Vortex-to-Polarization Phase Transformation Path in Ferroelectric Pb(Zr,Ti)O₃ Nanoparticles

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Phase transformation in finite-size ferroelectrics is of fundamental relevance for understanding collective behaviors and balance of competing interactions in low-dimensional systems. We report a first-principles effective Hamiltonian study of vortex-to-polarization transformation in Pb(Zr₀.₅Ti₀.₅)O₃ nanoparticles, caused by homogeneous electric fields normal to the vortex plane. The transformation is shown to (1) follow an unusual macroscopic path that is symmetry nonconforming and characterized by the occurrence of a previously unknown structure as the bridging phase, and (2) lead to the discovery of a striking collective phenomenon, revealing how ferroelectric vortex is annihilated microscopically. Interactions underlying these behaviors are discussed.

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Vortex is a circularly ordered structure phase of broad interest, which has been found in ferromagnets (FM) [1], superconductors [2], and Bose-Einstein condensed atoms [3]. Recently, the vortex phase formed by electric dipoles, as hinted by Ginzburg et al. when exploring the possibility of superdiamagnetism [4], was revealed to exist in ferroelectric (FE) nanoparticles [5]. It was shown [5] that the macroscopic toroid moment undergoes a spontaneous transition from being null at high temperature to nonzero at low temperature, acting as the order parameter of the vortex phase. In FE nanoparticles, another ordered structure of general concern is the ferroelectric phase with an out-of-plane polarization [6]. Transformation between these two ordered structures in FE nanoparticles, by electric fields perpendicular to the vortex plane, is a phase transition of fundamental importance, since (i) Phase transformation in finite-size systems has been long known as a fundamental subject [7]; (ii) The vortex-to-polarization transformation involves two phases of completely different order parameters (namely, toroid moment in vortex phase versus polarization in ferroelectric phase), and is a critical example to study collective mechanism in terms of how order parameter nucleates and/or disappears within a single domain; (iii) Participation of external electric fields during transformation alters and reorganizes the delicate balance among competing interactions inside FEs [8], and may lead to new structural phases that are not possible in the zero-field case; (iv) It concerns the interaction between FE-vortex and electric fields. Vortex, as a whole, does not interact with electric fields because of vanished net polarization, but individual dipoles do, which explains why collective behavior during the vortex transformation is interesting.

Technologically, the FE-vortex phase and the polarization phase both are of considerable significance [9,10]. The former promises to increase the storage density of nonvolatile ferroelectric random access memories by 5 orders of magnitude [5] while FEs in polarization phase exhibit large strain and electromechanical response, which is of widespread use in piezoelectric transducers and actuators [10,11]. Nowadays, FE particles [12], wires [13], and nanotubes [14] were all made possible in experiments.

Despite the fact that vortices exist both in FE and FM particles, they are different in key aspects arising from the profound difference between electrostatic and magnetostatic interactions. First, the demagnetizing energy in FM particles is 10⁴ times smaller than the depolarizing counterpart in FE particles of the same size, leading to the fact that for particles less than 10 nm, the dominant interaction in FMs is the short-range (SR) exchange interaction which favors magnetization, much like in bulk [15,16]. As size increases, the demagnetization energy (scaling approximately as N²/₃ where N is the number of dipoles in particle) becomes more important than the SR exchange energy (scaling as N); thereby, vortex turns favorable until domains start to play a role. Indeed, the minimum threshold size for magnetic Ni₉₀Fe₁₄Mo₉ particles to adopt a vortex structure is experimentally found as 100 nm in diameter (particles less than this size exhibit magnetization instead) [17]. This is in sharp contrast to the situation in FE nanoparticles where the depolarizing energy is dominant and which exhibit a vortex phase as small as 4 nm [5]. The balance between LR and SR interactions is thus profoundly different in two materials. Furthermore, because of the large depolarizing energy, the shape and anisotropy are insignificant for FE particles when size is small (<10 nm). In fact, FE vortices have been found in particles of cylindrical [5], cubic [18], and rectangular shapes. As a result of these differences, the knowledge of transforming magnetic vortex is not suitable for FE nanoparticles.

Here, we perform ab initio based simulations on vortex-to-polarization phase transformation, induced by homogeneous electric fields normal to the vortex plane, in nanoparticles made of technologically important Pb(Zr₀.₅Ti₀.₅)O₃ (PZT) solid solution. These studies lead to (1) the discovery of a critical new structure that bridges the transformation between two phases of unlike order parameters, (2) an unusual collective mechanism showing how FE vortex is annihilated, (3) the existence of a pre-
Polarization ratio and effective mass in InP nanowires: Effect of crystallographic axis

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Indium phosphide nanowires grown along different crystallographic axes—namely, the [001], [101], and [111] directions of zinc-blende structure—are investigated using a first-principles derived semi-empirical pseudopotential theory, aimed at understanding the effects of wire orientation on band structure, polarization ratio, and effective masses of semiconductor nanowires. Band energies over entire Brillouin zone are determined, and are found to exhibit different characteristics for three types of wires in terms of band dispersion and the location of orbital energy. A pronounced dispersion hump is revealed to exist in the lowest conduction band for the [001] and [111] wires, but not for the [101] wires. On the other hand, the [001] and [111] wires are shown to have very different orbital energy for the top valence state at the zone boundary X point—being \(-6.8\) eV in the former and \(-6.2\) eV in the latter. These differences provide specific and useful suggestion to encourage experimental determination of the band structure in InP nanowires. As another key result, we study the polarization ratio in wires of different orientations. Our calculations show that, given the same lateral size, the [111] wires yield the highest polarization ratio as compared to wires along the other two directions, while simultaneously possessing larger band-edge photoluminescence transition intensity. The [111] wires are thus suggested to be better suitable for optical device applications. Interestingly, we also found that polarization ratio displays a different size dependence than transition intensity does. More specifically, the polarization ratio is predicted to increase with the decreasing size, which is opposite to the behavior as exhibited by the optical transition intensity. The polarization ratios in the [101] and [111] wires of 11.7 Å diameter are shown to approach the limit of 100%. In addition to polarization ratio, we further determine the electron and hole masses for wires of different crystallographic axes. For the [101] and [111] wires, the hole masses are revealed to be \(\approx 0.25\), which are markedly smaller than the values \((\approx 1.0)\) along the same direction in bulk. This result demonstrates an interesting possibility of obtaining in nanowires a high hole mobility that is not available in bulk. An explanation for the anomaly in the hole mass is suggested and is associated with the existence of an electronic band transition.

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1. INTRODUCTIONS

Semiconductor wires with lateral size on the nanometer scale are of obvious importance for the eventual development of logic nanocircuits\(^{1-4}\) and semiconductor nanowire lasers,\(^{5,6}\) as well as for the generation of photo induced current in photodetector devices,\(^{7}\) which explains the need of understanding their electronic and optical properties. With respect to three dimensionally confined nanoparticles, nanowires (NW) are better suitable for the purpose of these applications, since (1) the existence of a large conductivity upon doping along the longitudinal wire axis allows carriers easy to transmit, and meanwhile, (2) quantum confinement along the lateral directions offers property tunability as well as efficiency enhancement. Nevertheless, theoretical studies and understanding on nanowires are much less than those on nanodots.\(^{8-19}\)

One additional and possibly interesting degree of freedom—which exists in wires but not prominently in nanoparticles, and may potentially be useful in modifying the properties of wires—is the crystallographic orientation of the wire axis. Different wires, with an equal diameter and yet formed along different axes (for instance, along the [111] or [101] directions of the zinc-blende structure), may show distinctive traits on band-edge wave function symmetry, luminescence wavelength, and/or transition intensity. It may thus be likely that only some wires along a certain orientation, but not others, can lead to preferable properties.

Another special property in NWs concerns the polarization ratio associated with optical absorption or emission. Different from photoluminescence (or absorption) intensity, polarization ratio often offers considerably higher resolution contrast and sensitivity,\(^{20,22}\) thereby being a more preferable quantity for use in sensors and optical communication. Recently, highly polarized luminescence, with a giant polarization ratio as high as \(-95\%\), was reported in single InP free-standing nanowires.\(^7\) The observed strong polarization was explained in terms of dielectric confinement, in which a smaller dielectric susceptibility of the environment surrounding nanowires allows the electric field of excitation laser to penetrate effectively into the wires only when the field is polarized along the wire axis.

