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Theoretical study of multiferroic thin films based on a microscopic model

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Abstract

The influence of the surface, film thickness, temperature and ion doping effects on the magnetic and electric properties in multiferroic thin films is studied by a combination of modified Heisenberg and transverse Ising models using a Green's function technique. It is demonstrated that the magnetization M , the polarization P , the critical temperatures T_N and T_C , the spin-wave energies E_m and E_e , and their damping are very sensitive to the exchange interaction constants on the surface (A_{1s} and J_s) and in the defect layers (A_{1d} and J_d). It has been found that the damping is enhanced compared to the case with no defect layers. We have obtained that M , P , T_N , T_C and the spin-wave energies could be increased or decreased by using different kinds of doping ions. The concurrent interaction mechanisms of the magnetic and electric subsystems are shown. The results are in qualitative accordance with the experimental data.

1. Introduction

In recent years multiferroics, defined as materials with the coexistence of at least two of the electric, elastic and magnetic orders in a single phase, have attracted considerable research interest. Ferroelectromagnets, also called magnetoelectric multiferroics, could be regarded as a subsystem of multiferroics, which possesses both electric and magnetic orders [1]. One of the well-known ferroelectromagnets is BiFeO₃ (BFO), which exhibits both ferroelectricity and antiferromagnetism (i.e. multiferroism), an intrinsic multifunctionality that would ostensibly make it a strong candidate for nanoscale electronics applications. Both its spontaneous polarization and saturation magnetization, however, are disappointingly low compared to many standard ferroelectrics and ferromagnets. Recently, Wang *et al* [2] reported an enhancement of the polarization (almost an order of magnitude higher than that of the bulk) and related properties in heteroepitaxially constrained thin films of BFO. The films also exhibit enhanced thickness-dependent magnetization compared to the bulk. This increase was attributed either to the formation of Fe²⁺ ions [3], to a homogenization of the magnetic spins [4] or to an increased canting angle [3]. Enhanced ferroelectric and magnetic properties in multiferroic thin films are obtained experimentally by many authors [5–7]. The values of the remanent polarization P_r and coercive field E_c are also

greatly enhanced [6, 7]. Nechache *et al* [8] have observed in Bi₂FeCrO₆ multiferroic thin films an increase in the macroscopic magnetization with decreasing thickness which could possibly be due to the increase of the canting angle and/or a re-ordering of the Cr and Fe cations. The dependence of the dielectric response on temperature in BFO thin films studied by Palkar *et al* [5] indicates an anomaly in dielectric constant $\epsilon(T)$ in the vicinity of the Néel temperature. This anomaly in $\epsilon(T)$ is explained as an influence of vanishing magnetic ordering on electric ordering of the BFO sample. The electric and magnetic properties of thin films could be affected by doping the sample with different ions. As shown in [9–17] the ferroelectric polarization and the saturation magnetization are greatly enhanced by doping with La, Ti, Sc, Nb and Cr ions. Doping with Mn ions does not lead to improvement of these properties [15], while doping with Ce ions reduces [18] the ferroelectric polarization of the thin film.

The deposition of a thin film on a substrate leads to the existence of considerable strain, resulting from differences in crystal lattice parameters, thermal expansion behavior between the film and the underlying substrate or defects formed during deposition. Consequently, the properties of thin films can be considerably different than the intrinsic properties of the corresponding bulk materials. The importance of substrate effects on phase transitions can be seen, for example, in STO thin films. STO is an incipient ferroelectric, remaining paraelectric down to 0 K. However, chemical substitution,

such as $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$, or stress by substrate effects can disturb this state, resulting in ferroelectricity. The most impressive experimental observation of biaxial strain coupling is that of Haeni *et al* [19]. STO thin films were grown coherently onto DyScO_3 in-plane tensile strain sufficient to not only raise the Curie temperature, but also to change an incipient ferroelectric into a genuine ferroelectric. A phenomenological thermodynamic theory of ferroelectric thin films epitaxially grown on cubic substrates is developed by Pertsev *et al* [20] using a new form of the thermodynamic potential, which is a function of polarization and strain. These two works on strain-induced ferroelectricity in STO is a clear and powerful demonstration as to how important substrate–film strain interactions can be. Liu *et al* [21] have considered the influence of the three-dimensional residual strain in multiferroic films. The authors have studied magnetically induced polarization using the Landau–Ginsburg–Devonshire thermodynamic theory. In the framework of a general Landau free energy function Jiang and Qiu [22] have investigated the ferroelectric and magnetic properties of BFO thin films. It was shown that the properties, such as lattice parameters, polarization and magnetization are functions of misfit strains. Based on the thermodynamic model, Lu *et al* [23] have studied the critical phase transition temperatures of the ferroelectric and ferromagnetic phases in multiferroic thin films. They are significantly affected by the induced elastic stresses arising from the ferroelectric/magnetic and the film/substrate interfaces. Using the Landau–Devonshire theory Ma *et al* [24] have investigated strain effects and the thickness dependence of the ferroelectric properties in epitaxial BFO thin films. Recently, density functional theory modeling of BFO and $\text{Bi}_2\text{FeMnO}_6$ epitaxial thin films was carried out by applying the generalized gradient approximation by Bi *et al* [25]. The electronic structure calculations are consistent with the electronic and optical properties of these films. The influence of the substrates on the properties of MF thin films will be studied in a future paper.

