Antiferroelectric hysteresis loops with two exchange constants using the two dimensional Ising model

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Monte-Carlo simulations are carried out to reproduce hysteresis loops of antiferroelectric single crystals using an Ising Hamiltonian in two dimensions where pseudospin interactions are defined by two constants. It is shown that with this approach, hysteresis loops can be obtained in very good qualitative agreement with the experiments. While our approach is similar to that of Milhazes *et al.* [Phys. Status Solidi B **242**, 1141 (2005)], we also demonstrate that the hysteresis loop shapes heavily depend on the ratio of the electrostaticlike term to the intrinsic Hamiltonian of the system. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2814059]

Studies on ferroelectric-to-antiferroelectric (FE-AFE) transitions in crystals such as $PbZrO_3$ (PZO) and hydrogen containing ones such as KH_2PO_4 (KDP) have been undertaken to gain an in-depth understanding of the interesting electrical properties of such crystals. Various approaches within the mean-field approximation and using Ising-type Hamiltonians have been developed to unveil the possible interactions taking place in crystals showing FE and AFE behaviors including defect related phenomena.[1–11] Moreover, superlattice and bilayer structures containing FE and AFE components have been both experimentally and theoretically analyzed to compare the impact of interfaces on electrical properties and hysteresis loop shapes.[11–15] Phenomenological approaches and mean-field approximation for the Ising model were adopted where the pseudospin of site i is a function of the average internal field due to the presence of neighboring pseudospins, and where the interaction energy of fluctuations of the spin variables around the mean-value is neglected.[16] Thus, choosing a range of J/kT ratios, where J is the interaction constant, k is the Boltzmann constant, and T is the temperature in Kelvin (K), various shapes of loops were obtained via different spin interaction strengths. The impact of electrostatics and intrinsic interactions have been simulated by Potter *et al.* and Li *et al.*, taking into account the domain orientations[17,18] using a double-well potential.

On the other hand, such extensive amount of work undertaken to shed light on characteristics of materials showing FE and AFE behaviors indicates that there exists an on-going debate to attribute the observed properties to various factors. Several studies have been published where the authors make use of various potentials to stand for the interactions in the crystals. The majority of these studies focus on the transverse Ising model[19] (TIM) where the transition of FE loops to AFE or mixed ones can be explained by the magnitude of the transverse field in which the exchange interactions take place, such as in KDP. In addition, strong AFE interface coupling between ferroelectric slabs and/or domains was theoretically shown to produce double loops.[11,12,14] However, there are only a few analytical[3,6,10] studies focusing on the energetics that give rise to the well-known double hysteresis loops in perovskites such as PZO.

In this letter, we carry out Monte-Carlo (MC) simulations to model the FE-AFE loops of a structure with hypothetical dipole moments by introducing two interaction constants, one of which represents head-to-tail coupling J_{FE} and the other sideways coupling J_{AFE}, where the latter can be perceived to give rise to the same effect as the transverse field term in TIM. We show that such a choice of Hamiltonian can qualitatively reproduce hysteresis loops of PZO. The simplicity of the approach allows one to effectively visualize the competition between the assigned intrinsic spin energy and the electrostaticlike energy of the applied field. The Ising model with spins $S_i = \pm 1/2$ is used on a two-dimensional 30×30 grid within the nearest neighbor exchange approximation. By employing a range of J_{FE}/J_{AFE} ratios, loops with various AFE behaviors are demonstrated. For this study, the value of the dipole moments of the sites determines the magnitude of the field at which the field-driven AFE-to-FE behavior takes place. J_{FE} has to be positive for parallel alignment, whereas J_{AFE} has to be negative for antiparallel alignment, which will impose a configuration of antiparallel columns of dipoles that are parallel in each column at zero applied field (Fig. 1). This approach is similar to that presented in Ref. 14 where domains of ferroelectric sites that couple to each other via an AFE interaction were introduced. In our case, instead of domains, one has columns of dipoles. Indeed, such a configuration imitates what has been predicted in the structural studies of PZO by Sawaguchi *et al.* and Jona *et al.*[20] The Hamiltonian we adopt in the light of the above statements is then

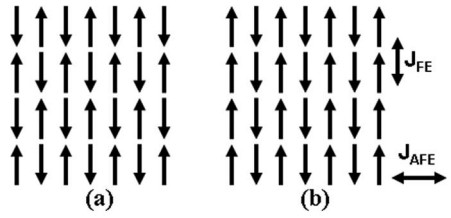

FIG. 1. (a) The usually adopted chessboard configuration with all antiparallel sites and (b) the configuration imposed on the system in the present work.

