



Hyperferroelectrics: Proper Ferroelectrics with Persistent Polarization

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All known proper ferroelectrics are unable to polarize normal to a surface or interface if the resulting depolarization field is unscreened, but there is no fundamental principle that enforces this behavior. In this work, we introduce hyperferroelectrics, a new class of proper ferroelectrics which polarize even when the depolarization field is unscreened, this condition being equivalent to instability of a longitudinal optic mode in addition to the transverse-optic-mode instability characteristic of proper ferroelectrics. We use first-principles calculations to show that several recently discovered hexagonal ferroelectric semiconductors have this property, and we examine its consequences both in the bulk and in a superlattice geometry.

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Ferroelectrics, which are materials with a nonzero spontaneous polarization that can be switched by an external electric field, have been extensively studied both experimentally and theoretically. Much of the work on ferroelectrics has focused on proper ferroelectrics, such as BaTiO_3 . These have a nonpolar reference structure that is related to the ferroelectric ground state by a polar distortion that lowers the energy in zero macroscopic electric field, corresponding to an unstable transverse optic (TO) mode. However, a slab of a typical proper displacive ferroelectric with insulating surfaces will not spontaneously polarize with polarization normal to the surface, because at quadratic order in the polarization the energetic cost of the resulting depolarization field is larger than the energy gain from freezing in the distortion [1]. In order to polarize, the depolarization field must be screened, as, for example, by a metallic electrode placed on the surfaces of the ferroelectric slab [2,3].

In contrast to proper ferroelectrics, improper ferroelectrics do not have an unstable polar distortion in their high-symmetry structure. Instead, these materials have one or more unstable nonpolar distortions. However, when these distortions assume nonzero values, they break inversion symmetry in the material, resulting in a nonzero polarization [4–7]. Because the primary energy-lowering distortion in an improper ferroelectric is nonpolar, the depolarization field is too weak to prevent the instability. Thus, a slab cut from such a material can develop a nonzero polarization normal to the surface [8].

In this work, we demonstrate a new class of “hyperferroelectrics.” These are proper ferroelectrics in which the polarization persists in the presence of a depolarization field. Using first-principles calculations, we identify hyperferroelectrics in the recently discovered class of hexagonal ABC semiconducting ferroelectrics [9]. Using first-principles-based modeling, we show that hyperferroelectrics have an electric equation of state that is qualitatively different from those of both proper and improper

ferroelectrics, resulting in persistent polarization regardless of screening and unique dielectric behavior. Finally, we discuss the potential applications of hyperferroelectrics, whose ability to polarize in ultrathin layers may allow the creation of highly tunable thin-film or superlattice structures displaying ultrafast switching behavior.

We perform first-principles density functional theory (DFT) calculations [10,11] within the local-density approximation [12] using the QUANTUM ESPRESSO code [13]. We use ultrasoft [14] pseudopotentials from the Garrity, Bennett, Rabe, Vanderbilt high-throughput pseudopotential set [15,16]. Phonon frequencies, Born effective charges, and electronic dielectric constants are calculated by using DFT perturbation theory [17–19], and polarization is calculated by using the Berry phase method [20].

We begin by reviewing the properties of normal proper ferroelectric materials, which in their high-symmetry phase have at least one unstable TO mode, specifically, a Γ mode that is unstable under zero macroscopic electric field ($\mathcal{E} = 0$) boundary conditions. The frequency of this mode can be obtained from first-principles computation of the force-constant matrix with the usual periodic boundary conditions. The longitudinal optic (LO) modes can then be obtained by adding to the force-constant matrix a nonanalytic long-range Coulomb term that schematically takes the form $(Z^*)^2/\epsilon^\infty$, where Z^* are the Born effective charges and ϵ^∞ is the electronic contribution to the dielectric constant, generating the well-known LO-TO splitting [21]. For normal proper ferroelectrics, this nonanalytic term is sufficiently large that all the LO polar modes are stable; in other words, the depolarization field resulting from the long-range Coulomb interaction will prevent the ferroelectric from polarizing under fixed $D = 0$ boundary conditions. For typical perovskite oxides, the strength of the depolarization field must be weakened by at least 90% to allow for a nonzero polarization with $D = 0$ [1].

