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Dependence of Curie temperature on the thickness of an ultrathin ferroelectric film

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The thickness dependency of the Curie temperature in stress-free $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ultrathin films under open-circuit conditions is revealed from the computation of some nontrivial statistical quantities (such as fourth-order cumulants), via a first-principles-based technique. For thicknesses above 16 Å, this dependency follows the usual finite-size scaling law with a critical exponent that is consistent with the one associated with the three-dimensional-random-Ising universality class. On the other hand, the Curie temperature-versus-film's thickness curve deviates from this scaling law below 12 Å while being rather well described by an empirical equation down to 8 Å.

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I. INTRODUCTION

Finite-size effects in dipolar (magnetic or ferroelectric) ultrathin films is a topic of growing interest for both technological and fundamental reasons—see, e.g., Refs. 1–8, and references therein. One particularly important issue in these low-dimensional systems is the dependency of their Curie temperature (that is, the highest temperature at which a spontaneous magnetization/polarization exists) on the film's thickness. The technological relevance of knowing such dependency partly stems from the possibility of designing improved devices since many properties fundamentally depend on the Curie temperature. Finite-size scaling theory predicts that this critical temperature shifts to lower temperatures than that of the bulk when one or more of the material's dimension(s) is reduced to an atomic size,⁹ with the shift being given by¹⁰

$$\delta T = [T_c(\infty) - T_c(d)]/T_c(\infty) = \left(\frac{\xi_0}{d}\right)^\lambda, \quad (1)$$

where $T_c(\infty)$ and $T_c(d)$ are the Curie temperatures of the bulk material and of the film having a thickness denoted by d , respectively. ξ_0 and λ are physically meaningful parameters for the corresponding *bulk* system: ξ_0 is its correlation length (interpolated down to $T=0$ K) while λ is a critical exponent characterizing the so-called universality class to which this system belongs to (examples of universality class are three-dimensional (3D) Heisenberg, two-dimensional Ising, etc.). However, a deviation of the $T_c(d)$ -versus- d curve from Eq. (1) was experimentally found in Refs. 11–13 for *magnetic films below a critical thickness* (note that such deviation carries important information, such as, e.g., the possible predominant role of surface on the transition temperature of ultrathin films). As a result, it was recently advocated^{14–16} that the behavior of the Curie temperature versus thickness can be fitted for a wider thickness range by considering $T_c(d)$ rather than $T_c(\infty)$ in the denominator of the relative shift in Curie temperature, that is by using

$$\Delta T = [T_c(\infty) - T_c(d)]/T_c(d) = \left(\frac{\xi'_0}{d}\right)^{\lambda'}, \quad (2)$$

where λ' and ξ'_0 do not possess any clear physical meaning,^{12,14} unlike λ and ξ_0 . Interestingly, the thickness dependency of the Curie temperature has been observed and tested against Eqs. (1) and (2) for a variety of low-dimensional magnetic systems^{11,14,17} but never in ferroelectrics, to the best of our knowledge. In other words, crucial characteristics of an important class of materials are currently unknown. In particular, one may wonder which relation among Eqs. (1) and (2) (if any) better describes the transition temperatures of ferroelectric thin films. In case that Eq. (1) holds in ferroelectric films (for any thickness or “only” above some critical thickness), one may also wonder if the involved critical exponent, λ , is consistent with a given universality class since there has been an intense debate for many years whether ferroelectrics belong to some universality classes or not (see, e.g., Ref. 18, and references therein). This paucity of knowledge may arise from the fact that many effects can affect the intrinsic $T_c(d)$ -versus- d curve in ferroelectric thin films. Examples of such effects are the increasing importance of depolarizing fields when decreasing the film's thickness¹⁹ or the increasing release of the strain arising from the substrate for thicker films.²⁰ First-principles-based approaches may thus be of great help to address the issues mentioned above since these methods have the flexibility to impose identical mechanical and/or electrical boundary conditions for ferroelectric films of different thicknesses—in addition to be accurate. However, predicting transition temperatures with these schemes is by no means trivial, and even when succeeding to do so, one has to face the undesirable fact that the computed critical temperatures of a given periodic system practically depend on the size of the supercell used to mimic such system.^{21,22}

