

## Electron paramagnetic resonance spectra near the spin-glass transition in iron oxide nanoparticles

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Electron paramagnetic resonance (EPR) in iron-oxide nanoparticles ( $\sim 2.5$  nm) embedded in a polyethylene matrix reveals the sharp line broadening and the resonance field shift on sample cooling below  $T_F \approx 40$  K. At the same temperature a distinct anomaly in the field-cooled magnetization is detected. The temperature dependences of EPR parameters below  $T_F$  are definitely different than those found for various nanoparticles in the superparamagnetic regime. In contrast to canonical bulk spin glasses, a linear fall-off of the EPR linewidth is observed. Such behavior can be explained in terms of the random-field model of exchange anisotropy.

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Oxide nanostructured media are considered as very perspective materials for high density magnetic recording.<sup>1</sup> This is the reason for the great interest in the maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) nanoparticles (NP).<sup>2</sup> The strong decreasing of the saturation magnetization in maghemite NP,<sup>3</sup> in comparison with the bulk counterpart, gave rise to a conception of spin canting.<sup>4</sup> The principle question is whether only the surface spins of a particle resist being aligned with even a large external magnetic field, or if such a property inheres in the core spins as well.<sup>5</sup> Recent studies of low field zero field cooled (ZFC) and field cooled (FC) magnetization curves of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NP evidence the existence of a spin-glass-like surface layer that undergoes a magnetic transition to a frozen state below  $\approx 42$  K.<sup>6</sup> Analogous spin-glass-like behavior below about 50 K was also found in oxygen passivated iron NP,<sup>7</sup> as well as in NiFe<sub>2</sub>O<sub>4</sub> NP.<sup>8</sup>

It seems natural to study these spin-glass-like phenomena in NP by an EPR technique, which has been proven to be a very useful tool for exploring spin dynamics in various ferromagnets and antiferromagnets<sup>9,10</sup> and, especially, in spin glasses,<sup>11</sup> including reentrant alloys.<sup>12,13</sup> Whereas measurements of the magnetic moment provide integral sample characteristics, EPR data give information about local magnetic properties and, in principle, about the nature of spin-spin interactions,<sup>13</sup> the distribution of internal fields,<sup>14</sup> and spin-spin correlations.<sup>15</sup> As a rule, in canonical bulk spin glasses (SG's) the EPR resonance field  $H_{\text{res}}$  and the EPR linewidth  $\Delta H$  are roughly temperature independent at high temperatures, but change rapidly [ $\Delta H \propto \exp(-T/T_g)$ ] if  $T < 2T_g$ , where  $T_g$  is the spin-freezing temperature. Contrary to usual magnetic phase transitions, for which the linewidth diverges at the critical temperature, bulk SG reveal a finite value of  $\Delta H$  at  $T_g$ . Due to the very complicated magnetism of spin glasses, there is no completely adequate theory of the linewidth temperature dependence. The increase in the linewidth is usually attributed either to a broadening from a distribution of internal local fields, or to a slowing down of the spin-relaxation rate on approaching  $T_g$ .<sup>16</sup>

Some microscopic features of SG and NP systems are similar, e.g., the maximum of ac and low-field ZFC susceptibility at a certain temperature  $T_m$ , as well as the irreversibility (splitting between ZFC and FC curves).<sup>17</sup> Spin-glass-like behavior in the NP systems is usually considered as a result of the random dipole-dipole interaction between NP at low enough temperatures, when all the particle moments are blocked along the anisotropy axes.<sup>17,18</sup> Correlations between the particle moments develop in a similar way to the correlations between spins in spin glasses. A lot of magnetic NP systems, similarly to SG, show a broadening and a low-field shift of EPR lines with a temperature decreasing.<sup>21-27</sup> Nagata and Ishihara<sup>21</sup> proposed a phenomenological description for these anomalies in superparamagnetic systems. They derived a simple power relation between the shift (relative to a high temperature value) of the resonance field  $\delta H_{\text{res}}$  and the EPR linewidth  $\Delta H$ . For randomly oriented particles it was found that  $\delta H_{\text{res}} \propto (\Delta H)^3$ . This theory does not take into consideration effects of magnetic transitions in nanoparticle systems and, probably, it should not hold below  $T_g$ . Some spin-glass concepts have been used for analysis of low-temperature anomalies of EPR spectra in NP.<sup>23,25-27</sup> However, qualitative differences in behavior of EPR spectra in NP and in bulk spin glasses are still lacking. It should be stressed, that the present work is devoted to the study of the intrinsic spin-glass state which takes place inside an individual particle, resulting from interactions between spins, which form its internal magnetic structure.

