Temperature oscillations of magnetization observed in nanofluid ferromagnetic graphite

2009 J. Phys.: Condens. Matter 21 495303

(http://iopscience.iop.org/0953-8984/21/49/495303)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **21** (2009) 495303 (4pp) doi:10.1088/0953-8984/21/49/495303

Temperature oscillations of magnetization observed in nanofluid ferromagnetic graphite

S Sergeenkov[1,3], **N S Souza**[1], **C Speglich**[1], **V A G Rivera**[1], **C A Cardoso**[1], **H Pardo**[2], **A W Mombrú**[2] **and F M Araújo-Moreira**[1,4]

[1] Materials and Devices Group, Department of Physics and Physical Engineering, Universidade Federal de São Carlos, São Carlos, SP 13565-905, Brazil
[2] Crystallography, Solid State and Materials Laboratory (Cryssmat-Lab), DEQUIFIM, Facultad de Química, Universidad de la República, PO Box 1157, CP 11800, Montevideo, Uruguay

E-mail: sergei@df.ufscar.br and faraujo@df.ufscar.br

Received 22 September 2009
Published 12 November 2009
Online at stacks.iop.org/JPhysCM/21/495303

Abstract

We report on unusual magnetic properties observed for nanofluid room temperature ferromagnetic graphite (with an average particle size of $l \simeq 10$ nm). More precisely, the measured magnetization exhibits a low temperature anomaly (attributed to the manifestation of finite size effects below the quantum temperature $T_l \propto \hbar^2/l^2$) as well as pronounced temperature oscillations above $T = 50$ K (attributed to manifestation of the hard-sphere type of pair correlations between ferromagnetic particles in the nanofluid).

(Some figures in this article are in colour only in the electronic version)

Recently, quite substantial progress has been made in developing suspended colloids of nanosized magnetic particles, including carbon, graphite and graphene based nanofluids and biocompatible ferrofluids (see, e.g., [1–9] and further references therein). In particular, Parkansky *et al* [6] successfully separated magnetic carbon particles (including chains of nanospheres with diameters from 30 to 50 nm, and nanorods with lengths from 50 to 250 nm and diameters from 20 to 30 nm) in the solutions obtained, by means of the bio-ferrography technique. At the same time, Widenkvist *et al* [9] suggested a new method for producing suspensions of graphene sheets (graphite flakes) by combining solution based bromine intercalation and mild sonochemical exfoliation.

In this paper, we report on the magnetic properties of nanofluid magnetic graphite (NFMG) obtained from the previously synthesized bulk organic magnetic graphite (MG) by stabilizing the aqueous ferrofluid suspension with the addition of active cationic surfactant. Two interesting phenomena have been observed in the temperature behavior of the magnetization: a low temperature anomaly (attributed to the manifestation of quantum size effects due to an average particle size of the order of $l \simeq 10$ nm), and pronounced temperature oscillations above $T = 50$ K (attributed to the manifestation of the hard-sphere type of pair correlations between ferromagnetic particles in the nanofluid).

Recall [10–13] that the chemically modified magnetic graphite (MG) was produced by a vapor phase redox controlled reaction in a closed nitrogen atmosphere with the addition of copper oxide using synthetic graphite powder. The modified graphite obtained in such a way has a strong magnetic response even at room temperature (which manifests itself through a visible attraction by a commercial magnet). After obtaining the MG, we have prepared the nanofluid suspension (NFMG) by dissolving graphite in acetone, adding a cetyltrimethylammonium bromide (CTAB) cationic surfactant, and bringing it to an ultrasonic edge. The structural characterization of NFMG was performed by transmission electron microscopy (TEM) using a Philips CM-120 microscope. The analysis of TEM images (shown in figure 1) reveals clusters (ranging from 100 to 300 nm) with an average size of the ferromagnetic particle in the nanofluid of the order of 10 nm (more details regarding the structure and chemical route for synthesis of the nanofluid magnetic graphite discussed here will be presented elsewhere [14]).

---

[3] Author to whom any correspondence should be addressed.

[4] Research leader.

