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Monte Carlo simulation of charge mediated magnetoelectricity in multiferroic bilayers

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ABSTRACT

Simulations of a bilayer ferroelectric/ferromagnetic multiferroic system were carried out, based on the Monte Carlo method and Metropolis dynamics. A generic model was implemented with a Janssen-like Hamiltonian, taking into account magnetoelectric interactions due to charge accumulation at the interface. Two different magnetic exchange constants were considered for accumulation and depletion states. Several screening lengths were also included. Simulations exhibit considerable magnetoelectric effects not only at low temperature, but also at temperature near to the transition point of the ferromagnetic layer. The results match experimental observations for this kind of structure and mechanism.

1. Introduction

Ferroelectric (FE) materials are dielectrics that maintain a net polarization even at zero electric field, property associated to the piezoelectric phenomenon. This characteristic is used in several technological applications, such as movement and pressure sensors, accelerometers, actuators and gyroscopes [1,2]. On the other hand, ferromagnetic materials (FM) retain magnetization even at zero magnetic field. They can be used in data store devices such as flash and hard drives. While ferroelectricity is associated to the charge, ferromagnetism is caused by the spin. Among the known materials, very few exhibit ferroelectricity and ferromagnetism simultaneously. Materials that show a direct relationship between both ferroelectric and ferromagnetic phenomena (magnetoelectric (ME) effect) are yet scarcer [3–5]. A new area in device design focuses on the possibility of building heterostructures that include, high performance ferroelectric and ferromagnetic materials with a considerable ME effect [6]. A first attempt for theoretically explaining the ME phenomenon was carried out in 1959 by Landau and Lifshitz. They proposed the existence of an additional term αHE in the free energy Hamiltonian, where α is a proportionality constant and H and E are magnetic and electric fields, respectively. Although this macroscopic description, followed by other authors [7,8], explains the relationship between the electric and magnetic fields, it lacks a more detailed correlation between the two elements that are involved in these systems, charge and spin. Janssen et al. [9,10] proposed an improved description of the interaction between the FE and FM components of the ME system. Using this model, they simulated the dynamics and configurations of domain walls for the unidimentional case. Given the difficulty of solving this model in greater dimensions, Li et al. [11] implemented an algorithm based on the Monte Carlo method for a two-dimensional lattice, in which magnetic and electric orders were imposed at each lattice point. Their results showed that the ME coupling, as well as the electric field, can produce a weak FM ordering.

Leufke et al. [12] grew $La_{0.87}Sr_{0.13}MnO_3/PbZr_{0.52}Ti_{0.48}O_3$ (PZT/LSMO) heterostructures by performing in situ magnetometry studies. These studies allowed precise measurements of the ME effects present between these materials. Such effects were associated to the charge accumulation at the interface, due to the PZT polarization under the effect of an electric field. This charge accumulation causes electron migration from the FM material toward the interface, creating a magnetic variation similar to that observed in manganite (LSMO) doping. According to the manganite phase diagram [13], this variation leads to greater critical temperatures and lower saturation magnetization. However, the decrease in the magnetization is higher than expected when only the charge accumulation effect is considered. Another study for $BaTiO_3/La_{0.67}Sr_{0.33}\ MnO_3$ (BTO/LSMO) heterostructures allows to conclude that the charge accumulation not only causes effects similar to the doping phenomenon, but also favors a modification of the kind of magnetic coupling in the first two layers of the magnetic material, shifting from the FM interaction in the depletion stage (charge carriers depletion from the interface) to an AF coupling in the accumulation stage (carriers accumulation at the interface).

In this work, Monte Carlo simulations of FE/FM bilayers in three-dimensional heterostructures were carried out. Magnetic and electric orders were individually imposed. Afterwards, the

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system was relaxed using the Metropolis dynamics and a model that included ME effects associated to the charge accumulation at the interface. The proposed Hamiltonian and the conditions given to it allowed to reproduce, for the first time, experimental behaviors through the Monte Carlo method (e.g. the shifting of the critical temperature in the ferromagnetic material and significant changes in the magnetic ordering type, when exposed to an external electric field). These behaviors were observed during accumulation and depletion periods in PZT/LSMO and PZT/BTO real systems.