Here it is useful to point out that the dielectric confinement model depends little on the explicit electronic structure of wires, and is more an extrinsic mechanism than an intrinsic one. Another mechanism that is able to cause a strong polarization of absorption involves the intrinsic electronic states of each individual wire. More specifically, when the dipole matrix elements between band-edge states show significant dependence on the polarization direction of the excitation electric field, the polarity of absorption occurs. This mechanism was originally proposed and demonstrated in Refs. 13–15 for embedded semiconductor quantum wires as a result of confinement induced heavy-hole–light-hole mixing, and was later examined in Refs. 16–18 for free-standing wires. The second mechanism could reveal more insight in...
Electric-Field-Induced Domain Evolution in Ferroelectric Ultrathin Films

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The electric-field-induced evolution of the recently discovered periodic 180° nanostripe domain structure is predicted in epitaxial Pb(Zr0.5Ti0.5)O3 ultrathin films from first principles. This evolution involves (1) the lateral growth of majority dipole domains at the expense of minority domains with the overall stripe periodicity remaining unchanged, (2) the creation of surface-avoiding nanobubbles, and (3) the formation of a single monodomain state. Analogies and differences (i) with ferroelectric thin films made of BaTiO3 and (ii) with ferromagnetic thin films under magnetic field are discussed.

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Ferroelectric thin films are receiving an enormous amount of attention because of their technological promise in leading toward miniaturized and efficient devices [1]. An ongoing intensive fundamental effort has also been made to determine if and understanding how properties of these low-dimensional systems can differ from those of the corresponding three-dimensional bulk. As a result, recent studies revealed striking unusual features that are related to a particular characteristic of thin films, namely, their internal depolarizing fields. An example of such features is the prediction of a minimal critical thickness below which no ferroelectricity can exist [2]. Another example is the occurrence of an unusual dipole pattern [3,4], which consists of 180° stripe domains that, unlike domains in bulks, are periodic (and thus propagate throughout the entire material) with its periodicity being exceptionally small, that is, on the order of a few nanometers. Despite its obvious technological and fundamental importance, we are not aware of any study revealing how this peculiar stripe pattern evolves—and depends on the inherent parameters of the film—when applying the external field that lies at the heart of many ferroelectric devices, namely, an external homogeneous electric field. In particular, one may wonder if a phenomenon seen in ferromagnetic films under magnetic fields also occurs in ferroelectric films under electric fields, that is, the formation of so-called bubbles [5]. The discovery of such bubbles would make ferroelectric thin films of even broader interest, and would raise the questions of similitude or difference between the morphology, size, shape, and formation mechanism of bubbles in ferromagnetic versus ferroelectric thin films.

The aim of this Letter is to reveal from first principles, the atomic configuration of the alloy [6]. The intrinsic energy of the ferroelectric film. Its expression and first-principles-derived parameters are given in Refs. [6,10] for Pb(Zr0.5Ti0.5)O3 bulk, except for the dipole-dipole interactions for which we implemented the formula derived in Refs. [11,12] for thin film under ideal open-circuit (OC) conditions. Such electrical boundary conditions naturally lead to the existence of a maximum depolarizing field (to be denoted by $E_{dep}$) inside the film, when the dipoles point along the [001] direction. $E_{dep}$ is exactly derived at an atomistic level, following the procedure introduced in Ref. [11]. The second term of Eq. (1) mimics a screening of $E_{dep}$ thanks to the $\beta$ parameter. More precisely, the residual depolarizing field, resulting from the combination of the first and second term of Eq. (1), has a magnitude equal to $(1-\beta)|E_{dep}|$. In other words, $\beta = 0$ corresponds to ideal OC conditions,
Properties of ferroelectric ultrathin films from first principles

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Advances in first-principles computational approaches have, over the past ten years, made possible the investigation of basic physical properties of simple ferroelectric systems. Recently, first-principles techniques also proved to be powerful methods for predicting finite-temperature properties of solid solutions in great details. Consequently, bulk perovskites are rather well understood nowadays. On the other hand, one task still remains to be accomplished by ab-initio methods, that is, an accurate description and a deep understanding of ferroelectric nanostructures. Despite the fact that nanometer scale ferroelectric materials have gained widespread interest both technologically and scientifically (partly because of novel effects arising in connection with the reduction of their spatial extension), first-principles-based calculations on ferroelectric nanostructures are rather scarce. For instance, the precise effects of the substrate, growth orientation, surface termination, boundary conditions and thickness on the finite-temperature ferroelectric properties of ultrathin films are not well established, since their full understandings require (i) microscopic insights on nanoscale behavior that are quite difficult to access and analyze via experimental probes, and (ii) the development of new computational schemes. One may also wonder how some striking features exhibited by some bulk materials evolve in the corresponding thin films. A typical example of such feature is the morphotrophic phase boundary of various solid solutions, where unusual low-symmetry phases associated with a composition-induced rotation of the spontaneous polarization and an enhancement of dielectric and piezoelectric responses were recently discovered. In this paper, recent findings resulting from the development and use of numerical first-principles-based tools on ferroelectric ultrathin films are discussed.

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1. Introduction
Ferroelectric materials are of unique importance for a variety of existing and potential device applications. Examples include piezoelectric transducers and actuators, nonvolatile ferroelectric memories, and dielectrics for microelectronics and wireless communication [1–3]. An important class of ferroelectric materials are the perovskites AB\textsubscript{0}\textsubscript{3}. The perovskite crystal structure AB\textsubscript{0}\textsubscript{3} can be regarded as a three-dimensional network of corner sharing BO\textsubscript{6} octahedra, with the B ions in the center of the octahedra. In a cubic perovskite, the A site is twelvefold surrounded by oxygen ions. As the temperature is reduced, many of these compounds undergo a phase transition and develop a switchable spontaneous electric polarization, thus becoming ferroelectric. Most of the perovskite compounds that are of greater interests are not simple systems, but rather complex solid solutions with the general formula A(B', B'')O\textsubscript{3}, i.e., with two kinds of B atoms

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Large electromechanical response in ZnO and its microscopic origin

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The electromechanical coefficient $d_{33}$ of wurtzite ZnO is determined by direct first-principles density functional calculations which are performed for solids under finite electric fields. Our theoretical $d_{33}$ value of 12.84 pC/N turns out to be in good agreement with experiment. This electromechanical response in ZnO (which is the largest among the known tetrahedral semiconductors) is found to originate from the strong coupling between strain and polarization, namely, a notably large $b$ parameter. We further show that the electromechanical response in wurtzite semiconductors bears a previously unknown resemblance to the polarization rotation mechanism in ferroelectric Pb(ZnNb)O$_3$-PbTiO$_3$ and Pb(MgNb)O$_3$-PbTiO$_3$ single-crystal solid solutions. Our results demonstrate that, different from what is commonly believed, the main effect of electric fields in wurtzite semiconductors is not to elongate the polar chemical bonds, but to rotate those bonds that are non-collinear with the polar axis. This finding also suggests that the electromechanical response in wurtzite materials is governed mainly by the ease of bond bending, which may provide an useful scheme for designing better piezoelectric semiconductors with enhanced performance.

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I. INTRODUCTION

Semiconductor ZnO is of growing technological importance due to its many favorable properties.\textsuperscript{1} ZnO possesses large band gap ($\sim$3.44 eV) and high electric conductivity upon doping, often used as a candidate for transparent conducting oxides.\textsuperscript{2} This material also shows strong bond strength, high melting temperature, large cohesive energy, and large exciton binding energy. The stability of ZnO is further ensured by its large shear modulus ($\sim$45 GPa). ZnO is thus more resistant to radiation and/or high temperature degradation, as compared to other semiconductors. Moreover, the drift mobility in ZnO saturates at higher fields and at higher values than most semiconductors, making it suitable for devices operating at high frequency.\textsuperscript{3} The inexpensive availability of ZnO substrates is also an advantage.

Among the known tetrahedral semiconductors, ZnO has another distinctive property, that is, it exhibits the largest electromechanical response that is used in transducers of converting electrical energy into mechanical energy. Along with its preferable electronic properties as a semiconductor, ZnO is thus an interesting candidate for functioning as a multi-purpose material that combines superior electronic, optical, electrical, and piezoelectric properties. Another possible example of similar type of multipurpose semiconductor is the metastable ScN of a hexagonal structure as suggested in Ref. 3, but this material has an indirect band gap that is not appealing in optical applications. While the electronic properties of ZnO have now been rather well studied,\textsuperscript{4,5} its electromechanical properties are nevertheless poorly understood.\textsuperscript{6,7} Previously, Dai Corso et al.\textsuperscript{8} studied the piezoelectric constant $e_{33}$ by computing the polarization response to applied strain under zero field and revealed that the clamped-ion contribution to the piezoelectric response cancels the internal atomic-relaxation contribution at the least degree in ZnO as compared to other semiconductors, thus giving rise to larger piezoelectric response.\textsuperscript{9} Hill and Waghamre studied (also at zero electric field) the interplay between strain and electronic properties, showing that stress can be used to effectively tune the piezoelectric coefficient $e_{33}$.\textsuperscript{10}