While large-band-gap oxide ferroelectrics, which typically have large Z^* 's and small ϵ^∞ 's, have all LO modes

stable, there is no fundamental principle that enforces this stability. For example, in a class of materials called “weak ferroelectrics” [22], the mode effective charge, and thus the LO-TO splitting, is negligible, and the polarization of the ferroelectric phase is produced by higher-order coupling to the hard polar modes. As we will demonstrate in detail below, unstable LO modes can also be found in semiconducting hexagonal ABC ferroelectrics. The crystal structure is shown in Figs. 1(a) and 1(b) (space group $P6_3mc$, LiGaGe structure type). The high-symmetry phase of these materials consists of layers of two atoms in an sp^2 -bonded honeycomb lattice separated by layers of a third “stuffing” atom, as shown in Figs. 1(a) and 1(b). The polar phase is reached by a single Γ^{2-} phonon mode, which consists primarily of a buckling in the honeycomb layers as the atoms move from an sp^2 environment towards sp^3 bonding, resulting in polarization in the z direction [9].

In Table I, we report the lowest TO and LO phonon frequencies and dielectric constants, as well as band gaps, $\Delta Z_{zz}^* = \sqrt{\sum_m (Z_{zz}^*)_m^2 / N}$, and polarizations for a variety of ABC ferroelectrics; those with imaginary LO frequencies are, by definition, hyperferroelectrics. The relatively small $\Delta Z_{zz}^* \approx 3$ and large $(\epsilon^\infty)_{zz} \approx 10$ –20 both contribute to the weak depolarization fields in these materials [for reference, cubic perovskites typically have $\Delta Z_{zz}^* \approx 5$ and $(\epsilon^\infty)_{zz} \approx 6$]. Both the small effective charges and large dielectric constants of ABC ferroelectrics are consequences of the covalent bonding and resulting small band gaps of these semiconductors. In Fig. 1(c), we show the phonon dispersion for the hyperferroelectric LiBeSb, which is a previously synthesized material [23,24]. We see that the lowest frequency phonon mode for $q \rightarrow 0$ is unstable regardless of the direction from which Γ is approached.

In order to investigate the electric equation of state of hyperferroelectrics, we use a simple first-principles-based model. We first define a dimensionless polar internal degree of freedom, u , as the buckling of the honeycomb layer, which varies from zero in the high-symmetry structure to one in the polar structure at $\mathcal{E} = 0$. Then, we expand the free energy up to second order in \mathcal{E} , and up to sixth order

in u , with the $\mathcal{E} = 0$ polarization included up to first order in u [25]:

$$F(u, \mathcal{E}) = -au^2 + bu^4 + cu^6 - P_s u \mathcal{E} - \frac{1}{2} \chi_e(u) \mathcal{E}^2, \quad (1)$$

where F is the free energy, $\chi_e(u) = \epsilon^\infty(u) - 1$ is the zero-field electronic susceptibility as a function of u , and P_s , a , b , and c are constants. The polarization P is then

$$P(u) = -\frac{\partial F}{\partial \mathcal{E}} = P_s u + \chi_e(u) \mathcal{E}, \quad (2)$$

which allows us to identify P_s as the spontaneous polarization of the ground-state structure at zero electric field ($u = 1$, $\mathcal{E} = 0$), justifying the notation for this constant. We fit this model to our materials by running a series of calculations with $\mathcal{E} = 0$ and u fixed between 0 and 1.1, allowing all of the other internal degrees of freedom as well as the lattice vectors to relax. In addition, we calculate $\epsilon^\infty(u)$ for each structure, which we fit to a cubic spline.

