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Study of magnetic properties of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ nanotubes by Monte Carlo simulation

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Abstract

Magnetic properties of a single nanotube whose walls are constituted by nanograins of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ are studied by means of Monte Carlo (MC) simulation. The system is considered as composed by ferromagnetic grains which couple via dipolar interaction. The grain size distribution is obtained from experimental measurements and the inter-grain distance distribution is obtained from a study of distance distribution among magnetic particles distributed in the tube walls. We show the magnetization behavior for a tube of 700 nm of diameter and 3.5 μm length. We discuss the simulation for different temperatures and external fields. As a main result, we show that the distribution of inter-granular distances has a unique behavior for tubular structures of similar diameter/length aspect ratio, independent of their sizes. This scaling relation allows us to perform the simulations using a tube of smaller dimensions. We succeed in explaining the magnetization curves, finding that dipolar interaction is necessary to explain the experimental behavior and that the grains behave as having magnetic dead layers.

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1. Introduction

Manganese oxides with mixed valence are systems that show colossal magneto resistance effect, consisting big changes in the electronic transport, through the system, as a function of an applied magnetic field [1–3]. Its technological importance lies in the fact that these systems can be used as sources of highly polarized electrons, as well as elements of magnetic memories [4]. In the present report our interest is the description, by means of MC simulation, of some magnetic properties of a nanostructured system, which was synthesized by a simple method already reported [5]. The considered system is a nanotube of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ whose walls are constituted by grains with a size distribution well described by a log-normal distribu-

tion. This system does not present phase separation as those nanotubes of $\text{La}_{0.325}\text{Pr}_{0.300}\text{Ca}_{0.375}\text{MnO}_3$ [6,7] and this fact allows us to consider each nanograin as a ferromagnetic monodomain. The sintering of manganite nanotubes has opened a set of new applications, which have motivated us to do this study [8].

2. Simulation

From experimental measurements the sintered tubes present lengths L of 3–4 μm and diameters of about 700 nm; with an external radius of $R = (1/10)L$ and a wall thickness $w = (1/7)R$. Therefore, the study was made for a nanotube of $L = 3.5 \mu\text{m}$ length. We also know that the tube walls are filled with grains whose size distribution can be well described by a log-normal distribution as shown in Fig. 1. Since the total number of grains in a single tube of this dimension is too high to perform magnetic simulations

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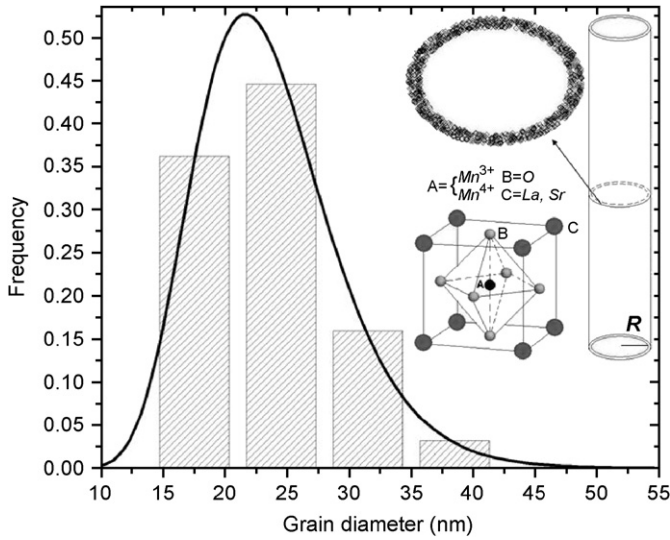


Fig. 1. Size distribution of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ nanograins distributed at the walls of tube. Inset: schematic of nanotube and crystal structure of compound.

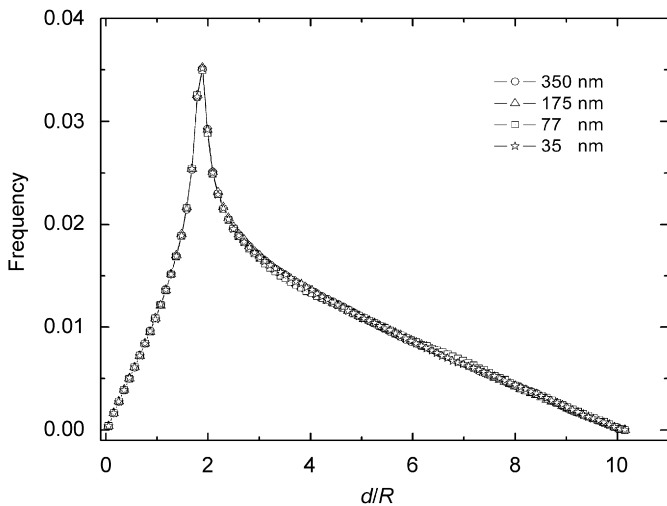


Fig. 2. Inter-grain distance distribution of grains at the tube wall, to four different external radius.

