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## **Effect of surface ionic screening on polarization reversal and phase diagrams in thin antiferroelectric films for information and energy storage**

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### **Abstract**

Emergent behaviors in antiferroelectric thin films due to a coupling between surface electrochemistry and intrinsic polar instabilities are explored within the framework of the modified 2-4-6 Landau-Ginzburg-Devonshire (LGD) thermodynamic approach. By using phenomenological parameters of the LGD potential for a bulk antiferroelectric and a Stephenson-Highland (SH) approach, we study the role of surface ions with a charge density proportional to the relative partial oxygen pressure on the dipole states and their reversal mechanisms in the antiferroelectric thin films. The combined LGD-SH approach allows delineating the boundaries of antiferroelectric, ferroelectric-like antiferroionic and electret-like paraelectric states as a function of temperature, oxygen pressure, surface ions formation energy and concentration, and film thickness. This approach also allows the characterization of the polar and antipolar orderings dependence on the voltage applied to the antiferroelectric film, as well as the analysis of their static and dynamic hysteresis loops. The applications of the antiferroelectric films covered with surface ion layer for energy and information storage are explored and discussed.

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## I. INTRODUCTION

Ferroelectric (FE) phase stability requires effective screening of the polarization bound charge at surfaces and interfaces with non-zero normal component of polarization [1, 2, 3]. Rapid growth of FE thin film applications in 90ies necessitated the analysis of the microscopic mechanisms acting at ferroelectric interfaces, preponderantly effects stemming from non-zero spatial separation between a spontaneous polarization and screening charges [4, 5, 6, 7, 8]. These effects are often introduced via the dead layer [2] or physical gap [9] concepts, postulating the presence of the thin non-ferroelectric layer or gap separating the ferroelectric surface from the electrode. The validity of this approximation was confirmed by the microscopic density functional theory studies [10, 11, 12].

However, the dead layer approximation largely ignores the realistic details of the screening process at the open surfaces and ferroelectric-semiconductor interfaces. In particular, the stabilization of FE state in ultrathin perovskite films can take place due to the chemical screening (see e.g. [13, 14, 15]), and the screening via ionic adsorption is intrinsically coupled to the surface electrochemical processes [16, 17, 18]. This screening mechanisms was confirmed by multiple experimental observations including the polarization retention above Curie temperature [19], temperature induced domain potential inversion [20], formation of bubble domains during tip-induced switching [21, 22, 23], chaotic switching [7] and domain shape instabilities [24]. Macroscopically, it is confirmed via the chemical switching in ferroelectrics [13, 25]. Finally, multiple anomalous observations such as tip pressure induced switching [26, 27] or continuous polarization states in ultrathin films can be partially attributed to the ionic screening [28]. This coupling results in non-trivial influence on the FE phase stability and phase diagrams [25, 29], albeit the overall research effort in this area is fairly small.

The early theoretical analyses, though studied the properties of ferroelectric material in details, typically ignored the nonlinear tunable characteristics of surface screening charges. A complementary thermodynamic approach was developed by Stephenson and Highland (SH) [25, 29], who consider an ultrathin film in equilibrium with a chemical environment that supplies (positive and negative) ionic species to compensate its polarization bound charge at the surface.

Recently, we modified the SH approach allowing for the presence of a gap between the ferroelectric surface covered by ions and a SPM tip [30, 31, 32, 33, 34], and developed the analytical description for thermodynamics and kinetics of these systems. The analysis [30 – 34] leads to the elucidation of ferroionic states, which are the result of nonlinear electrostatic interaction between the ions with the surface charge density obeyed Langmuir adsorption isotherm and ferroelectric dipoles. The properties of these states were described by the system of coupled 1D equations and corresponding phase diagrams have been established.

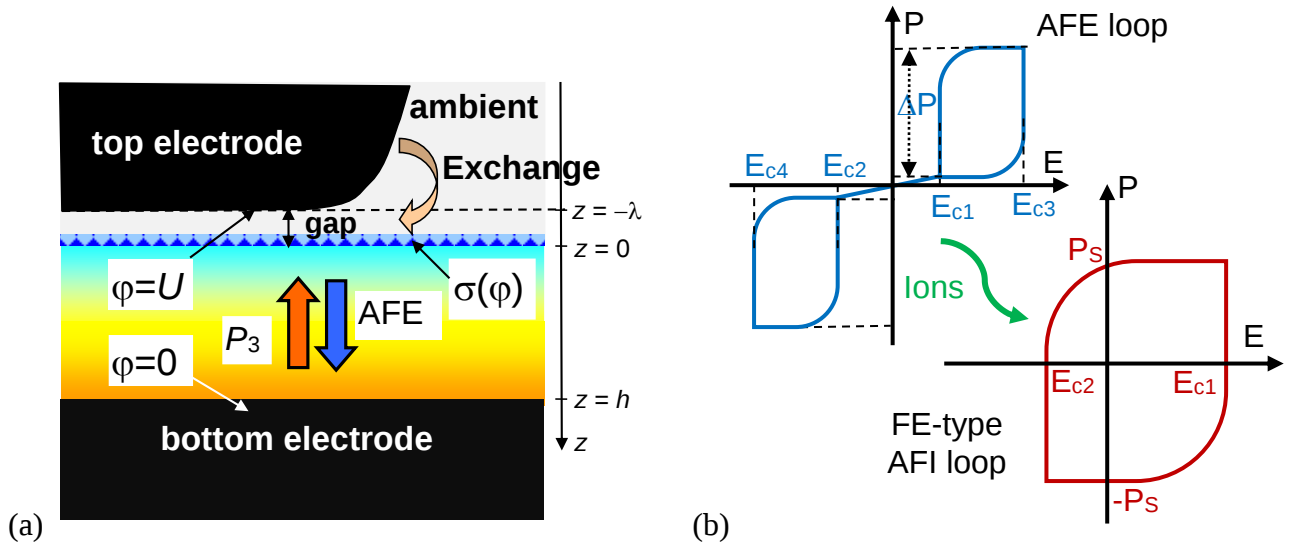
Here we study the role of the surface ions with a charge density proportional to the partial oxygen pressure on the dipole states and its reversal mechanisms, and corresponding phase diagrams of antiferroelectric (AFE) thin films. We use the SH approach combined with the 2-4-6 Landau-Ginzburg-

Devonshire (**LGD**) thermodynamic potential for the description of the polar and antipolar long-range orderings. Appeared, that, compared to FE materials, the considered AFE systems reveal more complex dynamics of polarization and surface charge due to presence of the FE-like antiferroionic (**AFI**) states. We analyze corresponding phase diagrams and associated hysteresis loops, as well as the application of the AFE films covered by surface ion layer for information and energy storage, and multi-bit nonvolatile random-access memory.

The manuscript is structured as following. **Section II** contains the basic LGD equations and SH problem formulation with boundary conditions. **Section III** presents free energy of the considered system. Numerical results (phase diagrams, hysteresis loops), their discussion and analysis are presented in **Section IV**. **Section V** is an outlook and brief summary. Parameters used in calculations and auxiliary figures are listed in **Appendices A-E** of **Suppl. Mat.** [35].

## II. BASIC EQUATIONS WITH BOUNDARY CONDITIONS

Here we consider the system consisting of an electron-conducting bottom electrode, an AFE film, and a layer of surface ions with a charge density  $\sigma(\phi)$ . An ultra-thin gap of thickness  $\lambda \sim (0.2 - 2)$  nm separates the film surface and the top electrode, that is either ion-conductive planar electrode or flatted apex of SPM tip. The gap provides a direct ion exchange with an ambient media, as shown in **Fig. 1(a)**. In the case of perfect electric contact,  $\lambda = 0$ , the ion exchange is impossible. A mathematical statement of the problem is listed in **Appendix A** [35].



**FIGURE 1. (a)** Layout of the considered system, consisting of an electron-conducting bottom electrode, an AFE film of thickness  $h$ , a layer of surface ions with a charge density  $\sigma(\phi)$ , an ultra-thin gap separating film surface, and a top electrode providing (from bottom to the top). The film thickness is  $h$ , the gap thickness is  $\lambda$ . Adapted from Ref. [31]. **(b)** Schematics of the transition from an AFE-type polarization hysteresis to an FE-type AFI hysteresis loop induced by electric coupling with the charge of surface ions.

Due to the presence of an ultra-thin dielectric gap between the top electrode and the surface of AFE film, the linear equation of state  $\mathbf{D} = \varepsilon_0 \varepsilon_d \mathbf{E}$  relates an electric displacement  $\mathbf{D}$  and field  $\mathbf{E}$  in the gap. Here  $\varepsilon_0$  is a universal dielectric constant and  $\varepsilon_d \sim (1 - 10)$  is a relative permittivity in the gap filled by an air with controllable oxygen pressure. A wide band-gap AFE film can be considered insulating, and here  $\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}$ . A potential  $\phi$  of a quasi-static electric field inside the film satisfies the Laplace equation in the gap and the Poisson equation in the film. The boundary conditions for the system are the equivalence of the electric potential to the applied voltage  $U$  at the top electrode (modeled by a flattened region  $z = -\lambda$ ); and the equivalence of the difference  $D_3^{(gap)} - D_3^{(film)}$  to the ionic surface charge density  $\sigma[\phi(\vec{r})]$  at  $z = 0$ ; the continuity of the  $\phi$  at gap - film interface  $z = 0$ ; and zero potential at the conducting bottom electrode  $z = h$  [see **Fig. 1**].

The polarization components of the uniaxial AFE film depend on the electric field  $E_i$  as  $P_i = \varepsilon_0(\varepsilon_{ii}^f - 1)E_i$  and  $P_3 = P_3^f + \varepsilon_0(\varepsilon_{33}^b - 1)E_3$ , where  $\varepsilon_{ii}^f$  is a relative dielectric permittivity of AFE,  $i = 1, 2$ , and  $\varepsilon_{33}^b$  is a relative background permittivity of antiferroelectric,  $\varepsilon_{33}^b \leq 10$  [36].

The polarization component  $P_3^f$  is further abbreviated as  $P_3$ . To determine the spatial-temporal evolution of  $P_3$ , one can use either the simplest two-sublattice Kittel model [37], or combine much complex models incorporating antipolar distortions related with oxygen octahedra rotations in antiferrodistortive perovskites [38] (such as  $\text{PbZrO}_3$ ) with the LGD approach. In fact, the seminal works of Haun et al. [39, 40] *does not* follow the classical Kittel model. In the Kittel model certain relations exist between the expansion coefficients of the free energy in the polarization and antipolarization powers, whereas such relations are not imposed in the Haun model. The topical review of Rabe et al. [41], where the earlier studies of antiferroelectrics are overviewed, concludes that available experimental facts about AFE structure of complex oxides can be relatively well described by a simple Landau theory (e.g., [38] and [39]). In these theories, the antiferroelectric distortion is described by an order parameter that does not specifically require a two-sublattice character for the distortion.

Tagantsev et.al. [42] suggest that a “missed” incommensurate phase exists in  $\text{PbZrO}_3$ , and that the transition to the AFE phase is driven by the softening of a single lattice mode via the flexoelectric coupling. Later on Hlinka et al. [43] proposed a so-called trilinear coupling between the antipolarization and oxygen octahedra rotations as the source of the antiferroelectricity in  $\text{PbZrO}_3$ . The complex models [42-43] are promising for such AFE as  $\text{PbZrO}_3$ , but, at the same time, they can be hardly included in the phenomenological LGD treatment.

Within the Kittel model one can introduce the one-component polar and antipolar long-range order parameters,  $P = \frac{1}{2}(P_i^{(1)} + P_i^{(2)})$  and  $A = \frac{1}{2}(P_i^{(1)} - P_i^{(2)})$ , where  $P_i^{(j)}$  is the  $i$ -th component of the  $j$ -th sublattice polarization. Within more complex models [38-39] the antiferroelectric distortion is described by an order parameter, that does not specifically require a two-sublattice character for the distortion.

Keeping the possible complexities in mind, we combine the above models with a 2-4-6-LGD thermodynamic potential for the description of long-range polar and antipolar orderings. At that the nature of the antipolar ordering is still controversial for many AFE perovskites, such as  $\text{PbZrO}_3$ , and the classical Kittel, Haun, Whatmore and Glazer models do not provide a complete quantitative description of their polar and structural properties, while it does not mean that the models are not applicable (at least semi-quantitatively) for other AFEs.

