Theory of ferroelectrics: A vision for the next decade and beyond

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Abstract

In the last ten years significant advances have been made in our understanding and ability to compute and predict properties of ferroelectrics and piezoelectrics using fundamental physics. Phase diagrams, electromechanical and elastic properties, and effects of defects and surfaces are now amenable to computation. Most importantly, new techniques have been developed, and new understanding of the meaning of polarization in dielectrics has been developed. Prospects for the future are discussed.

Key words: ferroelectrics; electronic structure; piezoelectricity; piezoelectrics; first-principles; phase diagrams; surfaces, defects

1 Introduction

About ten years ago a concerted effort began to apply modern first-principles band structure methods to the problems of ferroelectricity, with a vision that electromechanical properties could perhaps one day be designed computationally [1]. This effort has been at least as successful as hoped, and a range of problems that we didn’t even realize existed at the time have been identified and solved. Understanding electromechanical response has turned out to be a rich problem, both from a fundamental condensed matter physics perspective, as well as from the applied physics and even engineering perspectives. There is much expanded interest in the field now that a new class of materials have been discovered, single crystal piezoelectrics with ultra-high electromechanical couplings such as PMN-PT (PbMg\(_2\)Nb\(_3\)O\(_3\)-PbTiO\(_3\)) which will revolutionize fields ranging from sonar and hydrophones to medical ultrasonic imaging [2]. The current state of the field, as will be discussed below, is that we now can compute all of the parameters related to electromechanical coupling, particularly the piezoelectric constants, for pure, ordered, single crystal phases [3,4].
This can be done with good accuracy at zero temperature, and indications are that quite reliable results can also be obtained as functions of temperature [5]. The problems now being studied are how to treat disordered solid solutions, and to understand the underlying physics behind the observed material behavior—why is one material better than another. In the future, using the computational techniques developed, and the insights obtained from theory and experiment, we will be able to predict material properties of as-yet unsynthesized complex materials. The current state of the field and future prospects are outlined here. This is not intended as a comprehensive review, but should be a useful introduction to the field of first-principles studies of ferroelectrics and piezoelectrics.

The reason to use first-principles methods is that (1) one is not reliant on parameterized theories or (2) on fitting possible inaccurate experiments, (3) one has access to the underlying potential surfaces, (4) can clearly see the origin of observed behavior, and (5) they can be applied to hypothetical or not yet synthesized materials, or (6) for temperature, pressure or compositions for which data are not available. By “first-principles,” we mean that experimental data are not used to constrain parameters; rather one starts from the fundamental interactions among electrons and nuclei. Most of the first-principles methods that have been applied to ferroelectrics are based on the density functional theory (DFT) [6] and some are based on Hartree-Fock theory. The DFT states that the ground state properties of a system are given by the charge density, and Kohn and Sham [7] showed how to compute the charge density and energy self-consistently, using an effective exchange-correlation potential ($V_{xc}$) that accounts for the quantum mechanical interactions between electrons. The local density approximation (LDA) takes the exchange-correlation potential from the uniform electron gas at the density for each point in the material. The Generalized Gradient Approximation (GGA) includes the effects of local gradients in the density [8]. Given a form for the exchange correlation energy $E_{xc}[\rho]$, one can find the self-consistent charge density and compute the energy for any arrangement of nuclei (atoms). From the energies, zero temperature phase diagrams, phonon frequencies, and elastic constants can be computed. In the frozen phonon method, for example, one displaces atoms and computes the change in energy as a function of displacement, from which the potential surface for an instability, or phonon frequencies, can be derived. In principle one can also compute finite temperature properties, for example using Monte Carlo or molecular dynamics methods. In practice, self-consistent methods are extremely computationally demanding, especially for large systems, so instead one can find effective potentials or Hamiltonians fit to the first-principles results to obtain finite temperature properties.