Most of the theoretical works [21–24] are based on the phenomenological Landau theory. In our previous papers we have proposed an alternative approach, investigating different static and dynamic properties of hexagonal multiferroic RMnO_3 compounds using a combination of the transverse Ising and Heisenberg models, taking into account the magnetoelectric coupling term [26, 27]. The coupling term between the ferroelectric and magnetic subsystems is considered to be biquadratic. The aim of the present paper is to study the magnetic and ferroelectric properties in multiferroic thin films based on the same microscopic model which is modified to describe thin film properties.

2. The model

The Hamiltonian of the multiferroic system can be presented as

$$H = H^e + H^m + H^{\text{me}}. \quad (1)$$

H^e denotes the Hamiltonian for the electrical subsystem within the framework of the transverse Ising model (TIM). Thus H^e

can be written as

$$H^e = -\Omega \sum_i S_i^x - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z, \quad (2)$$

where S_i^x, S_i^z are the spin-1/2 operators of the pseudo-spins, J_{ij} denotes the nearest-neighbor pseudo-spin interaction and Ω is the tunneling frequency. In this system the mean electric polarization is proportional to the z component of the pseudo-spins introduced in the TIM. In the ordered phase we have the mean values $\langle S^x \rangle \neq 0$ and $\langle S^z \rangle \neq 0$, and it is appropriate to choose a new coordinate system, rotating the original one used in (2) by the angle θ in the xz plane [26]. The rotation angle θ is determined by the requirement $\langle S^x \rangle = 0$ in the new coordinate system.

H^m is the Hamiltonian for the magnetic subsystem, which is given by the Heisenberg Hamiltonian:

$$H^m = -\frac{1}{2} \sum_{\langle ij \rangle} A_1(i, j) \mathbf{B}_i \cdot \mathbf{B}_j - \frac{1}{2} \sum_{[ij]} A_2(i, j) \mathbf{B}_i \cdot \mathbf{B}_j, \quad (3)$$

where \mathbf{B}_i is the Heisenberg spin at the site i and the exchange integrals A_1 and A_2 represent the coupling between the nearest and next-nearest neighbors, respectively. H is the external magnetic field parallel to the z axis. $\langle ij \rangle$ and $[ij]$ denote the summation over the nearest neighbors and the next-nearest neighbors, respectively.

The most important term in the model is H^{me} which describes the coupling between the magnetic and the electric subsystems in the ferroic compound:

$$H^{\text{me}} = -g \sum_{\langle ij \rangle} \sum_{kl} S_k^z S_l^z \mathbf{B}_i \cdot \mathbf{B}_j. \quad (4)$$

Here g is the coupling constant between the magnetic and the electric order parameters.

3. The Green's functions

The retarded Green's functions to be calculated are defined as the Green's function for the ferroelectric subsystem:

$$G_{ij}(t) = \langle \langle S_i^+(t); S_j^-(0) \rangle \rangle. \quad (5)$$

where S^+ and S^- are the spin- $\frac{1}{2}$ operators in the rotated system, and the retarded Green's function for the magnetic subsystem:

$$g_{ij}(t) = \langle \langle B_i^+(t); B_j^-(0) \rangle \rangle, \quad (6)$$

where B^+ and B^- are the Heisenberg spin operators. On introducing the two-dimensional Fourier transform $G_{n_i n_j}(\mathbf{k}_{\parallel}, E)$ (and analogously for $g_{n_i n_j}(\mathbf{k}_{\parallel}, E)$), one has the following form:

$$\begin{aligned} G^{+-} &= \langle \langle S_i^+; S_j^- \rangle \rangle_E \\ &= \frac{2\langle S^z \rangle}{N'} \sum_{\mathbf{k}_{\parallel}} \exp(i\mathbf{k}_{\parallel}(\mathbf{r}_i - \mathbf{r}_j)) G_{n_i n_j}(\mathbf{k}_{\parallel}, E), \end{aligned} \quad (7)$$

where N' is the number of sites in any of the lattice planes. $P(T) = 2\langle S^z \rangle$ is the relative polarization in the direction of the mean field. \mathbf{r}_i represents the position vectors of site i and

$n = 1, \dots, N$ denotes the layer ordering number beginning with one surface ($n = 1$) and terminating with the other surface ($n = N$). $\mathbf{k}_{\parallel} = (k_x, k_y)$ is a two-dimensional wavevector parallel to the surface. The summation is taken over the Brillouin zone. For the approximate calculation of the Green's functions we use a method proposed by Tserkovnikov [28], which is appropriate for spin problems. After a formal integration of the equation of motion for the Green's function, for example in (5), one obtains

$$G_{ij}(t) = -i\theta(t)\langle [S_i^+; S_j^-] \rangle \exp(-i\epsilon_{ij}(t)t) \quad (8)$$

where

$$\epsilon_{ij}(t) = \epsilon_{ij} - \frac{i}{t} \int_0^t dt' t' \left(\frac{\langle [j_i(t); j_j^+(t')] \rangle}{\langle [S_i^+(t); S_j^-(t')] \rangle} - \frac{\langle [j_i(t); S_j^-(t')] \rangle \langle [S_i^+(t); j_j^+(t')] \rangle}{\langle [S_i^+(t); S_j^-(t')] \rangle^2} \right) \quad (9)$$

with the notation $j_i(t) = \langle [S_i^+, H_{int}] \rangle$. The time-independent term

$$\epsilon_{ij} = \frac{\langle [[S_i^+, H]; S_j^-] \rangle}{\langle [S_i^+; S_j^-] \rangle} \quad (10)$$

is the soft mode energy in the generalized Hartree–Fock approximation (GHFA). The time-dependent term in equation (9) includes damping effects.