We report the results of static magnetization and EPR measurements on iron-oxide NP embedded in a polyethylene matrix. The samples were prepared by the high-speed thermal decomposition of an iron-containing compound in a solution/melt of polyethylene in vaseline oil in an inert atmosphere at 220 °C. This method allows for the fabrication of particles with bimodal lognormal diameter distribution  $F(D)$  and effective sizes below 10 nm.<sup>27</sup> For the samples studied, our small-angle x-ray diffraction measurements

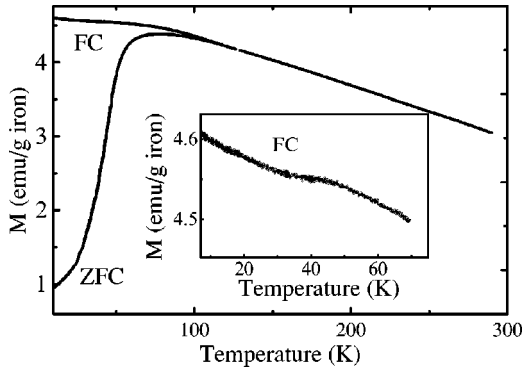


FIG. 1. ZFC and FC magnetization curves of the iron-oxide nanoparticles. The applied field is equal to 480 Oe. The inset shows the sudden increase of the FC magnetization at about 40 K.

show that the maximum of  $F(D)$  is near 2.5 nm. A room-temperature Mössbauer spectrum of the samples can be considered as a superposition of two doublets of nearly equal intensity, with the isomer shift  $0.35 \pm 0.01$  mm/s (with reference to  $\alpha$ -Fe) and values of the quadrupole splitting  $0.75 \pm 0.01$  mm/s and  $1.27 \pm 0.02$  mm/s. These parameters are close to those for  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> superparamagnetic NP.<sup>28</sup> The iron content in powderlike samples is approximately 30 wt. %.

The ZFC-FC magnetization curves were recorded in the temperature region from 4 K up to 300 K with help of the vibrating sample magnetometer PARC-M-155. The maximum of the ZFC magnetization curve at about 75 K and the splitting between ZFC and FC curves below approximately 100 K (Fig. 1) are typical of the blocking process of an assembly of superparamagnetic NP. The average blocking temperature can be estimated as  $T_B \approx 75$  K.<sup>17,18</sup> The inset of Fig. 1 shows details of the FC branch with a distinct increase of the magnetization below  $T_F \approx 40$  K. The magnetic behavior of this type was observed earlier in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NP, for which the appearance of the surface spin-glass transition has been supposed.<sup>6</sup> The sudden increase of the FC magnetization has been considered as the onset of the freezing process.<sup>6</sup> Although the ZFC curve peak at 75 K could reflect, in principle, a collective SG ordering due to dipole-dipole interactions between NP,<sup>17</sup> a relatively weak temperature dependence of the EPR linewidth from 110 down to 70 K (see

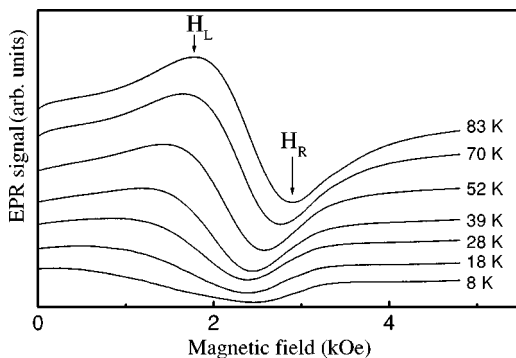


FIG. 2. Low-temperature EPR spectra in iron-oxide nanoparticles.  $H_L$  and  $H_R$  are left and right spectrum peaks, correspondingly.