Properties of ferroelectrics are extremely sensitive to volume (pressure), which can cause problems since the present first-principles methods are not perfect, and small errors in volume (typically several percent, or more in some cases)
can result in large errors in computed ferroelectric properties. The GGA is generally an improvement over the LDA, but still many computations for ferroelectrics so far have been done at the experimental lattice. The GGA gives reasonable $c/a$ at the experimental volume. For PbTiO$_3$ at the experimental volume (427.27 bohr$^3$), for example, we found $c/a$ equal to 1.12 (90% high) for LDA (Hedin-Lundqvist), 1.09 for LDA (Wigner), and 1.073 for GGA (PBE), compared to the experimental value of 1.063. However, the volume is still too large in GGA and $c/a$ is thus overestimated. A new form for the exchange and correlation called the Weighted Density Approximation (WDA) shows much promise, and gives excellent results for the lattice constants and energetics [9], so there is hope that in the future all properties of ferroelectrics could be computed truly *ab initio* without recourse to the experimental volume.

2 Milestones

2.1 Total energy and electronic structure

At first it was unknown whether first-principles methods within the LDA would even give ferroelectric ground states where they should. If fact, in the initial computations for BaTiO$_3$ (read “initial” as over one year!) the author’s LAPW computations did not give a ferroelectric ground state due to a minor bug that apparently did not effect other systems! After this problem was fixed, the ferroelectric instability was found at the experiment volume, though it was extremely sensitive to pressure. The initial questions then after finding the instability were (1) what is the underlying cause of the ferroelectric instability and (2) why do different similar materials behave differently; particularly why does BaTiO$_3$ show a series of phase transitions from cubic, to tetragonal, to orthorhombic, and to rhombohedral with decreasing temperature whereas PbTiO$_3$ has a single phase transition to tetragonal? The potential surface was initially mapped out using the LAPW method, and the charge density and electronic structure were analyzed [10–12]. PbTiO$_3$ showed a much deeper well when the tetragonal strain was included, whereas in BaTiO$_3$ the rhombohedral phase had the lowest energy. Thus the tetragonal strain is responsible for the tetragonal ground state in PbTiO$_3$. Analysis of the charge densities and densities of states showed that the ferroelectric instability is due to hybridization between the O 2p states and the Ti 3d states, and if the 3d variational freedom was removed from the problem, the ferroelectric instability vanished [10]. In BaTiO$_3$, the Ba is quite ionic and spherical, whereas the Pb in PbTiO$_3$ is very not spherical in the ferroelectric phase, and polarization of the Pb helps stabilize the large strain and the tetragonal ground state in PbTiO$_3$.

Thus the following picture emerged. All Coulomb lattices are unstable with
respect to ferroelectric displacements; the short-range repulsive forces tend to stabilize crystals with respect to off-center displacements. In perovskite like BaTiO$_3$ and PbTiO$_3$, the O 2p states strongly hybridize with the d$_0$ cation, in this case Ti$^{4+}$, reducing the short-range repulsions thus allowing off-center displacements. Without strain, or when strain effects are minor, the lowest energy off-center displacements are along the (111) directions. Thus the ground state is rhombohedral. As temperature is raised, the off-center displacements disorder over two directions, giving an average orthorhombic symmetry, then there is a disordering over four directions giving tetragonal symmetry, and final a disordered cubic phase at high temperatures. The same features are found in BaTiO$_3$ and KNbO$_3$ [13,14]. One should not overemphasize this order-disorder picture too much, however. In the ideal order disorder picture, the atoms are in off-center sites at all temperatures, and there should be a large configurational entropy change at the ordering phase transitions, which is not observed. Furthermore, in the ideal disorder picture, the local potential for displacing a single B-site cation such as Ti or Nb is unstable, but calculations show that the diagonal, self-force constant, is positive, and so there would be a restoring force for displacing a single cation from its ideal position in the perfect cubic perovskite, and only when groups of ions are moved (for example in a Γ-point displacement) is there a multiple well potential surface [15].