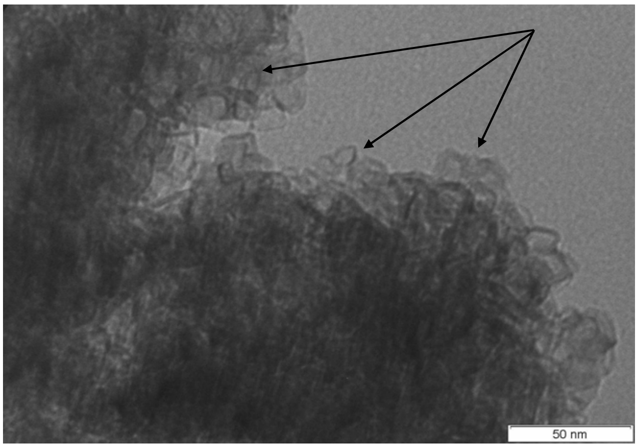

Figure 1. TEM image of the NFMG sample.

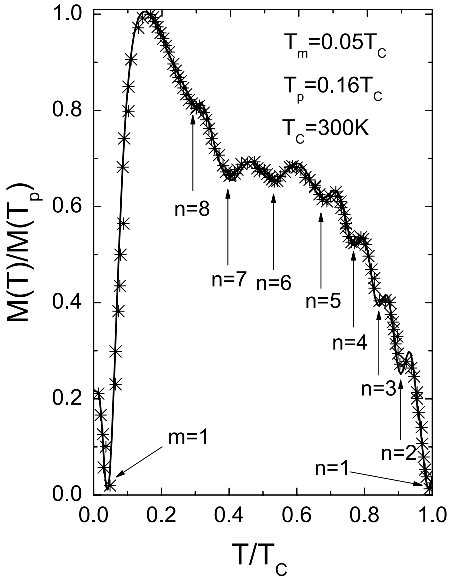

Figure 2. The temperature dependence of the normalized magnetization of NFMG (after subtracting the paramagnetic contribution). The solid line is the best fit according to equations (1)–(3).

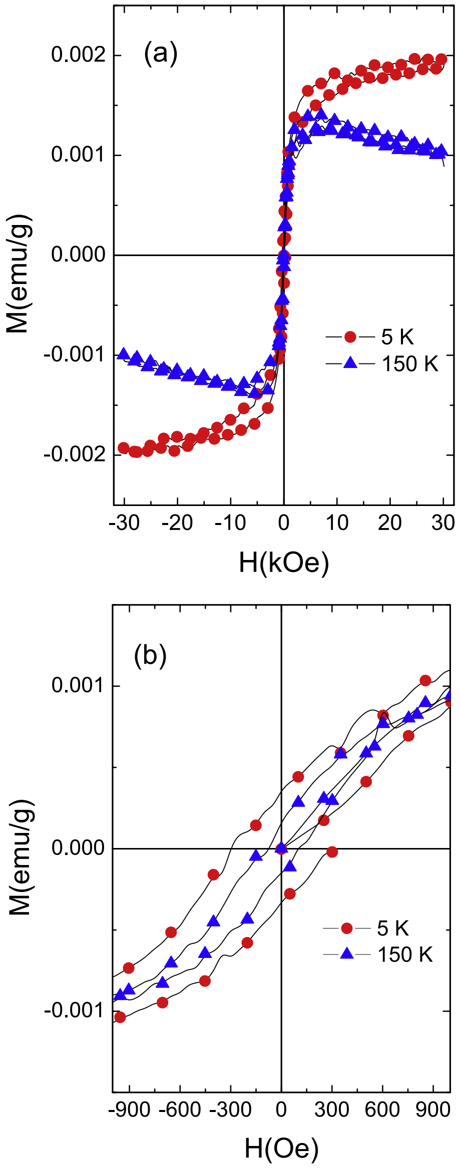

Figure 3. The hysteresis curves (taken at two temperatures, 5 and 150 K) for high (a) and low (b) applied magnetic field regions, showing a ferromagnetic like behavior of the NFMG sample.

