The effect of a weak ferromagnetic matrix on a system of nanomagnetic particles

S. Chakraverty1, A. Frydman2, V.G. Pol3, S. V. Pol3 and A. Gedanken3

1. Nanoscience Unit, S. N. Bose National Center for Basic Sciences, Block-JD, Sector-III, Salt Lake, Kolkata - 700098, India.
2. Dept.of Physics, Bar Ilan University, Ramat Gan 52900, Israel
3. Department of Chemistry and Kanbar Laboratory for Nanomaterials at the Bar-Ilan University Center for Advanced Materials and Nanotechnology, Bar-Ilan University, Ramat-Gan, 52900, Israel.
(Dated: March 23, 2022)

The study of system of magnetic nano-particle has received increasing attention recently both because of the novel physical concepts involved and also because of their vast potential for application. The influence of background material (the substrate coating) on magnetic properties of such systems is a relatively open topic and often a full understanding is missing. In the present work we discuss our experiments and interpretation for two systems: Ni nanoparticles coated with graphitic carbon and Ni nanoparticles coated with Au. While the latter system exhibits behavior typical of superparamagnetic particle systems the former shows several puzzling results such as extremely high blocking temperature \(T_B\), very fast relaxation time well below \(T_B\), temperature independent field-cooled magnetization and very small coercivity and remanent magnetization. We interpret these findings as being a result of weak ferromagnetism, characteristic of the graphitic carbon. This induces strong magnetic interactions between the Ni particles in the presence of small magnetic fields. Such systems give rise to a dramatic difference in blocking temperature between measurements performed at zero field and those performed at very small magnetic fields.

PACS numbers: 75.75.+a, 75.50.Lk, 75.50.Tt, 75.20.-g

Systems of magnetic nanoparticles have been gaining increasing attention over the past few years both because they introduce novel physical concepts and because of their vast potential for applications in the fields of nano-electronics, storage media and medicine. For practical devices, the nanoparticles are usually imbedded in a matrix or placed on a solid substrate. The influence of different background materials on the magnetic properties of the nanoparticle system is a relatively open topic. Though it is clear that different materials can have various effects on the magnetic coupling between the particles (depending on the magnetic nature of the matrix) a full understanding of these issues is lacking.

In this letter we study the effect of a special matrix material, i.e. a weak ferromagnet. We compare the magnetic behavior of Ni nanoparticles embedded in gold (a diamagnetic material) to that of Ni particles embedded in graphitic carbon which has been shown to exhibit weak ferromagnetic properties. The latter exhibit a set of surprising and contradictory findings. These are attributed to the coupling between the nanomagnetic particles via the weak ferromagnetic material in the presence of a small magnetic field. We show that this is an unique case in which the magnetization and blocking temperature of the system strongly depend on whether a small external field is applied.

The synthesis of Ni-C (graphitic) core-shell nanostructures was carried out through thermal dissociation of nickel acetylacetonate, Ni(C5H7O2)2, in a closed vessel cell assembled from stainless steel Swagelok parts. The full process is described elsewhere. Due to the lack of a commercially available gold precursor to carry out a similar synthesis, we produced Ni-Au core-shell using a two step process. In the first, the nuclei of Ni nanoparticles were formed in a solution of nickel (II) acetate tetrahydrate [99.998, Aldrich Chemical Co.] in EG (Ethylene glycol). A 100mL glass flask was placed in a microwave oven (spectra 900W) that was connected to the water condenser. A 50 mL of a solution of 0.2M Ni(AC)2 in EG was purged by argon for 10 min, after which the microwave oven was turned on at the power level of 60 watt with a continued flow of the argon gas. A black suspension appeared after 15 minutes of microwave irradiation. In the second stage, 0.15mL chloroauric acid (HAuCl4) was added by a microliter size syringe (Hamilton Co.) in the black suspension of Nickel nanoparticles. Once again microwave irradiation was turned on and maintained for 20 minutes at a power of 60 watt. The resulting pale-black solid product was washed thoroughly with ethanol thrice and centrifuged at 8000 rpm. The as-prepared product was dried in a vacuum chamber for 12h.