It is clear that the polarizability of Pb plays a special role in ferroelectrics. PbTiO$_3$ has a very large strain (6%) where tetragonal BaTiO$_3$ has only a 1% strain. The ground state of PbZrO$_3$ is antiferroelectric and it has a complex phase diagram [16], whereas BaZrO$_3$ is cubic [17]. PbZrO$_3$ has a complex structure at low temperatures, and it was structural total energy relaxations within the LDA that clarified the crystal structure [16]. Thus first-principles theory has the power now to find problems with experimental determinations of complex structures.

Another example of theory finding problems with experimental analysis is LiNbO$_3$. In the LiNbO$_3$ structure there are chains of oxygen octahedra with Li ions shared between two octahedra. Based on neutron scatter experiments, it was suggested that the Li atoms hopped between two octahedra at high temperatures in the high temperature phase, and ordered to occupied one set of octahedra at low temperatures in the polar phase [18]. Analysis of experimental data suggested that the underlying potential surface had a triple well structure for Li displacements, and all models considered the Li motions to the important physics driving the ferroelectricity. Inbar and Cohen performed LAPW frozen phonon computations and found a quite different picture [19]. They found no triple well, and they found that the double well for Li displacements was quite shallow, and the double well for oxygen displacements much deeper. The deepest wells were found for coupled displacements of Li and O. They found that the ferroelectric instabilities in LiNbO$_3$ and LiTaO$_3$ are quite similar to the instabilities in the oxide perovskites, and that a primary driving
force is the $d_0$ configuration of the $\text{Nb}^{5+}$ and $\text{Ta}^{5+}$ ions, and hybridization with the surrounding oxygens that allows the $d_0$ cation to go off-center. This sets up local fields that drive or order the Li off-centering.

Though static total energy computations are very powerful, and further examples will be given below, they are limited in the ability to find phonon or instability eigenvectors or behavior for arbitrary wavevector. Advances that give the linear response for arbitrary wavevector are discussed next.

2.2 First-principles lattice dynamics–linear response

Using conventional methods, first-principles methods with the LDA or GGA scale as $N^3$, where $N$ is the size (say number of atoms) of the system. This makes it prohibitive to study arbitrary wavevectors. For small wavevectors a very large supercell would be required. In linear response computations that problem is circumvented, and one can compute the response of the system to small perturbations with arbitrary wavevector with approximately the same cost as the primitive cell computation. Yu and Krakauer developed a linear response LAPW code and applied it to phonon dispersion in $\text{KNbO}_3$ [13,20]. They found the ferroelectric instability to be dispersive in certain directions, indicating correlations in displacements in real space. In other words, if the unstable band were flat, it wouldn’t matter how the atoms were displaced in one cell relative to the next. Analysis of the instability dispersion showed that there should be chain-like correlations, consistent with streaking observed in x-ray diffraction [21]. Linear response methods also allow computation of Born effective charges (discussed below) and the dielectric constant.

A number of different ferroelectric perovskites have now been studied using linear response methods. The unstable modes of $\text{KNbO}_3$ and $\text{BaTiO}_3$ show very similar dispersion, consistent with the same sequence of phase transitions for the two. The soft branch has primarily B-ion character. $\text{PbTiO}_3$ shows a much more flat soft branch, indicating that correlations between cells are less important than in $\text{KNbO}_3$ or $\text{BaTiO}_3$. The soft modes also have appreciable A-ion character (Pb) in $\text{PbTiO}_3$ compared with $\text{KNbO}_3$ or $\text{BaTiO}_3$. $\text{PbZrO}_3$ is similar to $\text{PbTiO}_3$ in that the soft branch remains unstable for any wavevector, but the zone boundary R- and M-point instabilities are deeper than the $\Gamma$-point instability, consistent with the fact that the ground state in $\text{PbZrO}_3$ is antiferroelectric, and $\text{PbTiO}_3$ is ferroelectric.
Although self-consistent methods are very powerful, they generally cannot provide anything but static, essentially zero temperature, properties, at least for the complex systems we are discussing. Ferroelectric phase transitions, however, occur with increasing temperature from one ferroelectric state to another, or to the high temperature paraelectric state. Dielectric and piezoelectric properties are strongly dependent on temperature, especially around the phase transitions. Thus we want techniques that can give finite temperature behavior. One approach is to use a Gordon-Kim based model and Molecular Dynamics or Monte Carlo [22,23], but these models have not been successful so far to compute finite temperature properties for ferroelectrics. An effective Hamiltonian approach has, however, been very successful [24,25]. One develops a symmetrized expansion of the free energy in terms of local mode coordinates, effective charges, and strains. Only the important local modes are used, and thus the number is degrees of freedom is reduced from the full atomic Hamiltonian. Local modes are important if they are related to the soft mode, and the choice of local modes is key to the success of the method. A rigorous formulation of local modes as Wannier-like functions has been developed [26]. Though the effective Hamiltonian method contains all of the physics to give qualitatively correct results, one might question whether it would be quantitatively accurate since it neglects the higher frequencies modes, and does not even try to estimate their average self-consistent effects on the ferroelectric behavior. One such example is the importance of thermal expansivity, which is not included in the effective Hamiltonian models so far. Since ferroelectricity is very sensitive to volume, one would think that neglect of thermal expansivity might lead to serious errors. This might be partly responsible for the shifts in predicted transition temperatures relative to experiment. So far, however, it appears, that the effective Hamiltonian models are very accurate, and they are the only game in town for finite temperature properties of ferroelectrics at the present time. Since the underlying first-principles calculations are also not perfect, it is surprising and encouraging that such high accuracy can be obtained.