($\sim 8 \times 10^4$), we had to resize the whole system and so lowering the number of grains considerably, conserving fixed concentration of grains in the tube.

For this purpose, the distribution of distances (d) between grains forming the single tube was studied. Fig. 2 shows the inter-grain distance distribution as a function of the ratio d/R , for tubes with different sizes, but the same R/L and w/L ratios. It is interesting to see that these distance distributions when plotted scaled by the tube radius, is independent of the tube size, as long as the indicated ratios are kept constant. The behavior indicates that for any grain at the tube, the fraction of grains located at a distance d/R is the same in the bigger system as well as in the small tube. This geometric scaling property of the

tubes allows us to use a much smaller tube, and to realize the simulations.

The nanotube considered in our simulations has a radius of $R = 77$ nm, length $L = 770$ nm and it is constituted by $N = 908$ grains with a size distribution as shown in Fig. 1. Each grain is considered a ferromagnetic monodomain, where its magnetic moment is proportional to their volume, i.e. $m_i = M_S V_i$ with M_S corresponding to the $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ compound. We considered that grains have magnetic uniaxial anisotropy with random orientation, interacting via dipole–dipole interaction and all systems are under an external magnetic field H . Therefore the Hamiltonian of the system is as follows:

$$H = - \sum_{i=1}^N \vec{m}_i \cdot \vec{H}_i^{\text{eff}}$$

with an effective field on i -th grain

$$\vec{H}_i^{\text{eff}} = - \left[\sum_{j>i}^N \left\{ \frac{\vec{m}_j - 3(\vec{m}_j \cdot \hat{r}_{ij})\hat{r}_{ij}}{r_{ij}^3} \right\} + \vec{H} + \kappa \left(\frac{\vec{m}_i \cdot \hat{n}_i}{m_i} \right) \hat{n}_i \right]$$

where κ is a constant (related to grain anisotropy field), r_{ij} is the distance between the i -th and j -th grains, and n_i (with unitary modulus) is the uniaxial anisotropy axis vector of the i -th grain.

The MC calculations were performed using the metropolis dynamic algorithm, which considers random and independent changes in the orientation of the magnetic moments of the system.

3. Results and discussion

In Fig. 3, we show the hysteresis curves for a temperature of 90 K (experimental and simulation) and, as it is seen, both curves agree very well in all range of external fields. The agreement is found when the magnetic moment per

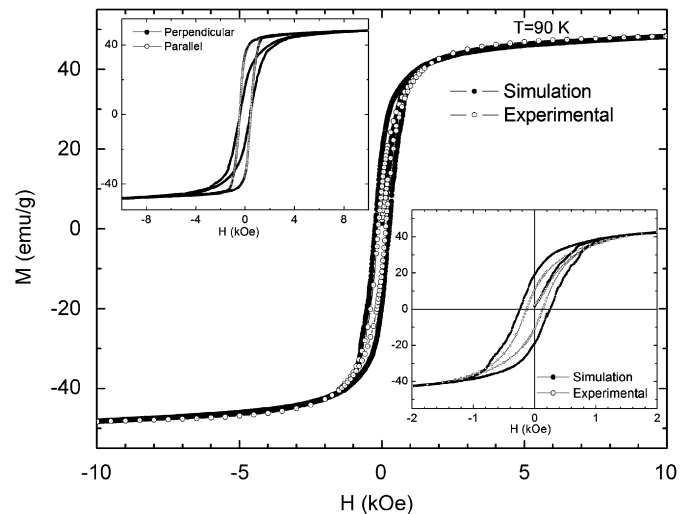


Fig. 3. M vs. H hysteresis loop of a nanotube with external field oriented at 45° respect to the axial axis at 90 K. Inset: Upper: M along axis and perpendicular to it. Lower: hysteresis loop in a lower range of field.

grain considered in the simulation is about 50.2% of the theoretical saturation value. This theoretical value of the moment is obtained considering all the grains as a perfect ferromagnetic domain, i.e., with all magnetic atoms aligned in the same direction; resulting the value $M_S = 91.13$ emu/g.