The polarization rotation is possible in multiaxial FEs and AFEs only. For the film of a uniaxial AFE (or FE), which polar axis is normal to the film surfaces, only the “out-of-plane” components of the polar ( $P_3$ ) and antipolar ( $A_3$ ) long-range order define their polar properties (one-component approximation). For a single-domain state, which is stabilized by the electric field induced by oxygen ions (see e.g. Refs.[13-15, 25, 29]), the properties weakly depend on the transverse coordinates, but can strongly vary with the distance  $z$  from the film surface (1D approximation). The validity of the one-component and 1D approximation used hereinafter requires grounds.

An appropriate (as a rule, compressive) mismatch strain, caused by the difference between the film and the substrate lattice constants, favors the stability of a “uniaxial” tetragonal phase with an out-of-plane polarization direction in thin epitaxial multiaxial perovskite films [44], which includes  $\text{PbZrO}_3$ . Hence the application of an appropriate strain corroborates the validity of the one-component approximation. For a single-domain case the mismatch strain leads to the renormalization of the coefficients in LGD potential via the electrostriction coupling coefficients in a well-known way (see Eqs.(3) in Ref.[44]). On the other hand, the coupling coefficients between the antipolar order parameter and the strains are unknown. On the one hand, the circumstance allows to assume that a compressive strain (e.g., about 0.5% or higher) induces the tetragonal phase with an out-of-plane polarization in an AFE film, but on the other hand the obtained results include a large uncertainty to be quantitatively valid for a concrete perovskite, such  $\text{PbZrO}_3$  film.

Hence, the evolution and spatial distribution of the polar ( $P$ ) and antipolar ( $A$ ) order parameters are given by the coupled time-dependent 2-4-6 LGD equations:

$$\Gamma_P \frac{\partial P_3}{\partial t} + 2\alpha_p P + 4\beta_p P^3 + 2\chi P A^2 + 6\gamma_p P^5 - g \frac{\partial^2 P}{\partial z^2} = E_3, \quad (1a)$$

$$\Gamma_A \frac{\partial A}{\partial t} + 2\alpha_a A + 4\beta_a A^3 + 2\chi P^2 A + 6\gamma_a A^5 - g \frac{\partial^2 A}{\partial z^2} = 0. \quad (1b)$$

Eqs.(1) follow from the variation of LGD free energy (see **Appendix A** for details). Here  $\Gamma_{P,A}$  are the positive kinetic coefficients defining the Khalatnikov relaxation of the order parameters. The coefficients  $\alpha_p = \alpha_T(T_P - T)$  and  $\alpha_a = \alpha_T(T_A - T)$  change their sign at Curie temperature  $T_P$  and AFE temperature  $T_A$ , respectively,  $T$  is the absolute temperature, and  $\alpha_T > 0$ . The inequalities  $\gamma_a > 0$ ,  $\gamma_p > 0$  and  $g > 0$  should be valid for the LGD potential stability. The AFE-FE coupling coefficient  $\chi$  should be positive for the stability of the AFE phase, and negative for the stability of the FE phase. Let us underline that no other specific relations are imposed on the coefficients in Eqs.(1), expanding their applicability well beyond the oversimplified Kittel model.

The boundary conditions for  $P$  and  $A$  at the film surfaces  $z = 0$  and  $z = h$  are of the third kind

$$\left(P \mp \Lambda_P \frac{\partial P}{\partial z}\right)\Big|_{z=0,\square} = 0 \text{ and } \left(A \mp \Lambda_A \frac{\partial A}{\partial z}\right)\Big|_{z=0,\square} = 0; \quad (1c)$$

and include extrapolation lengths  $\Lambda_{A,P}$  [45, 46]. Note, that the value of the extrapolation length is a poorly known parameter in LGD phenomenology. It can vary by order of magnitude due to the structure of surface or interface. In particular, Ref.[46] gives  $\Lambda_P = 2$  nm for the perovskite SrRuO<sub>3</sub>/PZT interface, while for the other film surface the parameter  $\Lambda_P$  is close to zero. For the ferroelectric-electrochemically active ambient medium the values of the extrapolation length can differ strongly from the case of the interface between two perovskites. We did not find any reliable data for the  $\Lambda_A$  value calculated or measured for AFE surfaces. For typical perovskite parameters the boundary conditions (1c) determine the behavior of polarization and anti-polarization in the layer of thickness not more than several correlation lengths in  $z$ -direction,  $L_z^C \cong \sqrt{\varepsilon_0 \varepsilon_{33}^b g} < 0.5$  nm, which is much smaller than the temperature-dependent correlation length in  $x$ -direction,  $L_x^C \cong \sqrt{\frac{g}{|\alpha_p|}} \sim (1 - 5)$  nm, due to the presence of the depolarization field in  $z$ -direction and its practical absence in  $x$ -direction for a single-domain state. So, the scale of the out-of-plane polarization variation related with the extrapolation length effect is typically smaller than the lattice constant [47]. Allowing for the applicability of LGD approach for the length-scale significantly higher than the lattice constant, the short-range effects related with the extrapolation length can be neglected.

An equation for the surface charge is analogous to the Langmuir adsorption isotherm used in interfacial electrochemistry for adsorption onto a conducting electrode exposed to ions in a solution [48]. To describe the dynamics of surface ions charge density, we use a linear relaxation model,

$$\tau \frac{\partial \sigma}{\partial t} + \sigma = \sigma_0[\phi], \quad (2)$$

where the dependence of an equilibrium surface charge density  $\sigma_0[\phi]$  on the electric potential  $\phi$  is controlled by the concentration of surface ions,  $\theta_i(\phi)$ , at the interface  $z = 0$  in a self-consistent manner, as proposed by Stephenson and Highland [25, 29]:

$$\sigma_0[\phi] = \sum_{i=1,2} e Z_i N_i \theta_i(\phi) \equiv \sum_{i=1,2} e Z_i N_i \left(1 + \rho^{1/n_i} \exp\left(\frac{\Delta G_i^{00} + e Z_i \phi}{k_B T}\right)\right)^{-1}, \quad (3)$$

where  $e$  is an elementary charge,  $Z_i$  is the ionization degree of the surface ions/electrons,  $N_i$  are saturation densities of the surface ions. A subscript  $i$  designates the summation on positive ( $i = 1$ ) and negative ( $i = 2$ ) charges, respectively;  $\rho = \frac{p_{O_2}}{p_{O_2}^{00}}$  is the relative partial pressure of oxygen (or other ambient gas) introduced in the Ref. [25],  $n_i$  is the number of surface ions created per gas molecule. Two surface charge species exist, since the gas molecule had been electroneutral before its electrochemical decomposition started. The dimensionless ratio  $\rho$  varies in a wide range from  $10^{-6}$  to  $10^6$  in the SH approach [25, 29].

Positive parameters  $\Delta G_1^{00}$  and  $\Delta G_2^{00}$  are the free energies of the surface defects formation at normal conditions,  $p_{O_2} = p_{O_2}^{00}$ , while the latter is set equal to 1 bar, and zero applied voltage  $U = 0$ . The energies

$\Delta G_i^{00}$  are responsible for the formation of different surface charge states (ions, vacancies, or their complexes). Specifically, exact values of  $\Delta G_i^{00}$  are poorly known even for many practically important cases, and so hereinafter they are regarded varying in the range  $\sim(0.1 - 1)$  eV [25]. At that the difference  $\Delta G_1^{00} - \Delta G_2^{00}$  can play a crucial role in the overall behavior of a ferroelectric film covered by the ions [25]. Notably, the developed solutions are insensitive to the specific details of the charge compensation process [49], but are sensitive to the thermodynamic parameters of corresponding reactions [50].

### III. FREE ENERGY OF THE ANTIFERRO-IONIC SYSTEM AND CALCULATION DETAILS

#### A. Free energy of the antiferroionic system

The stabilization of a single-domain polarization in ultrathin FE perovskite films takes place due to the chemical switching (see e.g. Refs.[13-15, 25, 29]), because the built-in field induced by the surface ionic charge is relatively high even when relative oxygen pressure  $\rho$  deviates from the equilibrium value  $\rho = 1$  not very strongly (e.g., for  $10^{-2} \leq \rho \ll 10^{-2}$ ), and the high field supports the out-of-plane orientation of polarization [30-34]. The domain structure is absent in the AFE phase of the film, but it may appear in the FE-like state due to the gap presence (i.e., for  $\lambda > 0$ ). However, as it will be shown below, the FE-like state can be induced by the strong oxygen excess or deficiency (e.g., for  $\rho \ll 10^{-2}$ ). As a rule, a single-domain configuration is stable in the case  $\rho \ll 1$  (or  $\rho \gg 1$ ) because both factors, the built-in field and the screening degree produced by the oxygen ions, are high enough to support the unipolar orientation of polarization. Since both factors are present in the considered case, as well as the gap width is typically very small, i.e.,  $\frac{\lambda}{h} \ll 1$ , a single-domain approximation can be used hereinafter.

Thus, we will assume that the distributions of  $P(x, y, z)$  and  $A(x, y, z)$  do not deviate significantly from their values, averaged over the film thickness, which are further abbreviated as “**polarization**”  $P \cong \langle P \rangle$  and “**anti-polarization**”  $A \cong \langle A \rangle$ . In this case, the behavior of the polarization  $P$ , and anti-polarization  $A$ , and surface charge density  $\sigma$  can be described via nonlinear coupled algebraic equations, similar to the ones derived in Refs. [30 - 34] for  $P$  and  $\sigma$ .

Below we consider either the stationary case or adiabatic conditions, when  $\sigma = \sigma_{0f}$ . The expression for the free energy density per unit area,  $f$ , which minimization gives the coupled equations for polarization dynamics, is the sum of the LGD polar and antipolar ordering energy  $f_{AP}$ , and the electrostatic energy  $f_\psi$ . The energy  $f_\psi$  includes the polarization interaction energy with the overpotential  $\Psi$ , the energy of the electric field in the AFE film, and in the gap, correspondingly, and the surface charge energy. So that  $f = f_{AP} + f_\psi$ , and the individual contributions are:

$$f_{AP} = h[\alpha_p P^2 + \alpha_a A^2 + \chi P^2 A^2 + \beta_p P^4 + \beta_a A^4 + \gamma_p P^6 + \gamma_a A^6], \quad (4a)$$

$$f_\psi = -\Psi P - \varepsilon_0 \varepsilon_{33}^b \frac{\Psi^2}{2\lambda} - \frac{\varepsilon_0 \varepsilon_a (\Psi - U)^2}{2\lambda} + \int_0^\Psi \sigma_0[\varphi] d\varphi. \quad (4b)$$

Here  $\alpha_p = \alpha_{pT}(T - T_p) + \frac{2g}{h\Lambda_p}$  and  $\alpha_a = \alpha_{aT}(T - T_A) + \frac{2g}{h\Lambda_A}$  are the thickness-dependent and temperature-dependent functions. The terms  $\sim g/h$  originate from "intrinsic" gradient-correlation size effects. The voltage  $U$  is applied between the electrodes.

The free energy given by Eqs.(4) has an absolute minimum at high  $\Psi$ . According to the Biot's variational principle [51], we can further use a thermodynamic potential, which partial minimization over  $P$  will give the coupled equations of state, and, at the same time, it has an absolute minimum at finite  $P$  values.

## B. Calculation details

So, a formal minimization of Eqs.(4),  $\frac{\partial f}{\partial P} = -\Gamma_P \frac{\partial P}{\partial t}$ ,  $\frac{\partial f}{\partial A} = -\Gamma_A \frac{\partial A}{\partial t}$ , and  $\frac{\partial f}{\partial \Psi} = 0$ , leads to the coupled time-dependent relaxation-type differential equations for the polarization and anti-polarization, and overpotential:

$$\Gamma_P \frac{\partial P}{\partial t} + 2(\alpha_p + \chi A^2)P + 4\beta_p P^3 + 6\gamma_p P^5 = \frac{\Psi}{h}, \quad (5a)$$

$$\Gamma_A \frac{\partial A}{\partial t} + 2(\alpha_a + \chi P^2)A + 4\beta_a A^3 + 6\gamma_a A^5 = 0, \quad (5b)$$

$$\frac{\Psi}{h} = \frac{\lambda(\sigma_0 - P) + \varepsilon_0 \varepsilon_d U}{\varepsilon_0(\varepsilon_d \square + \lambda \varepsilon_{33}^b)}. \quad (5c)$$

The overpotential  $\Psi$  contains the contribution from surface charges proportional to  $\sigma_0$ , the depolarization field contribution proportional to  $P$ , and the external potential drop proportional to  $U$ .

