Temperature dependence of magnetization of a nanosize Heisenberg ferromagnet

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Saturation magnetization of nanosize ferromagnets (nanoparticles and nanoclusters) does not follow the Bloch $T^{3/2}$ law, known to be valid for macroscopic materials. In the absence of the „small size" formula of magnetization one usually uses a phenomenological power law T^{α} with a size dependent exponent α, which is motivated simply by its flexibility in fitting the observed behavior. We argue on the inconsistency of such a desciption and present an analytic derivation of the respective expression for magnetization in which generalizes the Bloch formula to a finite size system. Comparison to the experimental data on nanoclusters and nanoparticles demonstrates a good agreement with this expression and its utility for a better understanding of the underlying physics.

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1. Introduction

During the last two decades, traditionally idealized examples of solid state physics, like atomic or spin chains [1], ultra-thin (one-layer) magnetic films [2], etc., have been obtained experimentally and investigated theoretically [3 - 6]. Moreover, systems of reduced size and dimensionality like, e.g., magnetic nanostructures (particles, clusters, wires etc.) serve as key components in a growing range of applications from electronics to medicine. One of the important consequences of device miniaturization is that their properties differ significantly from those of the bulk systems. There may be multiple reasons responsible, such as a high surface to volume ratio, strong size and shape dependence, modification of electronic properties, more prominent role of quantum effects etc. [7]. Thus, a dramatic decrease of saturation magnetization and critical temperature with the size of nanoparticles at about 3-5 nm (called "small" nanoparticles in [8]) can be explained by the dominant contribution of the surface layer with a depleted polarization, e.g. [9]. On the other hand, since the effects of demagnetization field and domain wall formation are reduced with sample size, the nanoscale is favorable to magnetism because of the possibility to support single domain fully polarized structures extending to hundreds of nanometers [10, 11]. However, even in this case large deviations from the Bloch "$T^{3/2}$" law for the temperature variation of the saturation magnetization $M(T)$ [12] are known both from numerical solution of self-consistent equations describing Heisenberg spin clusters [13] and from experiments on nanoparticles [14]. This law has been derived by considering magnon excitations in a $3D$ infinite crystal and gives an adequate description of bulk ferromagnetic materials below the Curie temperature, T_c, e.g. 1043 K for iron. The common practice in describing experimental data or numerical simulations on nanoparticles is to use a modified Bloch formula, e.g. [8,11,13, 15].

$$M(T) = M_0\left(1 - \gamma T^{\alpha}\right). \tag{1}$$

The three parameters fitted to the observed values are strongly size dependent and approach the bulk limit for larger samples, over hundreds of nm . It turns out that values of α show little regularity with size variation, and can be both larger and smaller than in the bulk, 3/2, depending on their preparation technology, see e.g. [9]. It is also often argued that the obtained values of γ are „much larger" in nanoparticles than in the bulk material, although this quantity differs even the measure units. Such confusing arguments are induced by, e.g., the expectation of magnon softening in smaller particles (e.g. Ch. 6.9 of the review [9]) and the known decrease with magnon stiffness of the Bloch factor B in the corresponding temperature dependence $B \times T^{3/2}$ of the bulk material. However, aside from the conveniency and flexibility of the modified form (0) of the Bloch law in representing the observed behavior of magnetization, its microscopic motivation was not discussed before and remains unclear. Moreover, it seems impossible to connect the decimal numerical values of α obtained from this fitting formula to the fractional powers generated by magnon spectra (see the derivation below).

In the analysis presented in the next sections we

consider the low temperature expansion within a microscopic model of a finite size ferromagnet and derive an explicit expression for the main terms. This leads to a different form of the finite size modification of the Bloch law, which is then compared to the available data. It has to be mentioned that at sufficiently low temperatures (which may reach dozens of Kelvin for small nanoparticles) the modified form becomes totally inadequate for the description of the magnetization because it is unable to capture the observed qualitative change in the temperature dependence (e.g. an inflection point [16]). There exist different scenarios proposed in the literature to explain this lower temperature deviation from the Bloch law [17, 9], e.g., the discrete, quantized nature of the magnon spectrum in confined systems [17, 18], magnetic properties related to the surface or finite width shell of nanoparticles [8], etc. Our consideration does not include the surface effects and does not refer to this lower temperature regime, but rather to the intermediate temperatures above this interval and below T_c, where Eq.(0) is used as a standard tool of data analysis.