We have considered the ferroelectric subsystem with a simple cubic lattice. The pseudo-spin-wave energy is in the generalized Hartree–Fock approximation:

$$E_c(\mathbf{k}_{\parallel}) = 2\Omega \sin \theta + \frac{1}{2}P \cos^2 \theta J_{\text{eff}} - \frac{1}{4}P \sin^2 \theta J_{\text{eff}}(\mathbf{k}_{\parallel}) - \frac{1}{NP} \sum_{q_{\parallel}} \left(\cos^2 \theta J_{\text{eff}}(\mathbf{k}_{\parallel} - \mathbf{q}_{\parallel}) - \frac{1}{2} \sin^2 \theta J_{\text{eff}}(\mathbf{q}_{\parallel}) \times \langle S_{q_{\parallel}}^- S_{q_{\parallel}}^+ \rangle \right) \quad (11)$$

with

$$J_{\mathbf{k}_{\parallel}} = \frac{1}{2} J_{ij} (\cos(k_x a) + \cos(k_y a)). \quad (12)$$

The quantity $P(T)$ is the relative polarization in the direction of the mean field and is equal to $2\langle S^z \rangle$. $M(T) = \langle B^z \rangle$ is the relative magnetization and must be calculated from the Green's function (6). It can be seen that the pseudo-spin exchange interaction constant J_0 is renormalized due to the interaction constant between the electric and magnetic subsystems g to J_{eff} :

$$J_{\text{eff}} = J_{ij} + 2g(\langle B_i^- B_j^+ \rangle + \langle B_i^z B_j^z \rangle). \quad (13)$$

The following two solutions have been obtained for the rotation angle θ :

$$(1) \cos \theta = 0, \quad \text{i.e. } \theta = \frac{\pi}{2}, \quad \text{if } T \geq T_C;$$

$$(2) \sin \theta = \frac{4\Omega}{PJ_{\text{eff}}} = \frac{P_c}{P}, \quad \text{if } T \leq T_C.$$

The relative polarization is given by

$$P = \frac{1}{2N} \sum_{\mathbf{k}_{\parallel}} \tanh \frac{E_c(\mathbf{k}_{\parallel})}{2k_B T}. \quad (14)$$

For the magnetic subsystem the spin-wave energy from equation (6) in the generalized Hartree–Fock approximation is calculated to be

$$E_m(\mathbf{k}_{\parallel}) = \frac{1}{2\langle B^z \rangle} \frac{1}{N} \sum_{q_{\parallel}} (A_1^{\text{eff}}(\mathbf{q}_{\parallel}) - A_1^{\text{eff}}(\mathbf{k}_{\parallel} - \mathbf{q}_{\parallel})) \times (2\langle B_{q_{\parallel}}^z B_{-q_{\parallel}}^z \rangle - \langle B_{k_{\parallel}-q_{\parallel}}^z B_{k_{\parallel}-q_{\parallel}}^+ \rangle) + \frac{1}{2\langle B^z \rangle} \frac{1}{N} \sum_{q_{\parallel}} (A_2(\mathbf{q}_{\parallel}) - A_2(\mathbf{k}_{\parallel} - \mathbf{q}_{\parallel})) \times (2\langle B_{q_{\parallel}}^z B_{-q_{\parallel}}^z \rangle - \langle B_{k_{\parallel}-q_{\parallel}}^z B_{k_{\parallel}-q_{\parallel}}^+ \rangle). \quad (15)$$

The spin exchange interaction constant between next-nearest neighbors A_1 is also renormalized to A_1^{eff} , due to the coupling between the electric and magnetic subsystems g :

$$A_1^{\text{eff}} = A_1 + 2gP^2 \cos^2 \theta. \quad (16)$$

The relative magnetization M for arbitrary spin value S is given by

$$M = \frac{1}{N} \sum_{\mathbf{k}_{\parallel}} [(S + 0.5) \coth[(S + 0.5)\beta E_m(\mathbf{k}_{\parallel})] - 0.5 \coth(0.5\beta E_m(\mathbf{k}_{\parallel}))]. \quad (17)$$

4. Numerical results and discussion

This section presents results from the numerical calculations for the following model parameters: $A_{1b} = 158$ K, $A_{2b} = -60$ K, $\Omega_b = 2$ K, $J_b = 910$ K, $g = 50$ K, $S = 2$ for the magnetic spins and $S = 0.5$ for the pseudo-spins. They are appropriate for the description of BFO with critical temperatures $T_N = 640$ K and $T_C = 1100$ K. Due to the changed number of next-nearest neighbors on the surface and to the reduced symmetry, the exchange interaction constants A_1 and J can take values on the surface A_{1s} and J_s different from those of the bulk A_{1b} and J_b . First of all, we have studied the surface effects by calculating the magnetization, the critical temperature, the spin-wave energy and the damping for different values of the surface exchange interaction A_{1s} , constant film thickness N and wavevector $\mathbf{k} = 0$. The results for a thin film with $N = 5$ layers are presented in figures 1 and 2. It can be seen that the magnetization, spin-wave energy and phase transition temperature are highly sensitive to the strength of A_{1s} . For the case where the exchange interaction on the surface layer is smaller than the bulk one, $A_{1s} < A_{1b}$, for example $A_{1s} = 70$ K (figures 1 and 2, curve 1), the magnetization M , the spin-wave energy E_m and the critical temperature T_N are reduced compared to the case $A_{1s} = A_{1b}$ (curve 2). For $A_{1s} = 230$ K (figures 1 and 2, curve 3), i.e. $A_{1s} > A_{1b}$, an opposite behavior is observed; M , E_m and T_N are enhanced compared to the bulk (curve 2). The results obtained for the dependences of the ferroelectric properties, polarization P , energy E_c and the phase transition temperature T_C , on the exchange interaction on the surface J_s (figures 3 and 4) clearly illustrate the coupling between the two order parameters below T_N . This coupling is observed as a kink at the magnetic phase transition temperature in the $P(T)$ and $E_c(T)$ plots. This anomaly can be explained as an influence of