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$$\bar{H} = -J_{\mathrm{FE}}\sum_{1}^{n} S_i S_{i\pm1} - J_{\mathrm{AFE}}\sum_{1}^{n} S_j S_{j\pm1} - 2E_{\mathrm{app}}\mu_i\sum_{1}^{2n} S_i, \quad (1)$$

where the first summation is over the sites having coupling along z, the second term along x, and the last term is the electrostaticlike energy with E_{app} being the external field. μ_i is the magnitude of the dipole moment at site i, which in a way scales the strength of the last term in Eq. (1) to the rest. $2n$ is the number of sites in the grid, which is 900. Infinite boundary conditions in the plane $[x, S(1,z)=S(30,z)]$ are adopted with free upper and lower surfaces, resembling a thin film case. A Markov chain is constructed with random site selection and the kinetic Glauber formula[21] is used to find the probability of flipping a spin P in the form

$$P = \begin{cases} 1 & \text{if } \Delta\bar{H} < 0 \\ \dfrac{1}{2\tau_{\mathrm{MC}}}\left[1 - \tanh\left(\dfrac{\Delta\bar{H}}{2k_B T}\right)\right] & \text{if } \Delta\bar{H} > 0, \end{cases} \quad (2)$$

where τ_{MC} is a time step taken as unity and $\Delta\bar{H}$ is the energy difference between two consecutive configurations of the grid that differ by a single spin flip. Average spin versus applied field hysteresis loops of the structures are obtained by applying a sinusoidal electric field (amplitude varying from zero to $E_{\max}$ where $E_{\max} \geqslant 4J_{\mathrm{FE}}$ and is constant for all simulations) whose frequency is about 1/70 MC steps^{-1}[1], enabling the structure to evolve in a relaxed manner, eliminating polarization relaxation and loop swelling. The average spin (av.S) at any instant is given by

$$\mathrm{Av}.S = \frac{1}{2n}\sum_{1}^{2n} S_i. \quad (3)$$

Any flip of a spin at site i should lower the energy of the system with respect to its previous configuration. A flip that increases the energy of the system is accepted with the probability given in Eq. (2).

In Fig. 2(a), an experimentally obtained loop is given for an epitaxial PZO film on $SrTiO_3$ with $SrRuO_3$ electrodes having $[001]_{\mathrm{film}}/[001]_{\mathrm{substrate}}$ (Ref. 22) measured at room temperature, and in Fig. 2(b), results are given for different ratios of $J_{\mathrm{FE}}/J_{\mathrm{AFE}}$ keeping J_{FE}/kT constant for each of the two sets of plots. We note that well-defined AFE loops are produced if $\mu_i < S_i$ and $J_{\mathrm{FE}}/J_{\mathrm{AFE}} \geqslant -1/2$. In Fig. 3, the configurations at two different values of applied field are given, where the AFE configuration can remain stable before any FE cluster formation, unless the last summation in Eq. (1) reaches a comparable value with the second summation in our simulations. This indicates that there is a competition between the head-to-tail exchange and sideways exchange to attain minimum energy, and the FE clusters do not nucleate unless a critical electrostatic energy is reached due to an applied field. On the other hand, the AFE-to-FE transition also happens quite abruptly in real experiments implying a critical electrostatic energy to overcome the antiparallel configuration [Fig. 2(a)] that is strongly dependent on temperature.

The above discussion for a MC simulation is of course not so straightforward applicable to reality because the magnitude of the dipole moment in a real crystal will have a susceptibility to the applied field and to strain, making the situation much more complicated. For a perfect AFE crystal,

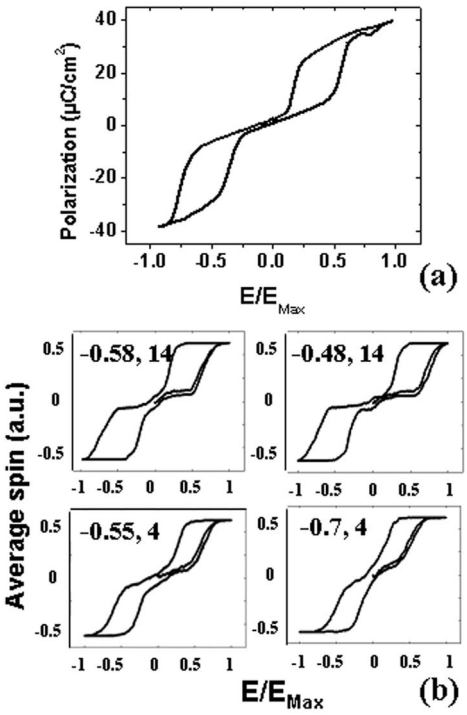

FIG. 2. (a) The experimentally obtained AFE loop for a 100 nm thick PZO film. (b) Hysteresis loops obtained from the MC simulations for four different $J_{\mathrm{FE}}/J_{\mathrm{AFE}}$ and J_{FE}/kT ratios (insets). E_{Max} in the experiment was 7×10^7 V/m.