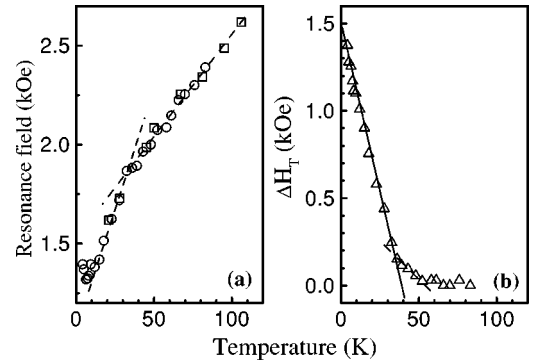


FIG. 3. Thermal behavior of the effective EPR resonance field (a) and the temperature-dependent contribution to the EPR linewidth (b). All dashed lines are guides for the eye. Solid line presents the linear fall-off of  $\Delta H_T = H(0)(1 - T/T_F)$  with  $H(0) = 1500$  Oe,  $T_F = 40$  K.

below) allows one to challenge this possibility. Indeed, in systems with an SG transition, the EPR linewidth usually starts notably broadening below about  $2T_g$ .<sup>11</sup> On the other hand, because of very different characteristic measuring times for a static magnetization and EPR spectra ( $\tau_m = 10^2$  s and  $\tau_{\text{EPR}} = 10^{-10}$  s, correspondingly), the transition from the superparamagnetic to the blocking state, which manifests itself in the ZFC peak, could not noticeably affect EPR spectra. The Néel theory of the superparamagnetic relaxation gives the relation  $T_B^{\text{EPR}}/T_B = \ln(\tau_m/\tau_0)/\ln(\tau_{\text{EPR}}/\tau_0)$ , where  $T_B^{\text{EPR}}$  is the temperature, at which the superparamagnetic relaxation time  $\tau$  equals  $\tau_{\text{EPR}}$ , and  $\tau_0$  is in the range  $10^{-10} - 10^{-12}$  s.<sup>19,20</sup> Since  $\tau_{\text{EPR}}$  could be very close to  $\tau_0$ , we suppose that  $T_B^{\text{EPR}}$  is many times higher than  $T_B$  and unattainable in our experiments.

EPR measurements were carried out by using the X-band spectrometer Varian E-109 with a flow helium cryostat. At room temperature the EPR spectrum consists of a single line with the peak-to-peak linewidth  $\Delta H \approx 400$  Oe and an effective  $g$  value of about 2.07. Upon cooling this line is monotonically broadened and shifts to the lower magnetic fields ( $\Delta H \approx 1100$  Oe and  $g \approx 2.9$  at 80 K). This is the typical high-

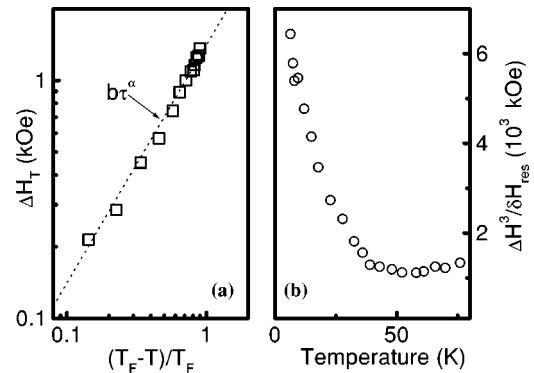


FIG. 4. (a) Double-logarithmic plot of excess linewidth vs reduced temperature  $\tau = 1 - T/T_F$ ,  $T_F = 40$  K. The dashed line is a result of the rms fit:  $b = (3.15 \pm 0.01)$  kOe;  $\alpha = 1.03 \pm 0.03$ . (b) The violation of the Nagata-Ishihara relation below  $T_F$ .  $\delta H_{\text{res}} = H_0 - H_{\text{res}}$ ,  $H_0 = 3290$  Oe.

temperature EPR behavior found in various magnetic NP systems.<sup>21,24,25</sup> The low-temperature EPR spectra are shown in Fig. 2. For the sake of convenience, the field positions of left and right spectrum peaks  $H_L$  and  $H_R$  are introduced (Fig. 2). We also define the effective resonance field as  $H_{\text{res}} = (H_L + H_R)/2$ . The thermal variation of  $H_{\text{res}}$  is shown in Fig. 3(a). To a first approximation,  $H_{\text{res}}(T)$  may be considered as two linear functions with a crossover at  $\sim T_F$ . The decrease of  $H_{\text{res}}(T)$  starts being more pronounced below  $T_F$ . The linewidth begins growing noticeably below approximately 70 K [Fig. 3(b)]. It is adopted for systems with low-temperature phase transitions to present the EPR linewidth as a sum of a temperature-dependent contribution  $\Delta H_T$  (the excess width<sup>10,29</sup>) and a constant high-temperature constituent  $\Delta H(\infty)$ .<sup>15</sup> Taking into account that  $\Delta H$  changes insignificantly in the temperature range from 70 to 110 K, it is allowable to put  $\Delta H(\infty) = 1100$  Oe. Below about 40 K the excess width shows linear variation  $\Delta H_T \propto (1 - T/T_F)$  [Fig. 4(a)] which is not typical of bulk magnetics near a transition point.<sup>10,11</sup> It is important that the ratio  $(\Delta H)^3/\delta H_{\text{res}}$  increases significantly below  $T_F$  [Fig. 4(b)] and, hence, the Nagata-Ishihara relation does not work.