2. Model and simulations

The simulations, considered a Hamiltonian for a tridimensional cubic system of $L \times L \times d$ dimensions, with periodic boundary conditions in the x–y plane and free boundary conditions out of the plane (z axis). Such a system is composed by two layers with thicknesses of $d1$ and $d2$; FE and FM order parameters were imposed to lower and upper layers respectively, through the electrical displacement ($\vec{u}$) and the Heisenberg spin ($\vec{S}$). Additionally, interactions between electric and magnetic systems were considered. According to the model described in [9,10], the following Hamiltonian was proposed:

$$H = H_{FE} + H_{FM} + H_{ME}, \tag{1}$$

where H_{FE} and H_{FM} represent the contributions of the electric and magnetic systems, respectively, and H_{ME} corresponds to the interaction between both, magnetic and electric layers. For the FE system, the following DIFFOUR Hamiltonian [10] was assumed:

$$H_{FE} = \sum_i \left(\frac{P_0^2}{2m} - \frac{a}{2}\vec{u}_i^{\,2} + \frac{b}{2}\vec{u}_i^{\,4} \right) - \sum_{nn} U_{ij}\left(\vec{u}_i \times \vec{u}_j\right) - \sum_i \vec{u}_i^{\,z} \times \vec{E} \tag{2}$$

Here, $\vec{u}_i$ is the ferroelectric dipole associated to the ith site, $(P_0^2/2m)$ is the kinetic energy, a and b are the double-well potential parameters for the ferroelectric spins, and U_{ij} is the FE exchange coefficient. Being $u\vec{}_i$ constant in magnitude and under a suitable reference system, the Hamiltonian can be rewritten [14] as

$$H_{FE} = -\sum_{nn} U_{ij}\left(\vec{u}_i \times \vec{u}_j\right) - \sum_i \vec{u}_i^{\,z} \times \vec{E}, \tag{3}$$

where $\vec{u}_i^{\,z}$ is the component of $\vec{u}_i$ in the z axis and E represents the electric field acting on the z direction.

For the magnetic system, a Heisenberg Hamiltonian was considered [15], given by

$$H_{FM} = -J\sum_{nn} \vec{S}_i \times \vec{S}_j - h\sum_i S_i^x - K\sum_i (S_i^x)^2, \tag{4}$$

being J the FM exchange constant, K the anisotropy constant, h the external magnetic field, $\vec{S}_i$ and $\vec{S}_j$ the spins associated to the ith and jth sites, respectively, and S_i^x the component of $S\vec{}_i$ in the x direction. In this model, J takes a $J1$ value for the interaction between one spin and its nearest neighbors, as long as this ion is out of the screening length (number of FM layers that provide charge carriers to the interface). Otherwise, J takes a $J2 > J1$ value if the ion is placed into that length and contributes to the screening.

For the ME coupling or interaction between the two subsystems, the subsequent model is proposed:

$$H_{me} = \sum_k g_{me} u_k^z \vec{S}_i \times \vec{S}_j. \tag{5}$$

In this expression, g_{me} is the parameter that fits the ME coupling intensity between the z component of the electrical displacement u_k^z and the magnetic interaction between spins. While the sums in Eqs. (3) and (4) consider nearest neighbor interactions (n.n.), in Eq. (5), $\vec{S}_i$ and $\vec{S}_j$ correspond to neighbor spins of $d1+1$ and $d1+2$ layers, exactly above the electric dipole u_k, which belongs to the $d1$ layer that is closest to the interface. Unlike the Janssen model, spatial and temporal inversion symmetries are not required, since both are broken at the interface between FE and FM materials, allowing the odd power term in u_k^z.

