$  (see Fig. 2a),  $k$  is found to decrease to small values as  $T \rightarrow T_g$ ,  $k \approx 0.01$  in both cases (Fig. 4). As discussed previously (Kleemann *et al.*, 2000b) these values seem to hint at three-dimensional glass-like freezing rather than at the two-dimensional one, where larger  $k$  values are expected (Sandlund *et al.*, 1989). In future experiments it will therefore be interesting to reduce the number  $n$  of *DMIM* bilayers towards the two-dimensional limit,  $n = 1$ , where significant changes, viz.  $k \approx 0.04$  and  $T_g \rightarrow 0$ , are expected.

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## References

- Andersson, J.-O., Djurberg, C., Jonsson, T., Svedlindh, P. and Nordblad, P. (1997) Monte Carlo studies of the dynamics of an interacting monodisperse magnetic-particle system. *Phys. Rev. B* **56**, 13983.
- Brown, Jr., W. F. (1963) Thermal fluctuations of a single-domain particle. *Phys. Rev.* **130**, 1677.
- Djurberg, C., Svedlindh, P., Nordblad, P., Hansen, M. F., Baker, F. and Mrup, S. (1997) Dynamics of an interacting particle system: evidence of critical slowing down. *Phys. Rev. Lett.* **79**, 5154.
- Dormann, J. L., Fiorani, D. and Tronc, E. J. (1997) Magnetic relaxation in fine-particle systems. *Adv. Chem. Phys.* **98**, 283.
- Dormann, J. L., Fiorani, D. and Tronc, E. J. (1999a) On the models for interparticle interactions in nanoparticle assemblies: comparison with experimental results. *J. Magn. Magn. Mater.* **202**, 251.
- Dormann, J. L., Fiorani, D., Cherkaoui, R., Tronc, E., Lucari, F., D’Orazio, F., Spinu, L., Nogues, M., Kachkachi, H. and Jolivet, J. P. (1999b) From pure superparamagnetism to glass collective state in  $g$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticle assemblies. *J. Magn. Magn. Mater.* **203**, 23.
- Fischer, K.H. and Hertz, J.A. (1991) *Spin Glasses* (Cambridge Univ. Press, Cambridge).
- Gunnarsson, K., Svedlindh, P., Nordblad, P. Lundgren, L., Aruga, H. and Ito, A. (1988) Dynamics of an Ising spin glass in the vicinity of the spin glass temperature. *Phys. Rev. Lett.* **61**, 754.
- Gunnarsson, K., Svedlindh, P., Nordblad, P. Lundgren, L., Aruga, H. and Ito, A (1991) Static scaling in a short-range Ising spin glass. *Phys. Rev. B* **43**, 8199.
- Jonsson, P., Hansen, M. F., Svedlindh, P. and Nordblad, P. (2000) Spin glass like transition in highly concentrated Fe-C nanoparticle system. *J. Magn. Magn. Mater.*, to appear (cond-mat/0007464).

- Jonsson, T., Svedlindh, P. and Hansen, M. F. (1998) Static scaling on an interacting magnetic nanoparticle system. *Phys. Rev. Lett.* **81**, 3976.
- Kakazei, G. N., Freitas, P. P., Cardoso, S., Lopes, A. M. L., Pereira de Azevedo, M. M., Pogorelov, Yu. G. and Sousa, J. B., (1999) Transport properties of discontinuous  $\text{Co}_{80}\text{Fe}_{20}/\text{Al}_2\text{O}_3$  multilayers, prepared by ion beam sputtering. *IEEE Trans. Mag.* **35**, 2895.
- Kakazei, G. N., Pogorelov, Yu. G., Lopes, A. M. L., Sousa, J. B., Cardoso, S., Freitas, P. P., Pereira de Azevedo, M. M. and Snoeck, E. (2000) Tunnel magnetoresistance in ion-beam sputtered  $\text{Co}_{80}\text{Fe}_{20}/\text{Al}_2\text{O}_3$  discontinuous multilayers. *J. Appl. Phys.* (submitted)
- Kleemann, W., Petravic, O., Binek, Ch., Kakazei, G. N., Pogorelov, Yu. G., Sousa, J. B., Cardoso, S. and Freitas, P. P. (2000a) AC susceptibility studies of discontinuous  $\text{Co}_{80}\text{Fe}_{20}/\text{Al}_2\text{O}_3$  multilayers. *J. Magn. Magn. Mater.* (in press); (2000b) Interacting ferromagnetic nanoparticles in discontinuous  $\text{Co}_{80}\text{Fe}_{20}/\text{Al}_2\text{O}_3$  multilayers: from superspin glass to reentrant superferromagnetism. *Phys. Rev. B* (submitted).
- Mydosh, J.A. (1993) *Spin Glasses: an Experimental Introduction* (Taylor and Francis, London).
- Néel, L. (1949) Théorie du trainage magnétique des ferromagnétiques en grains fins avec applications aux terres cuites. *Ann. Geophys.* **5**, 99.
- Ogielski, A. T. (1985) Dynamics of three-dimensional Ising spin glasses in thermal equilibrium. *Phys. Rev. B* **32**, 7384.
- Pfannes, H.-D., Mijovilovich, A., Magalhães-Paniago, R. and Paniago, R. (2000) Spin-lattice-relaxation-like model for superparamagnetic particles under an external magnetic field. *Phys. Rev. B* **62**, 3372.
- Sandlund, L., Granberg, P., Lundgren, L., Nordblad, P., Svedlindh, P., Cowen, J. A. and Kenning, G. G. (1989) Dynamics of Cu-Mn spin-glass films. *Phys. Rev. B* **40**, 869.

### Figure Captions

Fig. 1  $c'(f,T)$  and  $c''(f,T)$  vs.  $T$  of CoFe/Al<sub>2</sub>O<sub>3</sub> DMIMs with  $t = 0.9$  (a) and 1.0 nm (b) measured at frequencies  $f = 0.01, 0.02, 0.05, 0.1, 0.2, 0.5$  and 1 Hz (data points interpolated by spline functions; symbols explained in Fig. 2). Glass temperatures  $T_g$  are marked by arrows.

Fig. 2 Double-logarithmic plots of (a)  $t = (2pf)^{-1}$  vs.  $T_m/T_g - 1$  and (b)  $c_3$  vs.  $T/T_g - 1$  (obtained after waiting times  $t_w$  as indicated) for DMIMs with  $t = 0.9$  (a) and 1.0nm (a and b), where  $T_g = (45.6 \pm 4.6), (47.1 \pm 5.3)$  and  $(50.7 \pm 2.3)$ K, respectively, from best-fits to power laws (straight lines).

Fig. 3 Dynamic scaling plots  $(T/T_g - 1)^{-b} c''/c_{eq}$  vs.  $w(T/T_g - 1)^{-zn}$  of the susceptibility data shown in Fig. 1a and b for  $t = 0.9$  (a) and 1.0 nm (b) best-fitted by the parameter sets  $T_g = 44$ K,  $zn = 10.0$ ,  $b = 1.0$ ,  $c_{eq} = 0.115/(T - 42.5$ K) and  $T_g = 46$ K,  $zn = 10.0$ ,  $b = 0.6$ ,  $c_{eq} = 0.269/(T - 45$ K), respectively.

Fig. 4 Variation of the modulus  $k = (1/T_f)(\Delta T_f / \Delta \log w)$  with the freezing temperature  $T_f \approx T_m$  as obtained from  $c'$  vs.  $T$  as shown in Fig. 1a and b.