Using the model of Eqs. (1) and (2), we can parametrically plot $\mathcal{E}(u)$, $P(u)$, and $D(u) = \epsilon_0 \mathcal{E} + P$ versus each other, which we do for both the normal ferroelectric NaMgP and the hyperferroelectric LiBeSb in Figs. 2 and 3. In both cases, we indicate regions that are locally unstable, locally stable, and globally stable under fixed- \mathcal{E} boundary conditions. In locally unstable regions ($\partial P / \partial \mathcal{E} < 0$), the atomic degrees of freedom are at an unphysical maximum of the free energy, rather than a minimum. In NaMgP, P as a function of \mathcal{E} is multivalued at $\mathcal{E} = 0$, indicating that NaMgP is ferroelectric, with spontaneous polarization as given in Table I. However, P vs D is single valued, indicating that NaMgP will not polarize under fixed $D = 0$ boundary conditions and thus is a normal proper ferroelectric. In contrast, for the hyperferroelectric LiBeSb, both P vs \mathcal{E} and P vs D are multivalued, so

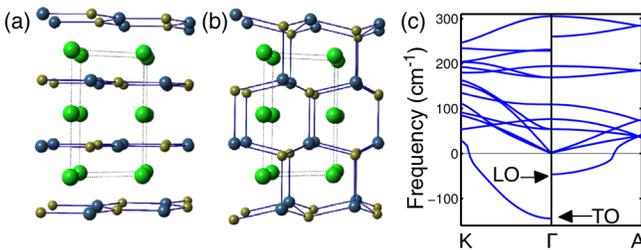


FIG. 1 (color online). Structures of (a) high-symmetry ($P6_3/mmc$) and (b) polar ($P6_3/mc$) ABC ferroelectrics. The large green atom is the stuffing atom. (c) Phonon spectrum of high-symmetry LiBeSb, from K ($\pi/3a, \pi/3a, 0$) to Γ ($0, 0, 0$) to A ($0, 0, \pi/2c$) (imaginary frequencies are plotted as negative numbers).

TABLE I. Properties of ABC hexagonal ferroelectrics. Compounds are listed with the stuffing atom first. First-principles results for the high-symmetry phase: ω_{TO} and ω_{LO} are frequencies of unstable polar modes approaching Γ along $\hat{q} = (100)$ and (001) , respectively; L_c is defined in the text; $(\epsilon^\infty)_{zz}$ is the zz electronic dielectric constant; ΔZ_{zz}^* is the rms zz Born effective charge; “Gap” is the band gap. $P^{(\mathcal{E}=0)}$ is the first-principles polarization at $\mathcal{E} = 0$. $P^{(D=0)}$ is the polarization computed from the model of Eqs. (1) and (2) at $D = 0$.

ABC	ω_{TO} (cm^{-1})	ω_{LO} (cm^{-1})	$(\epsilon^\infty)_{zz}$	ΔZ_{zz}^*	Gap (eV)	$P^{(\mathcal{E}=0)}$ (C/m^2)	$P^{(D=0)}$ (C/m^2)
LiZnP	134 <i>i</i>	49	13.3	3.0	1.27	0.80	0
NaMgP	131 <i>i</i>	150	10.6	2.9	0.89	0.52	0
LiZnAs	118 <i>i</i>	68 <i>i</i>	15.5	3.0	0.48	0.73	0.02
LiBeSb	144 <i>i</i>	47 <i>i</i>	19.9	2.9	0.93	0.59	0.02
NaZnSb	42 <i>i</i>	14 <i>i</i>	10.2	2.0	0.69	0.51	0.01
LiBeBi	171 <i>i</i>	132 <i>i</i>	22.1	2.9	0.83	0.54	0.02