Meiklejohn and Bean<sup>30</sup> showed that the uniaxial exchange anisotropy can exist in field-cooled NP with a single-domain ferromagnetic core and an antiferromagnetic (or spin-glass<sup>6</sup>) oxide shell. The exchange anisotropy can be characterized by

the effective field  $H_E$ , which depends on the temperature as  $H_E(T) = H_E(0)(1 - T/T_g)$ ,<sup>6</sup> according to the prediction of the random-field model for cubic anisotropy.<sup>31</sup> Therefore, the increasing of  $\Delta H(T)$  below  $T_F$  could be due to a spreading of resonance magnetic fields, which, in case of the random distribution of NP easy axes, is proportional to  $H_E$ .<sup>31</sup> Our results [Fig. 3(b)] show that  $\Delta H_T(0) = 1500$  Oe, which is in good agreement with the value of  $H_E(0)$  found by Martinez *et al.* from magnetization data.<sup>6</sup>

In summary, the thermal behavior of the EPR linewidth, the effective resonance field, as well as the FC magnetization curve demonstrate anomalies near 40 K, which can be related to the SG freezing in the NP surface layer. We found a linear increasing of the EPR linewidth excess below  $T_F$ , in good agreement with the thermal behavior of the exchange anisotropy field predicted by the random-field model. The violation of the Nagata-Ishihara relation suggests essentially different mechanisms of EPR line broadening in the superparamagnetic regime and below spin-glass freezing. Our data indicate that in iron-oxide NP the predominant cause of the EPR linewidth changing below the spin-freezing temperature is the influence of the exchange anisotropic field on the resonance conditions.