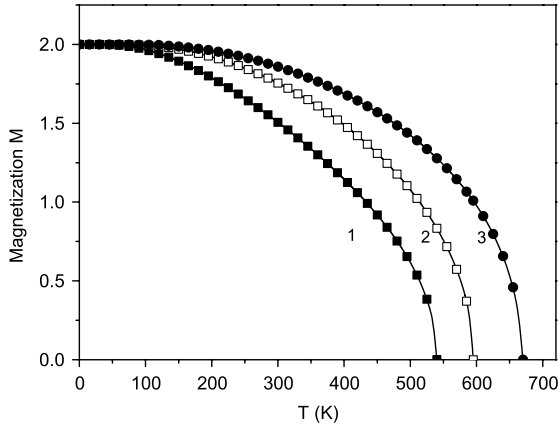


Figure 1. Temperature dependence of the magnetization M of a multiferroic thin film for $N = 5$, $J_s = J_b$ and different A_{1s} -values: 1— $A_{1s} = 0.45A_{1b}$; 2— $A_{1s} = A_{1b}$; 3— $A_{1s} = 1.5A_{1b}$.

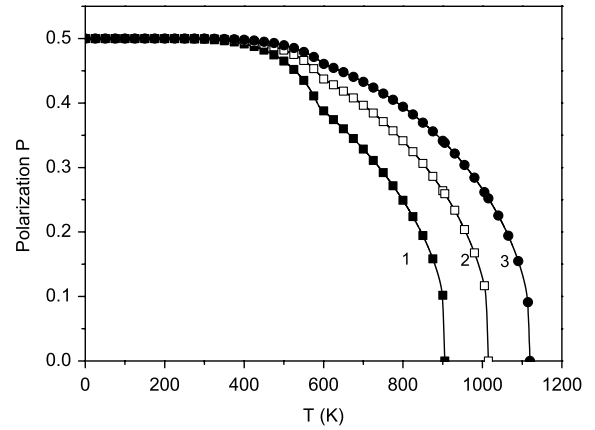


Figure 3. Temperature dependence of the polarization P of a multiferroic thin film for $N = 5$, $A_{1s} = A_{1b}$ and different J_s -values: 1— $J_s = 0.45J_b$; 2— $J_s = J_b$; 3— $J_s = 1.5J_b$.

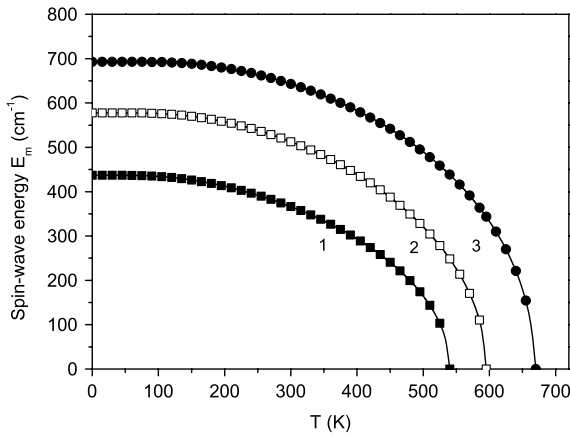


Figure 2. Temperature dependence of the spin-wave energy E_m of a multiferroic thin film for $N = 5$, $J_s = J_b$ and different A_{1s} -values: 1— $A_{1s} = 0.45A_{1b}$; 2— $A_{1s} = A_{1b}$; 3— $A_{1s} = 1.5A_{1b}$.

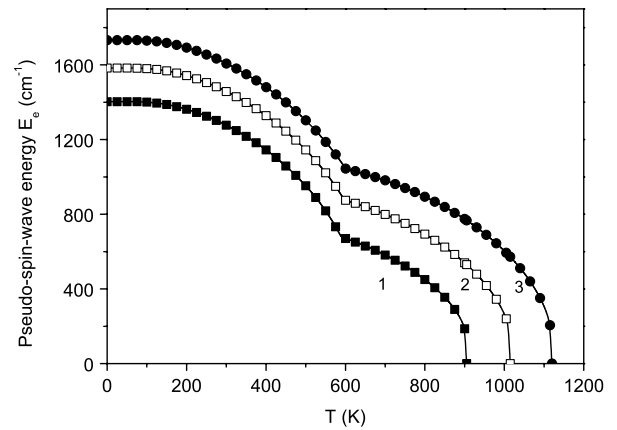


Figure 4. Temperature dependence of the pseudo-spin-wave energy E_e of a multiferroic thin film for $N = 5$, $A_{1s} = A_{1b}$ and different J_s values: 1— $J_s = 0.45J_b$; 2— $J_s = J_b$; 3— $J_s = 1.5J_b$.

vanishing magnetic ordering on electric ordering in the system. The dielectric response study with temperature in BFO thin films of Palkar *et al* [5] indicates an anomaly in the dielectric constant $\epsilon(T)$ in the vicinity of the Néel temperature. Lu *et al* [29] have also obtained a kink in the temperature dependence of the dielectric function ϵ in a magnetic field of multiferroic $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ thin films. The pseudo-spin-wave energies of the thin films could be larger or smaller compared to the bulk in dependence of J_s (figure 4), whereas the damping is greater than that of the bulk for both cases $J_s < J_b$ and $J_s > J_b$. The damping of the pseudo-spin waves is at low temperatures T very small, but with increasing T it increases very strongly.

