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Correlation between vacancies and magnetoresistance changes in FM manganites using the Monte Carlo method

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ABSTRACT

The Metropolis algorithm and the classical Heisenberg approximation were implemented by the Monte Carlo method to design a computational approach to the magnetization and resistivity of $La_{2/3}Ca_{1/3}MnO_3$, which depends on the Mn ion vacancies as the external magnetic field increases. This compound is ferromagnetic, and it exhibits the colossal magnetoresistance (CMR) effect. The monolayer was built with $L \times L \times d$ dimensions, and it had $L=30$ umc (units of magnetic cells) for its dimension in the x–y plane and was $d=12$ umc in thickness. The Hamiltonian that was used contains interactions between first neighbors, the magnetocrystalline anisotropy effect and the external applied magnetic field response. The system that was considered contains mixed-valence bonds: $Mn^{3+eg'}$–O–Mn^{3+eg}, Mn^{3+eg}–O–Mn^{4+d3} and $Mn^{3+eg'}$–O–Mn^{4+d3}. The vacancies were placed randomly in the sample, replacing any type of Mn ion. The main result shows that without vacancies, the transitions T_C (Curie temperature) and T_{MI} (metal–insulator temperature) are similar, whereas with the increase in the vacancy percentage, T_{MI} presented lower values than T_C. This situation is caused by the competition between the external magnetic field, the vacancy percentage and the magnetocrystalline anisotropy, which favors the magnetoresistive effect at temperatures below T_{MI}. Resistivity loops were also observed, which shows a direct correlation with the hysteresis loops of magnetization at temperatures below T_C.

1. Introduction

Manganites, which are metal oxides with perovskite structure, stimulate great scientific research because of their intriguing phenomenology. In particular, three phenomena are relevant: (a) colossal magnetoresistance (CMR), which is defined as large changes in the resistivity caused by small external magnetic fields, at temperatures near the Curie temperature (T_C), transition between the ferromagnetic (FM) and paramagnetic (PM) states. Frequently, T_C and the metal–insulator transition temperature (T_{MI}) are similar [1,2]. The occurrence of the peak in the resistance at this temperature strongly suggests that the behavior of the resistance is intimately connected [3]. (b) Exchange bias (EB), which is a hysteresis loop shifting, presents in compounds that have a combination of FM and anti-ferromagnetic (AFM) layers. This shifting is due to a directional anisotropy that is generated after cooling, starting from an intermediate temperature between T_C and the AFM–PM transition temperature (T_N) [4,5], and (c) phase separation, which consists of the presence of coexisting states, usually FM and AFM under specific conditions of temperature and stoichiometry [1,6]. This phenomenology influences the potential technological applications, such as magnetic sensors, readers of magnetic surface information through spin valves in magnetoresistive heads and storage of information in nonvolatile magnetic memory, among others. In particular, the CMR phenomenon has not been explained satisfactorily; although according to several reports, the double exchange theory (DE) can reproduce shapes and tendencies of the magnetoresistance curves, the magnitudes are usually lower than the experimental values. The Jhan Teller effect, which refers to distortions in the structures due to energy levels being partially unoccupied, and Coulomb interactions have been suggested as complements for explaining the phenomena; however, their influence is not as relevant as being caused by DE [3]. Other causes of MR should be lattice defects, essentially because they increase the resistivity due to the interruption of carrier paths and magnetic walls [7], which results in a distortion in the magnetic orientation and causes an increase in the percolation effect. Simulations of materials with similar structures using methods as Monte Carlo have been reported in the literature [8,9]; nevertheless, a deep study is required for understanding their behavior.

Experimental reports have shown that magnetic vacancies can

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be generated in thin films with percentages of up to 8% [7,10], and no many reports have been found about the influence of the interface imperfections on the magnetic properties of bilayers and multilayers can be found, as it presented by Boughrara et al. [11]. They carried out a Monte Carlo study of critical and compensation behavior of a ferrimagnetic superlattice on a simple cubic cell. The interfaces are characterized by a random arrangement of A and B atoms with different spins and coupling; nevertheless, more discussion about the study of the magnetic vacancies' influence on the magnetic properties of thin films is required. $La_{2/3}Ca_{1/3}MnO_3$ manganite has been selected because of the large number of experimental reports that conduct a comparative analysis.

The Monte Carlo method (MC) has shown suitable results in the simulation of magnetic and ferroelectric materials. With this method, the directions of the respective moments per unit cell are obtained in the stable states after a large number of iterations [12,13]. MC combined with the Metropolis algorithm and classical Heisenberg spin orientations was implemented previously in other reports. The results obtained reproduced satisfactorily the magnetic properties in thin films, in particular in the case of the magnetic phase diagram of $La_{1-x}Ca_xMnO_3$ [14] and critical exponents of ferromagnetic $La_{2/3}Ca_{1/3}MnO_3$ thin films [15]. This work presents a study of changes in the resistivity and CMR for FM materials as a function of the temperature and external magnetic field, as caused by magnetic vacancies in $La_{2/3}Ca_{1/3}MnO_3$. The simulations were conducted by using the Monte Carlo method combined with the Metropolis algorithm and classical Heisenberg model.