Unlike the piezoelectric constants $e_{ij}$, electromechanical coefficients $d_{ij}$ are the response of strain to nonzero electric field, and its determination requires the handling of finite electric fields. This is challenging since infinite solids under finite electric fields do not possess a ground state,\textsuperscript{9} and the general approach of searching for the lowest energy configuration using density-functional theory (DFT) thus cannot be applied in a straightforward manner. Direct determination of $d_{33}$ from first principles has been possible only recently.\textsuperscript{10\textsuperscript{-13}} By constraining the polarization direction, Fu and Cohen calculated the electromechanical response of BaTiO$_3$ to a non-collinear electric field by using only the DFT total energy.\textsuperscript{10} Sai et al.\textsuperscript{14} developed a systematic theory of "constrained polarization approach" by which the atomic structure and cell shape—for a given constrained polarization (including both direction and magnitude)—are determined using density-functional linear response theory.\textsuperscript{15} Souza et al.\textsuperscript{16} formulated a powerful "Bloch-theory approach" to determine both the electronic and ionic responses to finite electric fields by searching the metastable state of systems under finite electric fields.\textsuperscript{17} More recently, Fu and Bellaiche presented a simple and efficient "constrained-force approach" for determining the ionic response of insulators to finite electric fields.\textsuperscript{18}

Nevertheless, the electromechanical response in ZnO remains to be studied. First, determination of the $d_{33}$ coefficient in wurtzite ZnO using accurate DFT theory has not been done before and is of its own value itself. Furthermore, little is known about how each individual atom may respond to finite electric fields, and how the atomic displacement couples with strain in wurtzite structure. Similarly, it is not clear why electric fields are able to introduce large mechanical response in ZnO, but not in other semiconductors. Another interesting question is whether it is possible to discover a general mechanism that governs the electromechanical re-
Electronic properties and tunability in Si quantum rings

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We present an unconventional scheme that is able to dramatically modify single-electron states as well as their couplings in semiconductor nanostructures. The approach consists in perturbing the wave-function core (rather than the insignificant tail) of nanostructure states. We demonstrate this approach using a structure of silicon quantum rings. Anomalous interstate mixing, large tunability of orbital energy, and uncommon s/p level crossing are predicted. © 2005 American Institute of Physics. [DOI: 10.1063/1.2089165]

I. INTRODUCTION

To realize electronic structure by design is one of the ultimate goals that are being pursued in the growing science of nanostructures.1 With respect to bulk solids, threedimensionally reduced nanocrystallities (NCs) provide feasibility and advantage to tune and control quantum states by varying the size and/or shape. To achieve this goal, determining and understanding individual states of these NCs as well as their interaction are the keys.

Modifying the electronic properties by varying the size alone was demonstrated to be able to change the band-gap energy of II-VI and III-V NCs by as much as ~1 eV.2,3 However, simply scaling the size while keeping the shape of NCs fixed has been found by far not yielding significant effects neither on the level ordering nor on the interstate mixing between different NC states. For example, a pseudo-potential theory predicted that, in spherical InP dots, the valence state with an s-like envelope symmetry is always located in energy above the state with a p-like symmetry for all sizes, in other words, no crossover between these two states ever occurs.4 On the other hand, varying the shape of NCs was found to be able to cause much more pronounced effects, leading to an interesting level crossover in CdSe rods.5 More specifically, the valence-band maximum (VBM) of wurtzite CdSe rods undergoes a transformation from a state of Se 4p$_x$ and 4p$_y$ to a state of Se 4p$_z$, as the aspect ratio increases, consequently altering the absorption and emission from being circularly polarized in dots to being linearly polarized in rods.5

Here we propose an alternative approach by which one can simultaneously modify, in an efficient manner, (i) the orbital energies, (ii) level ordering, and (iii) interstate coupling in semiconductor nanostructures. Furthermore, these drastic and comprehensive modifications are all achieved by simply varying the size alone. The approach consists of, in general, perturbing the wave-function cores of individual electron states by creating a potential barrier at the geometric center of nanostructures. The rational of this approach is rather simple: most of band-edge states in NCs are spatially localized near the center of the considered structures, thereby the created potential barrier will impose a strong perturbation to the cores (and thus the major properties) of the electron wave functions. By contrast, previous studies achieve the modification of electronic states mainly by varying the perimeter of nanostructures that affects only the wave-function tails near the dot’s outer boundary; these tails are less significant in determining the level ordering and interstate mixing.

Another pursuit in nanomaterials is to synthesize and/or understand unusual nanostructures because of their properties and promising technological relevance, as demonstrated by the discoveries of fullerenes and nanotubes.6 Recently, much interest arises in quantum rings (QR) that allow a direct observation of the quantum Aharonov-Bohm phase-coherence effect as well as persistent current.7,8 Thus far, a shell-filling effect was observed in a charge-tunable InAs ring,10 multienergy spectra of AlGaAs/GaAs rings were also revealed.11 And yet, little is known about the individual quantum-ring states, mainly because the rings fabricated in these studies are too large (~200 nm). Here we choose to investigate individual states in silicon quantum rings and quantum disks (QDKs), aiming to provide a clear microscopic understanding of their properties. The structure of QRs is schematically illustrated in Fig. 1(a), where a hole, located at the center and with a varied size $r_1$, acts as the potential barrier (the case of $r_1=0$ corresponds to a QDK). Silicon rings have recently been fabricated via a nanosculpting technique,12 though the size of the inner hole of these rings is on the order of 50 nm which is too large to reveal the unusual properties that are reported here.

The purpose of this paper is twofold: (1) to demonstrate that the approach of perturbing the wave-function core will indeed introduce remarkable modifications to the electronic properties in semiconductor nanomaterials; and (2) to determine, characterize, and understand individual states in QDKs and QRs using an atomistic pseudopotential theory, and to establish an evolution between the electronic states in these two structures. We also provide possible technological impli-
Organic-inorganic hybrid semiconductor ZnSe(C2H8N2)½ under hydrostatic pressure

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Organic-inorganic hybrid semiconductor ZnSe(C2H8N2)½ under hydrostatic pressure is studied using a first-principles pseudopotential method with mixed-basis set, aimed at understanding its structural, mechanical, and electronic properties. The bulk modulus of the hybrid is determined to be 35.3 GPa, which is considerably smaller than that of bulk ZnSe and, in fact, smaller than most known tetrahedral bulk semiconductors. We find that, when the hybrid is exposed to pressure, the chemical bonds of the inorganic constituent, not those of the organic constituent, are significantly compressed. This is important and allows the band-edge electronic properties of hybrid chalcogenides to be effectively tuned by applying pressure, since these properties can be substantially modified only by changing the inorganic Zn-Se bonds. Our calculations further demonstrate that the pressure dependence of the band gap in hybrid semiconductor shows an unusual nonlinearity, with a bowing coefficient that is more than one order of magnitude larger than in bulk ZnSe. Moreover, our results reveal that the in-plane electron mobility mass is notably small (m_e^* ~ 0.27) and remains unchanged over a wide range of pressure. The hybrids will thus continue to maintain a fast electron mobility when they are under mechanical loading. However, and interestingly, the in-plane hole mass along the x and y direction is predicted to undergo at 2.14 GPa a dramatic change from 0.35 to 2.2 and from 2.0 to 0.24, respectively. A pressure-induced isostuctural phase transition is found to be responsible for this behavior of hole mass.

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I. INTRODUCTION

Organic-inorganic hybrid semiconductors are a new class of materials that have recently attracted substantial attention1-10 because of their promising potentials in technology and industry towards the ultimate goal of developing plastic microelectronics. These hybrid composites may integrate the advantages of semiconductors and organic polymers, both of technological relevance but with different uniqueness. Pure semiconductors have well-characterized and easy-controllable electrical, optical, and doping properties due to strong and directional covalent bonding.11 Furthermore, semiconductors have large carrier mobility that is suitable for fast-speed devices. In contrast, organic molecular crystals or polymers are inexpensive to produce and characterized by two different types of interactions between atoms. There are strong covalent bonding within molecules but weak van der Waals interaction between them. As a result, the organic materials tend to be mechanically flexible, structurally diverse, and light. The mechanical processability is attractive and has stimulated numerous studies in the area of flexible electronics and optically active polymers.12-15 However, the electron mobility in organic polymers is often slow, mainly caused by structural disorder and weak van der Waals interactions. Recently, a previously-nonexisting class of hybrid materials, namely, hybrid chalcogenide crystals16,17—in which II-VI chalcogenides are covalently bonded to short organic chains (Fig. 1)—have been successfully synthesized. These hybrid crystals provide an interesting and promising alternative to overcome the slow mobility in organics, while inheriting the superior functionalities of bulk semiconductors. Indeed, band-structure calculations showed that the band-edge electronic states in these hybrid chalcogenides are predominantly determined by the inorganic semiconductor part, with modifications arising from the strong quantum confinement provided by the insulating organic layer.18 Of particular interest, these hybrids possess a structure uniformity over a macroscopic scale by developing single-phase crystals in a periodic fashion, unlike most other hybrid composites in which the combined organic-inorganic structures are disordered.2-9 This structural uniformity, along with the covalent bonding within the inorganic layer, gives rise to unusual and large in-plane carrier mobility.18 Despite their technological importance, properties of these hybrid chalcogenide crystals remain largely unknown and unexplored, owing to their structural complexity. More investigations on

FIG. 1. Crystal structure of the hybrid ZnSe(C2H8N2)½. The crystal has an orthorhombic unit cell, with lattice vectors along the x, y, and z directions. The LDA-calculated lattice lengths along these directions are 6.55, 6.38, and 17.14 Å, respectively. Three nonequivalent bonds formed by a Zn atom with its neighboring Se atoms are labeled as B1, B2, and B3.
Atomistic treatment of depolarizing energy and field in ferroelectric nanostructures

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An atomistic approach allowing an accurate and efficient treatment of depolarizing energy and field in any low-dimensional ferroelectric structure is developed. Application of this approach demonstrates the limits of the widely used continuum model (even for simple test cases). Moreover, implementation of this approach within a first-principles-based model reveals an unusual phase transition—from a state exhibiting a spontaneous polarization to a phase associated with a toroid moment of polarization—in a ferroelectric nanodot for a critical value of the depolarizing field.