In order to show the influence of the magnetic subsystem on the electric one we have studied the temperature dependence of the polarization for different values of the magnetic surface exchange interaction constants. The results are shown in figure 5. In the case of $A_{1s} > A_{1b}$ (curve 2) the Néel temperature T_N increases with increasing A_{1s} and comes near to the critical temperature of the electric subsystem T_C . When A_{1s} is large enough, i.e. $A_{1s} \gg A_{1b}$ (curve 3), the kink disappears and T_C slowly increases.

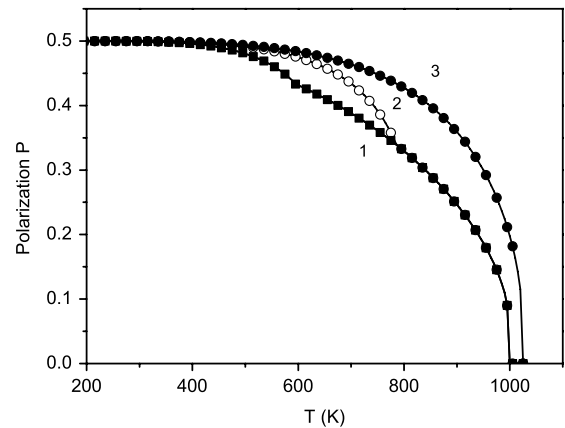


Figure 5. Temperature dependence of the polarization P of a multiferroic thin film for $N = 5$, $J_s = J_b$ and different A_{1s} values: 1— $A_{1s} = A_{1b}$; 2— $A_{1s} = 2A_{1b}$; 3— $A_{1s} = 3A_{1b}$.

Furthermore, we have investigated the dependence of the magnetization M , the polarization P , the phase transition temperatures, the spin-wave energies and their damping on the

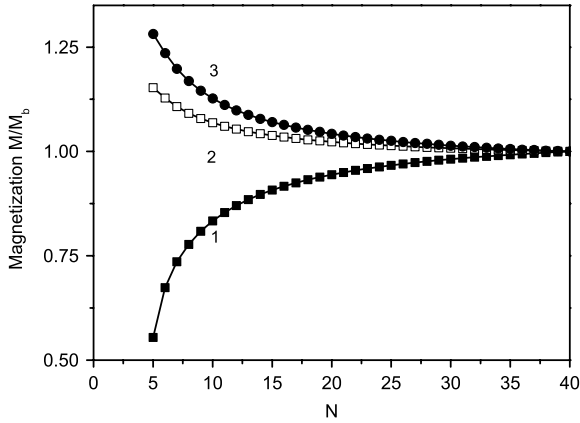


Figure 6. Thickness dependence of the magnetization M/M_b of a multiferroic thin film for $T = 500$ K, $J_s = J_b$ and different A_{1s} values: 1— $A_{1s} = 0.6A_{1b}$; 2— $A_{1s} = 2A_{1b}$; 3— $A_{1s} = 3A_{1b}$.

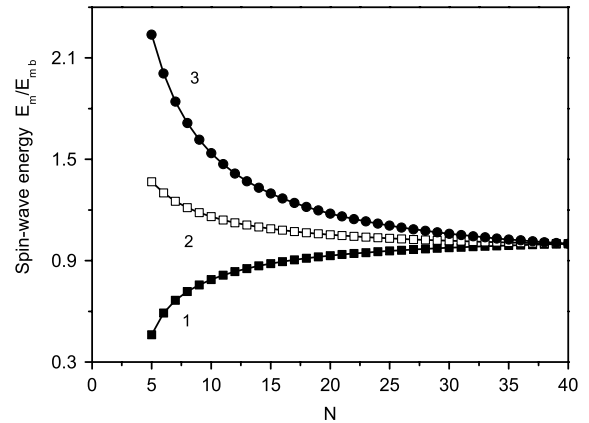


Figure 7. Thickness dependence of the spin-wave energy E_m/E_{mb} of a multiferroic thin film for $T = 500$ K, $J_s = J_b$ and different A_{1s} values: 1— $A_{1s} = 0.6A_{1b}$; 2— $A_{1s} = 2A_{1b}$; 3— $A_{1s} = 3A_{1b}$.

film thickness N . The physical properties of multiferroic thin films can be controlled by changing their thickness. The results are shown in figures 6–8. The magnetization M , figure 6, the spin-wave energy E_m , figure 7, as well as the critical temperature T_N could be decreased or increased by controlling N for both cases $A_{1s} < A_{1b}$ (curve 1) or $A_{1s} > A_{1b}$ (curves 2 and 3), respectively. The first case, where the surface exchange interaction constants are smaller compared to the bulk value, could be responsible for the experimentally observed decrease from Nechache *et al* [8] of the magnetization with decreasing film thickness in $\text{Bi}_2\text{FeCrO}_6$ (BFCO) thin films. The authors noted that this could be due to the increase of the canting angle and/or a re-ordering of the Cr and Fe cations. Neutron diffraction study of hexagonal manganite YMnO_3 and ErMnO_3 epitaxial films shows that the Néel temperature for the Mn^{3+} ions ordering is smaller compared to the bulk case [30] which corresponds to the case $A_{1s} < A_{1b}$. The second case, where the surface exchange interaction constants are larger compared to the bulk value, could explain the experimentally observed enhanced magnetic and ferroelectric properties in BFO [2–4, 31] and $\text{Bi}_4\text{Fe}_2\text{TiO}_{12}$ [32] thin films. This increase was attributed either to the formation of Fe^{2+} ions [3], to a homogenization of the magnetic spins [4] or to an increased canting angle [3]. Depending on the value of A_{1s} the spin-wave energies of the thin film, figure 7, could be larger or smaller compared to the bulk, while the damping in the thin film is always greater than that of the bulk due to the influence of the surface and size effects.