The equations (5) were solved numerically, and obtained stationary solutions were substituted in the energy (4) in order to determine the energy of the corresponding state. Since Eq.(5b) is homogeneous,

one can find the static solutions for  $A$ , namely  $A = 0$  or  $A^2 = \frac{2\beta_a \pm \sqrt{\beta_a^2 - 12\gamma_a(\alpha_a + \chi)P^2}}{6\gamma_a}$ , and substitute them in Eqs.(5a). Further substitution of the overpotential  $\Psi$  (as the function of  $\sigma_0[U]$ ,  $P$  and  $U$ ) from Eq.(5c) to Eq.(5a) allows to plot the parametric dependence  $U(P)$ , inverting which gives us the static  $P(U)$  and  $A(U)$  dependences.

The LGD thermodynamic potential can be further expanded in  $A$ ,  $P$  and  $\Psi$  powers, assuming that  $|eZ_i\Psi/k_B T| \ll 1$  (see **Appendices B** and **C** [35] for details). In result we obtain the expression for the free energy:

$$F[P, A] = \alpha_{pR}P^2 + \beta_{pR}P^4 + \gamma_{pR}P^6 - (E_{SI} + E_{act})P + \chi_R P^2 A^2 + \alpha_a A^2 + \beta_a A^4 + \gamma_a A^6. \quad (6)$$

Renormalized coefficients,  $\alpha_{pR}$ ,  $\beta_{pR}$ ,  $\gamma_{pR}$ , and  $\chi_R$ , a built-in field  $E_{SI}$  and an acting field  $E_a$  are

$$\alpha_{pR}(T, \rho, h) = \alpha_p(1 + S(T, \rho, h)) + \frac{\lambda}{2\varepsilon_0(\varepsilon_d \square + \lambda \varepsilon_{33}^b)}, \quad (7a)$$

$$\beta_{pR}(T, \rho, h) = (1 + S(T, \rho, h))\beta_p, \quad \gamma_{pR}(T, \rho, h) = (1 + S(T, \rho, h))\gamma_p, \quad (7b)$$

$$\chi_R(T, \rho, h) = (1 + S(T, \rho, h))\chi, \quad (7c)$$

$$E_{SI}(T, \rho, h) = \frac{\lambda}{\varepsilon_0(\varepsilon_d \square + \lambda \varepsilon_{33}^b)} \sum_{i=1,2} e Z_i N_i f_i(T, \rho), \quad E_{act}(U, h) = -\frac{\varepsilon_d U}{\varepsilon_d \square + \lambda \varepsilon_{33}^b}. \quad (7d)$$

The first term in Eq.(7a),  $\alpha_p(1 + S(T, \rho, h))$ , is renormalized by the influence of the surface charge caused by the adsorption/desorption of the oxygen ions via the function  $S(T, \rho, h)$ . The last term in Eq.(7a),  $\frac{\lambda}{2\varepsilon_0(\varepsilon_d \square + \lambda \varepsilon_{33}^b)}$ , originated from the depolarization field. The first expression (7d) is the built-in electric field created by surface ions,  $E_{SI}(T, \rho, h)$ , that is significant for thin films being proportional to the ratio  $\frac{\lambda}{h}$ . Since, as a rule,  $\varepsilon_d \square \gg \lambda \varepsilon_{33}^b$ , the acting field is close to an external field,  $E_{act} \approx -\frac{U}{h}$ . Also, we introduce positive functions in Eq.(7):

$$S(T, \rho, h) = \frac{\lambda h}{\varepsilon_0(\varepsilon_d \square + \lambda \varepsilon_{33}^b)} \sum_{i=1,2} N_i \frac{(e Z_i f_i(T, \rho))^2}{k_B T}, \quad f_i(T, \rho) = \left(1 + \rho^{1/n_i} \exp\left(\frac{\Delta G_i^{00}}{k_B T}\right)\right)^{-1}. \quad (7e)$$

It is seen from Eqs.(7) that the influence of the relative partial oxygen pressure on the AFE thin film reduces to the influence of the surface charge  $\sigma_0[\phi]$  caused by the adsorption/desorption of the oxygen ions. The influence is introduced via the positive function  $S(T, \rho, h)$  and the built-in electric field  $E_{SI}(T, \rho, h)$  penetrating the entire the depth of the film. Since  $\frac{\Delta G_i^{00}}{k_B T} > 3$  for  $\Delta G_i^{00} \geq 0.2$  eV and  $|T| < 500$  K,  $\exp\left(\frac{\Delta G_i^{00}}{k_B T}\right) \gg 1$  in the actual temperature range  $|T| < 500$  K. Thus, the function  $S(T, \rho, h)$  rapidly growth for high ( $\rho \gg 1$ ) and low ( $\rho \ll 1$ ) pressures, and so it can significantly increase the absolute value of the negative coefficient  $\alpha_p(1 + S(T, \rho, h))$ . In result the coefficient  $\alpha_{pR}(T, \rho, h)$  can become more negative than  $\alpha_a$  opening the possibility of the FE phase emergence at high excess ( $\rho \gg 1$ ) and deficient ( $\rho \ll 1$ ) relative partial pressures. Below we will show and analyze the possibility. The experimental evidences of this effect in FE films were given a while ago in Refs.[13-15, 25, 29]. This work states that the same mechanism of the FE phase induction by the oxygen exposure/deficiency should exist in AFE films, but unlikely it can be noticeable in the bulk AFE, because Eqs.(7) are valid for thin films only.

### B.1. The case of the second order phase transition (2-4 Landau expansion)

Note that in the case of the AFE film with the second order phase transitions, when  $\beta_{a,p} > 0$  and  $\gamma_{a,p} = 0$ , analytical solutions for the phase energy, order parameters and critical (or coercive) fields of double (or single) hysteresis loops are possible after a trivial minimization of the Landau energy (6). They are summarized in **Table I**. The boundaries between the AFE phase, mixed ferrielectric FEI phase, pressure-induced FE-like AFI phase, and paraelectric phase correspond to the condition of the phase energies equality. Below we will be specifically interested in the pressure-induced transition from the AFE phase to the FE-like AFI phase. The FE-like AFI phase becomes absolutely stable if  $\alpha_{pR} < 0$ , and  $F_{AFI} < 0$  is minimal in comparison with  $F_{AFE}$  and  $F_{FEI}$ . When  $\alpha_a > 0$  at  $T > T_A$  and we put  $\chi < 0$  for the AFE phase stability, the condition

$$\alpha_{pR}(T_A, \rho, h) \leq 0 \quad (8)$$

is sufficient for the absolute stability of the AFI phase.

**Table I.** Thermodynamic phases, order parameters, their energy and critical fields calculated for  $\beta_{a,p} > 0$  and  $\gamma_{a,p} = 0$ .

| Phase       | Order parameters at $E_{act} = E_{SI}$                                                                                                                                                              | Free energy at $E_a = E_{SI}$                                                                                                     | Critical field(s) $E_c$                                                                                                                                                                                                                       |
|-------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| AFE         | $A_S = \pm \sqrt{-\alpha_a/2\beta_a}$<br>$P_S = 0$<br>$\Delta P \cong \pm \sqrt{-\frac{\alpha_{pR}}{6\beta_{pR}}}$<br>(see <b>Fig. 1b</b> for definitions)                                          | $F_{AFE} = -\frac{\alpha_a^2}{4\beta_a},$<br>$\alpha_a < 0$                                                                       | $E_{c1,2} = \frac{\pm 1}{3\sqrt{3}} \frac{(-\alpha_{pR} + \frac{\chi_R \alpha_a}{2\beta_a})^{3/2}}{\beta_{pR} - \frac{\chi_R^2}{4\beta_a}} - E_{SI}$<br>$E_{c3,4} = \pm \frac{1}{3\sqrt{3}} \frac{(-\alpha_{pR})^{3/2}}{\beta_{pR}} - E_{SI}$ |
| FEI         | $P_S = \pm \sqrt{\frac{2\alpha_{pR}\beta_a - \chi_R \alpha_a}{4\beta_a\beta_{pR} - \chi_R^2}}$<br>$A_S = \pm \sqrt{\frac{2\alpha_a\beta_{pR} - \chi_R \alpha_{pR}}{4\beta_a\beta_{pR} - \chi_R^2}}$ | $F_{FEI} =$<br>$-\frac{\alpha_a^2\beta_{pR} + \alpha_{pR}^2\beta_a - \chi_R \alpha_a \alpha_{pR}}{4\beta_a\beta_{pR} - \chi_R^2}$ | $E_{c1,2} = \frac{\pm 1}{3\sqrt{3}} \frac{(-\alpha_{pR} + \frac{\chi_R \alpha_a}{2\beta_a})^{3/2}}{\beta_{pR} - \frac{\chi_R^2}{4\beta_a}} - E_{SI}$                                                                                          |
| FE-like AFI | $P_S = \pm \sqrt{-\frac{\alpha_{pR}}{2\beta_{pR}}}$<br>$A_S = 0$                                                                                                                                    | $F_{AFI} = -\frac{\alpha_{pR}^2}{4\beta_{aR}},$<br>$\alpha_{pR} < 0$                                                              | $E_{c1,2} = \pm \frac{1}{3\sqrt{3}} \frac{(-\alpha_{pR})^{3/2}}{\beta_{pR}} - E_{SI}$                                                                                                                                                         |
| PE          | $A_S = P_S = 0$                                                                                                                                                                                     | 0                                                                                                                                 | absent                                                                                                                                                                                                                                        |

We use a Gaussian Process model (**GPM**) for rapid exploration and prediction of phase diagrams and order parameters corresponding to the free energy (6) for the case  $\beta_{a,p} > 0$  and  $\gamma_{a,p} = 0$  in **Appendix D** of Ref. [35]. The material parameters are listed in **Table D1**. Results are shown in **Figs. D1-D4** [35]. In the GPM predicted image, we can see similar distinctive regions with different color coding and thus giving us the interpretation of individual phases. We can have better prediction of phases with more advanced acquisition function (exploration-exploitation) to sample as per user criteria (for example- we can conduct adaptive sampling where the objective function is higher). We observed that as  $\rho$  increase or decreases by the order of 10 for temperature  $T < T_p$ , we are approaching towards FEI phase where with further increase or decreases of  $\rho$  by the order of 10, the deeper wells for order parameter  $A$  are shifted to deeper wells for order parameter  $P$ . Also, as the parameters  $h$  and  $\Delta G_i^{00}$  decreases, the FEI region shrinks and expands respectively for the same parameter space of  $T, \rho$ . As per defined in **Table I**, we did not find the AFI region ( $A = 0, P_S \neq 0$ ) for any of **Figures D1-D4**. The codes are available at [52].

### B.2. The case of the first order phase transition (2-4-6 Landau expansion)

For the illustration of numerical results, we use an AFE film with the thickness  $h = (5 - 50)$  nm separated from the tip electrode by the gap of a thickness  $\lambda = (0 - 2)$  nm. Also, we regard that the ion formation energies are equal at normal conditions and small,  $\Delta G_1^{00} = \Delta G_2^{00} = 0.2$  eV. Using results of Haun

et al. [39, 40], we determine the LGD expansion coefficients for a model antiferroelectric PbZrO<sub>3</sub> (see **Appendix C** [35]). It appeared that  $\beta_{a,p} < 0$  and  $\gamma_{a,p} > 0$  for this material, and so 2-4-6 LGD expansion must be used. Corresponding expansion coefficients and other parameters are listed in **Table C1** in **Appendix C** [35].