For positive values of U and J, FE and FM interactions are activated, and for positive values of g_{me} and u_k^z, an antiferromagnetic (AF) coupling between $d1+1$ and $d1+2$ layers is favored. This AF coupling competes with the FM one generated by the exchange parameter J. In order to simulate the charge accumulation mechanism at the interface [16], a restriction is imposed to the Hamiltonian. According to this restriction, the ME contribution only occurs when the u_k^z in the FE system of the layer that is nearest to the interface reaches a positive value. The former is justified as the electric polarization at the interface is the source of the screening phenomenon, in which spins coming from the ferromagnetic layer take part. It is assumed that if the electric displacement at the interface is zero or takes negative values, the ME effect is not present, and the magnetic system, in the vicinity of this site, behaves as an independent system, without any coupling to the FE layer. Simulations take into account the carriers accumulation at the interface by means of g_{me}, $J1$, and $J2$ parameters, not only to show an AF interaction in the first two layers of the magnetic system, but also for modeling experimentally observed changes at the critical temperature for this kind of heterostructures [17]. In the system under study, it is assumed that the screening length goes beyond the first two layers, considering a carrier emptying from layers that are more distant from the interface. In the model, the hole generation in these layers, favors an FM ordering through the exchange constant $J2$.

As it has been stated, this change in the magnetic ordering has been identified in PZT/LSMO and BTO/LSMO bilayers. The hole accumulation at the LSMO interface is comparable to a higher Sr doping in the manganite, being responsible for a greater critical temperature and a lower magnetization. To include this behavior in the present model, $J1$ and $J2$ exchange parameters were taken for carrier depletion and accumulation states in the magnetic system. For the depletion process, the constant considered was lower than that for the accumulation one, in order to be consequent with the doping and critical temperature changes mentioned above.

Initially, high temperature or disorder conditions in the spin and dipole directions, were imposed to the system. To simplify the model, an electrical displacement of ± 1 was randomly assigned at each lattice point in the FE layer, in one of the six directions ($\pm x$, $\pm y$, $\pm z$). In the FM layer, spins with $|\vec{S}| = 1$ were also randomly assigned, but in any direction, following a uniform distribution. For this initial temperature, new random $\vec{S}_i$ or $\vec{u}_i$ were chosen, and the energy change caused by this movement was calculated. This change was accepted or rejected according to the Metropolis Algorithm [15]. In order to ensure the convergence in the calculus of the observables, the lattice was scanned 10,000 times, where each time is considered as a Monte Carlo step (mcs) that can be taken as the time scale of simulations. Observables of interest as electric polarization in z, P_z, and magnetization in x, M_x, were averaged over the following 5000 mcs. These quantities were calculated according to (6) and (7):

$$P_z = \sum_i u_i^z \tag{6}$$

$$M_x = \sum_i S_i^x. \tag{7}$$

The process was repeated, lowering the temperature in a range ensuring a disorder–order change in both FE and FM systems.

From the calculation of these observables, it was possible to determine polarization and magnetization curves depending on

the temperature, hysteresis loops and the ME interaction in the heterostructure.

Values of $J1$ and U were taken in such a way that the critical temperature of the FE layer was greater than for the magnetic layer, as it can occur in several systems of interest.

3. Results and discussion

3.1. Influence of the ME exchange parameter g_{me}

The ME exchange parameter g_{me} was varied during the accumulation period, in order to determine its influence on the system behavior. The magnetization curves exhibit a critical point at $g_{me} \approx 3.0$, from which marked differences in the magnetization magnitude were observed during the accumulation and depletion periods (Fig. 1(a)). At lower values of g_{me}, the system behaves as a classical ferromagnet, polarizing all the spins in a unique direction. On the other hand, at higher values of g_{me} and low temperatures, an AF ordering appears in the first two layers of the magnetic subsystem.

Finally, for $g_{me} = 0$, a square hysteresis loop was obtained, with a remanent magnetization corresponding with the tendency of all the dipoles to be ferromagnetically aligned in the $+x$ direction. Changes in g_{me} do not influence the coercive field; however, they have a strong influence on the remanent magnetization. This behavior is due to the fact that spin inversion out of the AF ordering continues being governed by the exchange constant $J1$. For $g_{me} = 5.0$, an analysis of the spin evolution on each lattice site allowed to identify the presence of an AF transition in the first two layers of the magnetic system. Nevertheless, for this value of g_{me}, the application of greater external fields can modify the dipoles alignment in AF state, forcing them to be oriented in the same direction (FM). This behavior is evidenced by the plateau exhibited in the corresponding hysteresis loop (Fig. 1(b)).