2. Model description

According to the orbital order pattern reported by Hotta et al. [16], $La_{2/3}Ca_{1/3}MnO_3$ presents perovskite structure with orbital order distribution of trivalent Mn^{3+eg}, $Mn^{3+eg'}$ and tetravalent Mn^{4+} ions placed in the unit cell center, considering a simple cubic lattice. FORTRAN 95 software was employed for program construction, and the Metropolis algorithm was implemented for energy minimization purposes. Vacancies were generated randomly. Periodic and free boundary conditions in the x–y plane and z direction were implemented, respectively. The sample dimension was $L \times L \times d$, where $L=30$ muc (magnetic units cell) and $d=12$ muc. These values were chosen because the bulk behavior was reproduced, according to the scaling finite size theory [17,18]. Bulk parameters that were considered were the metal–insulator transitions temperature T_{MI} and T_C, which are reported to be at approximately 260 K [10,19–22]. The Hamiltonian reads as follows:

$$H = -J \sum_{<i \neq j>} S_i \cdot S_j - K \sum_i (S_i \cdot \hat{a})^2 - h \sum_i s_i \cdot \hat{h} \tag{1}$$

where $\boldsymbol{S_i}$ and $\boldsymbol{S_j}$ represent the magnetic moments per muc that result from the Heisenberg spins model. The first term refers to the magnetic nearest neighbor interaction, which involves three types of exchange parameters (J) depending on the interaction type: Mn^{3+eg}–O–Mn^{3+eg}, Mn^{3+eg}–O–Mn^{4+d3} or $Mn^{3+eg'}$–O–Mn^{4+d3}. The second sum corresponds to the magnetocrystalline anisotropy effect, where K is the respective constant and $\hat{a}$is the easy axis direction. In the last term, h represents the external magnetic field, and$\hat{h}$ indicates the magnetic field directions. The values for J and K were taken from the literature [14,15].

At each temperature, 2×10^4 Monte Carlo steps (MCS) were used to reach the equilibrium before averaging the physical quantities over the following 1×10^4 MCS. After this procedure, the resistivity for the system in magnetic equilibrium is simulated.

For the resistivity measures, a model that is similar to it reported by Vandewalle for the CMR calculation was used [23]. In this model, the Heisenberg model for interacting spins, the Drude model for electrical conductivity, and domain wall scattering for electron hopping were combined. By using these basic elements, magnetic domain effects are taken into account. The model consists in, once the sample reaches the magnetic equilibrium, the electrons will be transmitted through the sample, following the next expression that gives the probability of the electron hopping:

$$p = \exp(-\gamma\delta) \tag{2}$$

Thus, the probability that the electron will be stopped is $1-p$. The factor γ is a dimensionless parameter that acts as a potential barrier ($\gamma=1$) and δ corresponds to the magnetic domain size that refers to the number of spins contained in a domain. Other types of scattering have been neglected. The collision frequency ν was computed by counting the number of times that the carriers are dispersed before they arrive to the topside of the sample. This collision frequency is obtained from a counter that is actualized each time that the electron cannot hop between two neighbor ions. The expression for calculating ν reads:

$$\nu = d + \frac{d}{\delta} \sum_{i=1}^{+\infty} (1-p)^i \tag{3}$$

where d is the sample thickness, $(1-p)^i$ is the probability that the electron remains blocked i successive times on a magnetic wall before being transmitted.

According to the magnetic criteria, the degrees of freedom in the magnetic moments per unit cell depend on the magnetic and thermal conditions. These conditions are governed by each term of the Hamiltonian, and the stability arises from the temperature influence in the metropolis algorithm [24]. Carriers have a hopping motion along and across the lattice, being in agreement with the Kronig–Penney model, while there are not vacancies that force carriers to move in other directions. Lorentz forces are neglected because the mean free path is short [23]. The carrier hopping depends on the relative angle between the neighbor spins (θ). According to Anderson and Hasegawa, the hopping probability is proportional to $\cos(\theta/2)$ [25]. The electron is stopped with a probability $(1-p)$ or is transmitted with a probability p. According to the tunneling effect, p is assumed to be decreasing exponentially as a function of the cluster size. The resistivity model is expressed in Eq. (4) according to the Drude Formula:

$$\rho = \frac{m_e \nu}{ne^2} \tag{4}$$

In this model, a relaxation time is not considered, and ν is the number of times per second that electrons collide before crossing a magnetic domain. The collision time is approximately 10^{-15} s. Here, m_e and e are the mass and charge of the electron, respectively. The carrier density is $n=1.144 \times 10^{28}$ electrons/m^3.

On the other hand, the Drude formula does not exhibit an explicit evidence of the vacancies influence; nevertheless, this influence is reflected in the collision frequency calculation during the process of electron hopping. In the resistivity model, when the electron finds a vacancy, there is an interruption in the electron trajectory, forcing it to change its direction. This situation changes the mean free path of the electron and consequently the resistivity. Then, because of this increase in the mean free path, the resistivity of the sample also increases.

The magnetoresistance (MR) is the resistivity change percentage evaluated in the presence of an external magnetic field h with respect to the resistivity without applying a magnetic field. The temperature step was 1 K for the resistivity as a function of the temperature; while in the case of the properties as a function of