However, the coefficients from **Table C1** do not capture all important features of a bulk PbZrO<sub>3</sub>, as we note several discrepancies in the temperature behavior of the calculated here and measured critical fields and polarization hysteresis shape [53, 54, 55, 56]. We relate the discrepancy with the strong influence of antiferrodistorsive subsystem (oxygen octahedra tilt) that is missed in the Kittel model and underestimated in the Haun model. The complete and self-consistent phenomenological description of PbZrO<sub>3</sub> antiferroelectric and electrocaloric properties [57], and anomalous ferroelectricity [42] allowing for an antiferrodistortion [38, 41, 43] is an important problem beyond the scope of this work. However, the ferroelectricity observed in thin PbZrO<sub>3</sub> films [58] is in scope of our work, at least partially.

When calculating the hysteresis loops of polarization  $P(U)$  at nonzero frequency  $\omega$  of the applied voltage,  $U = U_0 \sin(\omega t)$ , we use different kinetic coefficients  $\Gamma_P \gg \Gamma_A$  to make the characteristic relaxation time of  $P$  much longer than the relaxation time of  $A$ . The strong inequality  $\Gamma_P \gg \Gamma_A$  leads to the polarization relaxation with the characteristic time  $\tau = \frac{\Gamma_P}{2|\alpha_p|}$ , while the anti-polarization behaves adiabatically. Hence the dimensionless frequency  $w = \omega\tau$  govern the polarization response to external field.

To avoid “sticking” of the system at local minima, we applied a very small fictitious “antifield” (with an amplitude smaller than  $10^{-6}$  V/nm) acting on the anti-polarization  $A$ . The physical origin of the antifield is related with variations of the local electric field. The calculations were performed and visualized in Mathematica 12.2 ©Wolfram Research software and available at [59].

## IV. RESULTS

### A. A phase diagram, free energy relief and hysteresis loops of a thick antiferroelectric film without surface ions

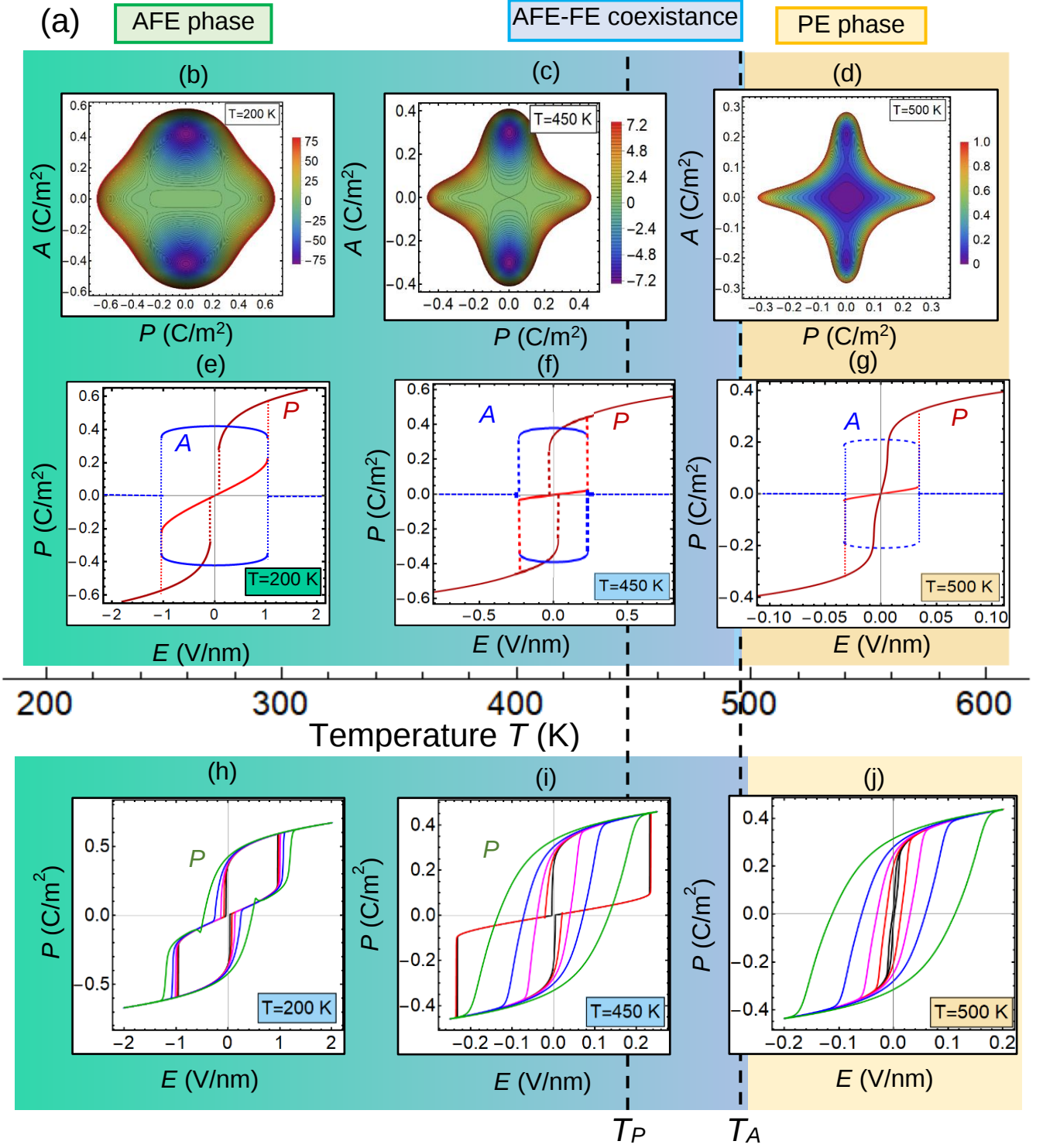
The phase diagram of a very thick AFE film as function of temperature is shown in **Fig. 2a**. Here the surface ions from ambient are absent and the gap is either absent or very small to approach the film close to bulk conditions. In accordance with available experimental results [38 - 43] the diagram contains the region of a AFE phase followed by an AFE phase coexisting with a “weak” FE phase, and then by a paraelectric (**PE**) phase. The first order phase transition between the AFE and the PE phase occurs at  $T_A \cong 490$  K, and the boundary between the AFE and the AFE-FE phases is very diffuse and located around  $T_P \cong 460$  K.

Contour maps of the free energy dependence on the polarization and anti-polarization are shown in the upper insets **(b)-(d)** to **Fig. 2** for different temperatures  $T = 200, 450$  and  $500$  K, and zero field  $E = 0$ . There are two relatively deep  $A$ -wells ( $A = \pm A_S, P = 0$ ) and two very shallow  $P$ -wells ( $P = \pm P_S, A = 0$ ) in the “deep” AFE-phase at the temperatures  $T \ll T_P < T_A$  [inset **(b)** for 200 K]. Both of  $A$ -wells have the

same depth, as well as both of  $P$ -wells have the same depth. The  $A$ -wells and  $P$ -wells are separated by the four saddle points. The  $A$ -wells become significantly shallower when the temperature approaches  $T_p$  [compare the minimal energy value (-7.2 rel. units) in the inset **(c)** for 450 K with -75 rel. units in the inset **(b)** for 200 K]. At temperatures  $T_p \leq T < T_A$  all wells still have negative energy, but the relative difference between the depth of  $A$ -wells and  $P$ -wells is much smaller than at  $T \ll T_p$ , indicating that the temperature range corresponds to the coexisting stable polar and anti-polar states. The wells energy become positive and so polar and anti-polar states become metastable at  $T > T_A$  [inset **(d)** for 500 K]. Then, the wells disappear completely in the deep PE phase at  $T \gg T_A$ .

The relief of the free energy determines the temperature behavior of polarization dependence on the external  $E$ -field,  $P(E)$ , where  $E = \frac{U}{h}$ . The quasi-static dependence  $P(E)$  is mostly hysteretic, and its shape gradually changes from a double antiferroelectric-type loop to a loop with a thin constriction, and then to a paraelectric-like curve with the temperature increase from 200 K to 500 K, respectively [see dark-red and red curves in the insets **(e)-(g)** to **Fig. 2**]. However, the transition from the red curves to a dark-red curves takes place only when  $E > E_{cr}$ , where  $E_{cr}$  is the static critical field. The dependence  $P(E)$  is quasi-linear at  $E < E_{cr}$  [see red parts of the  $P(E)$  curves]. Notable that  $P(E)$  curves are antisymmetric with respect to the  $E$ -axis, since the built-in field  $E_{SI}$  is absent due to the absence of surface ions.

Polarization hysteresis loops,  $P(E)$ , calculated for low dimensionless frequencies  $w \ll 1$ , almost coincide with the static  $P$ -curves [compare black loops in the plots **(h)-(j)** with red curves in the plots **(e)-(g)** in **Fig. 2**]. The frequency increase in the range  $1 \leq w \leq 3$  leads to the appearance of a thin constriction between the double loops in the AFE phase, as well as to the loop opening in the PE phase [see red loops in the plots **(h)-(j)** in **Fig. 2**]. The width of the constriction increases significantly with further increase of  $w$ , and the loop acquires a ferrielectric-like shape in the AFE phase [see magenta, blue and green loops in the plot **(h)**]. At the same time the frequency increase ( $3 \leq w \leq 10$ ) at higher temperatures leads to an opening of a ferroelectric-like loop, meaning that the opening is a purely dynamic effect [see magenta, blue and green loops in the plot **(i)**]. The dynamic effect allows us to classify the temperature region as AFE-FE coexisting region. The high frequency  $w \geq 10$  opens a pseudo-ferroelectric loop even in the PE phase [see magenta, blue and green loops in the plot **(j)**].



**FIGURE 2.** Phase diagram of an AFE film (a). Contour maps of the free energy dependence on the polarization ( $P$ ) and anti-polarization ( $A$ ) for the temperature values  $T = 200$  K (b),  $450$  K (c) and  $500$  K (d), and  $E = 0$ . Relative units are used for the energy color scale. Dependences of the anti-polarization  $A$  (dashed and dotted blue loops) and polarization  $P$  (dashed red and dark-red loops) on the static external electric field  $E$  calculated for temperature values  $T = 200$  K (e),  $450$  K (f), and  $500$  K (g), respectively. Polarization hysteresis  $P(E)$  calculated for dimensionless frequencies  $w = 0.3$  (black loops),  $3$  (red loops),  $10$  (magenta loops),  $30$  (blue loops), and  $100$  (green loops), and temperatures  $T = 200$  K (h),  $450$  K (i), and  $500$  K (j), respectively. For the plots (h)-(j) external electric field is  $E = 0$ .

$\frac{U_0}{h} \sin(\omega t)$ , and dimensionless frequency  $w = \frac{\omega \Gamma_P}{2|\alpha_p|}$ . The surface charges from ambient are absent. Gap thickness  $\lambda < 0.1$  nm, film thickness  $h > 500$  nm. Other parameters are listed in **Table C1** [35].

Note, that the phase set (AFE, AFE-FE and PE) calculated within 2-4-6 Landau expansion with material parameters from **Table C1** [35] and shown in **Fig. 2a** differs from the analogous set (AFE, FEI, PE) calculated within 2-4 Landau expansion with material parameters from **Table D1** and shown in **Fig. D1-D4** [35]. Since  $\beta_{a,p} > 0$  and  $\gamma_{a,p} = 0$  and  $\beta_{a,p} < 0$  and  $\gamma_{a,p} > 0$  for the 2-4 and 2-4-6 Landau expansions, respectively, as well as the effect of  $\rho$  is not considered in **Fig. 2a**, the difference in the phase set seems natural.

Comparing the diagram in **Fig. 2a** with well-known literature data [38 - 43], we concluded that our model with parameters from **Table C1** describes correctly all the main experimental features of the phase transitions in  $\text{PbZrO}_3$ , namely the sequence of phases: AFE phase  $\rightarrow$  AFE-FE coexistence  $\rightarrow$  PE-like state. Also, the experimentally observed transition from a double antiferroelectric-like hysteresis loop to a constricted ferroelectric-like loop and then to a PE-like dynamic loop with increasing temperature is correctly reproduced in **Fig. 2h-j**. However, the model does not describe several minor features of the hysteresis loops observed in some (but not all) experiments, such as the "stretched" constriction and AFE loops separated by long linear region (such as shown in **Fig. 1b**). It also does not reproduce correctly the temperature behavior of the critical fields.

