PHENOMENOLOGIC *VERSUS* MICROSCOPIC DESCRIPTION OF THE NANOPARTICLE MAGNETIZATION

S. COJOCARU [*1, 2], L. A. DOHOTARU [3] and V. A. MOSCALENCO [2, 4]

[1] Horia Hulubei National Institute for Physics and Nuclear Engineering, Magurele 077125, Romania
[2] Institute of Applied Physics, Chisinau 2028, Moldova
[3] Technical University, 2004 Chisinau, Moldova
[4] BLTP, Joint Institute for Nuclear Research, 141980 Dubna, Russia

Received December 14, 2012

Abstract. We critically discuss the existing phenomenological description of experimental and numerical simulation data on temperature dependence of nanoparticle and nanocluster magnetization in the context of the recently proposed microsopic theory. The latter leads to a qualitatively different form of the temperature dependence, is free of major inconsistencies of the former and reveals a clear connection of the observed behavior to the microscopic physical parameters.

Key words: nanomagnets, nanoparticles, magnetization, Bloch theory

1. INTRODUCTION

A current rapid growth in diversity of magnetic nanostructures (nanoparticles, nanoclusters, nanowires, ribbons, pillars, thin films, composites etc.) is driven by technological progress in their fabrication and a widening range of important applications (nonvolatile memory, permanent magnets, sensors, site specific drug delivery, hyperthermia treatment for malignant cells etc.) [1, 2]. At the origin of the large interest to these systems is not just the device miniaturization, but most importantly, a qualitative modification their properties undergo at the nanoscale. For instance, it is well known that bulk macroscopic ferromagnets contain a large number of magnetic domains which basically reduce to modest values the overall magnetization. The reason for this phenomenon is that although creation of domain walls costs an energy roughly scaling with the interface surface, the sample can reduce the energy of the stray demagnetization field (which scale with the volume *V i.e.* faster than the surface area) by breaking up its magnetic structure into a large number of domains. As a consequence, when the size of, *e.g.*, iron ferromagnet is smaller than 100 nm, the demagnetization energy falls below that of the domain wall, so that a single domain structure becomes energetically convenient. This leads to huge local magnetic fields of hundreds or thousands Tesla created by many thousands of collinear atomic spins. The major interactions governing magnetic

behavior of the nanostructures are due exchange coupling J responsible for their high Curie temperature T_c and the magnetocrystalline anisotropy K. Although the latter is several orders of magnitude smaller than J (typically J is 10-90 meV) and K is about 10 μeV (e.g., K(Fe) = 2.4 μeV/atom) it is responsible for the "blocking" and coercivity phenomena in nanoparticles [3]. Because the single domain particle reacts on an external field as a single giant magnetic moment proportional to its V, it can be characterized by a superparamagnetic relaxation time τ required to overcome the potential wall created by the anisotropy energy KV: $\tau = \tau_0 \exp(KV/T)$, where τ_0 is the atomic spin relaxation time, typically 10^{-13} - 10^{-19} sec. The blocking temperature T_B is the one when τ equals the timescale of the experimental observation technique. Above the blocking temperature, $T > T_B = KV / \ln(\tau/\tau_0)$ one measures an averaged effective magnetization μ_{eff} reduced from the full internal magnetization μ by the Langevin function

$$\mu_{eff} = \mu \mathcal{L}(\beta\mu VH) = \mu\left[\coth(\beta\mu VH) - \frac{1}{\beta\mu VH}\right],$$

while below T_B the small oscillations of the magnetic moment at the bottom of the potential well result in a linear temperature dependence $\mu = \mu_{eff}(1 - T/2KV)$ [4].

The above behavior is rather different from what one observes in the macroscopic bulk material, which corresponds to the limit $V \to \infty$. Indeed, in this case $\mu_{eff} = \mu$ the superparamagnetic response of the ferromagnet is then suppressed since T_B is larger than the Curie temperature T_C and the temperature dependence of the internal magnetization $\mu(T)$ below T_C is well accounted for by the famous Bloch law [5,6],

$$\mu_{Bloch}(T) = \mu(0)\ \left(1 - \Gamma \times T^{3/2}\right).$$

Thus, the actual problem investigated in many experimental and theoretical works is how does the internal magnetization behave when the size of the magnet is reduced to the nanometric scale.

2. PHENOMENOLOGIC AND MICROSCOPIC APPROACHES

In order to investigate this issue the authors of the seminal series of papers [7, 8] have carried out extensive numerical simulations and in-depth analysis on a variety of ferromagnetic clusters. They have shown that Bloch law is unable to follow the observed behavior and have proposed a phenomenological formula to modify its form by introducing two parameters $\Gamma \to \gamma$ and $3/2 \to \alpha$. This has indeed allowed to accurately reproduce the obtained numerical results and seemed to provide a natural continuity connection between nano- and macroscopic systems.