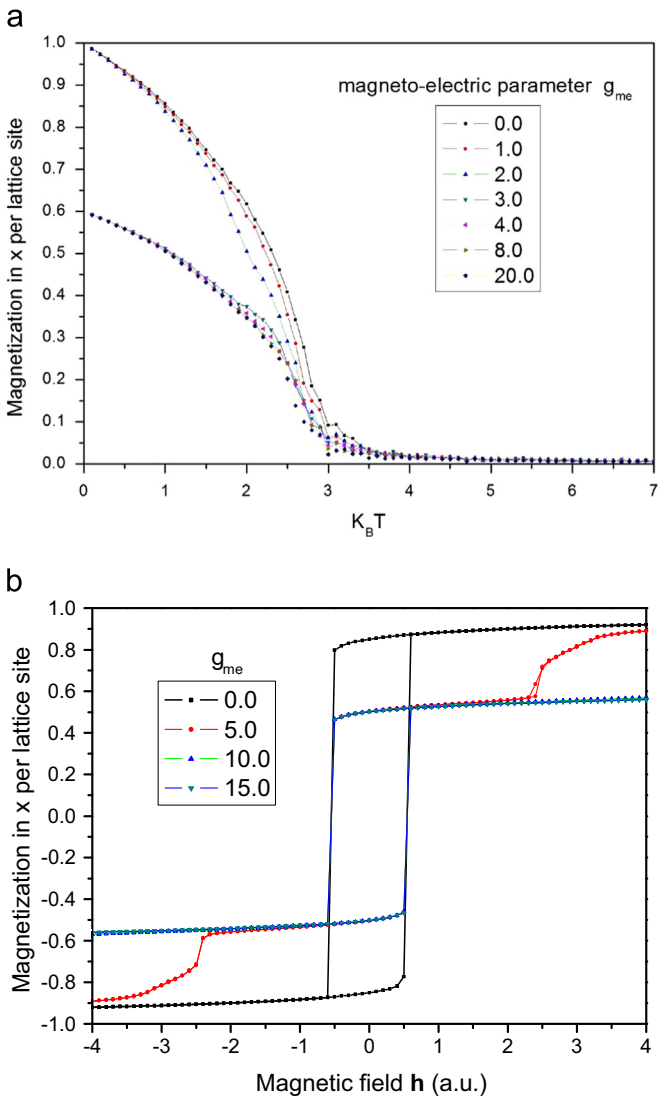

Fig. 1. (a) Magnetization per lattice site as a function of K_BT and (b) magnetic hysteresis loops, for different g_{me} values and $J1 = 1.0$.

3.2. Screening effect

As it was mentioned above, the screening effect of electrons coming from the FM layer was taken into account in the model by means of the magnetic exchange constant $J2$, characteristic of the accumulation period. When $J2$ is increased, the magnetization curves in the accumulation period exhibited a shifting of the transition temperature toward greater values (Fig. 2(a)). Then, two general situations can be observed: (i) at lower values of $J2$, the magnetization curves in accumulation and depletion states are separated until they reach their maximum saturation value ($Mx = 1.0$); and (ii), from a value of $J \approx 1.5$, the shifting in the critical temperature is high enough for generating three regions of interest between these curves (Fig. 2(a) and (b)). In the first region, characterized by high temperatures, accumulation and depletion curves are practically indistinguishable, and the paramagnetic character takes precedence. In the second region, which is close to the transition temperatures, until a cutoff temperature $T_x \approx 1.5$, the accumulation curve shows greater values of magnetization than in the one corresponding to the depletion period. Finally, in the third region, determined for $T < T_x$, an opposite behavior was observed: there were lower values of magnetization in the accumulation period in comparison with the depletion period. This three regions have been experimentally reported in PZT/LSMO heterostructures [16,17]. In the works referenced, authors showed that the ME effect is associated to the charge density at the interface. Calculating the magnetization difference between the accumulation and depletion states as a function of the temperature (Fig. 3(a)), a significant ME effect was observed not only at low temperatures, but also at values near the critical temperature of the ferromagnetic material. In theory, this behavior allows the study and application of the ME effect at room or even greater temperatures, depending on the kind of FM compound included in the heterostructure. Experimentally, in [17] the ME of (PZT/LSMO) samples was measured as a function of the temperature, finding a behavior very similar to the observed in our simulations. On the other hand, an increase in the value of $J2$ produces greater coercive fields and remanent magnetizations in the hysteresis loops (Fig. 3(b)). The former is explained by the corresponding increase in the FM interaction and the requirement of greater magnetic fields for causing the spins inversion.