We have also studied the thickness dependence of the polarization P , the phase transition temperature T_C , the energy E_e and its damping of the ferroelectric subsystem for different values of the surface exchange interaction constants. For the case $J_s > J_b$, where the surface exchange interaction constant of the electric subsystem is larger compared to the bulk value, we have obtained that the polarization increases with decreasing film thickness (figure 8, curve 1), whereas for the case $J_s < J_b$ (curve 4, for the same value of A_{1s} as in curve 1) it decreases. It is interesting to investigate the influence of the surface exchange interaction constant of the magnetic subsystem A_{1s} on the polarization P . In the case of $J_s > J_b$

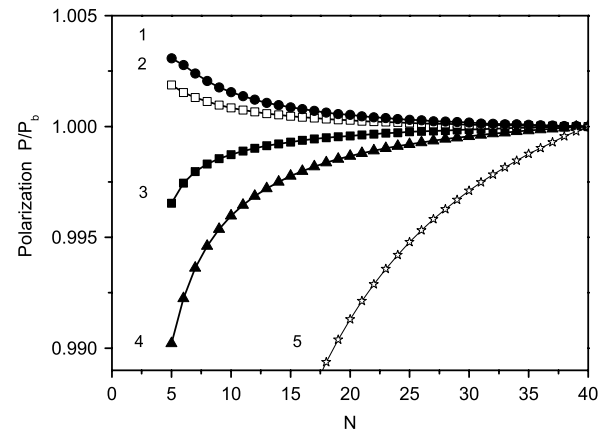


Figure 8. Thickness dependence of the polarization P/P_b of a multiferroic thin film for $T = 500$ K and different A_{1s} and J_s values: 1— $A_{1s} = 4A_{1b}$ and $J_s = 3J_b$; 2— $A_{1s} = 0.6A_{1b}$ and $J_s = 5J_b$; 3— $A_{1s} = 0.6A_{1b}$ and $J_s = 3J_b$; 4— $A_{1s} = 4A_{1b}$ and $J_s = 0.6J_b$; 5— $A_{1s} = 0.6A_{1b}$ and $J_s = 0.6J_b$.

different values of A_{1s} can lead to different film thickness behavior of P . For $J_s > J_b$ and $A_{1s} > A_{1b}$ we have obtained an increase of P with decreasing N (curve 1), whereas for $J_s > J_b$ and $A_{1s} < A_{1b}$ P decreases with decreasing N (curve 3). This behavior could be reversed for large enough values of J_s , $J_s \gg J_b$, which is shown on curve 2. This demonstrates the complexity of the interactions between the magnetic and the electric subsystems which leads to various interesting, from an applications point of view, properties of these multiferroic thin films. In the other case $J_s < J_b$ we have obtained a decrease of the polarization with decreasing film thickness N for all values of A_{1s} , $A_{1s} > A_{1b}$ (curve 4), and $A_{1s} < A_{1b}$ (curve 5), and we notice that the last curve is steeper. In that case the influence of the magnetic system is not strong enough to change the behavior of the polarization. Generally, the absolute change of P with film thickness is stronger when $J_s < J_b$ than the case $J_s > J_b$. The Curie temperature T_C and the pseudo-spin-wave energy E_e have an analogous behavior. For $J_s > J_b$ and $A_{1s} > A_{1b}$ we have obtained larger T_C and E_e values compared to the bulk ones. This could explain the

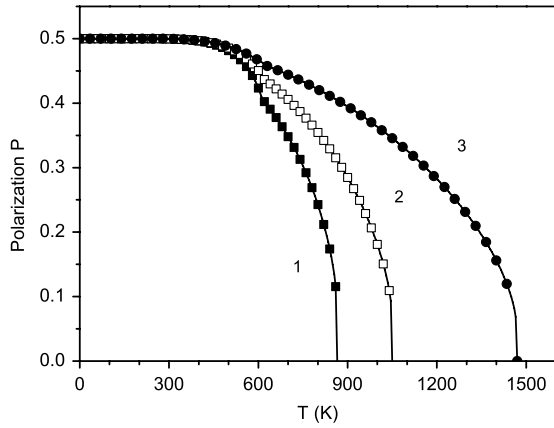


Figure 9. Temperature dependence of the polarization P of a multiferroic thin film for $N = 7$, $A_{1s} = A_{1b}$ and different J_d values: 1— $J_d = 0.6J_b$; 2— $J_d = J_b$; 3— $J_d = 2J_b$.