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- <sup>1</sup>D. E. Speliotis, J. Magn. Magn. Mater. **193**, 29 (1999).  
<sup>2</sup>J. L. Dormann, E. Tronc, and D. Fiorani, Adv. Chem. Phys. **98**, 283 (1997), and references therein.  
<sup>3</sup>A. E. Berkowitz, W. J. Shuele, and P. J. Flanders, J. Appl. Phys. **39**, 1261 (1968).  
<sup>4</sup>J. M. D. Coey, Phys. Rev. Lett. **27**, 1140 (1971).  
<sup>5</sup>F. T. Parker, M. W. Foster, D. T. Margulies, and A. E. Berkowitz, Phys. Rev. B **47**, 7885 (1993).  
<sup>6</sup>B. Martinez, X. Obradors, Ll. Balcells, A. Rouanet, and C. Monty, Phys. Rev. Lett. **80**, 181 (1998).  
<sup>7</sup>L. Del Bianco, A. Hernandez, M. Multigner, C. Prados, J. C. Sánchez-López, A. Fernández, C. F. Conde, and A. Conde, J. Appl. Phys. **84**, 2189 (1998).  
<sup>8</sup>R. H. Kodama, A. E. Berkowitz, E. J. McNiff, and S. Foner, Phys. Rev. Lett. **77**, 394 (1996).  
<sup>9</sup>F. J. Owen, Phase Transit. **5**, 81 (1985), and references therein.  
<sup>10</sup>M. S. Seehra and D. L. Huber, in *Magnetism and Magnetic Materials—1974*, edited by C. D. Graham, Jr., G. H. Lander, and J. J. Rhyne, AIP Conf. Proc. No. 24 (AIP, New York, 1975), and references therein.  
<sup>11</sup>D. Leslie-Pelesky and J. A. Cowen, Phys. Rev. B **48**, 7158 (1993); F. Mehran *et al.*, *ibid.* **35**, 5286 (1987); P. Monod *et al.*, J. Magn. Magn. Mater. **59**, 132 (1986); H. A. Sayad and S. M. Bhagat, Phys. Rev. B **31**, 591 (1985); W.-yu Wu, G. Mozurkevich, and R. Orbach, *ibid.* **31**, 4557 (1985); S. Oseroff, M. Mesa, M. Tovar, and R. Arce, *ibid.* **27**, 566 (1983); E. M. Gullikson, D. R. Fredkin, and S. Shultz, Phys. Rev. Lett. **50**, 537 (1983); F. R. Hoekstra, K. Baberschke, M. Zomack, and J. A. Mydosh, Solid State Commun. **43**, 109 (1982); S. Shultz, E. M. Gullikson, D. R. Fredkin, and M. Tovar, Phys. Rev. Lett. **45**, 1508 (1980).  
<sup>12</sup>Y. Oner, B. Aktas, F. Apaydin, and E. A. Harris, Phys. Rev. B **37**, 5866 (1988); B. Aktas, Y. Oner, and E. A. Harris, *ibid.* **39**, 528 (1988).  
<sup>13</sup>I. A. Campbell, H. Hurdequint, and F. Hippert, Phys. Rev. B **33**, 3540 (1986).  
<sup>14</sup>C. Rettori, D. Rao, S. B. Oseroff, G. Amoretti, Z. Fisk, S.-W. Cheong, D. Vier, S. Schultz, M. Tovar, R. D. Zysler, and J. E. Schirber, Phys. Rev. B **47**, 8156 (1993).  
<sup>15</sup>D. L. Huber, Phys. Rev. B **6**, 3180 (1972).  
<sup>16</sup>J. P. Jamet and A. P. Malozemoff, Phys. Rev. B **18**, 75 (1978); M. B. Salamon, Solid State Commun. **31**, 781 (1979).  
<sup>17</sup>T. Jonsson *et al.*, Phys. Rev. Lett. **75**, 4138 (1995); S. Morup, Europhys. Lett. **28**, 671 (1994); D. Fiorani, in *Magnetic Properties of Fine Particles*, Proceedings of the International Workshop, Rome, Italy, 1991, edited by J. L. Dormann and D. Fiorani (Elsevier Science Publishers, British Vancouver, 1992), p. 135.  
<sup>18</sup>W. Luo, S. R. Nagel, T. F. Rosenbaum, and R. E. Rosensweig, Phys. Rev. Lett. **67**, 2721 (1991).  
<sup>19</sup>L. Néel, Ann. Geophys. (C.N.R.S.) **5**, 99 (1949).  
<sup>20</sup>S. Mørup, F. Bødker, P. V. Hendriksen, and S. Linderorth, Phys. Rev. B **52**, 287 (1995).  
<sup>21</sup>K. Nagata and A. Ishihara, J. Magn. Magn. Mater. **104–107**, 1571 (1992).  
<sup>22</sup>R. Zysler, D. Fiorani, J. L. Dormann, and A. M. Testa, J. Magn. Magn. Mater. **133**, 71 (1994).  
<sup>23</sup>R. Massart, D. Zins, F. Gendron, M. Rivoir, R. V. Mehta, R. V.

- Upadhyay, P. S. Goyal, and V. K. Aswal, *J. Magn. Magn. Mater.* **201**, 73 (1999).
- <sup>24</sup>M. M. Ibrahim, G. Edwards, M. S. Seehra, B. Ganguly, and G. P. Huffman, *J. Appl. Phys.* **75**, 5873 (1994).
- <sup>25</sup>F. Gazeau, V. Shilov, J. C. Bacri, E. Dubois, F. Gendron, R. Perzynski, Yu. L. Raikher, and V. I. Stepanov, *J. Magn. Magn. Mater.* **202**, 535 (1999), and references therein; F. Gazeau, J. C. Bacri, F. Gendron, R. Perzynski, Yu. L. Raikher, V. I. Stepanov, and E. Dubois, *ibid.* **186**, 175 (1998).
- <sup>26</sup>G. A. Petrakovskii, V. P. Piskorskii, V. M. Sosnin, and I. D. Kosobudsky, *Sov. Phys. Solid State* **25**, 1876 (1983).
- <sup>27</sup>Yu. A. Koksharov, S. P. Gubin, I. D. Kosobudsky, M. Beltran, Y. Khodorkovsky, and A. M. Tishin, *J. Appl. Phys.* **88**, 1587 (2000).
- <sup>28</sup>L. Zhang, G. C. Papaefthymiou, and J. Y. Ying, *J. Appl. Phys.* **81**, 6892 (1997).
- <sup>29</sup>G. Mozurkevich, J. H. Elliott, M. Hardiman, and R. Orbach, *Phys. Rev. B* **29**, 278 (1984).
- <sup>30</sup>W. H. Meiklejohn and C. P. Bean, *Phys. Rev.* **102**, 1413 (1956).
- <sup>31</sup>A. P. Malozemoff, *Phys. Rev. B* **35**, 3679 (1987); *J. Appl. Phys.* **63**, 3874 (1988).