In this paper, we combine first-principles-derived approaches with statistical (e.g., Binder-cumulant²³) techniques to determine the thickness dependency of the Curie temperature in $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (PZT) thin films that are under stress-free and open-circuit electrical boundary conditions. As we

will see, such determination provides the answer to the questions stated above. In particular, we numerically found that (i) Eq. (1) holds for thicknesses above 16 Å with a λ parameter being consistent with the corresponding critical exponent of the 3D-random-Ising universality class; and (ii) there is a breakdown of Eq. (1) for thicknesses below 12 Å while Eq. (2) fits rather well the transition temperatures of the films for any thickness down to $d=8$ Å.

The paper is organized as follows. Section II describes the first-principles-based approach used in this work. Section III reports and discusses our predictions while Sec. IV provides some conclusions.

II. METHOD

Here, we investigate (001) disordered $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ thin films that are PbO terminated. Such films are mimicked by $L \times L \times m$ supercells that are periodic along the x and y axes while finite along the z axis—where the x , y , and z axes are along the pseudocubic [100], [010], and [001] directions, respectively. The number of B sites in each (001) layer of the supercell is thus $L \times L$ while m is the number of (001) B -site layers (the thickness of the film is thus around $d=4m$, when expressed in Å). For computational reasons, we will limit ourselves to m varying between 1 and 12. The total energy E_{tot} of such low-dimensional system is written as²⁴

$$E_{\text{tot}}(\{\mathbf{u}(i)\}, \{\mathbf{v}(i)\}, \boldsymbol{\eta}, \{\sigma_i\}) = E_{\text{mat}}(\{\mathbf{u}(i)\}, \{\mathbf{v}(i)\}, \boldsymbol{\eta}, \{\sigma_i\}) + P \sum_j u_z(j) + T \sum_j v_z(j), \quad (3)$$

where $\mathbf{u}(i)$ is the (B -centered) local soft mode in the unit cell i of the film and is directly proportional to the electrical dipole at that site. $\mathbf{v}(i)$ is the inhomogeneous strain around the i site while $\boldsymbol{\eta}$ is the homogeneous strain tensor.²⁵ The local modes and both strains are allowed to fully relax in order to mimic a stress-free film. $\{\sigma_i\}$ characterizes the alloy configuration²⁶—which is chosen to provide a realization of a disordered system and is frozen in our simulations. E_{mat} represents the intrinsic ferroelectric and elastic interactions inside the film. Its analytical expression and first-principles-derived parameters are those given in Ref. 26 for PZT *bulk*, except for the dipole-dipole interactions for which we use the analytical expressions derived in Refs. 27 and 28 for films under ideal open-circuit electrical boundary conditions. E_{mat} includes terms describing on-site local-mode self-energy, short-range, and dipole-dipole interactions between local modes, elastic energy, the coupling between local modes and elastic variables, and alloying-related terms. Moreover, the P and T parameters appearing in Eq. (3) quantify how the existence of the (free) upper surface affects the out-of-plane components (u_z and v_z) of the local modes and inhomogeneous strains, respectively, at the j sites closest to this upper surface [such parameters are determined from first-principles calculations on a PbO-terminated (001) 17-atom slab²⁴]. Furthermore, no term analogous to the last two expressions of Eq. (3) is considered at the lower surface since this latter characterizes the substrate/film interface and that we consider the substrate to be inert. Technically, we use the total