To test the magnetic properties of the NFMG samples, we performed the standard zero-field cooled (ZFC) and field cooled (FC) measurements using an MPMS-5T SQUID magnetometer from Quantum Design. Figure 2 presents the temperature dependence of the normalized magnetization $M(T)/M(T_{\mathrm{p}})$ (taken under the applied magnetic field of 1 kOe) after subtraction of paramagnetic contributions ($T_{\mathrm{p}} = 0.16T_{\mathrm{C}} = 48$ K is the temperature where $M(T)$ has a maximum with the absolute value of $M(T_{\mathrm{p}}) = 0.1$ emu g^{-1}). Notice that there are two distinctive regions, below and above the peak temperature T_{p}. Namely, below T_{p} there is a well-defined low temperature minimum (around $T_m = 0.05T_{\mathrm{C}} = 15$ K), while for $T > T_{\mathrm{p}}$ we have pronounced temperature oscillations. To verify that the observed peak originates from true quantum effects in a ferromagnetic sample (rather than from superparamagnetic behavior due to the thermal energy domination over the anisotropy energy), we also measured the hysteretic M–H curves for two characteristic temperatures, $T = 5$ K $< T_m$ (in the region of fully fledged quantum effects) and $T = 150$ K $= 0.5T_{\mathrm{C}}$ (in the middle of the oscillations pattern). According to figure 3, the low temperature hysteresis is quite strong (with coercive magnetic field $H_{\mathrm{C}} = 338$ Oe) and it does not disappear with increasing temperature ($H_{\mathrm{C}} = 200$ Oe for $T = 150$ K). Thus, we can safely assume that the temperature features observed for our sample do originate from a true ferromagnetic behavior.

Turning to the analysis of the results obtained, let us begin with the low temperature region ($T < T_{\mathrm{p}}$) and discuss the origin of the observed minimum of magnetization near $T_m = 0.05T_{\mathrm{C}}$. Recall that the finite temperature quantum effects manifest themselves for the size of the particle $l < \Lambda(T)$ (where $\Lambda(T) = \sqrt{2\pi\hbar^2/m^*k_{\mathrm{B}}T}$ is the thermal de Broglie

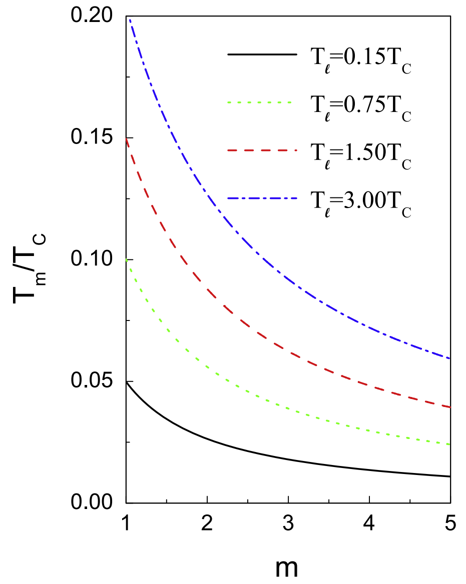

Figure 4. The predicted dependence of the reduced temperature T_m/T_C on the oscillations minima m for different values of the particle size l related quantum temperature T_l.

wavelength) or, alternatively, for temperatures $T < T_l$ (where $T_l = 2\pi\hbar^2/m^* k_B l^2$ is the quantum temperature). Using $l \simeq 10$ nm for an average size of the single particle in our samples (and assuming the free electron mass for m^*), we get $T_l = 0.15T_C = 45$ K for the onset temperature below which the manifestation of quantum size effects is expected (notice that T_l is very close to the peak temperature $T_p = 0.16T_C$). To fit the low temperature experimental data, we assume the following normalized (to the peak temperature T_p) periodic dependence of the finite size magnetization:

$$\frac{M_l(T)}{M_l(T_p)} = \left[\frac{l}{\Lambda(T)}\right] \sin\left\{\left[\frac{M_\infty(T)}{M_\infty(T_p)}\right]\left[\frac{\Lambda(T)}{l}\right]\right\} \tag{1}$$

where $M_\infty(T)$ is the bulk magnetization of a single magnetic particle.

It can be easily verified that equation (1) reduces to $M_\infty(T)$ when the quantum effects become negligible. More precisely, $M_\infty(T)/M_\infty(T_p) = \lim_{l \gg \Lambda(T)}[M_l(T)/M_l(T_p)]$.