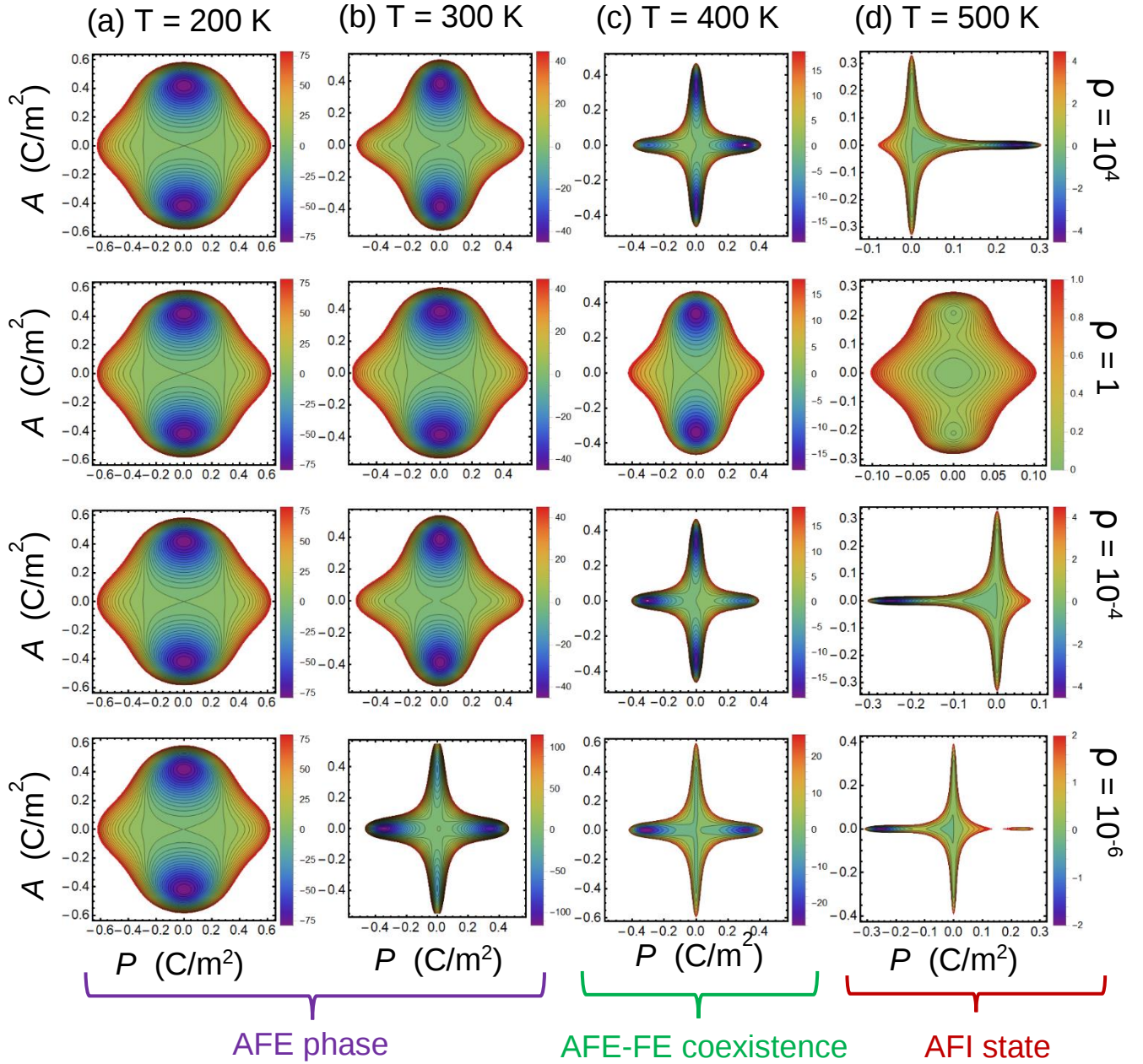
Next question is what will change in **Fig. 2** if a bulk  $\text{PbZrO}_3$  is placed in an oxygen environment? In our model, the bulk is achieved by considering a very thick  $\text{PbZrO}_3$  film with one (or both) surfaces exposed to oxygen pressure. It appeared that the effect of the partial oxygen pressure is significant only in the immediate vicinity of the film surface, since the depolarization field, the built-in electric field induced by ions, and the renormalization of the free energy coefficients are proportional to the ratio of the gap width  $\lambda$  to the film thickness  $h$ . Therefore, the consideration of a very thick film with  $h \gg 10^{-3}\lambda$  leads to results that are barely distinguishable from those shown in **Fig. 2**.

## B. The influence of surface ions on the phase diagram, free energy relief and hysteresis loops of antiferroelectric films

The free energy as a function of polarization ( $P$ ) and anti-polarization ( $A$ ) calculated for several temperatures  $T$  and relative partial oxygen pressures  $\rho$ , which values are listed for each column/row, is shown in **Fig. 3**. There are two very deep  $A$ -wells ( $A = \pm A_S$ ,  $P = 0$ ) and two very shallow  $P$ -wells ( $P = \pm P_S$ ,  $A = 0$ ) in the deep AFE phase at the temperatures well below  $T_p \approx 460$  K and  $10^{-6} < \rho < 10^4$  [see columns **(a)-(c)** for (200 – 400) K]; and the wells become shallower at  $T \rightarrow T_A$  and eventually disappear with the temperature increase well above  $T_A \approx 490$  K [see the column **(d)** for 500 K]. Both of  $A$ -wells have the same depth independently on the values of  $\rho$  and  $T$ . The relative depth of  $P$ -wells depends on  $\rho$  and  $T$

values. The right well ( $P = +P_S$ ) is evidently deeper for  $\rho \gg 1$  and  $T > T_A$ ; they are almost equal for  $10^{-4} < \rho < 10^4$  and  $T < 400$  K; and exactly equal for  $\rho = 1$  independently on  $T$ ; and the left well ( $P = -P_S$ ) becomes evidently deeper for  $\rho \ll 1$  and  $T > T_A$  [compare the top, middle and bottom rows]. The origin of the  $P$ -wells asymmetry is the built-in electric field,  $E_{SI}$ , induced by the surface ions charge. This field is approximately proportional to the difference  $(\rho^{1/n_i} - \rho^{-1/n_i})$ , and thus the magnitude of  $E_{SI}$  increases with the deviation of  $\rho$  from unity, and the sign of  $E_{SI}$  changes when  $\rho \rightarrow \frac{1}{\rho}$ , that is a direct consequence of Eqs.(7d) and (7e) at  $\Delta G_1^{00} = \Delta G_2^{00}$ . The sign change of  $E_{SI}$  explains the left (or right) asymmetry of the  $P$ -wells.

The  $A$ -wells and  $P$ -wells are separated by the four saddle points. At temperatures lower than  $T_A$  both  $A$ -wells and  $P$ -wells have negative energy, i.e., they correspond to stable polar and anti-polar states. The energy of  $A$ -wells becomes positive and corresponding states become metastable at  $T > T_A$  [see the column **(d)** for 500 K]. The  $A$ -wells disappear at  $T \gg T_A$ . Both  $P$ -wells acquire positive energy at  $T > T_p$  and disappear at  $T \gg T_A$  only when  $10^{-2} < \rho < 10^2$ . Either right or left negative well appears when  $\rho > 10^2$  or  $\rho < 10^{-2}$ , respectively. This means that the built-in electric field  $E_{SI}$  induced by the surface ions charge creates and supports an FE-like AFI state, that is characterized by the asymmetric potential relief, and the asymmetry increases with excess ( $\rho \gg 1$ ) or deficiency ( $\rho \ll 1$ ) of oxygen ions at the film surface [see Eq.(7d) for details].



**FIGURE 3.** The free energy as a function of polarization ( $P$ ) and anti-polarization ( $A$ ) calculated for the temperatures  $T=200, 300, 400$  and  $500$  K [columns (a), (b), (c) and (d)], and relative partial oxygen pressures  $\rho = 10^4, 1, 10^{-4}, 10^{-6}$ , which values are listed for each column/row. Relative units are used for the energy color scale. An external electric field is absent,  $E = 0$ . The thickness of AFE film  $h = 50$  nm, gap thickness  $\lambda = 2$  nm, and ion formation energies  $\Delta G_1^{00} = \Delta G_2^{00} = 0.2$  eV.

Since the case  $\rho \gg 1$ , corresponding to high oxygen excess, is hard to realize in practice, below we mainly discuss the easier realizable case of the oxygen deficiency,  $\rho \leq 1$ , keeping in mind that the physical picture at  $\rho \geq 1$  differs the one at  $\rho \leq 1$  only by the asymmetry with respect to the  $P$ -axis of the potential relief (the left or the right well is deeper), since corresponding built-in fields lead to the left or right shift of polarization loops/curves, respectively.

The dependences of the anti-polarization  $A$  (blue curves) and polarization  $P$  (red and dark-red curves) on the static electric field  $E$  are shown in **Fig. 4** for temperatures  $T = (200 - 500)$  K (columns **a-d**) and relative oxygen pressures  $\rho = 1, 10^{-4}, 10^{-6}$  (from the top to the bottom rows), which values are listed for each column/row. The red and dark-red polarization curves are two nonzero stable solutions of Eq.(5a). Dotted vertical lines show the thermodynamic transitions between different polar and anti-polar states.

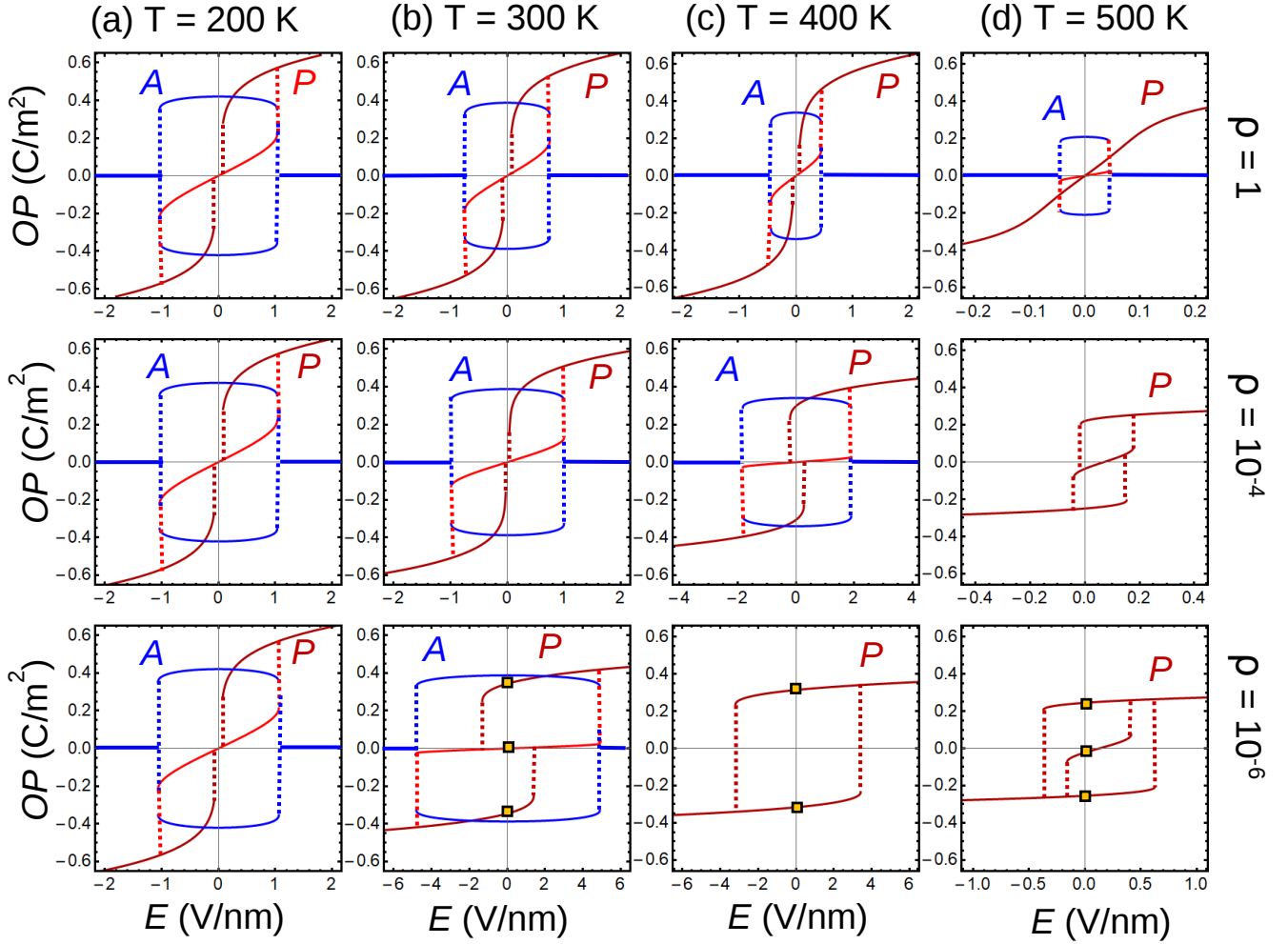
Changes, which occur with the shape of the loops in vertical columns **(a, b, c)** and **(d)**, with the increase in temperature, mainly consist in a decrease in the width and height of  $A$ - and  $P$ - loops, and the appearance of a noticeable asymmetry of  $P$ -loops between negative and positive values of polarization under the change in the relative oxygen pressure  $\rho$  from 1 to  $10^{-6}$ .