This has been further confirmed by a large number of later works and the modified form of the Bloch law has become an ubiquitous tool used for the description of the experimental and numerical data on magnetization of nanoparticles, nanoclusters, nanowires, etc., see *e.g.* the reviews in [9].

However, in analyzing a large number of diverse nanostructures (nanoparticles etc.) it has been noted on many occasions, *e.g.* [10, 11], that the fitted values of the parameters γ and α do not show any regular size dependence. For instance α can be found both above (up to *2*) and below (even less than 1) the Bloch value upon decreasing the sample size to a few nm. For instance, Fig. 1 shows the Bloch exponent as a function of Fe crystallite size [12].

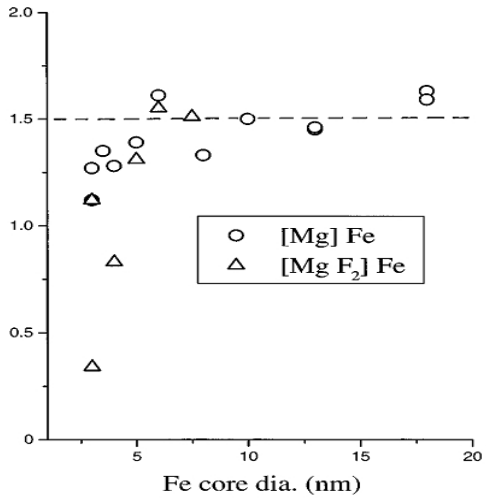

Fig. 1 – Bloch exponent as a function of Fe crystallite size [12].

Moreover, the phenomenological formula implies that the γ parameter is measured in units which depend on the value of the other parameter. It should be noted that the physical content of the Bloch parameter Γ relates to the stiffness of the magnon excitation spectrum. The numerical values of γ are found to be significantly larger the respective bulk values Γ and the confusion introduced by the phenomenological expression has lead to the claims that this behavior is due to a softening of the spin-wave spectrum in nanostructures [11]. Another problem with this description is that its interpretation in terms of spin-waves is in fact impossible. Indeed, as we have shown in an earlier paper [13] the extension of the magnon microscopic theory to finite systems can only generate powers of temperature which are multiples of 1/2. The above arguments lead to the necessity of reconsidering the existing phenomenological description from the viewpoint of microscopic theory. It is also clear that such a theory needs to go beyond the mean-field treatment.

An important starting point is the choice of the model required for a microscopic description. The Table below summarizes the analysis of relevant interactions dominating the magnetic behavior on different length-scales [14].
This analysis shows that for nanoparticles of a few dozens of nanometers one should consider the discrete quantum nature of the magnetic excitations dominated by the exchange coupling. The generic model for such a theory is based on the lattice Heisenberg spin-*S* exchange Hamiltonian. However, the major difficulty in this case is that most of the theoretical approaches refer to the quasiclassical continuum description based on the Landau-Lifshitz equations which ignore the discreteness of the excitation spectrum. In our earlier paper we have proposed an approach which allows to investigate the thermodynamics of discrete finite quantum spin structures of arbitrary dimensionality. In the present paper we show the results of applying this approach to a sample of rectangular shape and a simple cubic lattice structure.

Table

Wavevector q range of the relevant type of magnetic excitations described within respective models [14].

Region	Waveveetor range	theory
Exchange region,*J*	$q > 0.1$ mm^{-1}	Microscopic discrete models
Magnetic dipole interaction	0.1 mm^{-1} > q > 0.01 nm^{-1}	Macroscopic continuum models including the macroscopic dipolar field and effective exchange field
Magnetostatic region	0.01 nm^{-1} > q > 30 cm^{-1}	Macroscopic models with Maxwell equations of effectromagnetism, neglecting the effects of retardation
Electromagnetic region	30 cm^{-1} > q	Macroscopic models with Maxwell equations of efectromagnetism, including the effects of retardation

We consider the coupling between nearest neighbors *J* and neglect the contribution of the magnetocrystalline anisotropy *K* in calculating the magnon dispersion

$$\varepsilon_q = 2JS \sum_{\alpha=x,\,y,\,z} \left(1 - \cos\left(a_\alpha q_\alpha\right)\right), \tag{1}$$

where α are the lattice spacings. The latter assumption is justified by the fact that, *e.g.* for iron, *K* is three orders of magnitude smaller than *J*. The quantized momenta q_α are determined by the linear sizes of the sample $V = N$ x N x L and by the conditions set on the spins belonging to its surface. To simplify the discussion we assume that these are periodic, so that, *e.g.* $q_x = 2\pi m/a_x$ and $m=0,1,...,N-1$. The