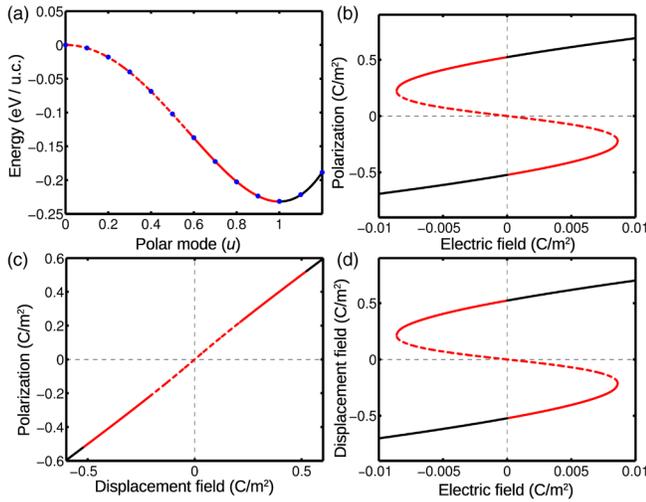


FIG. 2 (color online). Computed energy landscape and electric equations of state for normal ferroelectric NaMgP. (a) Energy vs polar mode u . Dots are first principles; the line is a fit to the model. (b) P vs $\epsilon_0 \mathcal{E}$. (c) P vs D . (d) D vs $\epsilon_0 \mathcal{E}$. Dashed red lines are locally unstable at fixed \mathcal{E} ; solid red lines are locally stable; solid black lines are globally stable.

that the material will spontaneously polarize under both fixed $\mathcal{E} = 0$ and fixed $D = 0$ boundary conditions. In addition, the slope of D vs \mathcal{E} indicates $\epsilon^0 = \partial D / \partial \mathcal{E}|_{\mathcal{E}=0} > 0$, despite the unstable polar mode. As shown in Table I and Fig. 3(c), the $D = 0$ polarization of hyperferroelectrics, $P^{(D=0)}$, which we compute with the model of Eqs. (1) and (2), is small compared to $P^{(\mathcal{E}=0)}$; however, the amplitude of the polar mode remains surprisingly large. The polar distortions of the materials at $D = 0$ are 25%–75% of their $\mathcal{E} = 0$ values, but the resultant ionic polarization is largely canceled by the electronic

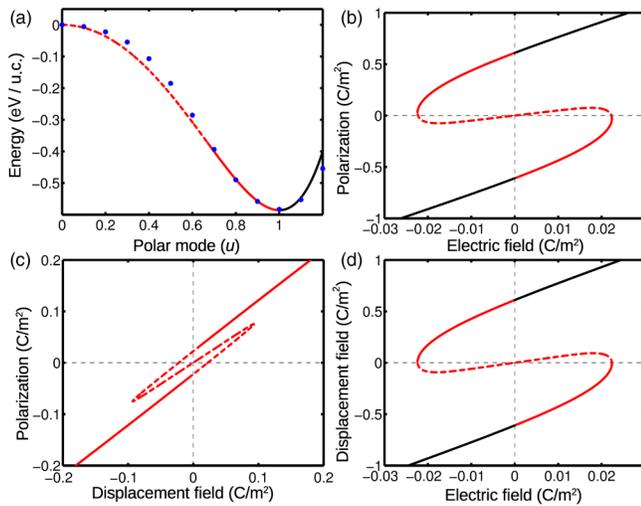


FIG. 3 (color online). Computed energy landscape and electric equations of state for hyperferroelectric LiBeSb. Details are as in Fig. 2.

polarization $\chi_e(u)\mathcal{E}$ induced by the depolarization field, resulting in a small net polarization. Similarly, we find that the $D = 0$ energy differences between the polar and nonpolar structures are reduced at least 70% relative to their $\mathcal{E} = 0$ values, due to the energetic cost of the depolarization field, but in several cases these differences remain comparable to room temperature.

To emphasize the difference between hyperferroelectrics and improper ferroelectrics, we briefly review a model of an improper ferroelectric. In the simplest improper ferroelectrics, the primary order parameter v is nonpolar, but it couples to a stable polar mode u with the form uv^3 . Then u , which appears only to quadratic order, can be minimized over analytically, resulting in an effective coupling between v^3 and \mathcal{E} [26]:

$$F(v, \mathcal{E}) = -av^2 + bv^4 - cv^3\mathcal{E} - \frac{1}{2}\chi_e\mathcal{E}^2. \quad (3)$$

In Fig. 4, we plot P vs D and D vs \mathcal{E} for this model with typical parameters. Similar to hyperferroelectrics, improper ferroelectrics allow for a nonzero polarization at $D = 0$; however, the overall shape of the curves is very different. In particular, improper ferroelectrics lack a structure with $D = P = 0$. This reflects the fact that our model of improper ferroelectrics always has a barrier to homogeneous switching via an external field ($\partial P / \partial \mathcal{E} > 0$ everywhere), as the effective coupling between the field and third power of the nonpolar distortion cannot overcome the primary quadratic instability. Clearly, then, the physical behavior of improper ferroelectrics and hyperferroelectrics is qualitatively different.