We were able to successfully fit the low temperature data using the following explicit expression for the single-particle bulk magnetization:

$$M_\infty(T) = M_s \tanh\sqrt{\left(\frac{T_C}{T}\right)^2 - 1} \tag{2}$$

which presents an analytical (approximate) solution of the Curie–Weiss mean-field equation for spontaneous magnetization valid for all temperatures [15, 16]. The solid line in figure 2 presents the best fits for the low temperature region ($T \leqslant T_p$) according to equations (1) and (2) with $M_s = 0.95M(T_p)$, $M(T_p) = 0.1$ emu g^{-1}, $T_C = 300$ K and $l = 10$ nm.

Notice also that, for a given temperature, the above periodic function $M_l(T)$ has minima m at $T = T_m$ where T_m is the solution of the implicit equation $M_\infty(T_m)\Lambda(T_m) = \pi m M_\infty(T_p)l$ with $m = 1, 2, \ldots,$ being the number of oscillation minima. Using the Curie–Weiss expression for bulk magnetization $M_\infty(T)$ and the previously defined thermal de Broglie wavelength $\Lambda(T)$, in figure 4 we depict the solution of the above equation as the dependence of the reduced temperature T_m/T_C on m for different values of the particle size l (in terms of the quantum temperature $T_l \propto \hbar^2/l^2$). According to this picture, the smaller the particle size (and hence, the larger the quantization temperature T_l), the greater the number of finite size related oscillations (minima) that should be observed in the temperature dependence of the magnetization $M_l(T)$. For example, in our particular case (with $l = 10$ nm and $T_l = 0.15T_C$) only the first minimum ($m = 1$) is expected to be visible at the non-zero temperature $T_m = 0.05T_C = 15$ K, in agreement with the observations (see figure 2).

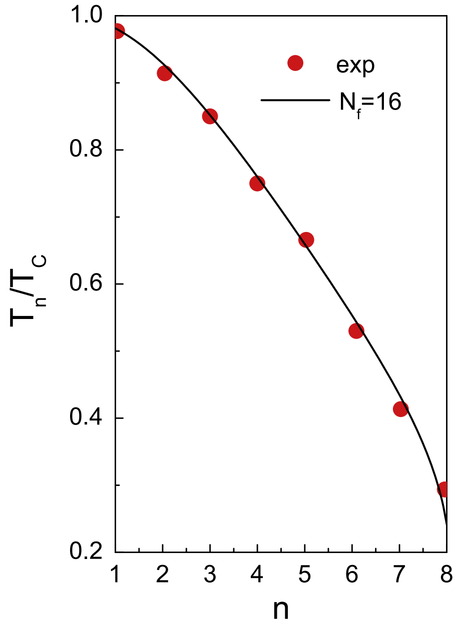

Figure 5. The predicted dependence (solid line) of the reduced temperature T_n/T_C on the number of oscillations minima n for $N_f = 16$ (according to equation (4)) along with the extracted (from figure 2) experimental points.

Turning to the discussion of the high temperature region (above T_p), it is quite natural to assume that the observed oscillations can be attributed to the local variation of the magnetization $\tilde{M}_f(r) = M_0 g(r)$ defined in terms of the periodic radial distribution function $r^2 g(r) = \sin kr$ in the hard-sphere fluid model [17, 18] with $k(T) = \pi M_\infty(T)/M_\infty(T_p)l$ where $M_\infty(T)$ is the above-introduced bulk magnetization of the single particle. Within this scenario, the temperature dependence of the fluid contribution to the magnetization reads

$$M_f(T) = \frac{1}{L}\int_0^L r^2\,dr\,\tilde{M}_f(r) = M_0\left[\frac{1 - \cos k(T)L}{k(T)L}\right] \tag{3}$$

where $L = N_f l$ and $M_0 = [\pi N_f/(1 - \cos\pi N_f)]M_f(T_p)$.

The best fits of the high temperature data, using equations (2) and (3), produced $N_f = L/l = 16$ for the number of particles contributing to the observed oscillating behavior of nanofluid magnetization (which correlates reasonably well with an average cluster size of $L = 160$ nm, revealed by the TEM images of the nanofluid; see figure 1).