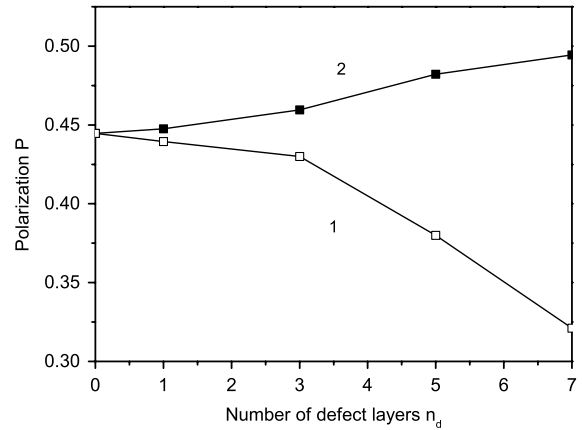


Figure 10. Dependence of the polarization P of a multiferroic thin film for $N = 7$ on the number of defect layers n_d , $T = 550$ K, $J_s = 200$ K, $J_b = 910$ K, $A_{1s} = A_{1b}$ and different J_d values: 1—500; 2—1500 K.

experimentally observed enhanced ferroelectric properties in BFO thin films [2, 6, 7]. Recently Chu *et al* [33] have studied the size effects in multiferroic BFO thin films and obtained ferroelectricity down to at least 2 nm film thickness. Using x-ray photoelectron spectroscopy (XPS) in $\text{Bi}_4\text{Fe}_2\text{TiO}_{12}$ thin films Lu *et al* [27] have reported that the XPS peaks of the film are shifted to the lower-energy end by 1.4 eV in comparison with that of $\text{Bi}_4\text{Fe}_2\text{TiO}_{12}$ ceramics and that the peaks are broader, i.e. the damping which corresponds to the full width of the half-maximum (FWHM) of the peaks is greater in thin films. The FWHM of the peaks in thin films usually comes from various additively factors, e.g. crystalline size, surface effects, strain, defects, substrates, film/substrate interface, etc. Singh *et al* [34] have obtained that the FWHM in multiferroic LCMO/BTO superlattices decreases at higher film thicknesses of BTO due to strains in the film. The x-ray diffraction peaks studied by Hu *et al* [35] in Gd-doped BFO thin films are broadened even for a low Gd content. For temperatures above T_N where only the electric phase exists we have obtained that the polarization increases for $J_s > J_b$ or decreases for $J_s < J_b$ for all values of A_{1s} . This shows that above the Néel temperature the magnetic system cannot influence the electric one. It must be noted here that different kinds of substrates could also influence the properties of multiferroic thin films. This will be discussed in a separate paper.

In order to study the effects of doping on the ferroelectric and magnetic properties of multiferroic thin films we assume that one or more of the layers can be regarded as a defect. The interaction strength of these defect layers is described by $J_d(r_i - r_j)$ (or $A_{1d}(r_i - r_j)$) which depends on the distance between the neighboring spins. For example, such a defect could originate from localized vacancies or impurities, doping ions with larger radii and respectively larger distances between them compared to that of the host material. In this case it is reasonable to assume that the exchange interaction J_d in one or more defect layers is smaller than the value of the interaction when there are no defects J_b , i.e. $J_d < J_b$. In that case we have obtained that the polarization P (figure 9), the pseudo-spin-wave energy E_e and the Curie temperature T_C are smaller than the case without defects, $J_d = J_b$. While for $J_d > J_b$,

i.e. J_d is larger than the value without defects J_b (for example, when the impurities have a smaller radius compared with the constituent ions), the opposite behavior is observed, i.e. P , E_e and T_C are larger than the case $J_d = J_b$. The electric properties of the thin films are enhanced in comparison to those without defects due to the presence of larger values of the exchange interaction constant J_d . The changes of the exchange interaction constants due to defects, ion doping or strain effects reflect on the magnetoelectric coupling constant g (because J^{eff} or A^{eff} , equations (13) and (16), are depending on g) and the interaction constants influence each other. For example, Bi ions of multiferroic BiMnO_3 were substituted with La by Yang *et al* [36] in order to induce an overlap of the ferroelectric and ferromagnetic transitions in temperature. The authors have obtained a dynamically enhanced magnetoelectric effect in La-doped BiMnO_3 thin films. Magnetoelectric coupling enhanced by two orders of magnitude is reported by Nugroho *et al* [37] in Ga-doped YMnO_3 single crystals.

The next figures 10–12 show the dependence of the polarization, the critical temperature, the pseudo-spin-wave energy and its damping on the number of defect layers, i.e. on the concentration of defects. The polarization (figure 10) and analogously the Curie temperature could be increased or decreased depending on the value of J_d . For the case $J_d = 1500$ K (curve 2), i.e. J_d is larger than the value without defects J_b , the polarization and the critical temperature are larger than the case when there are no defects, $J_d = J_b$. The electric properties of the films are enhanced in comparison to those without defects due to the presence of larger J_d values. An opposite behavior is observed in the case $J_d = 400$ K, $J_d < J_b$ (curve 1). The first case, $J_d > J_b$, could explain the experimentally obtained increase of the ferroelectric properties by doping of BFO films with ions, such as Ti [13], Sc [14], Nb [9, 15], Cr [16, 17] and Tb [38, 39]. In this case the doping ions (for example, Sc, Ti, Nb and Cr) have smaller radii in comparison to the host material ions (Fe) or, for example, Tb in comparison to Bi, i.e. $J_d > J_b$, and the properties are increased. In the case of Mn the radius of the doping ion Mn and the host ion Fe are nearly the same and the

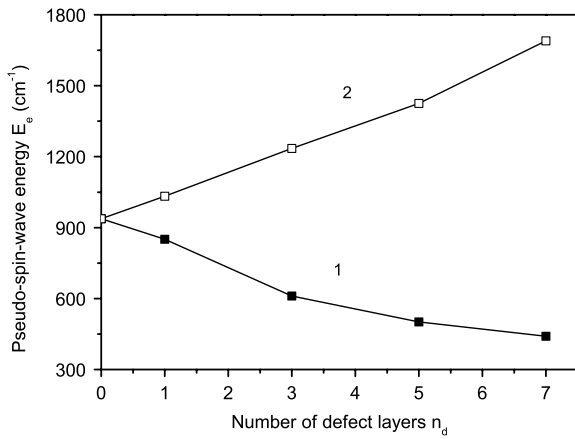


Figure 11. Dependence of the pseudo-spin-wave energy E_e of a multiferroic thin film for $N = 7$ on the number of defect layers n_d , $T = 550$ K, $J_s = 200$ K, $J_b = 910$ K, $A_{1s} = A_{1b}$ and different J_d values: 1—500; 2—1500 K.