The morphology and crystal structure for both samples were studied by TEM and HR-TEM. Figure 1a depicts the TEM analysis of a Ni nanoparticle (with sizes ranging from 30-150nm) embedded in graphitic carbon. The inserted top right image confirms the formation of ordered graphitic carbon shell of 15nm. The interlayer spacing between these graphitic planes is 3.41 Å, which is very close to that of the graphitic layers. The inserted bottom image provides further verification for the identification of the core as Ni. It illustrates the perfect arrangement of the atomic layers and the lack of defects. The measured distance between these (111) lattice planes is 0.200 nm.
FIG. 1: Transmission electron micrographs of (a) Ni nanoparticles embedded in graphitic carbon, and (b) Ni particles coated by gold nanocrystals. The left panels are conventional low magnification TEM images and the right panels are high resolution TEM images taken at different sections of the samples.

which is very close to the distance between the planes reported in the literature (0.203 nm) for the face-centered cubic lattice of the Ni ((PDF No. 03-065-2865).

The TEM analysis of Ni particles (sizes of 100-200nm) coated by gold nanocrystals with diameters of 7nm is shown in Figure 1b. The inserted (HR-TEM) top image confirms the interlayer spacing for Au nanocrystals and the bottom image provides further evidence for the Ni core.

Fig. 2 depicts the field cooled - zero field cooled (FC -ZFC) magnetization measurements for the Ni-C and Ni-Au samples as measured in a SQUID magnetometer. In ZFC mode the system is cooled to the lowest temperature in the absence of magnetic field, H, and M(T) is measured while heating the sample in the presence of H=100Oe, while in FC, M(T) is measured during cooling the sample in the presence H=100Oe. For superparamagnetic systems the ZFC magnetization curves are expected to show a peak corresponding to the average blocking temperature while the FC curves always increase as the temperature is decreased due to the alignment of the spins in the direction of the field. Our measurements show that for the Ni-Au system $T_B$ is found to be of the order of 150K (which is a reasonable value for Ni particles with diameters of 150 nm). Since the Ni particles in the carbon coated systems are smaller, the average blocking temperature is expected to be smaller as well (a rough estimation yields $\sim 30K$). Surprisingly, for the Ni-C case the block-

FIG. 2: FC and ZFC M(T) plots for Ni-C (top) and Ni-Au (bottom) nanoparticle systems.

ing temperature is found to be well above 400K (which was the highest available temperature). Moreover, the temperature dependance of the magnetization in these samples is very peculiar. The FC C-Coated Ni particles exhibit magnetization that remains almost constant even down to temperatures of 15K.

Another peculiarity of these systems is demonstrated in fig. 3 which depicts the low-field regime of the room temperature M-H curves of both samples. It is seen that the coercive field, $H_C$ is smaller for the carbon coated sample ($\sim 60Oe$) than that of the gold coated sample ($\sim 170Oe$). This seems to be in striking contradiction to the fact that the blocking temperature extracted from the FC-ZFC measurements is much larger for the Ni-C sample.

An even more surprising finding is related to relaxation-response measurements below the blocking temperature. In this measurement, the sample is cooled to a temperature of 40K (well below the measured $T_B$ for both types of samples) in the absence of magnetic field. At this temperature a 50 Oe field is abruptly switched on and the magnetization is measured as a function of time. After a few hours the field is switched back off and the M(t) is measured again. Figure 4 compares the relaxation-response measurements for the Ni-Au and Ni-C samples. It is seen that the Au coated Ni sample shows slow response to changes in the external magnetic field. When the field is switched on the magnetization increases slowly and when it is switched back off there is a long time related to the magnetization decay. This is expected because the magnetic orientation of a particle is blocked at temperatures smaller than $T_B$. The Ni-C
sample, on the other hand, responds almost immediately (within the measuring time scale of SQUID) to the magnetic field changes. Upon switching the field off the magnetization drops immediately to zero and upon switching the magnetic field back on the magnetization restores its maximal value instantaneously. This behavior is very unexpected for a system of particles with blocking temperatures above 400K.