Notice also that, according to equation (3), the number of oscillation minima n of the magnetization (observed at $T = T_n$) is given by the solution of the implicit equation $k(T_n)L = 2\pi n$ where $n = 1, 2, 3, \ldots$. Using the Curie–Weiss expression for bulk magnetization $M_\infty(T)$, the above equation results in the following explicit dependence of T_n on n and N_f:

$$T_n = \frac{T_C}{\sqrt{1 + \{\tanh^{-1}(2n/N_f)\}^2}}. \qquad (4)$$

Figure 5 demonstrates very good agreement between the predicted n dependence of T_n/T_C (given by equation (4) with $N_f = 16$) and the experimental points extracted from figure 2.

In summary, we reported the magnetic properties of recently synthesized nanofluid room temperature ferromagnetic graphite (with the single-particle size of $l \simeq 10$ nm). We observed, in addition to a low temperature magnetic anomaly (attributed to the manifestation of quantum size effects below 50 K), strong temperature oscillations of the spontaneous magnetization (attributed to the manifestation of the hard-sphere type of pair correlations between ferromagnetic particles in the nanofluid above 50 K).

Acknowledgments

This work was financially supported by the Brazilian agencies CNPq, CAPES and FAPESP.

References

[1] Miller J S and Drillon M (ed) 2002 *Magnetism: Molecules to Materials III* (Weinheim: Wiley–VCH)

[2] Ying Y, Grulke E, Zhang G and Gefei W 2005 *J. Nanosci. Nanotechnol.* **5** 571

[3] Zhu H, Zhang C, Tang Y, Wang J, Ren B and Yin Y 2007 *Carbon* **45** 226

[4] Phillip J, Shima P D and Raj B 2008 *Appl. Phys. Lett.* **92** 043108

[5] Tombacz E, Bica D, Hajdu A, Illes E, Majzik A and Vekas L 2008 *J. Phys.: Condens. Matter* **20** 204103

[6] Parkansky N, Alterkop B, Boxman R L, Leitus G, Berkh O, Barkay Z, Rosenberg Yu and Eliaz N 2008 *Carbon* **46** 215

[7] Jagodie M, Gyergyek S, Jaglicic Z, Makovec D and Trontelj Z 2008 *J. Appl. Phys.* **104** 074319

[8] Wu D, Zhu H, Wang L and Liu L 2009 *Curr. Nanosci.* **5** 103

[9] Widenkvist E, Boukhvalov D W, Rubino S, Akhtar S, Lu J, Quinlan R A, Katsnelson M I, Leifer K, Grennberg H and Jansson U 2009 *J. Phys. D: Appl. Phys.* **42** 112003

[10] Araújo-Moreira F M, Pardo H and Mombrú A W 2005 *Patent Specification* WO/2005/123580 World Intellectual Property Organization, Singapore

[11] Mombrú A W, Pardo H, Faccio R, de Lima O F, Lanfredi A J C, Cardoso C A, Leite E R, Zanelatto G and Araújo-Moreira F M 2005 *Phys. Rev.* B **71** R100404

[12] Pardo H, Faccio R, Mombrú A W, Araújo-Moreira F M and de Lima O F 2006 *Carbon* **44** 565

[13] Faccio R, Pardo H, Denis P A, Yoshikawa Oeiras R, Araújo-Moreira F M, Veríssimo-Alves M and Mombrú A W 2008 *Phys. Rev.* B **77** 035416

[14] Souza N S, Sergeenkov S, Speglich C, Rivera V A G, Cardoso C A, Pardo H, Mombrú A W, Rodrigues A D, de Lima O F and Araújo-Moreira F M 2009 *Appl. Phys. Lett.* at press

[15] Sergeenkov S, Bougrine H, Ausloos M and Cloots R 1999 *JETP Lett.* **69** 858

[16] Sergeenkov S, Mucha J, Pekala M, Drozd V and Ausloos M 2007 *J. Appl. Phys.* **102** 083916

[17] Hansen J P and McDonald I R 2006 *The Theory of Simple Liquids* (London: Academic)

[18] Scheffold F and Mason T G 2009 *J. Phys.: Condens. Matter* **21** 332102