The features of  $A(E, T)$  behavior depend on  $T$  and  $\rho$  much weaker than the features of  $P(E, T)$ . The  $A$ -loop is absent only for  $\rho < 10^{-4}$  and above (350 – 450) K, which indicate the transition to the FE-like AFI state due to the absence of "ionic support" of the AFE state. At lower partial oxygen pressures, the shape of  $A$ -loop is close to rectangular, its width and height depend on temperature and pressure. The  $A$  - loop disappears at external fields larger than the critical value  $E_c$ , since the anti-polarization  $A$  no longer exists.

A decrease of  $A$  magnitude with increasing an electric field  $E$  in the range  $E < E_c$  corresponds to the increase of  $P$ , and the  $A(E)$  curves are almost symmetric with respect to the  $E$ -axis, while the  $P(E)$  curves acquire a more noticeable asymmetry between positive and negative  $P$ -values with the decrease of  $\rho$  from 1 to  $10^{-6}$ .

$P(E)$ -curves supplemented with red dotted vertical lines are virtually static double loops at  $\rho = 1$  and become hysteresis-less only at  $T > 500$  K. The coercive field and the loop height decrease with temperature at  $\rho = 1$  (as it should be). The double  $P$ -loops transforms to the loops with a thin constriction in the vicinity of  $E = 0$  with  $\rho$  decrease and temperature increase. Then the constriction significantly increases for  $\rho = 10^{-4}$  and  $T \geq 300$  K, and eventually the static loop with a wide constriction transforms to a ferroelectric-like single loop for  $\rho = 10^{-6}$  and  $T \geq 400$  K. The FE-like single  $P$ -loops correspond to the AFI state, because the surface ions support the FE polarization, and suppress the antipolar AFE order.

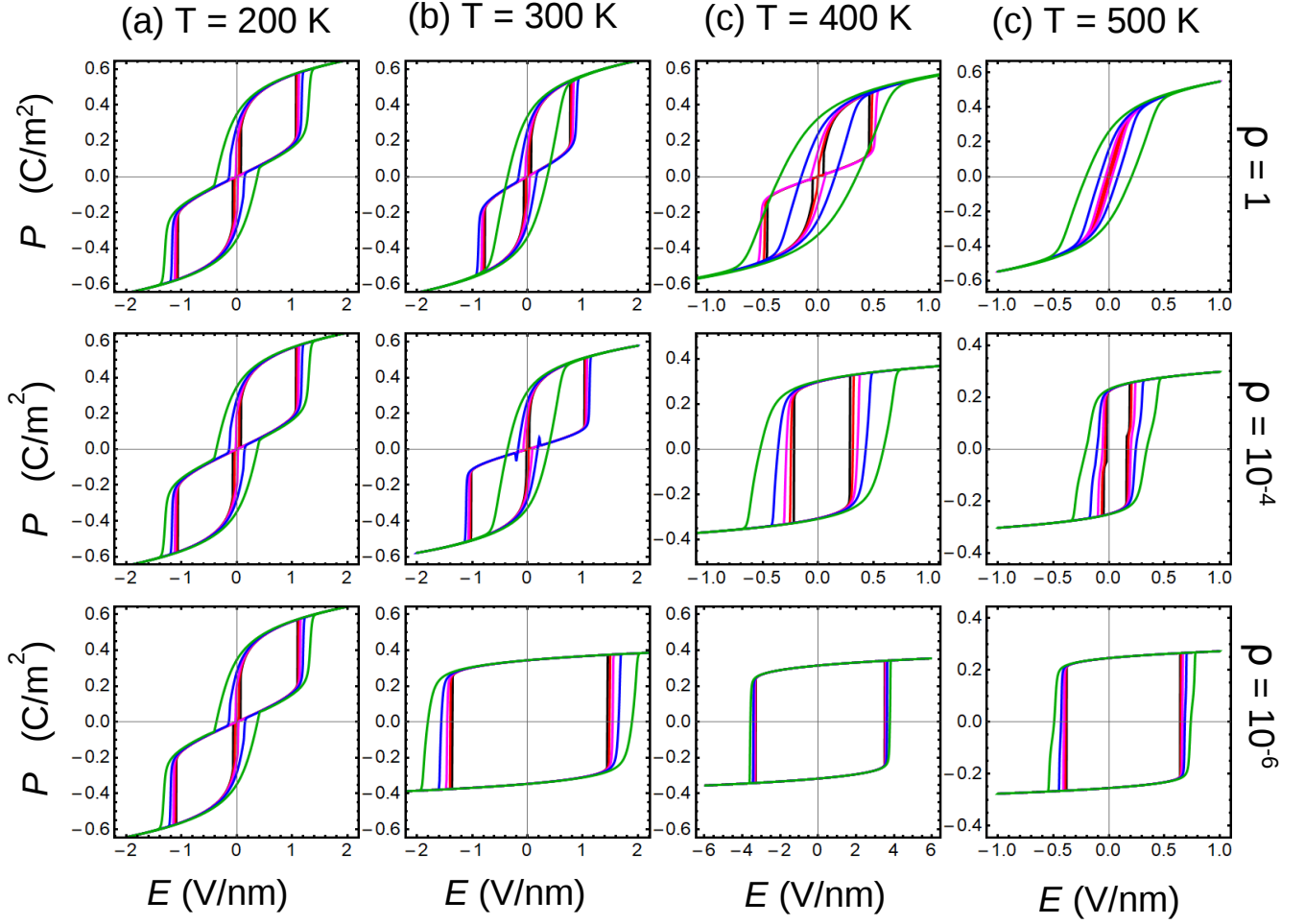
Note that the  $P(E)$ -curves have no asymmetry for  $\rho = 1$ , since the built-in field  $E_{SI}$  is absent in the case. The  $P(E)$ -curves are slightly right-shifted for  $\rho < 1$ , since  $E_{SI}$  is positive. The shift increases significantly with  $\rho$  decrease below  $10^{-4}$  and  $T$  increase above 400 K. The  $P$ -curves for  $\rho = 10^{-4}$  are left-shifted, since  $E_{SI}$  is negative in the case; they are shown in **Fig. E1** in **Appendix E** [35].



**FIGURE 4.** Static dependences of the order parameters (OP) – anti-polarization  $A$  (solid blue curves) and polarization  $P$  (solid red and dark-red curves) on external electric field  $E$  calculated for temperature  $T = 200, 300, 400$  and  $500$  K [columns (a), (b), (c) and (d)] and relative partial oxygen pressures  $\rho = 1, 10^{-4}, 10^{-6}$ , which values are listed for each column/row. Dotted vertical lines show the thermodynamic transitions between different polar and antipolar states; yellow rectangles mark 2 or 3 stable polarization states. An external electric field is  $E = \frac{U}{h}$ . Other parameters are the same as in **Fig. 3**.

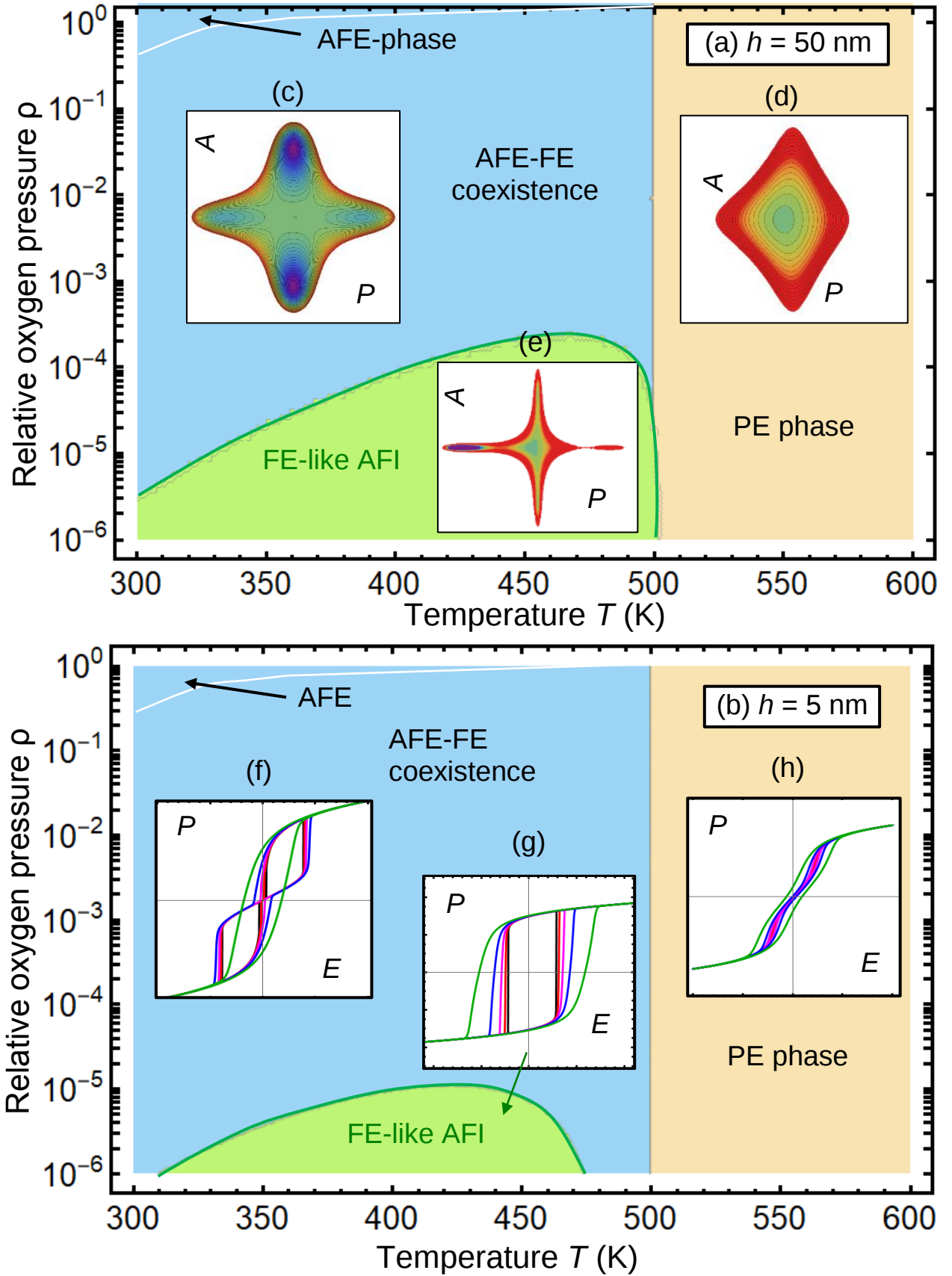
Polarization hysteresis loops  $P(E)$  calculated for dimensionless frequencies  $w = 0.3 - 100$ , temperatures  $T = (200 - 500)K$  and relative oxygen pressures  $\rho = 1 - 10^{-6}$  are shown in **Fig. 5**. Under the relative pressure decrease from 1 to  $10^{-4}$  and relatively low frequencies  $w \leq 10$  the loop shape demonstrates a continuous transition from a double loop in the AFE phase to a single loop in the AFI state, and then the loop disappears in a PE phase. Only a single loop exists at  $\rho = 10^{-6}$  and  $T \geq 300$  K, and it gradually degrades to a shifted hysteresis-less PE curve with a temperature increase far above 600 K (that is not shown in the figure). The frequency increase ( $w \geq 30$ ) transforms a double loop to a loop with constriction, and then it “opens” a single loop. The loop opening is a dynamic effect similar to the one, shown in **Figs. 2h-j**. Both quasi-static ( $w \leq 10$ ) and dynamic ( $w \geq 30$ ) loops are slightly right-shifted at  $\rho < 1$ , and the shift is proportional to the built-in field  $E_{SI}$ . The shift increases with  $\rho$  decrease below  $10^{-4}$

and  $T$  increase above 400 K. The  $P$ -curves for  $\rho = 10^4$ , which are left-shifted (since  $E_{SI}$  is negative in the case), are shown in **Fig. E2** in **Appendix E**.