2.4 Physics of Polarization

2.4.1 Polarization in Periodic Boundary Conditions

Contrary to intuition and many textbook discussions, polarization cannot be determined directly from the self-consistent charge density or changes in the charge density alone within periodic boundary conditions. Rather one must consider changes in polarization as current flow, and this can be determined
from the phases of the wave functions. King-Smith and Vanderbilt showed how
this can be computed using a Berry’s phase approach [27]. A more intuitive
approach is the realization that polarization changes can also be considered
as the charge transport on displacing Wannier functions [28]. Practical cal-
culations generally use the Berry’s phase approach, and the development of
this technique was a key advance in the ability to compute electromechanical
properties. A review of the theory of polarization is given by Resta [29].

Born effective charges are defined as the change in polarization with displace-
ment of a nucleus, $Z_{i\alpha\beta} = dP_\beta/du_{i\alpha}$, for the change in $\vec{P}$ moving ion $i$; note
that the effective charge is a tensor. The effective charges are not necessarily
equal to the nominal ionic charges, and can be quite different. In oxide ferro-
electrics they tend to be greatly enhanced for certain directions, with values up
to several times the nominal values. The enhancement of the effective charges
is due to strong covalent hybridization [30–32]. Effective charges have been
predicted for a number of ferroelectric systems now. They are accessible to
experimental determination, for example by optical measurements of LO-TO
splitting. Very large values were experimentally obtained for BaTiO$_3$ many
years ago [33], but there was no theoretical basis for understanding the results
for many years. It would be of great interest for experimentalists to measure
these values for a variety of ferroelectrics and compare with the theoretical
predictions.

Piezoelectric constants can also be determined theoretically from changes in
polarization with respect to strain, as discussed below, using the Berry’s phase
 technique.

2.4.2 Density polarization theory

Another area of much discussion is in even more fundamental problems of po-
larization under Kohn-Sham theory. It was argued that DFT did not properly
account for electronic polarization, and implied that previous calculations were
incorrect, and that the gap problem and low dielectric constants in LDA were
due to this failure [34]. Mazin and Cohen [35] questioned this, and showed
that there is no problem with established methods such as the LDA. The
situation has been clarified [36,37] and it appears that to obtain the proper
polarization in exact Kohn-Sham theory (which no one knows how to do for
real bulk systems of interest, anyway) one would have to consider the polar-
ization as well as the charge density. Realistic estimates of this effect suggest
it may be very small (3%, [38]). Regardless of the theoretical importance of
density polarization in the exact Kohn-Sham theory, it is questionable if it
is solely responsible for the gap problem and LDA dielectric constants. The
gap problem varies considerably from one material to another, as do dielectric
constants. For example, although the LDA high frequency dielectric constant
is 20% too high in BaTiO$_3$, it is very close to experiment in PbTiO$_3$ [39]. A study of a set of 11 materials gives an r.m.s. error of 8% from experiment for $\epsilon_\infty$ using LDA [40]. It is not at all clear than there is a uniform cause for these deviations.