uniform precession of the magnetic particle, $|q| = 0$ should be excluded, as explained in the introduction. It can be shown that other boundary conditions do not qualitatively modify the results. The magnetization is obtained by quantum statistical averaging of the magnetization over the above magnon states. This calculation is carried out on the basis of the original method developed in a series of earlier papers [13], [15,16,17]. The final result is as follows:

$$\begin{aligned} N<L: \frac{\mu(T)}{\mu(0)} &= 1 - T^{3/2} \times \zeta(3/2)\ (4\pi J)^{-3/2} S^{-5/2} + T \times \frac{4 - L/N}{N} (4\pi J S^2)^{-1}, \\ N>L: \frac{\mu(T)}{\mu(0)} &= 1 - T^{3/2} \times \zeta(3/2)\ (4\pi J)^{-3/2} S^{-5/2} + T \times \frac{3 - 2\ln(N/L)}{L} (4\pi J S^2)^{-1}. \end{aligned} \tag{2}$$

The Equation (2) is the microscopic generalization of the Bloch theory to a ferromagnetic sample of rectangular shape (prolate and oblate). It contains the bulk limit ($L,N \to \infty$) in an explicit form as well as the size and shape dependent part. Its validity is confined by the temperature interval below the Curie $T_C \sim JS^2$ and above $T^* \sim JS / V^{2/3}$. The latter temperature scales with the energy spacing of the quantum discrete magnon levels and can be as high as *10* Kelvin, for comparison, T_C of bulk iron is about 1000 Kelvin and is not dramatically smaller in nanoparticles. When the temperature falls lower than T^* the temperature dependence switches to exponential so that magnetization is almost at its saturation value $\mu(0)$. In Fig. 2 we compare the above result to the numerical cluster simulations and their phenomenological fitting for the Fe *(S=1)* nanocluster with 339 atoms [7].

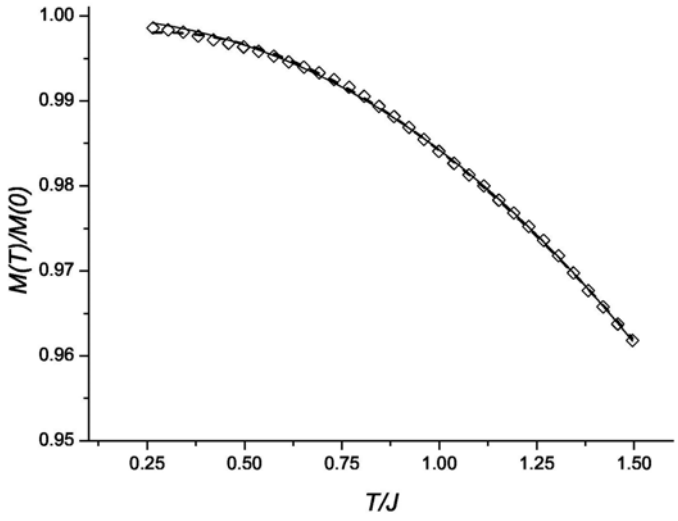

Fig. 2 – Comparison of the numerical cluster simulations and their phenomenological fitting for the Fe *(S=1)* nanocluster with *339* atoms [7] to the expression in Eq. (2).

It can be seen that differences occur only at rather low temperatures near saturation which correspond to the crossover at T^* to the exponential regime, as explained above. Above this point the results of the two approaches are almost indistinguishable. In Fig.3 we show another example where the experimentally measured temperature dependence of the γ-Fe_2O_3 particle of 6.4 nm size (crosses) [18] is well reproduced by our theory.

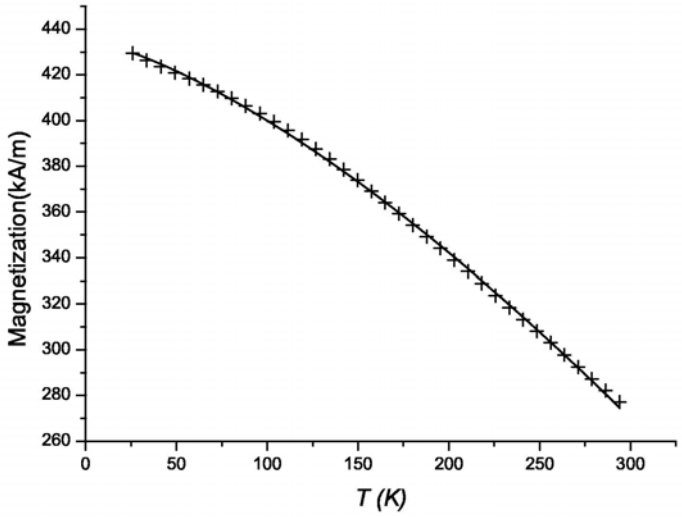

Fig. 3 – Experimental temperature dependence of the magnetization for the γ-Fe_2O_3 particle of 6.4 nm size (crosses) [18] reproduced by the Eq. (2).