**FIGURE 5.** Polarization hysteresis loops,  $P(E)$ , calculated for dimensionless frequencies  $w = 0.3$  (black loops), 3 (red loops), 10 (magenta loops), 30 (blue loops), and 100 (green loops), temperatures  $T = 200$  K, 300 K, 400 K and 500 K [columns (a), (b), (c) and (d), respectively], and relative partial oxygen pressures  $\rho = 1, 10^{-4}, 10^{-6}$ , which values are listed for each column/row. External electric field is  $E = \frac{U_0}{h} \sin(\omega t)$ , and  $w = \frac{\omega \Gamma_P}{2|\alpha_p|}$ . Other parameters are the same as in **Fig. 3**.

A typical phase diagram of a thin AFE film in dependence on the temperature  $T$  and relative oxygen pressure  $\rho \leq 1$  is shown in **Fig. 6a** for  $h = 50$  nm and in **Fig. 6b** for  $h = 5$  nm. There are an AFE phase, an AFE phase coexisting with a weak FE phase, a FE-like AFI phase, and an electret-like PE phase. The insets (c, d, e) in **Fig. 6a** illustrate the typical free energy relief is the AFE-FE, FE-like FEI and electret-like PE phases, respectively. The insets (f, g, h) in **Fig. 6b** are typical hysteresis loops in these phases. The phase diagram plotted for the relative pressures from  $10^{-6}$  to  $10^6$  is shown in **Fig. E3** in **Appendix E** [35].



**FIGURE 6.** Typical phase diagrams of thin AFE films with thickness  $h = 50$  nm **(a)** and  $h = 5$  nm **(b)** in dependence on the temperature  $T$  and relative partial oxygen pressure  $\rho$ . There are an AFE phase coexisting with a weak FE phase, a FE-like AFI phase, and an electret-like PE phase. Typical free energy maps at  $E = 0$  **(b-d)** and polarization

hysteresis loops  $P(E)$  (**e-g**). The description of the insets is the same as in **Figs. 3** and **5**, respectively. Other parameters are the same as in **Fig. 3**.

The wide light-blue AFE-FE coexistence region increases with  $h$  decrease (compare **Fig. 6a** and **Fig. 6b**), but it is located at the temperatures lower than 500 K (that is slightly higher than  $T_A \cong 490$  K) independently on the film thickness, because the anti-polarization is insensitive to the depolarization field. The relatively small light-green region of the AFI phase decreases significantly with  $h$  decrease (compare **Fig. 6a** and **Fig. 6b**), because the polarization is very sensitive to the depolarization field  $E_d$ , which is inversely proportional to the film thickness,  $E_d \sim -\frac{\lambda P}{\varepsilon_0(\varepsilon_d \square + \lambda \varepsilon_{33}^b)}$  [see Eq.(5c)]. The AFI phase corresponds to rather low relative oxygen pressures ( $\rho \leq 2 \cdot 10^{-4}$  for  $h = 50$  nm or  $\rho \leq 10^{-5}$  for  $h = 5$  nm), but exists in a relatively wide temperature range ( $250 \text{ K} \leq T \leq 500 \text{ K}$  for  $h = 50$  nm, or  $310 \text{ K} \leq T \leq 475 \text{ K}$  for  $h = 5$  nm). The boundary between the AFE-FE region and the AFI phase is close to a rounded corner. The boundary between the AFE-FE, the AFI and the PE phase (local inside a sand-colored region) is close to the vertical line  $T \cong 500 \text{ K}$ .

Note, that the phase set, namely AFE, AFE-FE, FE-like AFE, and electret-like PE, shown in **Figs. 6** differs from the analogous set (AFE, FEI, PE) shown in **Fig. D1-D4** [35]. The difference originated from the difference in Landau expansion coefficients,  $\beta_{a,p} > 0$  and  $\gamma_{a,p} = 0$  for 2-4 Landau expansion, apart  $\beta_{a,p} < 0$  and  $\gamma_{a,p} > 0$  for the 2-4-6 Landau expansion (compare material parameters from **Table C1** with material parameters from **Table D1**[35]).

### C. The influence of surface ions on the energy and information storage in thin AFE films

It is well-known that an energy loss is an area inside a hysteresis loop  $P(E)$ , further abbreviated as **LA**, and a stored energy is equal to an area above the loop (in other words, the area between the loop and P-axis), further abbreviated as **SA**. The nonvolatile information storage requires high remanent polarization and not very small coercive field, and, thus the optimal loop area **LA**. If the loop is absent and  $P \cong \chi E$ , the loss is absent, and the stored energy is  $\frac{\chi}{2} E^2$ . However, the nonvolatile information storage is impossible in the case.

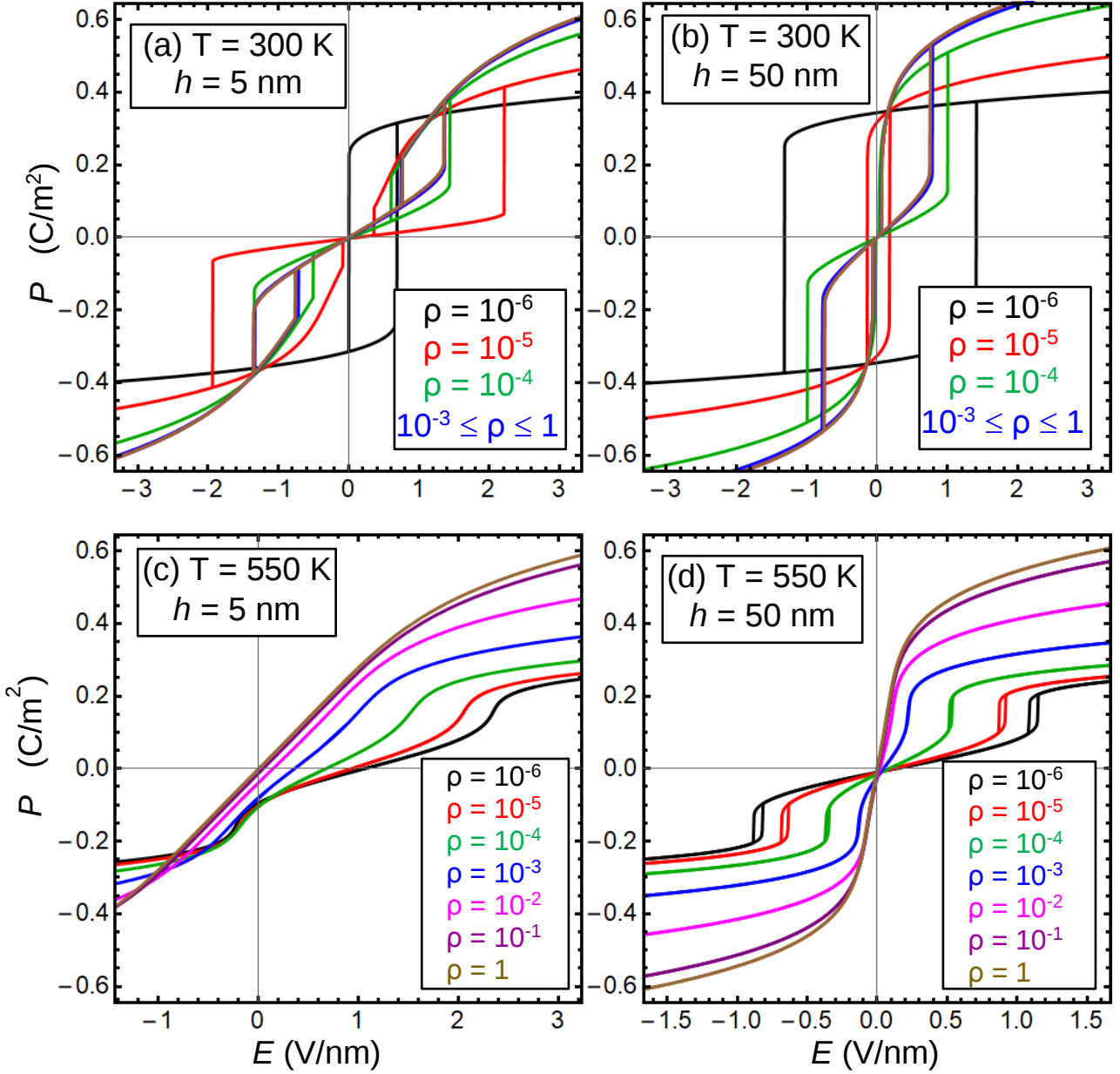
For a single quasi-rectangular ferroelectric hysteresis loop with polarization saturation above the coercive field the stored energy is small (zero in the limit of a rectangular loop), and the loop area is given by the approximate expression  $LA = 2P_S(E_{c2} - E_{c1})$  (see **Fig. 1b**). The expressions for the spontaneous polarization  $P_S$  and coercive fields  $E_{ci}$  in the case of the second order phase transitions are given in **Table I**. The area of a double loop is given by approximate expression  $LA = \Delta P(E_{c3} - E_{c1}) + \Delta P(E_{c2} - E_{c4})$ , and the stored energy is  $SA = \frac{\varepsilon}{2}(E_{c1}^2 + E_{c2}^2) + \Delta P(E_{c1} - E_{c2})$ . For the case of polarization saturation above the critical fields a rough approximation  $\frac{LA}{SA} \sim \frac{E_{c3} - E_{c4}}{E_{c1} - E_{c2}} - 1$  is valid. If all four coercive field exists, we obtain

that  $\frac{LA}{SA} \sim \left(1 - \frac{\chi_R \alpha_a}{2\alpha_p \beta_a}\right)^{-3/2} - 1$  for the AFE film with the second order phase transitions [ $\beta_{a,p} > 0$  and  $\gamma_{a,p} = 0$  in Eq.(6)].

It follows from the above expressions that one needs a large step-like (or quasi-linear with a small slope) hysteresis-less region (e.g.,  $P \cong \varepsilon E$ , where  $\varepsilon$  is small) for the maximal energy storage. Without the region the loop shape optimization for the energy storage in the space of parameters  $\{\rho, T, h\}$  leads to a trivial result - no loop at all, i.e., to the hysteresis-less curve in the PE phase. The presence of the linear region adds additional trapezoidal area above the  $P(E)$  curve (or between the  $P(E)$  loop and P-axis), and the energy storage becomes favorable in the AFE phase also (see **Fig. 1b**). Since we have shown that the oxygen deficiency (or excess) can transform a double AFE loop to a single FE-like one (compare loops in **Fig. 5**), the usage of AFI film for the energy storage can be not beneficial, at the same time, the information storage in AFI films can possess several advantages. Let us discuss the question in more details for the AFE film with the first order phase transitions [ $\beta_{a,p} < 0$  and  $\gamma_{a,p} > 0$  in Eq.(6)].