The difference between both values for the magnetic moment of grains can be associated to the presence of magnetic dead layers that have negligible contribution to the moment of grains [2–9]. Hence, any grain is constituted by a ferromagnetic core and a paramagnetic shell whose contribution to magnetism is noticed only at high fields and which has been taken into account in the simulation curves. The found value is consistent with the fact that the number of atoms at the surface is comparable to the number in the bulk, in nanometric particles.

The value of grain anisotropy field satisfying the experimental curve is 100 Oe, and satisfies that observed by Lofland et al. [10]. We have also found magnetization dependence on the orientation of applied field, and as observed in the upper inset of Fig. 3, the axial axis is the easy axis. Simulations neglecting dipole-dipole interaction between magnetic grains never adjust to the experiment; resulting that simulated magnetization always saturates quicker than the experimental one. Hence, the grains in the tube wall are interacting particles, i.e. the tube present shape anisotropy.

Here, we assumed that each grain behaves as a single magnetic moment, whose magnitude does not change with temperature. A particular task which is worth to be investigated by itself is the ferromagnetic behavior of a grain of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ as a function of temperature. In a grain of nanometer size the magnetic coupling between Mn^{3+} and Mn^{4+} is due to double-exchange interaction through the O atoms [11] and when the temperature of the system is increased, the double-exchange coupling, which tend to keep the system as a ferromagnetic domain is opposed by the thermal noise which disorders the magnetic atoms (favoring the paramagnetic phase) and as a consequence the moment of grains diminishes. Hence a complete study of the system involves the simulation of the internal magnetic structure of each grain and the dipolar coupling among them, simultaneously. This is beyond our present capabilities because the number of degrees of freedom is very large, and due to the different order of magnitude of interactions (exchange and dipolar), the time scale for thermalization in both processes is very different.

Therefore, we proceeded by the following way: the saturation magnetization curve of the sample at high field (10 kOe) as a function of temperature is known from experiments (in particular the saturation at 90 K with 50.2% of magnetic atoms aligned as ferromagnetic monodomain corresponds to a point in that curve), so at a given temperature we can estimate the percent of ferromagnetic phase of each grain, and so we can carry on the magnetic simulations.

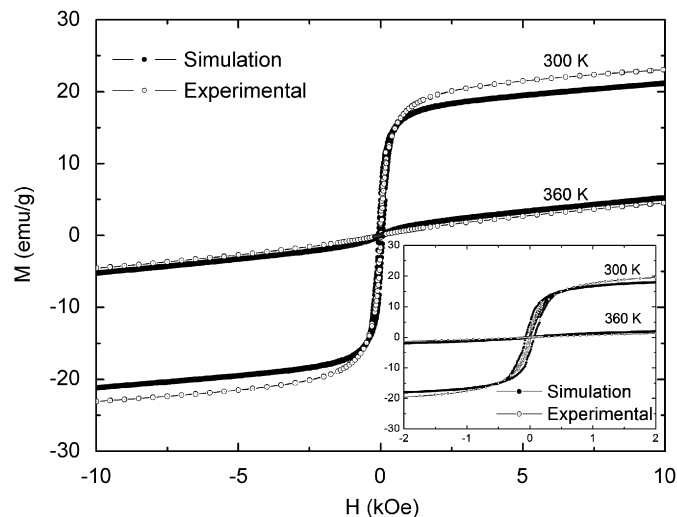


Fig. 4. M vs. H hysteresis loop of a nanotube at 300 and 360 K. Inset: hysteresis loop in a lower range of field.

In Fig. 4, we show the magnetization curves at 300 and 360 K simulated, using the indicated procedure. As seen these adjust reasonably with the experimental curves, with slight differences especially at higher fields for 300 K.

This effect is due to the inter-grain magnetic coupling that reduces the saturation value of the magnetic moment at 10 kOe. Therefore, these observed differences indicate that, at this temperature, the actual values of the individual magnetic moments are slightly greater than the values obtained from the experimental saturation curve.

4. Conclusions

The electronic and transport properties of highly correlated $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ system are still far from being understood. However, the macroscopic magnetic properties of these tubular samples, can be well described employing classical MC simulation, by supposing that grains behave as ferromagnetic domains that couple via dipole-dipole interaction. This achievement, is possible due to the scaling law that the inter-grain distances distribution satisfy, allowing us to perform simulations, on a smaller system.

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