one could assume that the dipole moments do not change dramatically with applied field [linear region in Fig. 2(a) before loop splitting] as long as the crystal is away from the Curie point (or Neel, for PZO). Thus, the relative magnitudes of the first two summations and the last term in Eq. (1) can act as a qualitative guide to evaluate the governing energetics and trends in real AFEs. In our simulations, the ratio of the dipole moment to the absolute value of spins is certainly an abstract assumption to check trends. A comparison of the hysteresis for $\mu_i/S_i = 0.4$ and $\mu_i/S_i = 1$ are given in Fig. 4.

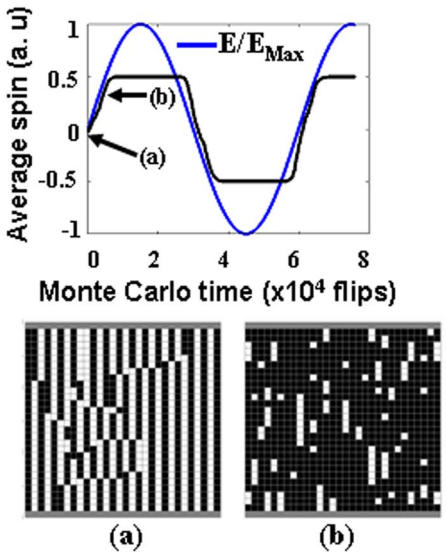

FIG. 3. (Color online) Snapshots of configurations (arrows numbered as a and b) at various stages of the simulations for $J_{\mathrm{FE}}/J_{\mathrm{AFE}} = -1/2$; (a) equilibrium at near-zero field and (b) low field configuration. Horizontal axis indicates number of flip attempts.

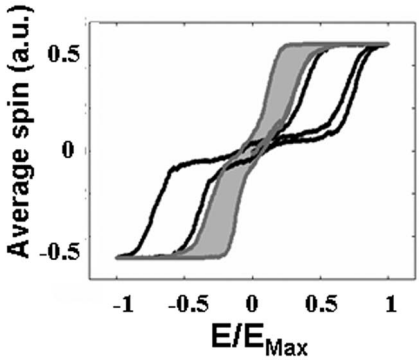

FIG. 4. Hysteresis loops for $\mu_i/S_i=0.4$ (black) and $\mu_i/S_i=1$ (shaded) for $J_{\mathrm{FE}}/J_{\mathrm{AFE}}=-1/2$ and $J_{\mathrm{FE}}/kT=4$.

The system has two different behaviors for two different μ_i/S_i ratios chosen. Hence, even if $\mathrm{abs}(J_{\mathrm{FE}}/J_{\mathrm{AFE}})\leqslant 1$, loops with FE-like character can be exhibited when $\mu_i/S_i>1$. This could somewhat imply a scenario for real life cases, where overcoming the energy barrier of an antiparallel alignment to induce parallel alignment is dependent on the strength of the dipole moments impacting the hysteresis loop shapes in addition to thermal fluctuations (J_{FE}/kT ratios in the simulations).

This study demonstrates that a system undergoing a FE-to-AFE (or vice versa) transition can be characterized by two interaction constants within the two-dimensional Ising approach, providing qualitative insight into experimentally obtained hysteresis loops. An equilibrium configuration of antiparallel columns of parallel dipoles is imposed on the system at zero field. Despite the simplicity of the model, a very good qualitative agreement with the experiment is attained. Another implication of the current analysis is the significance of the ratio of the electrostatic energy to the internal interaction energy that determines the nucleation of the parallel aligned clusters and their coalescence to form field-induced FE. Simulations in three dimension would yield slightly different results for the same $J_{\mathrm{FE}}/J_{\mathrm{AFM}}$ ratios used in two-dimension two dimension simply due to the change in number of neighbors of each site. This will impact the magnitude of the domain-wall energy but the main characteristics of the system should remain.

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