**Figure 7a** illustrates that the double hysteresis loops with a pronounced linear region between the loops can exist at room temperature only in ultra-thin AFE films ( $h \leq 10$  nm) if the relative oxygen pressure does not deviate significantly from the normal conditions,  $10^{-3} \leq \rho \leq 1$ . At the same time the linear region is almost absent for thicker films (see **Fig. 7b**). At the temperatures above  $T_A$  an ultra-thin film becomes either paraelectric for  $\rho \cong 1$ , or electret-like for  $\rho \ll 1$ , and corresponding hysteresis-less  $P(E)$  curves cannot be used for the information storage, because their area is zero (see **Fig. 7c**), while double hysteresis loops with a very small loop area (and, consequently, very small losses) can exist in a thicker film for  $\rho \leq 10^{-4}$  and  $T \geq T_A$  (see **Fig. 7d**). Similar plots for the film thickness 5, 10, 20 and 50 nm are shown in **Fig. E4** in **Appendix E** [35].

Hence, we can conclude that the energy storage at room temperature is viable only in ultra-thin AFE films ( $h \leq 10$  nm) when the relative oxygen pressure does not deviate significantly from the normal conditions,  $10^{-3} \leq \rho \leq 1$ . Also, the energy storage is favorable in thicker films ( $50 \leq h \leq 100$  nm) at elevated temperatures slightly above  $T_A$  and relative pressures  $\rho \leq 10^{-4}$ .



**FIGURE 7.** Polarization field dependence  $P(E)$  calculated for a very low dimensionless frequency  $w = 10^{-3}$ , temperature  $T = 300 \text{ K}$  (**a**, **b**) and  $550 \text{ K}$  (**c**, **d**), relative partial oxygen pressure  $\rho = 10^{-6}$ , (black curves),  $10^{-5}$  (red curves),  $10^{-4}$  (green curves),  $10^{-3}$  (blue curves),  $10^{-2}$  (magenta curves),  $10^{-1}$  (purple curves) and 1 (brown curves). The film thickness  $h = 5 \text{ nm}$  (**a**, **b**), and  $50 \text{ nm}$  (**c**, **d**). External electric field is  $E = \frac{U_0}{h} \sin(\omega t)$ , and  $w = \frac{\omega \Gamma_P}{2|\alpha_P|}$ . Other parameters are the same as in **Fig. 3**.

To quantify the conclusion, we calculate the dependence of the hysteresis loop shape, LA and SA on the relative pressure, temperature and film thickness, and these results are shown in **Figs. E5-E7** in **Appendix E** [35]. After analyzing the results shown in **Fig. 7** and **Fig. E5-E7**, we compose a schematic diagram of the correlation between the loop shape, the energy loss, and the stored energy in dependence on the relative pressure  $\rho$  and temperature  $T$ . It is shown in **Fig. 8a**. Color maps of the stored energy SA and loop area LA are shown in **Fig. 8b** and **8c**, respectively. The hysteresis loops map (black curves) is

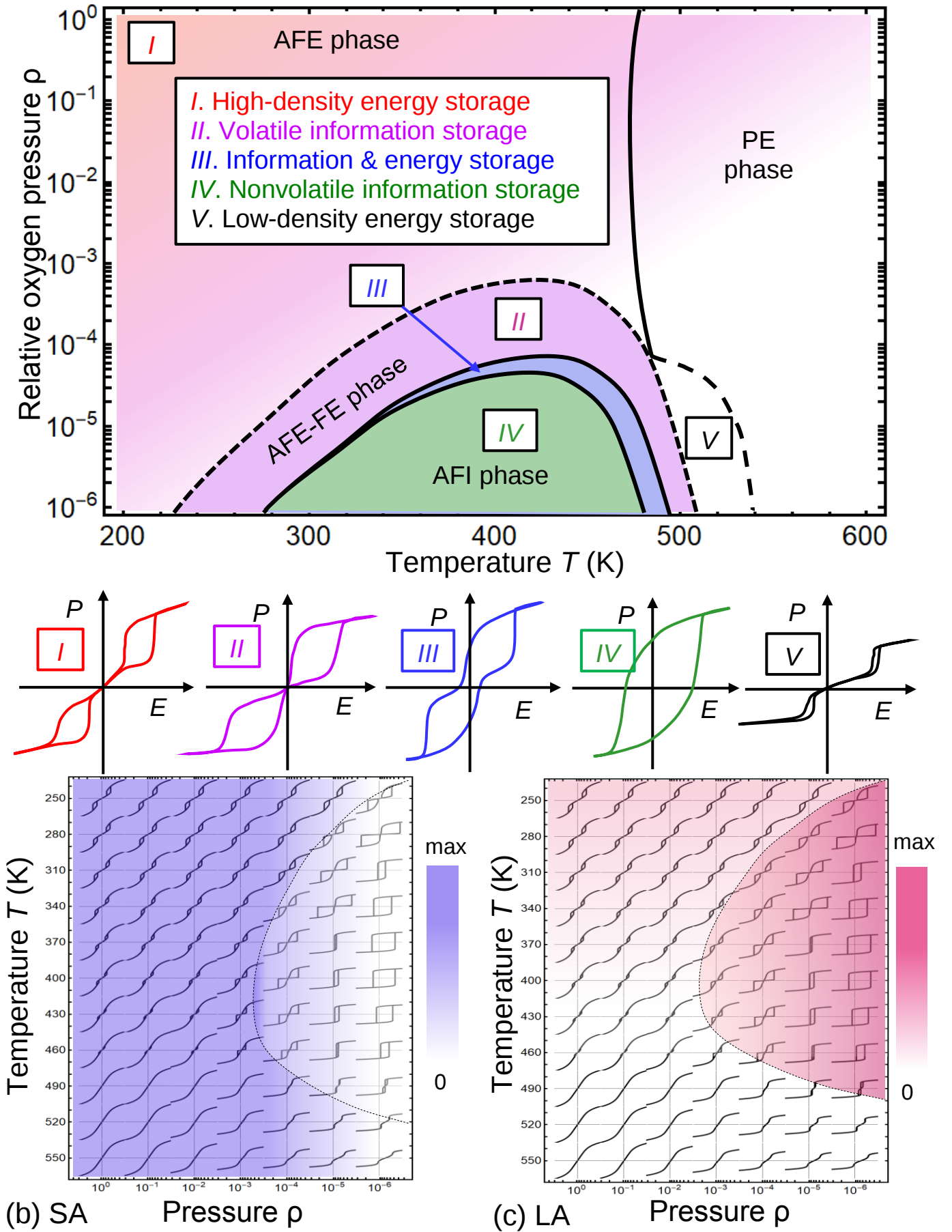
superimposed on the SA and LA color maps. As expected, the loop shape, and the SA and LA areas definitely correlate with the efficiency of the energy and information storage in the AFE films exposed to oxygen pressure.

From the diagram we conclude that the region *I* of double loops with a pronounced linear region is the most suitable for the high-density energy storage, and less suitable for the volatile information storage, because LA is high and SA is relatively small for them. The nonvolatile information storage is impossible for this type of double loops, since the spontaneous polarization  $P_S$  is absent at zero and small voltages,  $P_S(0) = 0$ . The region *I* is the biggest: it corresponds to the pressures  $10^{-3} \leq \rho \leq 1$  and temperatures  $T < T_A$ , and the area of the region slowly decreases with  $\rho$  decrease or/and  $T$  increase.

A region *II* corresponds to double loops without a linear region. The loops are characterized by high losses and thus are neither suitable for nonvolatile information storage (since  $P_S(0) = 0$  for the loops), nor for the effective energy storage (since their area LA is small). However, the type of loops is ideally suitable for a resistive-type (i.e., volatile) information storage, since SA is high for each minor loop. The region *II* has a shape of a curved stripe. This region corresponds to the pressures  $10^{-3} \leq \rho \leq 1$  and temperatures  $T < T_A$ , its area increases with  $\rho$  decrease; and it borders with the above region *I*.

The narrowest region *III* contains single loops with a pronounced constriction, which are suitable for the information storage that is mostly nonvolatile, but the loops are less suitable for the energy storage, since LA is rather high and SA is very small. The boundaries of this region are diffuse, and it is located at pressures  $10^{-6} \leq \rho \leq 10^{-3}$  and wide temperature range  $T < 500$  K.

A region *IV* contains FE-like single AFI loops without a pronounced constriction, which are suitable for the nonvolatile information storage, but non-suitable for the energy storage. This region is a bit wider than region of AFI phase shown in **Fig. 6**. A region *V*, that is mostly PE phase, is suitable for the low-density-energy storage in a definite sense, because the height of the polarization step is relatively small, but the loop area LA is very small and SA is large (see green, black and red curves in **Fig. 7d**).



**FIGURE 8.** (a) A schematic diagram relating the loop shape, information and energy storage abilities in dependence on the relative pressure  $\rho$  and temperature  $T$ . Roman letters I - V are for the five regions described in the text. Color

maps of the stored energy SA **(b)** and loop area LA **(c)** of the  $P(E)$  dependences. Hysteresis loops (black curves) are superimposed on the color maps. The film thickness  $h = 5$  nm. The other parameters are the same as in **Fig. 3**.

## V. DISCUSSION AND OUTLOOK

Using the phenomenological parameters of LGD thermodynamic potential, we explore the role of the surface ion layer with a charge density proportional to the partial oxygen pressure on the dipole states and their reversal mechanisms, and corresponding phase diagrams of AFE thin films using a Stephenson-Highland approach. The combined LGD-SH approach allows to delineate the boundaries of the AFE, FE-like AFI, and electret-like PE states as a function of temperature, oxygen pressure, surface ions formation energy and concentration, and film thickness. This approach also allows the characterization of the polarization and anti-polarization dependence on the voltage applied to the antiferroelectric film, and the analysis of the static and dynamic hysteresis loop features. Important, that LGD-SH approach proposes an alternative model for the frequently observed ferroelectricity in AFE thin films [58] and provides a numerical model for the energy storage in the materials with AFI state.

For applications, our modeling is able to select parameters, which can tune the position, where a transition to FE-like AFI state happens, minimize (or maximize) the area of hysteresis loops. Also, our results can be interesting for the implementation a multi-bit nonvolatile random-access memory (**NRAM**). As a matter of fact, a “single” hysteresis loop  $P(E)$  with two values of the spontaneous polarization,  $\pm P_S$ ; implements a “binary” bit in uniaxial ferroelectrics. In the case of a thin film of multiaxial ferroelectric, the coexistence of several phases with different directions of the polarization vector and its magnitude is possible. Recently, Baudry et al. [60] predicted the existence of a multi-well free energy relief in a thin strained  $\text{PbTiO}_3$  film, with the possibility of transitions between the wells under the action of an electric field. Depending on the misfit strain and temperature, 2 (c-phase), 3 (aa-phase) and 4 (r-phase) stable phases with different spontaneous polarizations are possible, which implements 4-bit, 3-bit or “normal” 2-bit. However, the transition between the multi-bits is possible only by changing the misfit strain, that is difficult to implement during the film exploitation in a memory cell. The considered AFI system, “antiferroelectric film + surface ions layer”, allows switching between 2 or 3 stable polarization states (see 2 or 3 yellow rectangles on the static loops in **Fig. 4**), which can implement ternary bits, and the transition of the nonvolatile memory cell to 3-bits is possible under the change of partial oxygen pressure, which can be easier from technological point of view and possible during the cell operation.

However, in this work we did not consider phases with several orientations of polarization and anti-polarization, leaving this for future studies, realizing that the multiaxiality can lead to the appearance of additional stable phases of the free energy and increase the number of multi-bits in the AFI-based NRAM.

To resume, our approach allows performing the overview of the phase diagrams of thin AFE films covered by surface ion layer and exploring the specifics of polarization reversal and antipolar ordering in the system, quantify the films applications for the energy and information storage, such as AFI NRAM. On

the other hand, many important questions, such as the polarization multiaxiality, finite size effect and its influence on domain formation and evolution, remain for further studies.

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**Authors' contribution.** S.V.K. and A.N.M. generated the research idea. A.N.M. proposed the theoretical model, derived analytical results and interpreted numerical results, obtained by E.A.E. A.B. used Gaussian Process model for rapid exploration and prediction of phase diagrams. A.N.M. and S.V.K. wrote the manuscript draft. Then S.V.K. and N.V.M. worked on the results discussion and manuscript improvement.

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