2.5 Piezoelectricity

The electromechanical response important in transducer applications is given by the piezoelectric constants, or by the figure of merit of the electromechanical coupling factors. Piezoelectric constants can be written in different ways and one can transform from one set to the other using thermodynamic transformations [41]. The set most easily computed are the piezoelectric strain coefficients $e_{ijk} = (\partial P_i/\partial \varepsilon_{jk})_{E=0}$, the change in polarization with strain at zero applied field, usually reduced to the Voigt form $\varepsilon_j$, $j = 1...6$. Since the polarization can now be computed using the Berry’s phase approach, one can compute the polarization versus strain and obtain the derivatives for the piezoelectric constants numerically. It is important then to allow the atomic coordinates to displace as functions of strain, because this is in fact the major contribution to the piezoelectric response. The piezoelectric constant can be written as

$$e_{ijk} = \left( \frac{\partial P_i}{\partial \varepsilon_{jk}} \right)_{E=0} = \sum_{\alpha} \left( \frac{\partial P_i}{\partial u_{\alpha}} \right)_{E} \left( \frac{\partial u_{\alpha}}{\partial \varepsilon_{jk}} \right)$$

where the first term, $e^h_{ijk}$, is the change of polarization with homogeneous strain, that is no atomic relaxations, and the second is from the displacements of the ions in response to strain, carrying effective charges $Z$.

This was first carried through for PbTiO$_3$ [3]. Ferroelectric PbTiO$_3$ is tetragonal, and there are three independent piezoelectric constants which can be found by three strains, tetragonal, orthorhombic, and a monoclinic strain. Two methods can be used, the direct method, that is finding the polarization versus strain, relaxing the internal coordinates at each strain, and using the effective charges as shown above. Both methods give the same final results, but the two step procedure also illustrates the relative importance of the two terms.

First one must find the optimum minimum energy structure at the volume of interest, in our case, the experimental zero pressure volume. Then, for example for $e_{33}$ (using Voigt notation), one varies the $c$-axis length, and computes the change in polarization, giving $e^h_{33}$. One finds the effective changes by displacing.
each ion separately, and computing the change in polarization in each case, and then finds how the atoms relax as a function of strain. Finally one can compute the polarization at the final relaxed strained lattice. This gives two computations of $e_{33}$, which we checked are identical, and give 3.23 C/m$^2$. The homogeneous contribution is -0.88, and the internal relaxations give 4.11, so the total is dominated by the atomic relaxations. Similarly, we found $e_{15}=3.15$ C/m$^2$ and $e_{31}=-0.93$ C/m$^2$. These are the proper moduli that do not include homogeneous deformations of the original spontaneous polarization, which are not observable. As pointed out later in this volume, the straightforward way to extract the proper piezoelectric response is to compute differences in Berry’s phases, and convert to piezoelectric constants only in the last step [42]. The computed moduli were very close to some experimental results, but there is a wide spread between different experiments even for PbTiO$_3$, indicating the importance of obtaining better values of experimental piezoelectric moduli under well-defined electrical boundary conditions in order to test theory.

We also computed $e_{33}$ for two ordered structures of PZT50/50, near the morphotropic phase boundary and obtained values significantly lower than experimental measurements for PZT ceramics (single crystals were never made successfully for PZT) extrapolated to low temperatures [4]. This lead us to conclude either that (1) extrinsic effects are very important even at low temperatures in PZT and/or (2) that the single crystal $e_{33}$ does not dominate the piezoelectric response in the poled direction in PZT.