3. DISCUSSION AND CONCLUSIONS

It can be seen that the proposed microscopic theory leads to a qualitatively different general form of the temperature dependent magnetization in nanoparticles and nanoclusters compared to the phenomenological description presently used in the literature on this subject. This theory gives a good agreement with the data obtained both in numerical simulations or experiments and reveals the connection to the microscopic parameters of the considered structures. Being a consistent generalization of the Bloch theory for bulk ferromagnets to the finite nanoscopic systems, it does not suffer from intrinsic contradictions and physical inconsistencies of the phenomenological expression. Most importantly, its relatively simple form turns out to be also sufficiently universal. Namely, it is valid not only for *3D* structures, such as particles, but also to quasi-two and quasi-one-dimensional structures like strips and wires. We therefore propose that the new general form should replace the existing phenomenological expression:

$$\frac{\mu(T)}{\mu(0)} = 1 - T^{3/2} \times A + T \times B, \tag{3}$$

where the parameters A and B should be found by fitting the experimental data. Their microscopic interpretation being now put on a more solid microscopic ground.

Acknowledgements. One of the authors (SC) gratefully acknowledges stimulating discussions with Dr. D.V. Anghel. The work has been financially supported by CNCSIS-UEFISCDI (project IDEI 114/2011) and by ANCS (project PN 09370102). The authors acknowledge the support of the CEI Cooperation Fund Project, Fostering Scientific cooperation in CEI countries through research and training in renewable energies and nanophysics, No: 1202.161-13.

REFERENCES

1. H.Hahn, A. Sidorenko, I. Tiginyanu, *Nanoscale Phenomena*, Springer-Verlag Berlin, Heidelberg, 2009.
2. S. Neralla, *Nanocrystals -- Synthesis, Characterization and Applications*, InTech Prepress, Novi Sad, 2012.
3. C. Binns, *Introduction to Nanoscience and Nanotechnology*, Wiley, New Jersey, 2010.
4. S. Morup, C. Frandsen, M.F Hansen, Uniform excitationsin magnetic nanoparticles, *Beilstein J. Nanotechnol.* **1**, 48–54 (2010).
5. F. Bloch, *Z. Phys*. **61**, 206–213 *(*1930).
6. C. Kittel *Introduction to Solid State Physics*, Wiley, 8th Edition, 2004.
7. P. V. Hendriksen P. Linderoth, A. Lindgard, Magneticproperties of Heisenberg clusters *J. Phys.:Condens. Matter* **5**, 5675–5693 (1993).
8. Hendriksen P. V., S. Linderoth, P.-A. Lindgard, Finite-size modifications of the magnetic properties of clusters, *Phys. Rev. B,* **48**, 7259–7273 (1993).
9. Schmid G. (Ed.), *Nanoparticles: From Theory to Application,* Wiley-VCH, Berlin, 2010.
10. Marie-Paule Pileni, *Nanocrystals Forming Mesoscopic Structures*, WILEY-VCH Verlag, Weinheim, Germany, 2005.
11. S.P. Gubin, Editor, *Magnetic Nanoparticles*, Wiley-VCH, Berlin, 2009.
12. D. Zhang, K. J. Klabunde, C. Sorensen, Magnetization temperature dependence in iron nanoparticles, *Phys. Rev. B*,58, 14167–14181, 1998
13. S. Cojocaru, Deviation from the Bloch law in a nanoscale Heisenberg ferromagnet, *Philosophical Magazine*, **91**, 4053–4062 (2011).
14. Zhang Zhi-Dong, p.141, in *Encyclopedia of Nanoscience and Nanotechnology*, Hari Singh Nalwa, Editor, American Scientific Publishers, N.Y. 2004.
15. S. Cojocaru, Green functions on finite lattices and their connection to the infinite lattice limit, *Philosophical Magazine,* **88**, 441–447 (2008).
16. S. Cojocaru, Green function of a finite chain and the discrete Fourier transform, *Int. J. Mod. Phys. B,* 2006, **20** (5): 593–605
17. S. Cojocaru, V. Bârsan, A. Ceulemans, Exact solution of the discrete Schrodinger equation for ferromagnetic chain, *Philosophical Magazine B*, **86**, 4983–492 (2006).
18. S. Cojocaru, V. Bârsan, A. Ceulemans, Spin excitations on finite lattices and the discrete Fourier transform, *Journal of Magn. and Magnetic Materials*, **307**, 62–73 (2006).
19. R. Aquin, J. Depeyrot, Sousa M. H. , Tourinho F. A., Dubois E., Perzynski R., Magnetization temperature dependence and freezing of surface spins in magnetic fluids based on ferrite nanoparticles, *Phys. Rev. B,* **72,** 184435–184446 (2005).