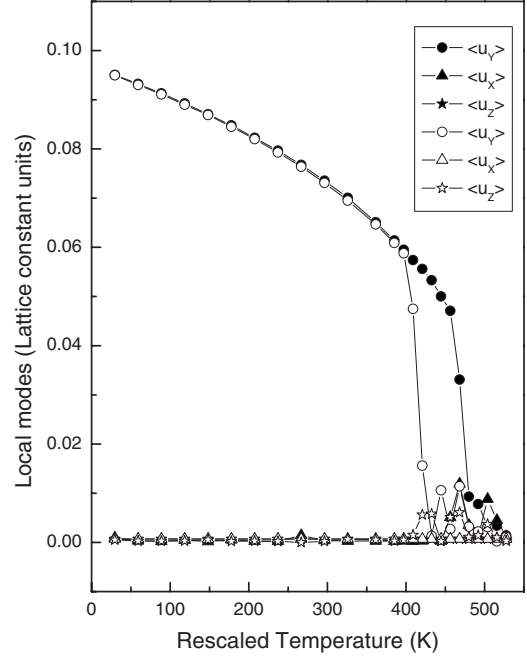


FIG. 1. Cartesian components of the supercell average of the local modes in a 20-Å-thick stress-free $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ film under open-circuit electrical boundary conditions, as a function of temperature. The open symbols refer to simulations performed with a $16 \times 16 \times 5$ supercell while the filled symbols display the results for a $26 \times 26 \times 5$ supercell. The temperature has been rescaled to match the experimental Curie temperature of PZT bulk.

energy of Eq. (3) in Monte Carlo (MC) simulations—performed with the Metropolis algorithm²⁹—and use a huge number of Monte Carlo sweeps (up to 20 million) for each temperature to reach convergency. The local soft modes and strains are collected at each Monte Carlo sweep, and the temperature is practically decreased by small steps.

III. RESULTS

Figure 1 displays the predicted temperature behavior of the Cartesian coordinates ($\langle u_x \rangle$, $\langle u_y \rangle$, and $\langle u_z \rangle$) of the local-mode vectors averaged over the supercell sites and over the Monte Carlo sweeps, in the 20-Å-thick ($m=5$) film.³⁰ Results for two different supercell sizes (namely, associated with $L=16$ or $L=26$) are shown there. For both sizes, each coordinate is close to zero at high temperature, indicating a paraelectric phase. As the temperature is decreased and passes through a critical value, $\langle u_y \rangle$ rapidly increases when the temperature decreases while $\langle u_x \rangle$ and $\langle u_z \rangle$ remain nearly null—as consistent with Ref. 24. This indicates the formation of a ferroelectric phase (via a second-order transition) with a polarization lying along an in-plane $\langle 010 \rangle$ direction, below this critical temperature. Such in-plane direction leads to a vanishing depolarizing field. Interestingly, Fig. 1 also shows that the computed critical temperature of PZT thin films having a given thickness strongly depends on the L lateral supercell length, and increases as L increases. Such size dependencies were previously reported for ferromagnetic thin films.^{31,32} They also indicate that determining the “real” Cu-

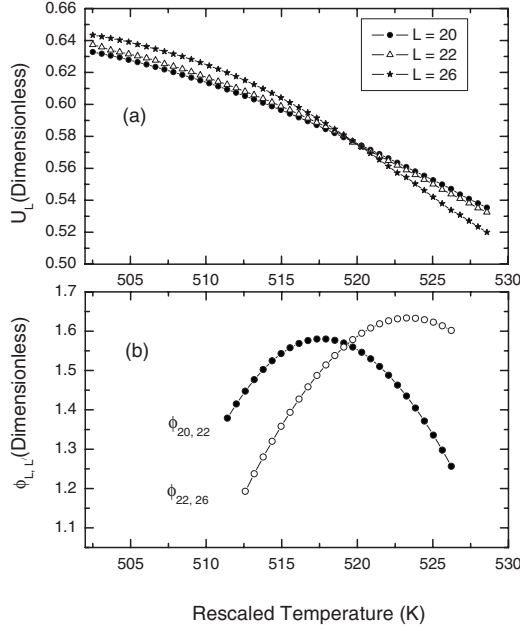


FIG. 2. Temperature dependency of fourth-order cumulants [part (a)] and of $\phi_{L,L'}(T)$ functions [part (b)], for different lengths of the periodic supercells, in a 20-Å-thick stress-free $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ film under open-circuit electrical boundary conditions. The temperature has been rescaled to match the experimental Curie temperature of PZT bulk.

