Temperature oscillations of magnetization observed in nanofluid ferromagnetic graphite

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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 bioferrography 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]).
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 $M(T)/M(T_p)$ (taken under the applied magnetic field of 1 kOe) after subtraction of paramagnetic contributions ($T_p = 0.16T_C = 48$ K is the temperature where $M(T)$ has a maximum with the absolute value of $M(T_p) = 0.1$ 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 $T_m = 0.05T_C = 15$ K), while for $T > T_p$ 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 $= 0.5T_C$ (in the middle of the oscillations pattern). According to figure 3, the low temperature hysteresis is quite strong (with coercive magnetic field $H_C = 338$ Oe) and it does not disappear with increasing temperature ($H_C = 200$ 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 ($T < T_p$) and discuss the origin of the observed minimum of magnetization near $T_m = 0.05T_C$. Recall that the finite temperature quantum effects manifest themselves for the size of the particle $l < \Lambda(T)$ (where $\Lambda(T) = \sqrt{2\pi\hbar^2/m^*k_B T}$ is the thermal de Broglie
To fit the low temperature experimental data, we assume the periodic function $M_l$ dependence of the finite size magnetization: that the manifestation of quantum size effects is expected (notice bulk magnetization: using the following explicit expression for the single-particle samples (and assuming the free electron mass for $m$ particle size $l$ 10 nm for an average size of the single particle in our samples (and assuming the free electron mass for $m$)).

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:

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

(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, $M_\infty(T)/M_\infty(T_p) \approx \lim_{T \to 0}(M_l(T)/M_l(T_p))$.

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

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

(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 ($T \leq T_p$) according to equations (1) and (2) with $M_s = 0.95 M(T_p)$, $M(T_p) \approx 0.1$ 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 $l$ for different values of the particle size $l$ (in terms of the quantum temperature $T_l \approx \hbar^2/l^2$). 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 $T_l = 0.15 T_c$) only the first minimum ($m = 1$) is expected to be visible at the non-zero temperature $T_m = 0.05 T_c = 15$ K, in agreement with the observations (see figure 2).

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 $M_l(r) = M_0 g(r)$ 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

$$M_1(T) = \frac{1}{L} \int_0^L r^2 dr \tilde{M}_1(r) = M_0 \left[ \frac{1 - \cos k(T)L}{k(T)L} \right]$$

(3)

where $L = N_l l$ and $M_0 = [\pi N_l/(1 - \cos \pi N_l)] M_1(T_p)$.

The best fits of the high temperature data, using equations (2) and (3), produced $N_l = L/l = 16$ 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 $N_f$:

$$T_n = \frac{T_C}{\sqrt{1 + \left[\tanh^{-1}(2n/N_f)\right]^2}}.$$  

(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).

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