In Fig. 4, the magnetization response to the external electric field is observed for temperatures lower and greater than the cutoff value T_x. According to this figure, for $T < T_x$, the magnetization decreases as the electric field is increased, whereas for $T > T_x$, the magnetization increases along with the electric field. Both loops show similar variations in the magnetization magnitude (loop height), although the ME loop at low temperature exhibits a greater width than the one obtained for $T > T_x$ near the critical point. This effect can be associated to the greater magnetic order present at low temperatures. Curves with similar tendencies have been reported in experimental works, previously mentioned, for this type of multiferroic structures [12,16,17].

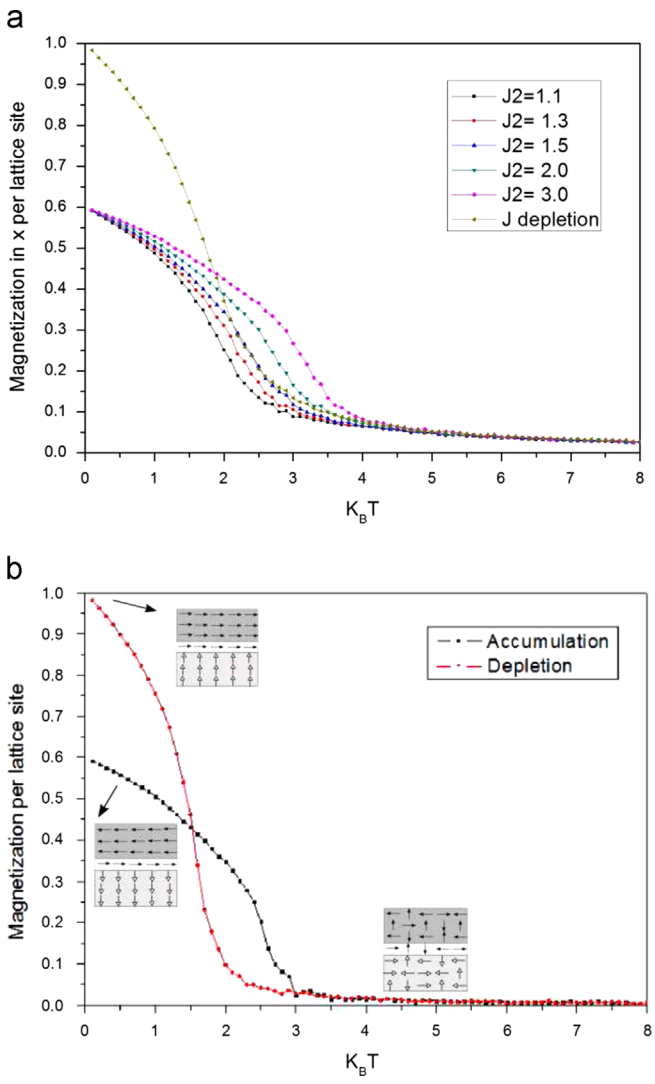

Fig. 2. (a) Magnetization per lattice site as a function of K_BT for several J2 values and (b) magnetization curves corresponding to the depletion (negative electric field) and the accumulation state (positive electric field) at $J1=1.0$ and $J2=2.0$. The insets show the orientation of magnetic spins (black arrows) and electric dipoles (open-headed arrows) for both states, at high and low temperatures.