In an attempt to understand the results observed in the Ni-C samples we considered the possibility that the large obtained blocking temperatures are due to dipole-dipole interactions between the magnetic moments of the Ni-nanoparticles (super-spin-glass behavior [11]) mediated by the ferromagnetic background. To check the relevance of this mechanism in our system we performed arrested cooling ZFC measurements. In this experiment the system is cooled in the absence of magnetic field from room temperature to 30K (well below the $T_B$ of the system) and the temperature is arrested for four hours. Then the system is cooled again in a constant rate to 15K in absence of external magnetic field. From 15K the sample is heated up to room temperature in the presence of 500e DC external magnetic field, while monitoring the magnetization constantly. An established sign of super-spin-glass interactions [11] is the occurrence of a dip in the M-T heating curve at the temperature that was arrested during the cooling process (30K in our case). Our Ni-C samples showed no sign for such a dip, thus ruling out the existence of pronounced spin glass interactions.

Nevertheless, the fact that the puzzling (and apparently contradicting) results were not observed in the Ni-Au systems leads us to suggest that the unique phenomena are due to interparticle (Ni-Ni) interaction mediated via the weak ferromagnetic carbon matrix. In the following paragraphs we suggest a model, based on such interactions, that may account for our experimental findings.

Let us consider an assembly of Ni nanoparticles coated by graphitic carbon, in which the easy axis of the Ni-particles are randomly oriented. The carbon is characterized by very weak ferromagnetism. Let $E_{nn}$ be the magnetic interaction between the atoms of Ni, $E_{nc}$ the interaction between Ni and C and $E_{cc}$ the interaction energy between carbon atoms. The dipolar interaction between Ni-nanoparticles is assumed to be weak due to small Ni particle size and large inter-particle separation. Let us further assume that $E_{nc} >> E_{cc}$. In the absence of magnetic field there is a spin disorder in the carbon shell coating the Ni particle due to the surface spin disorder of the Ni particles [12] and the random orientation of the easy axis. But as soon as an external magnetic field is applied, all the Carbon spins orient themselves in the field direction, producing a huge effective magnetic field on the Ni-nanoparticle, $H'$, thus forcing it to orient along the external field direction.

The apparent contradiction observed for Ni-C samples occurs due to the fact that two different classes of experiments (namely field measurements and zero field measurements) were compared. FC-ZFC belongs to finite applied field measurements while relaxation measurements belong to zero field measurements. Taking this fact into account, our experimental observations can be well explained within the framework of the above model. Let us first discuss the FC-ZFC measurement. Consider a single
domain uniaxial magnetic nanoparticle. The anisotropy energy of such a particle is given by:

\[ E = KV \sin^2 \theta \]  

(1)

where K is the anisotropy energy per unit volume, V is the volume of the nanoparticle and \( \theta \) is the angle between the magnetic moment of the particle and the easy axis for magnetization. In absence of an external magnetic field the probability of finding an up spin is equal to that of a down spin, leading to zero magnetization. If the temperature of the system is decreased in absence of the external magnetic field the situation remains the same and zero magnetization is observed. As soon as an external magnetic field is applied the energy of the system becomes

\[ E = KV \sin^2 \theta - \mu VH^* \cos \theta \]  

(2)

where \( \mu \) is the magnetic moment of the particle per unit volume and \( H^* = H + H^\prime \) is the effective magnetic field seen by the particle due to external magnetic field and the field produced by surrounding Carbon spins. In eq. 2 we have assumed, for simplicity, that the external magnetic field is applied along the direction of easy axis of the nanoparticle. Let \( \delta E_{0m} \) be the energy difference between the minima at \( \theta = 0 \) and that of the maxima \( E_{m1} \), and \( \delta E_{1m} \) be that between the energy at \( \theta = \pi \) and \( E_{m} \). Due to the contribution of large number of Carbon spins, \( H^* \), is extremely large. This leads to \( \delta E_{0m} \gg \delta E_{1m} \), which means that with increasing temperature the down spin will easily orient parallel to the applied magnetic field with the help of thermal energy. The magnetization can decrease with increasing temperature only if the thermal energy becomes comparable to \( \delta E_{0m} \), which is a very high value. Hence, unusually large effective blocking temperature are measured by the ZFC magnetization experiment. If now the system is cooled in the presence of an external magnetic field, the particles are already blocked along the direction of external field and the FC curve becomes independent of temperature.