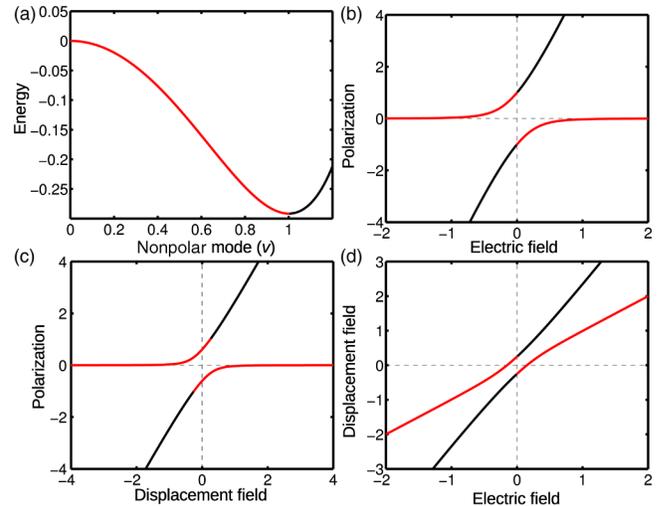


FIG. 4 (color online). Energy landscape and electric equations of state for improper ferroelectric model of Eq. (3). (a) Energy vs nonpolar mode v . (b) P vs \mathcal{E} . (c) P vs D . (d) D vs \mathcal{E} . All regions are locally stable at fixed \mathcal{E} ; globally stable regions in black; other regions in red.

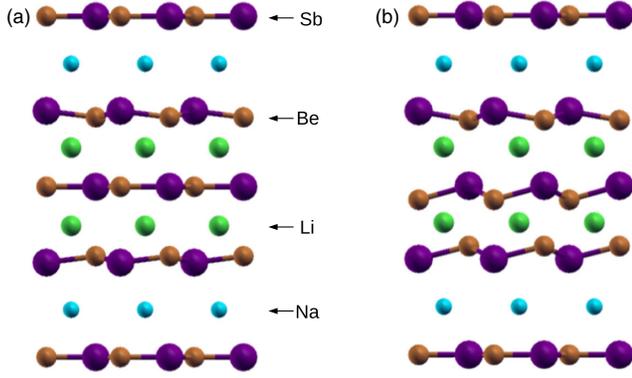


FIG. 5 (color online). Interfacial region of (a) nonpolar and (b) polar phases of the $1/7$ LiBeSb/NaBeSb superlattice. The full supercell has three additional unpolarized NaBeSb layers.

Returning to our main topic, we note that the unusual electric properties of hyperferroelectrics mean that the ferroelectric phase transition temperature, which decreases with decreasing screening, will still be nonzero even under $D = 0$ boundary conditions. At this temperature T_D , the LO mode becomes unstable and the material becomes a hyperferroelectric. As a hyperferroelectric goes through T_D under $D = 0$ boundary conditions, the inverse dielectric constant will diverge, rather than the dielectric constant, which can be understood by comparing the D vs \mathcal{E} plots of normal and hyperferroelectrics in Figs. 2(d) and 3(d), respectively. In order to transition from the normal to the hyperferroelectric state, the slope at the origin of the D vs \mathcal{E} curve, which is equal to the dielectric constant, must pass through zero.

In order to demonstrate the consequences of the most notable quality of hyperferroelectrics, their ability to polarize under fixed $D = 0$ boundary conditions, we place our ABC ferroelectrics in superlattice configurations with thick slabs of nonpolar ABC materials. We expect that normal ferroelectrics will not polarize in this geometry if there are no free charges, as a sufficiently thick nonpolar layer will have $P = 0$, which enforces $D = 0$ boundary conditions on the ferroelectric, but hyperferroelectrics will still polarize under these conditions.