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Ferroelectric nanostructures (FEN) are of increasing technological and fundamental interest because of the need in miniaturization of devices, as well as, the appearance of new phenomena (see, e.g., Refs. 1–6, and references therein). Unscreened polarization-induced charges at the surfaces of FEN generate a depolarizing field that is responsible for striking properties. Examples are the existence of a critical thickness below in which no ferroelectricity can appear,3 and the observation and prediction of laminar stripe nanodomains2,4 as well as the formation of polarization vortex.5,6 Internestingly, and despite its huge importance, we are not aware of any model being able to exactly calculate the depolarizing field and energy in any low-dimensional ferroelectric. For instance, the widely used continuum model (1) neglects the atomistic nature of materials, (2) is technically applicable only in the limit of large enough systems, and (3) cannot predict the depolarizing energy and/or field in the realistic cases of inhomogeneously polarized samples.

In this report we (i) demonstrate that it is possible to derive a scheme allowing the exact atomistic computation of the depolarizing field and energy in any low-dimensional FEN; (ii) use this scheme to check the accuracy of the continuum model for some simple test cases; (iii) report an unusual phase transition between two different kinds of order parameters in a ferroelectric nanodot that is driven by the depolarizing field.

To calculate the depolarizing energy in low-dimensional ferroelectrics, one first needs to realize that a system under perfect open-circuit (OC) electrical boundary conditions exhibits a maximum depolarizing field (if the polarization lies along a nonperiodic direction), while ideal short-circuit (SC) electrical boundary conditions leads to a complete screening of charges at the FEN surfaces that fully annihilates any depolarizing field. As a result, the depolarizing energy and field experienced by the FEN should involve a difference between the dipole-dipole interactions associated with these two extreme electrical boundary conditions. We shall write the energy of the dipole-dipole interaction in any system in the form

$$E_{dd}^{(p)} = \frac{1}{2V} \sum_{\alpha\beta ij} G_{ij}^{(p)} p_{\alpha}(r_j) p_{\beta}(r_i),$$

where $D=3,2,1$ stands for a system periodic in 3, 2, and 1 directions, respectively; $D=0$ corresponds to nonperiodic systems, and the sum runs over the atomic sites $i$ and $j$ that differ from each other and belong to a supercell (to be denoted by $S$) mimicking the system. Such a supercell is infinitely repeated along the periodic directions, if any. For instance, thin films are modeled by supercells that are repeated in two dimensions while the direction associated with the growth direction of the film is nonperiodic. For dots, the supercell is not repeated. $V$ is the volume of the supercell, $p(r_i)$ the dipole moment at the site $i$, and $\alpha=x,y,z$ denotes the Cartesian components. The quantity $Q^{(S,D)}$ depends on both the chosen supercell ($S$) and the periodicity of the system ($D$).

The elements of the $Q$ matrix for systems periodic in three, two $(x$ and $y$), one $(z)$ directions22 and nonperiodic systems are given by

$$Q_{\alpha\beta ij}^{(S,3)} = \frac{4\pi}{V} \sum_{\gamma \neq 0} G_{ij}^{(p)} \exp\left(-\frac{G^2}{4\lambda^2}\right) G_{\alpha\gamma\delta} \cos(\gamma \cdot r_i) - \frac{4\lambda^3 \delta_{\alpha\beta} \delta_{ij}}{3\sqrt{\pi}},$$

$$Q_{\alpha\beta ij}^{(S,2)} = 2\pi \sum_{\Lambda} G \cos(G \cdot r_i) \left[\gamma \left(1 - \frac{G^2}{2\lambda^2}\right) \delta_{\alpha\beta} \delta_{ij} + \frac{1}{G^2} \text{erfc}\left(\frac{G}{2\lambda}\right) G_{\alpha\gamma\delta} \frac{G_{\beta\gamma\delta}}{G^2} - \delta_{\alpha\beta} \delta_{ij} \cos(G \cdot r_i) - \frac{G_{\alpha\gamma\delta}}{G} \sin(G \cdot r_i) \frac{z_{ij}}{|z_{ij}|}\right]$$

$$- \frac{4\lambda^3 \delta_{\alpha\beta} \delta_{ij}}{3\sqrt{\pi}},$$

$$Q_{\alpha\beta ij}^{(S,1)} = 2 \sum_{\Lambda} G^2 \cos(G \cdot z_{ij}) \left\{ K_0(G p_{ij}) \delta_{\alpha\beta} \delta_{ij} + \delta_{\alpha\beta} \delta_{ij} + \frac{\delta_{\alpha\beta} \delta_{ij}}{G p_{ij}} K_1(G p_{ij}) - \frac{1}{\rho_{ij}} \frac{K_2(G p_{ij})}{G p_{ij}} \rho_{ij} \delta_{ij} \right\}$$

$$+ \frac{1}{\alpha} \left\{ k_0 \left(\frac{G p_{ij}}{\rho_{ij}}\right) - 1 \right\} \left(\delta_{\alpha\beta} \delta_{ij} + \frac{\delta_{\alpha\beta} \delta_{ij}}{G p_{ij}} K_1(G p_{ij}) \rho_{ij} G_{\alpha\beta ij} + \frac{1}{\alpha} \delta_{\alpha\beta} \delta_{ij}\right).$$
Phonon structure in SrTiO₃ under finite electric fields: First-principles density functional approach

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A first-principles approach within the density-functional theory is proposed to determine the phonon structure of infinite solids under finite electric fields. The approach is applied to perovskite SrTiO₃, confirming the existence of giant field-induced frequency shifts. Our theory further predicts a striking piezoelectric response as well as a wide-range dielectric tunability. A microscopic understanding for individual phonon modes under finite electric fields is also provided.

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The determination of a phonon structure in solids under finite electric fields from density functional theory (DFT) is a fundamental and challenging topic itself, which meanwhile can also enable many other studies such as field-induced phonon hardening, dielectric tunability, and finite-field structural phase transition. It has been nearly 40 years since Worlock and Fleury discovered by means of Raman scattering that the transverse-optical (TO) phonon in SrTiO₃ (Ref. 1) and in KTaO₃ (Ref. 2) exhibits a giant increase in frequency—by more than 40% of its zero-field value—when a very small but finite electric field of 12 kV/cm is applied. Despite its obvious importance in tuning the structural and dielectric properties, this giant field-induced shift of phonon frequency has not thus far been independently investigated and/or understood via the density-functional theory, which, on the other hand, has been amply applied in the past three decades on a variety of other material properties. The reason is due to the difficulty of handling finite electric fields within the direct DFT approach.1-9

SrTiO₃ is an incipient ferroelectric that is approaching, but does not in fact undergo, a paraelectric-to-ferroelectric phase transformation when lowering the temperature.10 However, being on the edge of phonon softening, SrTiO₃ shows an uncommon sensitivity on external electric fields that are able to drive easily the occurrence of phase transformation and thus lead to large structural responses. Given their technological importance, this and other ferroelectric incipients remain nevertheless poorly understood,11-15 in particular, when they are under finite electric fields. For example, it is not clear how different phonon modes may respond differently to the electric fields in terms of their frequencies and in terms of their atomic participations (that is, lattice-dynamic properties). Furthermore, little is known on how atomic displacements driven by external fields may couple with strain in incipient ferroelectrics, and whether SrTiO₃ under finite electric fields can be a good piezoelectric, in addition to being a good dielectric (that is, electromechanical properties). Finally, a direct DFT modeling of how electric fields may tune the dielectric constants (that is, dielectric properties) is very important and largely unknown.16

Our purpose in this paper is threefold: (1) to show that it is possible to devise a direct density-functional approach to determine and understand the phonon spectrum of infinite solids under finite electric fields; (2) to demonstrate that the approach works robustly for incipient SrTiO₃, and the theoretical predictions of the field-induced frequency shift are in excellent agreement with the results observed in experiments; (3) to present other unusual properties in SrTiO₃ that occur “only” under finite electric fields, that is, a gigantic piezoelectric response and a superior field-induced dielectric tunability.

