SIMULATION OF SURFACE ANISOTROPY IN $LA_{2/3}CA_{1/3}MNO_3$ NANOPARTICLES

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Introduction

Magnetic nanoparticles have been investigated for being employed because of their potential applications in medicine [1], in catalysis process [2], and as a precursor for the production of some materials and especially because in many applications, high purity and homogeneous nano-sized powders are required. Due to finite size effects, magnetic nanoparticles present changes in magnetic properties compared with materials in bulk.

For instance, J. Restrepo et al [3] employed Monte Carlo simulation and they reported the effect of surface anisotropy upon the magnetic structure of ferromagnetic maghemite γ-Fe_2O_3 nanoparticles in the limit of low temperature. They observed a marked decrease of the Curie temperature in the nanoparticles compared to bulk. Regarding to $La_{2/3}Ca_{1/3}MnO_3$, it has been widely study because its special magnetic thermal and electrical properties, and exhibits Colossal Magneto Resistance (CMR) employed in many applications as spin valves, magnetic sensors among others. The study of surface anisotropy is important for technological applications because in a magnetic field it influences strongly the magnetic behavior of these nanoparticles, and can produce changes in the magnetization reversal mechanism and may lead to the formation of different spin structures.

The aim of this work is to study magnetic properties of $La_{2/3}Ca_{1/3}MnO_3$ nanoparticles with different diameters. Finally, the effect of surface anisotropy upon the spin structure in the limit of low temperature is also presented.

Model and Simulation

The manganite $La_{2/3}Ca_{1/3}MnO_3$ is a ferromagnetic compound below 260 K. It is characterized for having three types of ions as Mn^{4+} (S=3/2), which is bonded with Ca^{2+} ions, Mn^{3+eg} and $Mn^{3+eg'}$ (S=2) that are related to La^{3+}. A scheme of the nanoparticle with diameter of 7.334 nm showing the three types of ions is presented en fig. 1. This material has perovskite type structure (simple cubic lattice), for the ideal case, having a coordination number of six.

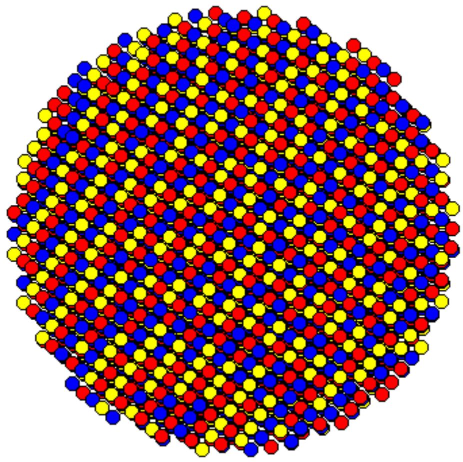

Fig. 1. Scheme of a $La_{2/3}Ca_{1/3}MnO_3$ nanoparticle with diameter 7.334 nm, showing the three types of ions.

Here the attention is focused on the properties of manganite nanoparticles with diameters between 2.316 nm (6 ions) and 10.422 nm (27 ions), employing a lattice parameter of 0.386 nm, by implemented free boundary conditions. The model employed is based on three-dimensional classical Heisenberg Hamiltonian with magnetocrystalline anisotropy, Néel´s surface anisotropy and interacting within first magnetic coordination shell [4].

The Hamiltonian used in this work is:

$$H = -\sum_{i\neq j} J_{ij}\vec{S}_i\cdot\vec{S}_j - K_B\sum_i \left(\vec{S}_i\cdot\hat{a}\right)^2 - K_s\sum_i \left(\vec{S}_k\cdot\hat{n}\right)^2 - h\sum_i \vec{S}_i\cdot\hat{h}$$

The first sum runs over nearest magnetic neighbors with a coordination number of six. The second term gives the core cubic magnetocrystalline anisotropy, where $K_B \approx 1.2484$ meV/nm^3 is the bulk anisotropy constant. The unit vector $\hat{a}$ indicates the easy axis direction. The third term accounts for single ion site surface anisotropy and the unit vector on the surface at each ith position is represented by the expression [4]:

$$\hat{n} = \sum_{i\neq j}(\vec{d}_j - \vec{d}_i) \Big/ \sum_{i\neq j}\left|(\vec{d}_j - \vec{d}_i)\right|$$

K_S is the surface anisotropy that will be varied for obtaining different ratios of K_S/K_B. The forth term in the Hamiltonian represents the influence of the external magnetic field, being $\hat{h}$ the direction of the magnetic field.