We consider superlattices consisting of ferroelectric ABC materials combined with nonpolar hexagonal ABC semiconductors, specifically normal ferroelectric NaMgP with nonpolar KZnSb and hyperferroelectric LiBeSb with nonpolar NaBeSb, as shown in Fig. 5. We epitaxially strain each superlattice to the in-plane lattice constant of the nonpolar material, allowing the z lattice constant to relax.

As shown in Table II, the normal ferroelectric NaMgP has essentially no polarization when in a superlattice with an insulating material. We attribute the tiny 10 meV energy lowering of the $1/7$ NaMgP/KZnSb superlattice to interface effects, as the interfaces between NaMgP and KZnSb consist of single layers of NaZnSb, which as shown in Table I is itself a hyperferroelectric. On the other hand, a

TABLE II. Properties of superlattices. An $n/m ABC/A'B'C'$ superlattice consists of $n BC$ atomic layers separated by A atomic layers, and $m B'C'$ atomic layers separated by A' atomic layers, with A layers at both interfaces. ΔE is the energy gained by allowing a polar distortion. “Gap(HS)” and “Gap(FE)” are the band gaps for the nonpolar and polar phases, respectively; m indicates a metal. For insulators, $P^{(\mathcal{E}=0)}$ is the polarization for $\mathcal{E} = 0$ boundary conditions.

Ferro.	Nonpolar	Period	ΔE (eV)	Gap(HS) (eV)	Gap(FE) (eV)	$P^{(\mathcal{E}=0)}$ C/m ²
NaMgP	KZnSb	1/7	-0.01	0.32	0.35	0.007
NaMgP	KZnSb	2/6	0	0.69	...	0
NaMgP	KZnSb	3/7	0	0.61	...	0
NaMgP	KZnSb	4/6	0	0.68	...	0
LiBeSb	NaBeSb	1/7	-0.07	0.75	0.39	0.03
LiBeSb	NaBeSb	2/6	-0.09	0.57	m	m
LiBeSb	NaBeSb	3/7	-0.25	0.28	m	m
LiBeSb	NaBeSb	4/6	-0.50	0.32	m	m
LiBeSb	NaBeSb	1/3	-0.08	0.77	0.46	0.07
LiBeSb	NaBeSb	2/2	-0.41	0.61	1.02	0.56

single polarized layer of the hyperferroelectric LiBeSb interfaced with NaBeSb has a significantly lower energy and reduced band gap relative to an unpolarized layer. A second LiBeSb layer already provides sufficient polarization to cause the system to become metallic, due to dielectric breakdown, a field-induced overlap of conduction and valence bands leading to charge transfer.

As already demonstrated, hyperferroelectrics can remain polarized down to single atomic layers even when interfaced with normal insulators. Such quasi-2D ferroelectric systems could have a variety of unusual properties. First, by adjusting the spacing of layers in a superlattice, the polarization, well depth, band gap, and internal electric field could all be tuned. More speculatively, these superlattice systems could display novel domain-wall motion or superfast switching behavior, as they consist of weakly coupled ferroelectric layers which may allow for easier domain nucleation, and they support head-to-head and tail-to-tail domain walls. Also, unlike a normal ferroelectric, which requires asymmetric screening charges to remain polarized, a hyperferroelectric can switch between two states without the motion of screening charges between its surfaces or interfaces, allowing hyperferroelectric slabs which are terminated by vacuum or by nonpolar insulators to be switched via an external field. In addition, in contrast to improper ferroelectrics, the primary order parameter of hyperferroelectrics couples directly to an applied electric field, which may allow for easier switching. Finally, ABC materials could be used to build an all-semiconducting ferroelectric field effect transistor, sidestepping many of the materials difficulties and interface effects that have hampered attempts to interface ferroelectric oxides with semiconductors [27–29].

In conclusion, we have introduced a new class of ferroelectrics, hyperferroelectrics, and we have identified examples among the *ABC* hexagonal semiconducting ferroelectric family. These new ferroelectrics have a variety of interesting and potentially useful properties, both in the bulk and as thin films. Furthermore, this work highlights the benefits of looking beyond well-studied materials systems in the search for functional materials with novel properties.

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