To determine the phonon frequencies and eigenmodes of a solid under finite electric fields, we begin with free energy $F = U - EF$, where $E$ and $P$ are the screened macroscopic field and polarization per cell, respectively. Field $E$ is assumed to be along the pseudocubic [001] direction throughout this paper. The force-constant matrix elements thus are

$$\frac{\partial^2 F}{\partial r_{i\alpha} \partial r_{j\beta}} = \frac{\partial^2 U}{\partial r_{i\alpha} \partial r_{j\beta}} - E \frac{\partial Z_{i\alpha}(i)}{\partial r_{j\beta}},$$

where $r_{i\alpha}$ is the position of atom $i$ along the $\alpha$ Cartesian direction, and $Z_{i\alpha}(i)$ is the Born effective charge tensor of this atom. Each term in Eq. (1) should be evaluated at the field-induced new atomic positions $\{R_{\text{new}}\}$ and cell-shape strain $\{\eta_{\text{new}}\}$ instead of the zero field $\{R_0\}$ and $\{\eta_0\}$. Since finite electric fields in incipients may induce very large atomic displacements, the linear response theory, while being suitable for systems close to their zero-field equilibrium, thus does not generally apply. Here we determine $\{R_{\text{new}}\}$ and $\{\eta_{\text{new}}\}$ under finite fields using a recently developed structure optimization method.17

Evaluation of the force-constant matrix requires us to determine the response of the macroscopic polarization $P$ with respect to atomic displacements [i.e., the second term in Eq. (1)]. This is nontrivial and its implementation is cumbersome, since polarization $P$—which is determined by the geometric phases of valence wave functions, as shown in the modern theory of polarization18,19—couples electron states at different $k$ points over the whole Brillouin zone, and its linear response to a given perturbation is complex.20 Here we present a simple and yet accurate approach to overcome this difficulty. We numerically found by performing finite-difference calculations that, even for an electric field as large as $0.5 \times 10^8$ V/m, the second term in Eq. (1) turns out to be less than 0.5% of the first term for all diagonal elements, and...
Spontaneous Polarization in One-Dimensional Pb(ZrTi)O₃ Nanowires

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Formation of spontaneous polarization in one-dimensional (1D) structures is a key phenomenon that reveals collective behaviors in systems of reduced dimensions, but has remained unsolved for decades. Here we report ab initio studies on finite-temperature structural properties of infinite-length nanowires of Pb(Zr₅Ti₄O₁₉) solid solution. Whereas existing studies have ruled out the possibility of phase transition in 1D chains, our atomistic simulations demonstrate a different conclusion, characterized by the occurrence of a ferroelectric polarization and critical behaviors of dielectric and piezoelectric responses. The difference is accounted for by the use of depolarizing effects associated with finite thickness of wires. Our results suggest no fundamental constraint that limits the use of ferroelectric nanowires and nanotubes arising from the absence of spontaneous ordering.

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Low-dimensional ferroelectrics (FE) are of considerable importance because of the demand in nonvolatile FE memory and device miniaturization [1–3], and because of their unusual properties that could be drastically different from bulks [4–9]. One-dimensional nanowire (1D NW) is an interesting system that bridges the 3D bulk ferroelectrics, for which no depolarizing fields exist along any dimension and possess at low temperature a ferroelectric ordering with formation of spontaneous polarization [10], and the 0D nanoparticles, for which depolarizing fields exist along all three possible dimensions and exhibit instead a peculiar ordering with formation of toroidal moment [9]. Experimentally, it has become possible to fabricate 1D ferroelectric nanowires and nanotubes out of different substances such as Pb(Zr₅Ti₄O₁₉), BaTiO₃, SrTiO₃, and SrBi₂Ta₂O₉ [11–14]. Theoretically, despite their obvious technological implication, the properties of these 1D systems—in particular, the structural, dielectric, and piezoelectric properties—remain unknown, which hampers the understanding of these novel forms of ferroelectrics.

Another key question of fundamental relevance is whether one-dimensional wires should exhibit any spontaneous ferroelectric ordering. The answer is not clear. On the one hand, it has been amply proved using a variety of statistical models that the 1D lattices with particle-particle interaction decaying as or faster than r⁻³ are impossible to have phase transformation at finite temperature [15–19], thereby imposing a fundamental constraint that limits the potential use of ferroelectric 1D nanowires and nanotubes. This conclusion has been widely accepted and formulated into a basic theory [20]. On the other hand, evidence of a ferromagnetic ordering was recently reported in a one-dimensional atomic chain on a metal supporting surface [21], questioning the applicability of the existing phase transition theory of 1D systems.

Here we investigate the fundamentals of phase transition in 1D FE system as well as study their dielectric and electromechanical properties, by means of two complementary techniques of (1) finite-temperature ab initio simulations on 1D wires made of Pb(Zr₅Ti₄O₁₉) (PZT) solid solution and (2) analytical minimization of a free energy applicable for a general 1D FE system. We demonstrate that ferroelectric long-range ordering remarkably exists, at finite temperature and under zero external fields, in real 1D wires of diameter larger than 2 nm. The result is in difference from what has been known from the statistical models. Our results further show that the ordering in 1D infinite wires does not form any toroid moment and bears no similarity to the phase transition in 0D nanoparticles [9,22]. As another key outcome of our study, we determine the scaling law of the polarization in 1D systems.

Our simulations are based on a first-principle derived effective Hamiltonian [23,24], in which total energy $E$ is a function of local modes $u_i$, inhomogeneous strain $v_i$, and alloy species $\sigma_i$ at site $i$, as well as homogeneous strain $\eta$,

$$E(u_i, v_i, \sigma_i, \eta) = E_{\text{vca}}^{\text{e}}(u_i, v_i, \sigma_i, \eta) + E_{\text{vca}}^{\text{p}}(u_i),$$

where the first two terms describe the nondipolar and dipolar interaction between perovskite 5-atom cells in the virtual crystal approximation (VCA), and the third term includes the energy associated with species-dependent alloy interaction. Expressions for $E_{\text{vca}}^{\text{e}}$ and $E_{\text{vca}}^{\text{p}}$ as well as parameters for PZT were given in Ref. [25], and were recently used for studying PZT nanoparticles [9]. The effective-Hamiltonian approach has been proved to be very successful in predicting the unusual low-symmetry monoclinic phase of PZT [24,26] and the phase diagram of BaTiO₃ with the presence of quantum zero-point motion [27]. The Hamiltonian in Eq. (1) was initially proposed for 3D bulks [23] and applicable to systems possessing periodicity along all three dimensions (i.e., with no depolarizing fields). To include the depolarizing energy due to charges at the lateral surfaces of 1D systems, we formulate a dual-space approach by using periodic Green’s function $G(r, r')$, for which the dipole energy $E_{\text{dip}}$ can be determined as [28].
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Unusual phase transitions in ferroelectric nanodisks and nanorods

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Bulk ferroelectrics undergo structural phase transformations at low temperatures, giving multi-stable (that is, multiple-minimum) degenerate states with spontaneous polarization. Accessing these states by applying, and varying the direction of, an external electric field is a key principle for the operation of devices such as non-volatile ferroelectric random access memories (NFERAMs). Compared with bulk ferroelectrics, low-dimensional finite ferroelectric structures promise to increase the storage density of NFERAMs 10,000-fold. But this anticipated benefit hinges on whether phase transitions and multi-stable states still exist in low-dimensional structures. Previous studies have suggested that phase transitions are impossible in one-dimensional systems, and become increasingly less likely as dimensionality further decreases. Here we perform ab initio studies of ferroelectric nanoscale disks and rods of technologically important Pb(Zr,Ti)O₃ solid solutions, and demonstrate the existence of previously unknown phase transitions in zero-dimensional ferroelectric nanoparticles. The minimum diameter of the disks that display low-temperature structural bistability is determined to be 3.2 nm, enabling an ultimate NFERAM density of $60 \times 10^{12}$ bits per square inch—that is, five orders of magnitude larger than those currently available. Our results suggest an innovative use of ferroelectric nanostructures for data storage, and are of fundamental value for the theory of phase transition in systems of low dimensionality.

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Modelling of nanoscale ferroelectrics from atomistic simulations

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Abstract

The recent development and use of atomistic approaches have revealed the occurrence of original features in zero- and one-dimensional ferroelectric systems, and have also indicated how properties of such nanostructures dramatically depend on boundary conditions.

Keywords: Ferroelectric nanostructures; Atomistic simulations; First-principles techniques; Nanodomains

1. Introduction

Ferroelectric nanostructures (FENs) are receiving a lot of attention for technological reasons, e.g., the need in devices miniaturization [1] and their potential for applications such as dynamic random access memories [2], non-volatile random access memories [3] and integrated devices [4]. Such low-dimensional systems are also attractive from a fundamental point of view by, e.g., determining if – and understanding how – their properties can differ from those of the corresponding (three-dimensional) bulk system.