2. Finite size modification of the Bloch law

The behavior of noninteracting separate nanoparticles can readily be studied experimentally [16, 19]. As a model of a single monodomain ferromagnetic particle we consider a simple finite $N \times N \times N$ cubic lattice with periodic boundary conditions described by the quantum Heisenberg Hamiltonian with nearest neighbor interaction:

$$H = -\sum_{\langle ij \rangle} J\left(\mathbf{S}_i \mathbf{S}_j - S^2\right). \tag{2}$$

There exist, of course, many additional factors that may be relevant for a more detailed description, like anisotropic interaction, different boundary conditions, shape of the sample etc. However, it is reasonable to assume that the generic features of the finite size effects should be present already in this "simplified" model. Moreover, in the present treatment we neglect the effect of magnon-magnon interaction, taking into account that, as has been proved by Dyson in a series of seminal papers, this effect shows up for higher powers of the low temperature expansion (for a $3D$ lattice it is T^4) due to the fact that the interaction cross-section goes as a product of magnon momenta [20, 21].

The magnetization density (in units of $\mu_B g$) is given by the expression

$$M(T) = S - \frac{1}{N^3}\sum_{n=1}^{\infty}\sum_{\mathbf{k}\neq\mathbf{0}} \exp\left(-\beta n \varepsilon_{\mathbf{k}}\right), \tag{3}$$

where the linear size N is in units of nearest neighbor distance, $\beta = \left(k_B T\right)^{-1}$ relates to the inverse temperature and the magnon spectrum for a simple cubic lattice is ($\mathbf{k} = \left(k_1, k_2, k_3\right)$):

$$\varepsilon_{\mathbf{k}} = JS \sum_{i=1,2,3} \left(1 - \cos k_i\right), \quad k_i = \frac{2\pi m_i}{N}, \quad m_i = 0,..., N-1. \tag{4}$$

Here a remark on the Eq. (2) can be made that "linearization" of ε_k to a parabolic dispersion, commonly assumed at low temperatures, is not justified at nanoscale because the difference between long and short waves is not well defined, the parameter $2\pi / N$ is not "infinitesimally small" anymore and the sum in Eq. (3) can not be replaced by an integral.

Thus, we have to calculate the quantity $\Delta M = M_0 - M(T)$:

$$\Delta M = \frac{1}{N^3}\sum_{n=1}^{\infty}\sum_{\mathbf{k}\neq\mathbf{0}} \exp\left(-\beta n \varepsilon_{\mathbf{k}}\right) \tag{5}$$

$$= \sum_{n=1}^{\infty}\left(\left(\frac{1}{N}\sum_{m=0}^{N-1}\exp\left(-2n\beta JS\sin^2\left(\frac{\pi m}{N}\right)\right)\right)^3 - \frac{1}{N^3}\right)$$

As has been shown earlier [22] the sum over wave-vector in Eq. (3) generates a series of modified Bessel functions:

$$\frac{1}{N}\sum_{m=0}^{N-1}\exp\left(-2n\beta JS\sin^2\left(\frac{\pi m}{N}\right)\right) \tag{6}$$
$$= \exp\left(-\beta nJS\right) I_0\left(\beta nJS\right) + 2\exp\left(-\beta nJS\right)\sum_{k=1}^{\infty} I_{kN}\left(\beta nJS\right).$$

The first term in (4) corresponds to the thermodynamic limit $N \to \infty$, with the leading contribution to the low temperature expansion representing the Bloch law

$$\Delta M_{TDL} = \sum_{n=1}^{\infty}\left(\exp\left(-\beta nJS\right) I_0\left(\beta nJS\right)\right)^3$$

$$= \zeta\left(3/2\right)\left(2\pi\beta JS\right)^{-3/2} + \frac{3}{16\pi}\zeta\left(5/2\right)\left(2\pi\beta JS\right)^{-5/2} + ...,$$

where $\zeta(x)$ is the Riemann $\zeta-$ function [23]. The finite N corrections are contained in the terms with the Bessel functions of higher order [24,25]. However in the present case the situation is more complicated because our series contains two "large" parameters (βJS and N), while their ratio may be finite. To develop a low temperature expansion of the remaining terms in (4) we use the integral representation of the Bessel function

$$\exp\left(-\beta nJS\right) I_{kN}\left(\beta nJS\right) = \int_0^{\pi} \exp\left(-2n\beta JS\sin^2\left(\phi/2\right)\right)\cos\left(\phi kN\right)\frac{d\phi}{\pi}.$$