rie temperature, $T_c(d)$, associated with a specific thickness d (i.e., the critical temperature corresponding to the case of $L \rightarrow \infty$) is practically impossible when solely using the simulations of a fixed periodic supercell. In fact, as we will see below, this determination can be accomplished by combining predictions offered by our numerical tool with particularly relevant statistical features. More precisely, one can compute the fourth-order cumulant U_L ,³² defined as

$$U_L = 1 - \frac{\langle u^4 \rangle}{3\langle u^2 \rangle^2}, \quad (4)$$

where “ $\langle \rangle$ ” denotes the average over the MC sweeps, and where u^2 and u^4 represent the square and fourth power of the magnitude of the local modes (averaged over the $L \times L \times m$ supercell sites for each MC sweep), respectively. Such latter quantities are provided by our computational scheme for each investigated temperature. Note that U_L is practically calculated by taking advantage of the so-called reweighting technique.³³ Interestingly, it is well established that U_L should be independent of L for a single temperature, that is $T_c(d)$.³² Such important fact is indeed numerically confirmed in Fig. 2(a), that shows the temperature dependency of the fourth-order cumulant of a PZT thin film with $m=5$ for three different lateral supercell sizes (namely, $L=20, 22$, and 26). One can indeed clearly see that these three different curves all intersect at a temperature equal to 520 K, which is thus taken to be the real Curie temperature of the 20-Å-thick PZT film.

To further confirm this value, we also computed the function defined as

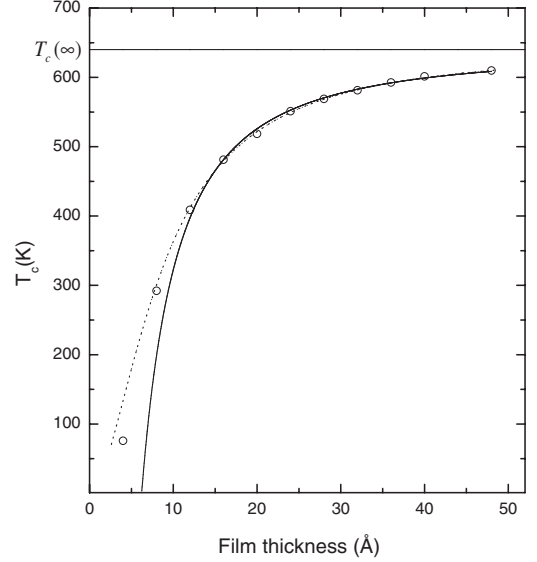


FIG. 3. Thickness dependency of the Curie temperature in stress-free $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ films under open-circuit electrical boundary conditions. The solid line shows the fit of the numerical data to Eq. (1) while the dashed line represents the fit of the same data but to Eq. (2). The uncertainties of the numerical data are smaller than the size of the dot used to display such data and are thus not shown for clarity. The horizontal bold line shows the Curie temperature of PZT bulk. The temperature has been rescaled to match the experimental Curie temperature of PZT bulk.

$$\phi_{L,L'}(T) \equiv \frac{\ln[\chi(L',T)/\chi(L,T)]}{\ln(L'/L)}, \quad (5)$$

where

$$\chi(L,T) = \frac{(L^2 d)[\langle u^2 \rangle - \langle |u| \rangle^2]}{T}, \quad (6)$$