Properties of perovskite thin and ultrathin films – that are two-dimensional systems – are now rather well understood thanks to an intense experimental and theoretical effort (see, e.g., Refs. [5,6] and references therein). On the other hand, studies on 0D-like and 1D-like FENs are rather scarce mostly because of the difficulty in growing, characterizing and modelling them [7–18]. Interestingly, such nanosystems should be exquisitely sensitive to many factors, such as their morphology and boundary conditions because: (i) the strong Coulomb interactions that give rise to ferroelectricity are drastically modified in the presence of surfaces and interfaces; (ii) a ferroelectric state is significantly affected by the mechanical boundary conditions due to a strong electrostrictive coupling; (iii) the fields arising either from space charge or from depolarization also interact strongly and directly with the ferroelectric order parameter. Thus, by altering the properties of ferroelectrics in unexpected ways, nanostructuring may result in both new science and new functional devices. Accurate atomistic simulations can thus be useful to provide local insights on nanoscale behavior that are difficult to access via experimental probes, and to guide synthesis of materials with new or improved properties.

The purposes of the present review are twofold: (1) to provide a description of different numerical atomistic schemes allowing the computation of properties of 0D and 1D FENs; (2) to summarize the understanding of these low-dimensional systems that has been gained in the last 3 years thanks to these numerical schemes.

2. Methodology

2.1. Dipole–dipole interaction in ferroelectric nanostructures under open-circuit conditions

One important issue associated with ferroelectric nanostructures is how to precisely compute their dipole–dipole interactions when they are under open-circuit electrical boundary conditions. As a matter of fact, at the exception of 0D systems that form the sole type of nanostructure having a finite number of atomic sites, the dipole–dipole interaction energy in other low-dimensional systems can not be
Ultrathin Films of Ferroelectric Solid Solutions under a Residual Depolarizing Field

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A first-principles-derived approach is developed to study the effects of depolarizing electric fields on the properties of Pb(Zr,Ti)O₃ ultrathin films for different mechanical boundary conditions. A rich variety of ferroelectric phases and polarization patterns is found, depending on the interplay between strain and the amount of screening of surface charges. Examples include triclinic phases, monoclinic states with in-plane and/or out-of-plane components of the polarization, homogeneous and inhomogeneous tetragonal states, as well as peculiar laminar nanodomains.

First-principles calculations with electrical conditions (see Refs. [4,8], namely, that they arise from different electrical boundary conditions. More precisely, real thin films are likely neither in ideal open-circuit (OC) conditions, for which unscreened polarization-induced surface charges can generate a large depolarizing electric field along the growth direction [9], nor in ideal short-circuit (SC) conditions, which are associated with a vanishing internal field resulting from the full screening of surface charges, but rather experience a situation in between. The amount of surface charges' screening in thin films can vary from one experimental setup to another, possibly generating different polarization patterns [4,5].

Phenomenological and atomistic models have provided deep insight into thin films, but “only” for ideal OC or SC conditions (see Refs. [6,7,10], and references therein). First-principles calculations with electrical conditions falling between these two extremes have been performed, but the small used supercell size may have prevented the prediction of domains [4]. Finally, experimentally extracting the magnitude of the internal field is a challenging task. A precise correlation between the amount of screening of surface charges and the morphology of the polarization pattern, and how this correlation depends on mechanical boundary conditions, are thus still lacking nowadays despite their importance. Atomic-scale details of multidomains—and their formation mechanism—are also scarce in ferroelectric thin films. One may also wonder if some uncompensated depolarizing fields can yield ferroelectric phases that do not exist in the corresponding bulk material. Candidates for these latter anomalies are films made of alloys with a composition lying near their morphotropic phase boundary (MPB), because of the easiness of rotating their polarization [11].

In this Letter, we develop a first-principles-based scheme to investigate the effects of uncompensated depolarizing fields on the properties of Pb(Zr₁₋ₓ,Tiₓ)O₃ (PZT) films near their MPB, for different mechanical boundary conditions. Answers to the problems summarized above are provided. We find a rich variety of ferroelectric phases, including unusual triclinic and monoclinic states. We also observe complex nanodomains and reveal their formation and atomic characteristics.

We model PZT thin films that (i) are grown along the [001] direction (to be chosen along the z axis), (ii) are “sandwiched” between nonpolar systems (mimicking, e.g., air, vacuum, electrodes, and/or nonferroelectric substrates), (iii) have Pb-O terminated surfaces, and (iv) have a 50% overall Ti composition. Such structures are modeled by large periodic supercells that are elongated along the z direction and that contain a few number of B layers to be denoted by m, with the atoms being randomly distributed inside each layer. Typically, we use 10 × 10 × 40 periodic supercells with m around 5. The nonpolar regions outside the film are thus altogether 40 – m lattice constant thick along the growth direction, which allows well-converged results for the film properties [6]. The total energy of such supercells is used in Monte Carlo simulations, and is written as

$$E_{\text{Eff}}(\{u_i\}, \{v_i\}, \{\eta_i\}) = \sum_i \beta 2\pi \frac{Z^2}{a^3\varepsilon_0} (u_{i,z}^2 + u_{i,z}).$$

where $E_{\text{Eff}}$ is the energy of the ferroelectric film per se. Its expression and first-principles-derived parameters are those given in Ref. [11] for bulk PZT. $u_i$ are the local soft modes in unit cells i of the PZT film whose components along the z axis are denoted as $u_{i,z}$. $v_i$ are inhomogeneous strain-related variables inside these films, while $\eta$ is the homogeneous strain tensor. The form of $\eta$ is relevant to stress-free (all the components of $\eta$ fully relax) versus...
Density-functional study of organic–inorganic hybrid single crystal 
ZnSe(C$_2$H$_8$N$_2$)$_{1/2}$

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Unusual properties (i.e., strong band dispersion, high carrier mobility, wide absorption-energy window, and sharp band-edge transition) that are desirable for hybrid-material electronics and for solar electric energy conversion are predicted to exist in the organic–inorganic chalcogenide single crystal ZnSe(C$_2$H$_8$N$_2$)$_{1/2}$ by using density-functional calculations. A simple mechanism, namely that the band-edge electronic states of the hybrid composite is predominantly determined by the inorganic constituent, is revealed to be responsible for governing these properties. Suggestions for further engineering hybrid semiconductors are also provided. © 2004 American Institute of Physics. [DOI: 10.1063/1.1665804]

I. INTRODUCTION

Organic materials—for example, short-chain oligomers or long-chain conjugated polymers—are of considerable interest in making low-cost and large-area electronic devices by use of printing technique. Moreover, these devices are mechanically flexible in the sense that bending and twisting affect little their performances. However, organic materials generally suffer low electron/hole mobility (which is caused by structure disorders due to weak van der Waals interactions between organic molecules), and the resulting organic devices thus tend to be slow and are difficult to meet the need of high-speed performances. By contrast, inorganic semiconductors—such as III–V and II–VI compounds—are known for having ordered crystal structures and exhibiting high carrier mobilities, as well as for possessing a variety of doping and temperature-controllable optical and electrical properties. Combining organic materials and inorganic semiconductors into organic–inorganic “hybrids” may thus integrate the favorable properties of both classes of materials, forming new and interesting “plastic” semiconductors. These hybrid materials promise to usher in a new age of semiconductor electronics by bypassing the costly molecular-beam epitaxial growth and lithography (thus drastically improve processability and reduce cost). Examples of hybrid materials include hybrid silica, hybrid perovskite tin iodide (C$_6$H$_5$C$_2$H$_4$NH$_2$)$_2$SnI$_4$ (Ref. 8) and CdSe nanocrystals heterostructured with polymers.

Recently, a new class of hybrid materials MX(C$_2$H$_8$N$_2$)$_{1/2}$ (where cation M can be Zn or Cd, and anion X can be S, Se, or Te) were synthesized from II–VI chalcogenides via chemical reaction with ethylenediamine C$_2$H$_4$N$_2$. The crystal structure of ZnSe(C$_2$H$_8$N$_2$)$_{1/2}$, as revealed by x-ray diffraction, is shown in Fig. 1(a), where an ordered ZnSe monolayer is chemically bonded to organic ethylenediamine (abbreviated as “en” in chemistry) by Zn–N coordination bonds. The hybrid composite is thus denoted as ZnSe(en)$_{1/2}$. Unlike other hybrids, the hybrid chalcogenides are single crystals, which, as will become clear later, results in many unusual and useful properties.