Then with exponential accuracy, $\exp\left(-2\beta JS\right)$, the low temperature expansion of (4) becomes

$$\Delta M = \sum_{n=1}^{\infty}\left\{\left[\frac{1}{\sqrt{2\pi n\beta J}}\left(1+\frac{1}{8n\beta J}+...\right)+\right.\right.$$
$$\sum_{k=1}^{\infty}\frac{2}{kN}\int_0^{\infty}\exp\left(-x^2/2\right)\sin\left(xkN/\sqrt{n\beta J}\right)\times \quad (7)$$
$$\left.\left.\left(x+\left(-\frac{1}{6}x^3+\frac{1}{24}x^5\right)/n\beta J+...\right)\frac{dx}{\pi}\right]^3-\frac{1}{N^3}\right\}$$

It can now be seen that consecutive terms in the last line correspond to an expansion in powers of temperature. The first line of the Eq. (5) corresponds to the limit $N\to\infty$ and the series under integration, containing the finite size correction, can be expressed in terms of Jacobi elliptic theta function, e.g.

$$\sum_{k=1}^{\infty}\frac{2}{kN}\int_0^{\infty}\exp\left(-x^2/2\right)\sin\left(xkN/\sqrt{n\beta JS}\right)x\frac{dx}{\pi}$$

$$=\frac{1}{\sqrt{2\pi n\beta JS}}\left(\theta_3\left(\exp\left(-N^2/2\beta nJS\right)\right)-1\right),$$

where

$$\theta_3\left(\exp\left(-x\right)\right)=1+2\sum_{k=1}^{\infty}\exp\left(-k^2x\right).$$

Next step is to use an important identity due to Jacobi which can be put in a suggestive form

$$\frac{\theta_3\left(\exp\left[-\pi P/n\right]\right)}{\theta_3\left(\exp\left[-\pi n/P\right]\right)}=\sqrt{\frac{n}{P}}, \quad (8)$$

where we have introduced the parameter

$$P=N^2/\left(2\pi\beta JS\right), \quad (9)$$

which plays a key role in the low temperature physics at nanoscale. Thus, it follows from the identity (7) that the value $P=n$ continuously connects the region of an exponential dependence of the θ_3 function upon P/n, when $P>n$, from an exponential in n/P, when $P<n$. The two exponential series ensure a fast convergence and this property allows to cast Eq. (6) in the following form

$$\Delta M=\sum_{n=1}^{\infty}\left(\left[\frac{1}{N}\frac{\sqrt{P}}{\sqrt{n}}\left(1+\frac{\pi}{4}\frac{P}{N^2}\frac{1}{n}+...\right)\right.\right.$$
$$\left.\left.+\theta\left(n<P\right)\left(\sum_{k=1}^{\infty}\exp\left(-\pi k^2P/n\right)\right)\left(\frac{2}{N}\frac{\sqrt{P}}{\sqrt{n}}\right)\right]^3-\frac{1}{N^3}\right)$$
$$+\theta\left(n>P\right)\frac{2}{N}\frac{\sqrt{P}}{\sqrt{n}} \quad (10)$$
$$\left.\times\left(\frac{1}{2}\sqrt{\frac{n}{P}}-\frac{1}{2}+\sqrt{\frac{n}{P}}\sum_{k=1}^{\infty}\exp\left(-\pi k^2n/P\right)\right)+...\right]^3-\frac{1}{N^3}\right),$$

where θ is the Heaviside theta function. The higher order terms in the second line of Eq.(8), which start with $O\left(\left(\beta JS\right)^{-3/2}\approx P^{3/2}/N^3\right)$, preserve the same structure as shown above. It can now be seen that the special role of the condition $P=1$ is due to the fact that at this point the familiar T expansion for the thermodynamic limit (in the first line) is completely canceled by the algebric terms of the finite N correction (the second line and higher order terms), signifying a qualitative change in the temperature behavior. Indeed, for $P>1,$ due to the presence of Heaviside theta functions in (8), which give the main contribution to the series are expressed through Harmonic numbers, e.g. like

$$\frac{P^{\frac{3}{2}}}{N^3}\sum_{n=1}^{P}\frac{1}{n^{\frac{3}{2}}}.$$

The remaining exponentials can be calculated by Euler-Maclaurin formula and give only a small correction. In this way we find that the finite size modification of the Bloch law is determined by the expression:

$$\Delta M \sim \frac{\zeta\left(3/2\right)}{\left(2\pi JS\right)^{3/2}}\left(k_BT\right)^{3/2}-\frac{1}{\pi JSN}k_BT. \quad (11)$$