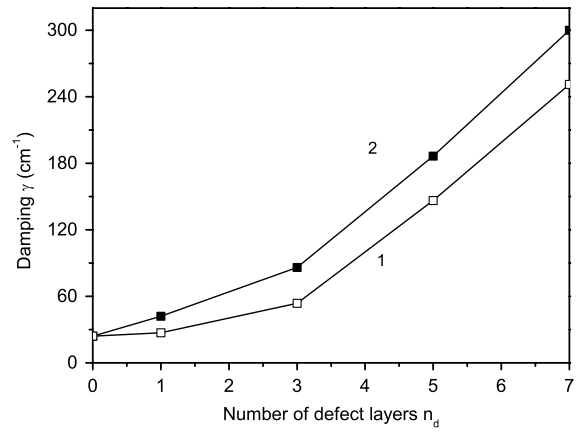


Figure 12. Dependence of the pseudo-spin-wave damping γ of a multiferroic thin film for $N = 7$ on the number of defect layers n_d , $T = 550$ K, $J_s = 200$ K, $J_b = 910$ K, $A_{1s} = A_{1b}$ and different J_d values: 1—500; 2—1500 K.

doping with Mn does not lead to improvement of the electric properties [15]. This corresponds to the case $J_d = J_b$ and the properties are the same as in the undoped thin films. Hu *et al* [35] have studied the effects of Gd substitution on structure and ferroelectric properties of BFO thin films. The results show that the remanent polarization P_r and the coercive field E_c decrease monotonically with the increase of Gd content. It is well known that the ionic radius of Gd^{3+} (0.938 Å) is much smaller than that of Bi^{3+} (1.03 Å). Therefore, we would expect higher values of the remanent polarization P_r induced by larger structure distortions in BFO films doped with Gd. This phenomenon can be ascribed to a decrease of the Curie temperature as observed in BFO thin films doped with La and Nd [40], to a decrease of grain size and, hence, more defects formed at the grain boundaries may deteriorate the ferroelectric properties. Naganuma *et al* [41] have observed an enhancement of the ferroelectric properties in BFO thin films by a small amount of cobalt addition. The saturation magnetization decreased when the cobalt content exceeded 15 at.%, whereas the ferroelectricity degraded when the cobalt concentration exceeded 9 at.% due to the formation of the secondary phases of Bi_2Pt . In the case of doping with La there is some discrepancy in the experimental data. In some papers [9–12] there is reported an increase of the polarization in multiferroic BFO thin films, but a decrease of the critical temperature T_C [40, 42, 43]. Some authors obtained an increase of the magnetization M [9–12], but others a decrease of M [44] and the Néel temperature T_N [42] as the La concentration increases. Our hypothesis about the influence of the doping ion radius cannot be applied here, because the ionic radii of Bi^{3+} (1.02 Å) and La^{3+} (1.04 Å) are nearly equal, so the difference in ion size does not have an effect on the phase transition temperature. There must be another reason which leads to the changes of the polarization or magnetization in BFO thin films doped with La and this will be considered in a future publication. The properties are depending also on the substrates, on the valence of the Fe ion (it can be Fe^{2+} or Fe^{3+}), etc. The saturation magnetization was enhanced about two times due to the Fe^{2+} ions in the BFO thin films [10].

In figures 11 and 12 there is demonstrated the dependence of the ferroelectric pseudo-spin-wave energies E_e and their damping γ on the number of defect layers, i.e. on the concentration of doping ions. It can be seen that E_e can be increased or decreased depending on the value of the exchange interaction constant J_d in the defect layer(s) (figure 11), whereas the damping is increased in thin films for all values of J_d (figure 12). The damping increases with temperature T and exchange interaction constant J_d . Unfortunately, there are not many experimental data about the spin-wave energies and their damping in multiferroic thin films. Nechache *et al* [8] have observed that the FWHM of the O 1s peak in the XPS spectra of BFCO thin films is slightly larger than that of BFO thin films, which could denote the presence of some atomic disorder in the BFCO layer (for instance, caused by disorder in the Fe–Cr sequence along $\langle 111 \rangle$ or by a slight deviation of the nominal Fe/Cr atomic ratio), possibly due to the surface proximity. The broadening of the diffraction peaks studied by Hu *et al* [35] in Gd-doped BFO thin films increases with the increase in Gd concentration.

5. Conclusion

Using a microscopic model and the Green's function technique we have calculated different static and dynamic properties of multiferroic thin films in the generalized Hartree–Fock approximation. The influence of the surface, film thickness, temperature and doping effects on the magnetic and electric properties of multiferroic thin films is studied. It is shown that the magnetization M , the polarization P , the critical temperatures T_N and T_C , the spin-wave energies E_m and E_e , and their damping are very sensitive to the exchange interaction constants on the surface. The physical properties of multiferroic thin films can be controlled by changing their thickness. We have obtained that M , P , T_N , T_C and the spin-wave energies could be increased or decreased by using different kinds of doping ions. The results show that the damping of the thin film is enhanced compared to that of the

bulk and furthermore enhanced compared to the case without defects.

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