Hybrid chalcogenides are poorly understood (with respect to inorganic semiconductor compounds and organic molecules) mainly because of their complex structures—and however, applications of these hybrids depend critically on acquiring and understanding their materials properties. For example, it is unknown how the inorganic bonds in hybrids are altered (with respect to the pure inorganic bulk semiconductors), though these chemical bonds are important in affecting the electronic properties. Also, the band structure of hybrid materials, which is essential for optical applications, remains as an intriguing mystery. Furthermore, it is unclear how the material properties of hybrids are affected by the chemical mixing of organic and inorganic constituents. In hybrid ZnSe(en)$_{1/2}$, as the inorganic layer [Fig. 1(A)] is only monolayer thick, strong and inevitable charge redistribution at the organic/inorganic interfaces implies that the electronic structure and related properties of the hybrid may deviate significantly from the parental bulk ZnSe and from molecule C$_2$H$_4$N$_2$. Indeed, a large blueshift of absorption edge was observed in hybrid ZnSe(en)$_{1/2}$ with respect to bulk ZnSe, indicating a drastic change in optical properties. Quantum size effect was suggested to be responsible for the shift, but this speculation thus far has not been proved. In fact, it is not even clear whether the band-edge absorption in the hybrid is from the inorganic part or from the organic part, both being able to produce the observed large shift. Provided that the material properties of the hybrids are mainly derived from the organic part, the slow carrier mobility associated with organic materials will then remain, and the use of hybrid composites in electronics will be limited. Also note that engineering the organic part is substantially more difficult and inefficient than engineering the inorganic part. The above concern is not merely for hybrid chalcogenides; it also exists for other hybrids. Moreover, virtually nothing is known about the electrical mobilities of the hybrid chalco-
A first-principles-based scheme is developed to simulate properties of (001) PbO-terminated Pb(Zr,Ti)O$_3$ thin films that are under stress-free and open-circuit boundary conditions. Their low-temperature spontaneous polarization never vanishes down to the minimal thickness, and continuously rotates between the in-plane (010) and (110) directions when varying the Ti composition around $x=0.50$. Such rotation dramatically enhances piezoelectricity and dielectricity. Furthermore, the order of some phase transitions changes when going from bulk to thin films.

Here, we extend the \textit{ab initio} effective Hamiltonian scheme proposed in Ref. 12 to mimic thin films that (1) are made of Pb(Zr,Ti)O$_3$ (PZT), (2) are grown on a substrate along the [001] direction; and (3) have vacuum above them. More precisely, the total energy $E_{\text{mat}}$ of such low-dimensional systems is written as

$$E_{\text{mat}}([u(i)], [v(i)], \eta, \{\sigma\}) = E_{\text{mat}}([u(i)], [v(i)], \eta, \{\sigma\}) + P \sum_j u_j + T \sum_j v_j + \sum_{\alpha=x,y} \sum_j u_{\alpha}(j)[u_{\alpha}(j + \hat{\alpha}) + u_{\alpha}(j - \hat{\alpha})],$$

where $u_j$ are the (B-centered) local soft modes in unit cells of the film, and are directly proportional to the electrical polarization. $v_j$ are inhomogeneous strains around the $i$ site, while $\eta$ is the homogeneous strain tensor. $\{\sigma\}$ characterizes the alloy configuration. $E_{\text{mat}}$ represents the intrinsic ferroelectric and elastic interactions inside the film, with its analytical expression and first-principles-derived parameters being those of PZT bulks. Only four (out of 26) parameters are composition dependent in $E_{\text{mat}}$; they are those associated with the so-called local-mode self-energy. The last three terms of Eq. (1) mimic explicit interactions between this film and the vacuum, with the $j$ index running over all the B sites that are the closest to the free surface. $u_{\alpha}(j)$, $v_{\alpha}(j)$, and $u_{\alpha}(j)$ denote the $(x, y, z)$ Cartesian components of $u_j$ along the pseudocubic [100], [010], and [001] directions, respectively. $\alpha$ runs over the $x$ and $y$ axes (i.e., it does not include the growth direction). $u_{\alpha}(j + \hat{\alpha})$ [respectively, $u_{\alpha}(j - \hat{\alpha})$] is the $\alpha$ component of the local mode centered on the $B$ site that is the closest from the $j$ site that is parallel (respectively, antiparallel) to the $\alpha$ axis. The $P$ and $T$ parameters quantify how vacuum affects the out-of-plane components ($u_x$ and $u_y$) of the local modes and inhomogeneous strains near the surface, respectively. $S$ characterizes the change, with respect to the bulk, of the short-range interaction between the in-plane components of the local modes near the surface. The $P$, $T$, and $S$ parameters are determined from first-principles calculations on a PbO-terminated (001) 17-atom slab (corresponding to 3 B-O and 4 A-O atomic layers) of a PZT alloy, as

The aims of this Rapid Communication are twofold: first, to present a first-principles-derived approach allowing accurate predictions of finite-temperature properties of complex ferroelectric thin films, under stress-free and open-circuit boundary conditions; second, to use this approach to better understand thin films by providing answers to the questions mentioned above.

Ferroelectric thin films are currently of enormous technological interest, mostly because of the need for miniaturization in devices.\[1\] Many fundamental questions are still unanswered and/or unsettled in these low-dimensional systems. For instance, whether or not there is a critical thickness below which no ferroelectricity can occur is still under debate.\[2-6\] Similarly, the precise effects of surface on properties of thin films are opened for discussion.\[5,7-10\] One may also wonder how the striking features exhibited by some bulk materials may evolve in the corresponding thin films. Typical examples of such features are the unusual low-symmetry phases (associated with a composition-induced rotation of the spontaneous polarization and with an enhancement of dielectric and piezoelectric responses), recently discovered in the morphotropic phase boundary (MPB) of various alloys.\[11-15\]

One reason behind this lack of knowledge is that thin (and particularly ultrathin) films are difficult to synthesize in a good quality form, and their characterization is by no means straightforward. Similarly, realistically simulating thin films is a theoretical challenge. For instance, while phenomenological and \textit{ab initio}-based models have already provided a deep insight into thin films (see Refs. 2 and 16–18 and references therein), such models do not usually incorporate some subtle surface-related phenomena, e.g., charge transfer and modification of ferroelectric interactions near the surface. On the other hand, direct first-principles techniques can easily include such effects.\[3-7,10\] However, their large computational cost currently prevents them from being used to study complex phenomena and/or complex systems (e.g., thin films made of disordered solid solutions), especially at finite temperature. The atomistic approach of Ref. 5 is a promising technique for investigating thin films at finite temperature, but its level of accuracy depends on the surface termination,\[5\] which emphasizes that mimicking well surface effects on physical properties is tricky.

The aims of this Rapid Communication are twofold: first, to present a first-principles-derived approach allowing accurate predictions of finite-temperature properties of complex ferroelectric thin films, under stress-free and open-circuit boundary conditions; second, to use this approach to better understand thin films by providing answers to the questions mentioned above.

FERROELECTRIC THIN FILMS UNDER STRESS-FREE AND OPEN-CIRCUIT ELECTRICAL BOUNDARY CONDITIONS

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First-Principles Determination of Electromechanical Responses of Solids under Finite Electric Fields

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We describe a first-principles, easy-to-implement, and efficient approach for determining the structural geometry of insulating solids under finite electric fields. This method consists of simultaneously minimizing the field-induced total ionic forces and the electric free energy. Moreover, we present a theory to analyze its predictions that provides a microscopic understanding of electromechanical responses in materials. We illustrate this approach by computing piezoelectric and dielectric responses of two rather different compounds, namely, ferroelectric PbTiO$_3$ and semiconductor GaN.

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Converting electricity to mechanical energies, via the application of an electric field in piezoelectric materials, is a process of both technological and fundamental interest [1–3]. For this process, the determination and microscopic understanding of the $d_{ij}$ piezoelectric coefficients—which characterize the response of strains $\gamma_i$ ($i = 1, 2, \ldots, 6$ using Voigt notation) to an electric field $E$ via $\gamma_i = \sum_j d_{ij}E_j$—is critical in light of discovering new materials having the promise to drastically improve the resolution and range of piezoelectric transducers and actuators. Measuring these coefficients in experiments is straightforward using Sawyer-Tower circuits [4]. On the other hand, unlike the calculation of the inverse piezoelectric coefficients $e_{ij}$ [5,6], the use of first-principles density-functional theory (DFT) [7] to compute the piezoelectric responses $d_{ij}$ of solids under finite electric fields proved to be exceptionally difficult [8,9]. More specifically, the difficulty lies in that an infinite solid in a static electric field has no ground state. Therefore, energy minimization cannot be directly performed using the variational principle that underlies the self-consistent tight-binding model [8]. On the other hand, unlike the calculation of the inverse piezoelectric coefficients $e_{ij}$ [5,6], the use of first-principles density-functional theory (DFT) [7] to compute the piezoelectric responses $d_{ij}$ of solids under finite electric fields proved to be exceptionally difficult [8,9]. More specifically, the difficulty lies in that an infinite solid in a static electric field has no ground state. Therefore, energy minimization cannot be directly performed using the variational principle that underlies the self-consistent tight-binding model [8].