Results and discussion

The temperature dependence of the modulus of the magnetization per spin for bulk with L=4.242 nm and spherical nanoparticles with diameters from 2.316 nm to 10.422 nm is showed in fig. 2. And the Magnetic Susceptibility is showed in fig.3.

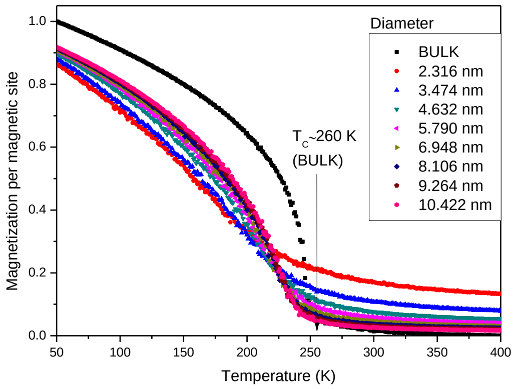

Fig. 2. Magnetization per magnetic site for the nanoparticles of $La_{2/3}Ca_{1/3}MnO_3$ with different diameters.

Results reveal a diminution of the Curie temperature T_c, compared to that obtained for a bulk when using periodic boundary conditions. Such a diminution in T_c is attributed to the decrease of the average coordination number and consequently to the smaller density of magnetic bonds. This fact is in turn a consequence of symmetry breaking occurring at the surface of the nanoparticle.

Fig. 4 shows the magnetization as a function of K_S/K_B. Changes in the magnetization meaning the mechanism by which the system undergoes the ferromagnetic to paramagnetic transition depends on the magnitude of surface anisotropy.

Conclusions

A shifting toward low temperatures of T_c was observed, these phenomenon is due to the surface anisotropy. Nevertheless, T_c is shifted toward bulk transition temperature (260 K) when the nanoparticle diameter is increased.

Magnetization and magnetic susceptibility per site were obtained as a function of the nanoparticle size and the results were compared with those obtained for bulk material.

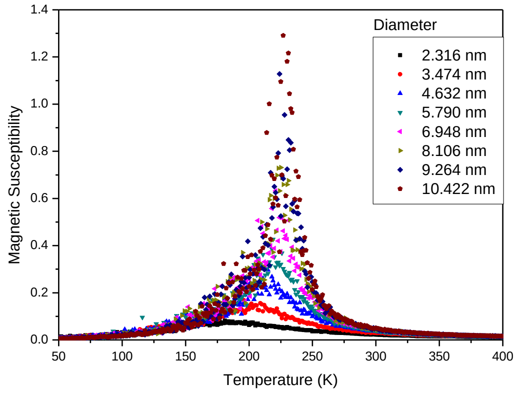

Fig. 3. Magnetic Susceptibility per magnetic site for the nanoparticles of $La_{2/3}Ca_{1/3}MnO_3$ with different diameters.

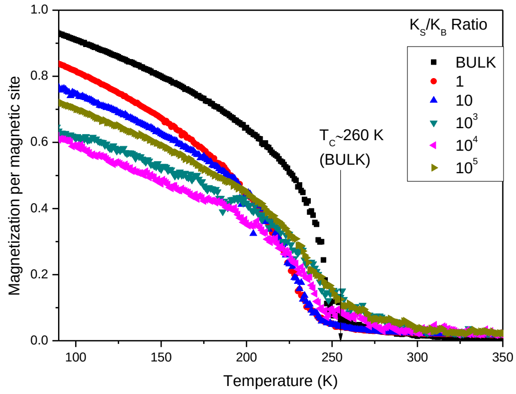

Fig. 4. Magnetization per magnetic site for different values of the relation K_S/K_B.

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