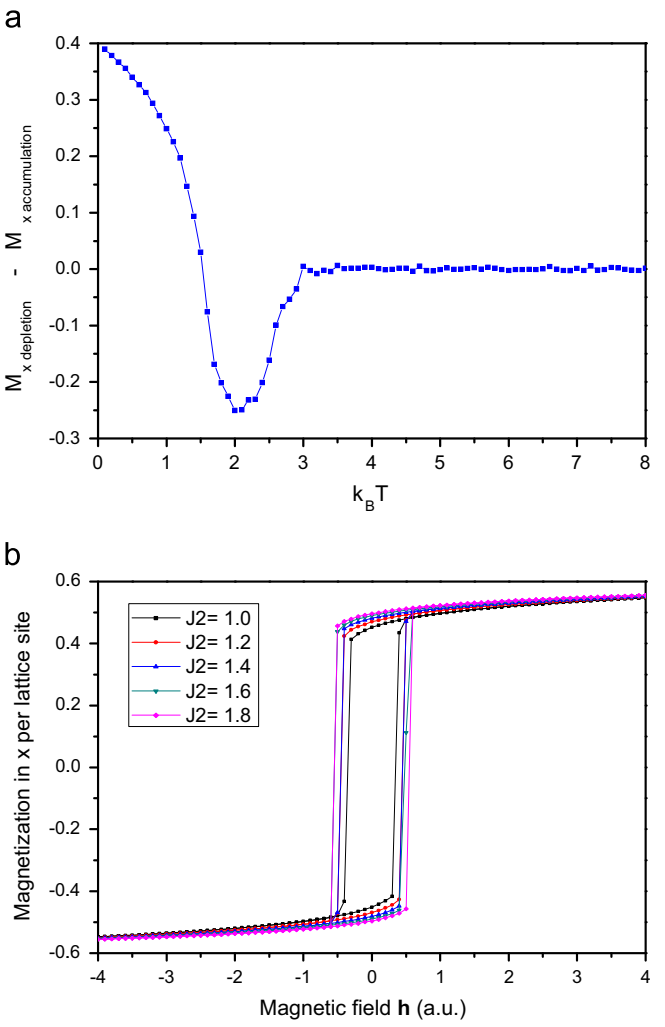

Fig. 3. (a) Difference between the magnetization in x direction for accumulation and depletion states as a function of K_BT corresponding to $J2=2.0$ and (b) magnetic hysteresis loops for different values of $J2$.

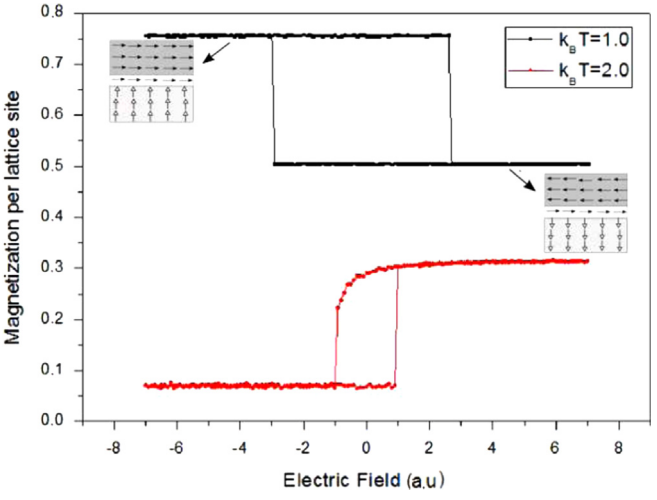

Fig. 4. Magnetoelectric effect. The electric field has been taken as positive in the direction that favors the hole accumulation in the magnetic material. The insets show the orientation of magnetic spins (black arrows) and electric dipoles (open-headed arrows) for both depletion and accumulation stages.

3.3. *Screening length effect*

Even though the ME effect mediated by charge has been associated to a purely interface phenomenon, it is well known that the screening can extend its influence to several lattice units far from the interface [18]. The effect of the screening intensity on this model is considered when the number of layers affected by the exchange interaction $J2$ is varied. In Fig. 5(a), results of simulations for screening lengths between 1 and 5 u.c (unit cells) are shown. According to these curves, the effect of increasing the number of layers contributing to the screening, results in an increase in the system magnetization, since more layers interact ferromagnetically with a greater exchange constant 2. For screening lengths of 1 or 2 layers, the magnetization increases, but not high enough for generating the three regions before described, as it occurs for the other simulated screening lengths. In real samples, the screening length is linked to several factors, such as the quantity of available charge carriers and the facility with which these carriers can move to the interface under an electrostatic field effect generated by the FE material. In PZT/LSMO and PZT/LCMO thin films, it was found that the inclusion of oxygen vacancies reduces the number of carriers in the material. This reduction can imply that a greater number of FM material layers might be required to compensate the electric polarization present in the FE system [19].