The magnetization response measurement are also understood using the above considerations. As soon as the magnetic field is switch on the system’s hamiltonian becomes that of eq. 2. Since \( H^* \) produces a large asymmetry in the energy profile. In this case the response time (the time it takes for the spins to flip along the external field) given by:

\[ \tau = \tau_0 \exp \left[ \frac{KV \sin^2(\theta) + \mu VH^* \cos(\theta)}{K_B T} \right] \]  

(3)

is very short compared to that of the Ni-Au samples in which the magnetic field is much smaller.

The magnetization relaxation measurement, on the other hand, is a zero field magnetic measurements. In effect these systems are characterized by two distinct blockings; a zero field, conventional blocking temperature, \( T_B(0) \), and a finite field blocking temperature \( T_B(H) \), which is much larger due to the effect of the carbon atoms. When the magnetic field is switched off, the carbon spins disorient immediately. Since \( T_B(0) \) of the Ni particles is estimated to be a few tens of degrees, at 40K they behave as isolated nano-magnets with a small barrier height. Hence, fast relaxation is expected. This is in vast contradiction to the situation for the FC-ZFC measurements in which a field is applied and the finite field blocking temperature, \( T_B(H) \), determines the magnetization properties. A similar argument is related to the coercive field, \( H_C \) which is the field associated with zero magnetization. Since very small external magnetic fields are sufficient to align the grains’ orientations, thus giving rise to large measured magnetization, the field for which zero magnetization is achieved in the Ni-C samples is expected to be very low.

In conclusion we note the the choice of substrate and spacing material is crucial for the magnetic performance of nano-particle based systems. A graphitic carbon spacer gives rise to very fast response to magnetic field changes while exhibiting relative insensitivity to temperature changes.

We thank R. Ranganathan for useful discussions. This research was supported by the Israel Science foundation (grant number 326/02).

[1] A.N. Goldstein, Hand Book of Nanophase Materials, New York: Marcel Dekker Inc. (1997).
[2] R.H. Kodama, J. Magn. Magn. Mater., 200, 359 (1999).
[3] Magnetic Properties of Fine Particles, edited by J.L. Dornman and D. Fiorani, North-Holland, Amsterdam (1992).
[4] K.M. Unruh and C.L. Chein, Nanomaterials: Synthesis, Properties and Applications edited by A.S. Edelstein and R.C. Cammarata, Bristol: Institute of Physics.
[5] I.S. Jacobs and C.P. Bean in Magnetism III (eds.) G.T. Rado and H. Suhl, (New York: Academic) (1963).
[6] Physical Principles of Magnetism, A.H. Morrish, John Wiley, New York, 1965.
[7] S.H. Sun, et-al, Science 287, 139701 (2000).
[8] T. L. Makarova, B. Sundqvist, R. Hohne, P. Esquinazi, Y. Kopelevich, ; P. Scharff, V. A. Davydov L. S. Kashevarova, and A. V. Rakhmanina, Nature, 413, 716 (2001).
[9] A. A. Ovchinnikov, and I. L. Shamovsky, THEOCHEM-J. Mol. Struct., 83, 133 (1991).
[10] S.V. Pol, V.G. Pol, A. Frydman, G. N. Churilov, and A. Gedanken, Journal of Physical Chemistry, in press.
[11] M. Sasaki, P.E. Jonsson, H. Takayama and P. Nordblad, Phys. Rev. Lett. 93, 139701 (2004).
[12] R.H. Kodama, A.E. Berkowitz, E.J. McNiff, Jr., and S. Foner, Phys. Rev. Lett. 77, 394, (1996).