The corrections are of the order $T^{5/2}$ and $1/N^3$. E.g., the correction coming from the renormalization of magnon dispersion with temperature $\sim T^3$ can also be neglected for $T\ll T_c$ [21]. This expression is valid for the condition that

$$k_BT>2\pi JS/N^2. \quad (12)$$

At lower temperatures, when $P<1,$ due to term cancelations discussed above, only the exponentials are left to govern the temperature behaviour:

$$\Delta M=\sum_{n=1}^{\infty}\left(\left[\frac{1}{N}+\frac{2}{N}\sum_{k=1}^{\infty}\exp\left(-\pi k^2n/P\right)+...\right]^3-\frac{1}{N^3}\right).$$

In this region, the deviation of magnetization from its maximal value is well represented by the leading exponential

$$\Delta M \sim \frac{6}{N^3}\exp\left(-2\pi^2\beta JS/N^2\right), \quad (TN^2<2\pi JS). \quad (13)$$

A similar expression has been used in a number of papers, e.g. [14, 17, 18], to fit the lowest temperature part (below 30 K) of the magnetization curve in nanoparticles.

As mentioned before, we are interested in the region of higher temperatures, as now defined by the condition (9a). Let us examine whether the new form of the modified Bloch law

$$M(T)/M_0 = 1 - BT^{3/2} + CT \qquad (14)$$

agrees with the existing numerical and experimental data. For instance, we may use the numerical analysis of iron magnetic clusters of different size described in [13, 26], which can be calibrated against the bulk ($N \to \infty$) behavior shown in Fig. 4 of Ref.[26]. Thus we find $\alpha = 3/2,\ \gamma = B = 0.057,\ C = 0,\ k_B T_c / JS \approx 6.7,\ k_B / JS \approx 0.0064.$ According to (c) this gives the estimate for the threshold temperature $T(P=1) \approx (20-30)K$ for the clusters of size $N^3 = 725$ and $N^3 = 339$ - in agreement with the values of the gap in magnon spectrum calculated in [26], Fig.3. It should be kept in mind that expression Eq. (11) may not be used to represent the data beyond this temperature, $T < T(P=1)$, where the exponential dependence, Eq. (10), takes over.

For the cubic cluster of $N^3 = 339$ atoms, i.e. around 2 nm size, we find $B = 0.134,\ C = 0.075$ (as compared to $\gamma = 0.064,\ \alpha = 1.96$ for Eq. (0)), (Fig. 1).

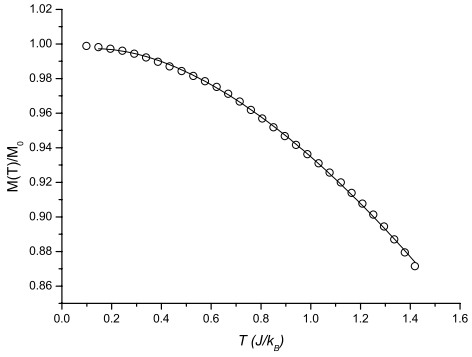

Fig. 1. Magnetization of the 339 atoms ferromagnetic cluster [26] (circles) and its fit by Eq. (14).

For an even smaller cluster of $N^3 = 137$ atoms the results are $B = 0.174,\ C = 0.1$ (respectively $\gamma = 0.078,\ \alpha = 2.07$), Fig. 2.

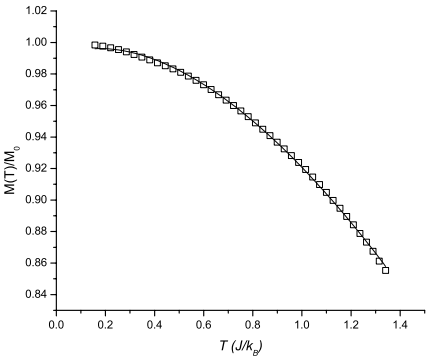

Fig. 2. Magnetization of the 137 atoms ferromagnetic cluster [26] (circles) and its fit by Eq. (14).