where T denotes the temperature, and where the statistical averages of the u -dependent terms are once again determined by our presently used numerical scheme for $L \times L \times m$ supercells. Reference 23 indicates that the $T_c(d)$ Curie temperature should be the temperature at which the $\phi_{L,L'}(T)$ and $\phi_{L',L''}(T)$ functions intersect for any two pairs of sizes, (L, L') and (L', L'') with $L'' > L' > L$. Figure 2(b) indeed shows that such intersection occurs between $\phi_{20,22}(T)$ and $\phi_{22,26}(T)$ for the PZT thin film having $m=5$. More precisely, this intersection happens at 519 K, which is in very good agreement with the Curie temperature previously obtained using the fourth-order cumulant, see Fig. 2(a). The (tiny) difference between the $T_c(d)$ obtained when using the crossing of the U_L 's or of the $\phi_{L,L'}(T)$'s practically provides our uncertainty for the Curie temperature of the investigated film. Moreover, the temperature crossings of the fourth-order cumulants and of the $\phi_{L,L'}(T)$ functions were numerically found to occur for all the considered thicknesses. We thus are in position to reveal the thickness dependency of the real Curie temperature in PZT thin films, as displayed in Fig. 3. Furthermore, the resulting data of this latter figure are fitted using the well-established Eq. (1), as well as the empirical law described by

Eq. (2).³⁴ Several striking features can be clearly seen. First of all, there is no critical thickness below which ferroelectricity vanishes in stress-free PZT film under open-circuit conditions, as consistent with Refs. 24 and 35. As a matter of fact, Fig. 3 indicates that the Curie temperature is equal to 76 K for the thinnest possible system (i.e., for $m=1$). Second, $T_c(d)$ decreases as the film becomes thinner, as previously found for magnetic and ferroelectric nanostructures.^{2,11,12,14,31,36} Third, such decrease is very well described by the usual finite-size scaling relationship of Eq. (1) *but only for thickness above or equal to 16 Å*. More precisely, $T_c(d)$ deviates more and more from the fit to Eq. (1) as the thickness decreases below 12 Å. Such kind of deviation has also been recently found in magnetic ultrathin films,^{11–13,37} and arises from the increasingly important role of surface effects relative to bulk effects when decreasing the film's thickness. Interestingly, the two degrees of freedom of Eq. (1) are numerically found to be $\xi_0=6.21 \pm 0.20$ Å, and $\lambda=1.47 \pm 0.03$. The former parameter indicates a correlation length corresponding to the third-nearest-neighbors' distance (in the B sublattice) for PZT bulks. The latter parameter confirms the prediction of Ref. 18, namely, that the critical exponents of $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ bulks are consistent with those of the 3D-random-Ising universality class—for which λ has been reported to be around 1.46.³⁸ Finally, Fig. 3 demonstrates that the empirical relationship of Eq. (2) can nicely reproduce the Curie temperatures down to a thickness of 8 Å, with $\lambda'=1.75 \pm 0.03$ and $\xi'_0=8.55 \pm 0.20$ Å. In other words, Eq. (2) somehow captures the effect of surface on the transition temperatures in ultrathin systems, as also found in low-dimensional magnets.^{12,14} However, the loss of a fundamental feature occurs with such capture, namely, the result-

ing λ' [which is always larger than λ (Refs. 12 and 39)] is *not* associated with an universality class.

Note that we have also tested the effect of the P and T parameters of Eq. (3) on the critical temperature, by turning off both of them in the simulations, and found that $T_c(d)$ is not affected by these parameters for any investigated thickness.⁴⁰

IV. CONCLUSIONS

In summary, we have revealed the thickness dependency of the Curie temperature in $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ultrathin films, by computing nontrivial statistical quantities (such as fourth-order cumulants) from first-principles-based schemes. It is found that the empirical relation of Eq. (2) reproduces rather well such dependency for thickness down to 8 Å, in contrast with the usual finite-size scaling law of Eq. (1) that breaks down below 16 Å. The resulting value for the parameter λ appearing in Eq. (1) (for thicknesses above 16 Å) also further confirms that the critical exponents of $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ bulks are consistent with the 3D-random-Ising universality class, as recently predicted.¹⁸ We are confident that our present work provides a deeper knowledge of nanoscience, phase transitions, and critical behaviors in dipolar systems.

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