Using an effective Hamiltonian and Monte Carlo, Garcia and Vanderbilt studied piezoelectric response of BaTiO$_3$ as a function of applied field and temperature [43]. They obtained good agreement with the temperature dependence of the piezoelectric constants, and found a field induced rhombohedral to tetragonal phase transition at very large fields. Rabe and Cockayne used an effective Hamiltonian for PbTiO$_3$ and found $d_{33}$ as a function of temperature using Monte Carlo, also finding good agreement with the experimental temperature dependence, which peaks strongly at the ferroelectric phase transition [5].

2.6 Solid solutions

Most useful piezoelectrics are solid solutions rather than pure ordered compounds. This allows their properties to be tuned to meet engineering specifications. But more than that, many complex solid solution ferroelectrics, for example, the new single crystal piezoelectrics with giant electromechanical coupling, like PMN-PT, have much enhanced properties relative to the pure compounds. Even the endmember PMN is complex, with ions of different valence, Mg$^{2+}$ and Nb$^{5+}$ on the same crystallographic site. There has been some work to study the ordering energetics in these systems. In PST-PT, for ex-
ample, the PIB (Potential Induced Breathing) model was used to study the relative energetics of ordering, and to find an order-disorder phase diagram basic on the Cluster Variation Method (CVM) [44]. More recently, self-consistent methods have been used along with Monte Carlo [45]. Even simple Madelung sums have been shown to illustrate some of the important behavior in these systems [46]. Only limited work so far has studied how ordering (short-range and long-range) interacts with ferroelectricity and piezoelectricity. Computations show that different ordering schemes can drastically affect piezoelectric response in one case [47], but how general this is not yet known.

2.7 Defects, domain boundaries, and surfaces

Real crystals are not perfect and infinite, and defects, domain boundaries, and surfaces play important roles in ferroelectrics. Park and Chadi studied oxygen vacancies in PbTiO$_3$, which may be important in fatigue. Domains have been studied using an effective Hamiltonian, and it was found that 180° domain boundaries are very sharp, and even one unit cell away the structure looks like bulk [48] Large scale LAPW computations were performed on periodic BaTiO$_3$ slabs. The computations showed that just one unit cell away from the surface, the charge density is indistinguishable from bulk BaTiO$_3$. There are two types of surfaces with either TiO$_2$ or BaO terminations. On the TiO$_2$ surface the dangling Ti-bond relaxes back onto the surface, but atomic relaxations are quite small. A surface state was found in the band structure. LAPW computations for symmetrically terminated surfaces were straightforward to interpret, and using results from slabs with two BaO and two TiO$_2$ surfaces, an average unrelaxed surface energy of 920 erg/cm$^2$ was determined by comparing with the bulk BaTiO$_3$ energy [49]. Using plane waves and pseudopotentials, Padilla and Vanderbilt found an average relaxed surface energy of 1260 erg/cm$^2$ [50]. Hartree-Fock calculations using Gaussian basis sets gave 1690 erg/cm$^2$ (unrelaxed) [51]. The differences in basis sets as well as Hartree-Fock versus LDA may be responsible for the differences. The effect of periodic slabs versus isolated slabs, as used in the Hartree-Fock study, amount to only about 3% in the average surface energy for symmetric slabs. Clearly these are exploratory studies, and we cannot confidently state the exact surface energy for BaTiO$_3$ except all agree it is high, which explains the difficulty of of cleavage in BaTiO$_3$ and the rough surfaces that form on fracture.

In the LAPW study, periodic asymmetric and polar slabs were also studied [49]. As discussed there, asymmetric or polar periodic slabs produce artificial potential gradients across the slab which is like an external applied field. This is an undesirable effect that makes it difficult to interpret the results. Nevertheless, it was interesting that the polar slab has a higher energy than the ideal slab, due to the unscreened depolarization field. The field is large enough
to cause the slab to be metallic with densities of states overlapping from one
side of the slab to the other. It is much less metallic than would be the case in
the rigid band picture, however, with oxygen density of states piling up at the
Fermi level. This is due to the fact that \( \text{O}^{2-} \) really wants to be closed shell,
and not metallic, even on surfaces.