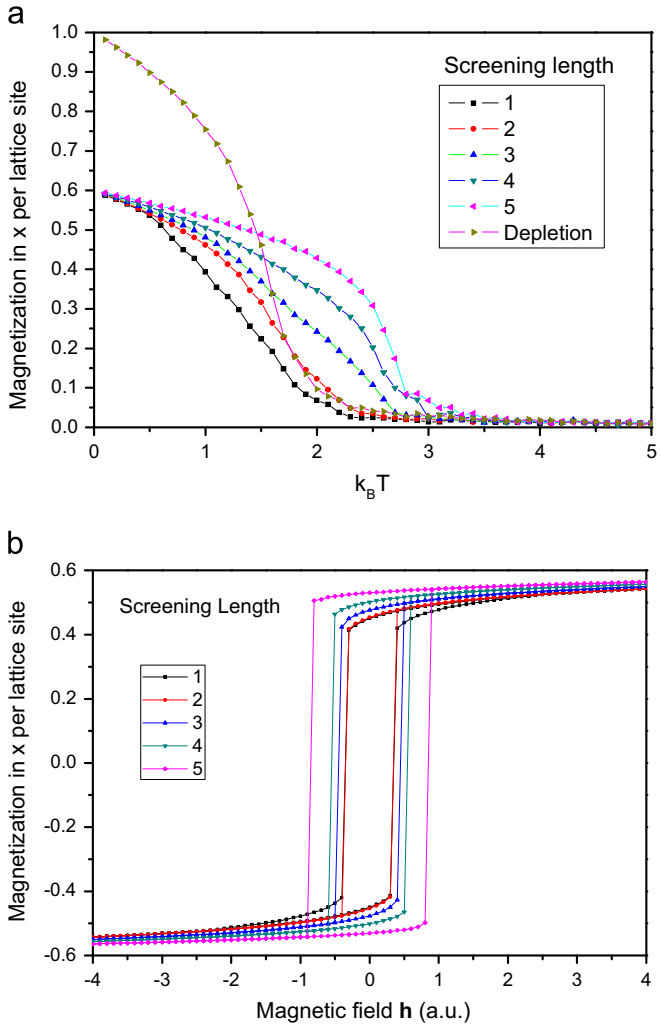

Fig. 5. (a) Magnetization per site as a function of K_BT and (b) hysteresis loops corresponding to several values of the screening length.

The increase in the screening length generates hysteresis loops with greater coercive fields and remanent magnetizations (Fig. 5(b)). From the point of view of this model, the increase of both loop width and remanent magnetization is caused by the increase in the magnetic lattice sites that interact with $J2 > J1$.

4. Conclusions

Simulations based on the Monte Carlo method and Metropolis dynamics, applied to multiferroic systems of FE/FM bilayers were carried out. A generic model based on a Janssen-like Hamiltonian was proposed, including characteristic conditions of an ME interaction explained by a charge accumulation mechanisms at the interface. Magnetic exchange constants were incorporated for the accumulation and depletion states of carriers, as well as several screening lengths. The inclusion of these parameters allowed us to obtain behaviors that were experimentally observed before for this kind of heterostructures and mechanism. Particularly, the model attains to reproduce the ME effect associated to the appearance of an AF phase at the interface, along with the change in the transition temperature of the magnetic layer, produced by the application of an external electric field. This phenomenon has been observed in PZT/LSMO and BTO/LSMO structures for certain doping concentrations in the manganite, ensuring the strong influence of the ME mechanism because of carrier accumulation at the interface, with neglected contributions of structure deformations.

The obtained results are consequent with the experimental observations that evidence the possibility to obtain a considerable ME effect, not only at low temperatures, but also at temperatures near the critical temperature of the ferromagnetic material. This set of features points to the potential design of devices that can work at temperatures close to or even greater than room temperature.

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