The past few years have witnessed an intense activity in seeking methods able to mimic electric-field effects in solids within the DFT. Several approaches have been developed. (i) The approach of Ref. [10] uses periodic real-space supercells, so that charges do not "run away" and that the system still has an energy minimum. This method is straightforward to implement, and was applied to compute the electronic response (i.e., electronic screening) to external electric fields. (ii) The scheme proposed in Ref. [8]—that uses field-dependent Wannier functions to prevent charge tunneling—was implemented in a non-self-consistent tight-binding model [8], as well as in self-consistent DFT calculations [11]. (iii) Another method, based on low-order DFT perturbative expansions of thermodynamic energy as a function of electric fields, has been recently developed [12]. This approach takes advantage of the fact that the problem of studying electromechanical responses in solids can be converted to the search of structural geometry under a constrained polarization [12], if one assumes a first-order expansion of energy in which the electric field is only coupled to the zero-field polarization. A simple and less powerful "constrained-polarization" technique was developed and used in Ref. [13]. (iv) Finally, a scheme yielding field-dependent Bloch functions at the local minimum of free energy, and using conjugate-gradient method, has been proposed and successfully developed in Ref. [14]. A similar scheme but implemented within the Car-Parrinello $ab$ initio molecular-dynamics method was independently developed in Ref. [15].

In this Letter, we propose and successfully apply an alternative approach that (i) allows an accurate structural minimization of solids under finite electric fields, and thus computation of piezoelectric and dielectric coefficients; (ii) is easily implementable in any DFT code; (iii) is computationally efficient; and (iv) naturally leads to the understanding of why some materials, and not others, exhibit large electromechanical responses.

The proposed method starts from the expression (within DFT) of the free energy ($F$) of an insulator under a uniform finite electric field:

$$F(R, \eta, E) = U_{KS}[R(E), \eta(E)] - P(R, \eta, E) \cdot E,$$

where $F$, the Kohn-Sham internal energy $U_{KS}$, and the macroscopic polarization $P$ for each unit cell all depend on atomic positions $R$, strain $\eta$, and electric field $E$. Note that the electric field $E$ in Eq. (1) is the screened macroscopic field inside the material [9]. Equation (1) implies that the total force $Q_{\text{tot}}$ acting on ion $i$ is simply $Q_{\text{tot}} = Q_{\text{HF}} + Z_i^* (R, \eta, E) E$, where $Q_{\text{HF}}$ is the (usual) Hellmann-Feynman force, and $Z_i^*$ is the Born effective-charge tensor of ion $i$. When the system is at its field-induced local minimum, the total force $Q_{\text{tot}}$ on each ion $i$ should vanish, or, equivalently, the Hellmann-Feynman force should thus satisfy

$$Q_{\text{HF}}^i = -Z_i^* (R, \eta, E) E,$$

for any ion $i$.  

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Ferroelectric in Barium Titanate Quantum Dots and Wires

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Properties of BaTiO$_3$ colloidal quantum dots and wires are simulated using a first-principles-based approach. Large atomic off-center displacements (that are robust against capping matrix materials) are found to exist in very small (<5 nm) dots. We further determine the size dependences of electrical and electromechanical responses in the studied nanostructures, as well as provide microscopic understanding of these responses.

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Intense experimental effort has been made recently in synthesizing and understanding ferroelectric (FE) nanostructures—e.g., BaTiO$_3$ dots [1], rods [2], wires [3], and nanotubes [4], and Pb(Zr,Ti)O$_3$ thin films [5,6] and nanoparticles [7]—mainly because of their promise in increasing FE nonvolatile-memory density thousands fold by reading and writing into individual nanoparticles [3,8,9]. Furthermore, these FE nanostructures are also critical in light of miniaturizing piezoelectric transducers and actuators, ultrasonic devices, and medical imaging detectors [10,11]. From a fundamental point of view, ferroelectricity is caused by atomic off-center displacements, resulting from a delicate balance between long-range (LR) Coulomb interaction and short-range (SR) covalent interaction [12]. In nanostructures, both interactions—and thus their balance—are altered with respect to the bulk, since the LR interaction is truncated due to lack of periodicity, while the SR one is significantly modified near the surface boundary. Consequently, it is commonly believed [13–16] that ferroelectricity in nanostructures would disappear entirely (i.e., there is no ferroelectric off-center instability) below a critical size. This belief has recently received support from a theoretical study on BaTiO$_3$ thin films [17]. For FE nanoparticles, while measurements of lattice structures (rather than polarization) are available only at large sizes (~500 Å, Refs. [14,15]), the critical size of ferroelectricity (if any) is unknown [1–3,7]. In fact, it is not even clear whether there are any ferroelectric displacements in FE dots and/or whether these displacements are aligned to form long-range ferroelectric phases. Similarly, virtually nothing is known about the electrical and mechanical responses of FE nanoparticles to electric fields.

The purpose of this Letter is to investigate, from first principles, the ferroelectric properties of BaTiO$_3$ colloidal nanoparticles—and, in particular, to answer whether there is ferroelectricity in FE nanoparticles and how these particles respond to applied electric fields. These properties are found to be unusual and differ from what is commonly believed.

Here, we further develop and use a first-principles-derived effective-Hamiltonian approach [18,19] coupled with Monte Carlo simulations. (Ideally, one would like to use direct first-principles density-functional theory, but this is currently computationally impracticable.) The effective Hamiltonians of Refs. [18,19], which are derived from first principles and possess a comparable accuracy, have been successfully applied to many FE materials, including simple BaTiO$_3$ [20], PbTiO$_3$ [21], and KNbO$_3$ [22] systems, and complex Pb(Zr,Ti)O$_3$ [19] and Pb(Sc,Nb)O$_3$ [23] solid solutions. In this approach, local modes $\{u_i\}$ ($i$ is the cell index) describe the ferroelectric instability in individual 5-atom cells; $u_i$ are associated with local electrical dipoles $P_i$ via $P_i = Z^* u_i$ (where $Z^*$ is the effective charge of the local mode).

Compared to the original method detailed in Ref. [18], two new developments are made here in order to be able to study FE nanoparticles: (i) No supercell periodic boundary conditions are imposed, and the LR dipole-dipole interaction is performed in real-space (inside the nanoparticles) rather than in reciprocal space. Our simulations with open-boundary condition precisely mimic the experimental situations [3,5,6] in which polarizations in FE wires and films are probed by noncontact electrostatic forces without metallic electrodes. By contrast, the calculations of BaTiO$_3$ thin films in Ref. [17] assume a short-circuit boundary condition with metallic electrodes surrounding the films. Also note that, in our real-space implementation without artificial periodicity for finite systems, the potential field generated by every dipole in the nanoparticles—including the depolarization field produced by the charges (i.e., uncompensated dipoles) at nanoparticle surfaces—is precisely computed and properly accounted for. (ii) Existence of the vacuum surrounding nanoparticles will cause surface-induced atomic relaxations and cell-shape changes (thus affecting both local modes and local inhomogeneous strains) near the nanoparticle surfaces. To account for the effect of atomic relaxations on local modes, an interaction between local modes at surfaces and the vacuum (denoted as mode-vacuum interaction) is added in the
Off-center atomic displacements in BaTiO₃ quantum dots

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Abstract. Structural properties of BaTiO₃ quantum dots are studied using a first-principles derived effective-Hamiltonian approach. Truncated long-range dipole-dipole interaction and modification of the short-range interaction due to the existence of vacuum are taken into account. Our calculations show that there are significant off-center atomic displacements in these dots; the amplitudes of such displacements are comparable with those occurring in bulk BaTiO₃. However, unlike in the bulk system, the net polarization in dots is found to be zero. Our results also show that the local displacements in the dots tend to flip across the distance of the entire dot, resulting in an unusual and complex pattern.

INTRODUCTION

As temperature decreases, bulk BaTiO₃ undergoes sequences of structural transitions[1]: from the paraelectric cubic phase to a tetragonal phase at 403K, then to an orthorhombic phase at 278K, and finally to a rhombohedral phase at 183K. Some of these phase transitions have an order-disorder character, as indicated by the existences of substantial atomic displacements at cubic phases and the broad Fourier spectrum over the Brillouin zone.[2] The microscopic mechanism that are responsible for the existence of ferroelectric phases are, in particular, the long-range (LR) dipole-dipole interaction and the short-range (SR) interatomic covalent coupling. The ferroelectric phases of bulk BaTiO₃ have now been understood, at a microscopic level, from both first-principles calculations[3] and effective Hamiltonian simulations.[2]

Compared to bulk materials, quantum dots (i.e., finite-size nanocrystals) do not have the imposed periodic boundary condition. As a result, the microscopic forces that determine the material phases are altered, and the delicate balance between the LR and SR interactions in bulk can be strongly modified with respect to the bulk case. It is therefore interesting to examine whether there are significant off-center displacements in dots, and whether these displacements will align themselves to form ferroelectric phases. Specifically, the following three differences exist between the bulk and dots: (1) The LR dipole interaction that is crucial to yield ferroelectric phases is truncated in dots. Unlike in bulk, the electrostatic potentials at different cells are thus not equal. (2) The SR interaction among the atoms near the boundary of dots are altered. The atomic displacements at the surfaces will thus be different from those inside the dots. (3) Depending on the sizes of dots, dielectric screening may be different from the bulk value, which will affect the LR dipole energy.

Here we study the off-center atomic displacements in BaTiO₃ dots using an effective