In the pseudopotential study, symmetric slabs were studied, but a polarization
parallel to the slab was also considered [50]. The isolated slab Hartree Fock
study is the most straightforward to interpret, and they found results similar to
bulk BaTiO\(_3\). The use of isolated, rather than periodic, slabs, greatly facilities
interpretation of results for asymmetric or polar slabs [51].

Padilla and Vanderbilt also studied SrTiO\(_3\) surfaces and found a very similar
surface energy of 1360 erg/cm\(^2\) compared with 1260 in BaTiO\(_3\). In SrTiO\(_3\),
they found without relaxation a value 14% higher, very close to the estimate
of 12% for the surface relaxation energy in BaTiO\(_3\) of Cohen [49].

3 The Future: A Vision

We see that in the last ten years significant advances have been made in com-
puting properties and understanding origins of ferroelectric behavior. We now
have the ability to predict ferroelectric instabilities, electromechanical cou-
pling, phonon dispersion and optical spectroscopy, elasticity, pressure behav-
ior, order-disorder, and some surface and defect properties of structurally and
chemically relatively simple pure compounds. Now the challenge is to address
problems in more complex solid solutions, some that are structurally and/or
chemically heterogeneous and some with frequency dependent properties.

3.1 Relaxor systems

In relaxor systems the dielectric response has a broad peak as a function
of temperature, rather than a sharp peak in a normal ferroelectric, and a
frequency dependent response. The origin of this behavior is still controversial,
but is most likely due to heterovalent disorder. It will be a challenge to compute
this behavior from first-principles, but models can be parametrized using first-
principles results, as in the effective Hamiltonian models discussed above, and
then molecular dynamics or Monte Carlo simulations could be used to simulate
still rather small disordered systems. To simulate much larger, mesoscopic,
systems, it may be necessary to parametrize models for interactions between
nanoregions, leaving the atomic domain all together. But this may be possible
using only \textit{ab initio} results.
3.2 New piezoelectrics

The discovery of new single crystal piezoelectrics with huge electromechanical coupling [2,52,53] are revolutionizing the field of piezoelectric transducers. Theory did not play a role in discovering these materials, but it may play an important role in showing how they work and helping design better materials. The new materials are rhombohedral, with a morphotropic phase boundary to a tetragonal phase nearby. The large response is $d_{33}$, which is an elongation along the cubic (001) direction, and parallel to the applied field. The rhombohedral phase though has polarizations locally about $(111)$. As the the field is increased, the numbers of domains with polarizations that project in the $(0,0,-1)$ direction decrease, and there is a large piezoelectric strain induced as the local polarizations are slowly rotated up towards the (001) direction. At a critical field, a field induced phase transition to true tetragonal symmetry occurs, and the piezoelectric response changes and becomes more normal. An idea of why the strain is so large in these materials can be understood by considering PbTiO$_3$. PbTiO$_3$ is tetragonal, with a large 6% strain at zero pressure and low temperatures. There is no rhombohedral phase stable in PbTiO$_3$ at zero or positive pressures, but if there was, one would see a small strain in that phase, and one would see a giant strain as one went from the rhombohedral to tetragonal phases. One can think of phases like PMN-PT as chemically engineered “rhombohedral PbTiO$_3$.” It is clear that the polarization of the Pb$^{2+}$ ion is key to this large strain behavior [12], though a thorough understanding of exactly how the Pb drives the strain has not yet been fully elucidated.

3.3 Materials by design

The goal of this research program is to lead to the ability to computationally design useful materials. We are clearly on that path, but it will be a few years before one can practically hope to routinely design materials by computer. On the other hand, it is also largely a matter of having the right good idea. We understood the role of Pb in the strain of PbTiO$_3$ some years ago, and if we smart enough to think of trying to make “rhombohedral PbTiO$_3$” we might have found this large strain effect before experiments. However, theoretical developments were just a few years behind to realistically do this, because the first first-principles computation of piezoelectric constants in pure tetragonal PbTiO$_3$ were only done this last year, and it has’t been that long since the Berry’s phase approach to computing polarization was discovered. As we make further advances, however, in the next revolution perhaps theory will lead the way rather than follow.
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