It can be seen that (11) agrees well with the results of [26] within a similar standard fitting error. Interestingly, the ratio of the size dependent coefficients in (11) $C(339)/C(137) = 0.75$ corresponds to the dependence $C \approx 1/N$ following from the expression (9), $(137/339)^{1/3} \approx 0.74.$ However, it should be kept in mind that Figs. 1 and 2 refer to the total magnetization, which includes surface and central spins. Thus, it is natural to expect a higher value for the B coefficient than in the bulk, because the larger surface to volume ratio can be roughly thought of as a decrease of the effective coupling constant J . Numerical analysis allows to examine the magnetization of the central spins, which are more "3D coordinated". In this case fitting with the formula (11) leads to an even better quantitative agreement with the analytical expression (9): $B = 0.057,\quad C = 0.048.$ As can be seen from Fig. 4 of Ref. [26], the central spin magnetization increases for larger samples of cubic structure.

In Ref. [16] manganese and copper ferrite nanoparticles of up to 10 nm are investigated in the dilute regime, so that the observed properties can be attributed to individual particles. It is found that the modified Bloch law (0) can account well for the finite size effects on the temperature dependence of the saturation magnetization. At the same time, the values of the exponent α for particles of almost the same size are found above and below the bulk value, Table 3. In Figs. 3 and 4 we show that our formula can represent the experimental data equally well.

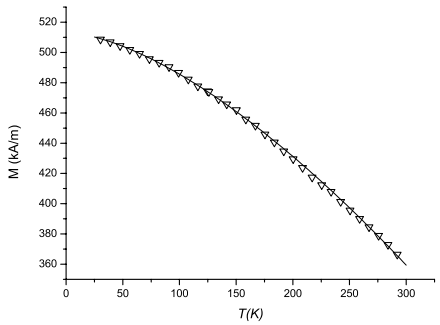

Fig. 3. Magnetization of the 9 nm nanoparticle [16] (circles) and its fit by Eq. (14).

In (Fig. 3) the magnetization of the 9 nm sample, denoted as $Mn1$ in Ref. [16], is matched by the continuous curve according to (11) with the following set of parameters: $M_0 = 513.1\ kA/m$, $B = 6.32\times10^{-5}\ K^{-3/2}$, $C = 0.95\times10^{-4}\ K^{-1}$. The parameters obtained in [16] for the expression (0) are: $M_0 = 515\ kA/m, \gamma = 7.1\ K^{-\alpha}$, $\alpha = 1.45$ (curve not shown).

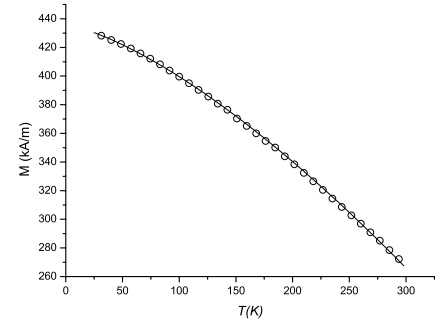

Fig. 4. Magnetization of the 7.4 nm nanoparticle [16] (circles) and its fit by Eq. (14).

In Fig. 4 the respective parameters corresponding to the continuous curve fitting the magnetization of the 7.4 nm sample $Mn2$ are: $M_0 = 435.9\ kA/m$, $B = 6.33\times10^{-5}\ K^{-3/2}$, $C = -2.06\times10^{-4}\ K^{-1}$. The ones obtained in [16] are: $M_0 = 430\ kA/m, \gamma = 6.46\ K^{-\alpha}$, $\alpha = 1.6$ (curve not shown).

It is interesting that in both cases we obtain the value of B close to that in the bulk [16], while the sign of the coefficient C differs in correspondence to the value of α being above or below 1.5. We note in this context that the sign and magnitude of this coefficient depend on the shape of the sample and this difference might be explained by a more asymmetric shape of the 7.4 nm nanoparticles.

3. Conclusions

The examples analyzed above demonstrate that the derived finite size generalization of the Bloch law in (11) is well suited for the description of the temperature dependence of the saturation magnetization of nanoclusters and ferromagnetic nanoparticles. Its advantage with respect to the phenomenological form usually employed for this purpose is that it has a clear microscopic motivation and gives a better understanding of the nature of their magnetic properties. In particular, it explains that the irregular size dependent pattern of the exponent α in (0) is caused by the shape asymmetry of the nanoparticles obtained in the technological process. The lower temperature limit for the formula has a clear physical explanation and emerges in a transparent way when trying to fit the data beyond this limit, signalling the crossover into a new physical regime. On the contrary, the "traditional" formula, due to its flexibility, tends to hide this qualitative change of behavior.

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