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Technical Objectives

The goal of this work has been to carry out realistic first-principles calculations of the structural, electronic, dielectric, magnetic, and piezoelectric properties of ferroelectric and other electroactive materials. Such materials are of pressing technological interest for Navy sonar applications (acoustic projection and detection) as well as for other piezoelectric (e.g., medical ultrasound imaging, micromanipulation), memory storage, and optoelectronic applications. We searched for novel ferroelectric materials with improved properties, including corundum derivatives, hexagonal ABC compounds, hybrid improper ferroelectrics, charge-ordered ferroelectrics, and multiferroics. Another goal has been to develop new methods for computing flexoelectric responses, in which an electric polarization is induced by a strain gradient. The work has been based on first-principles Kohn-Sham density-functional calculations using a plane-wave pseudopotential approach, both in the absence and presence of electric fields. Theoretical materials search strategies were carried out using well-tested pseudopotential libraries, and included evaluation of materials stability with respect to decomposition into other phases. Our overall objective has been to develop a thorough atomistic understanding of the structural and electronic properties of novel ferroelectric, piezoelectric, flexoelectric, and magnetic materials, so as to provide guidance in the search for new materials that may be of improved utility in technological applications.

Technical Approach

Over the last 20 years we have developed a battery of robust first-principles methods for computing almost all dielectric-related properties of functional oxides, including electric polarization, linear and nonlinear piezoelectric couplings, responses to applied electric fields, magnetoelectric couplings, and flexoelectric responses. Many of these methodologies are built on the Berry-phase theory of polarization introduced by us in 1993. Technically, we carry out first-principles calculations of total energies, forces, and dielectric properties at "zero temperature" using plane-wave based first-principles methods as implemented in standard code packages such as PWSCF, ABINIT, and VASP. When zero-temperature calculations on simple parent materials cannot answer the questions at hand, we use a second step in which we fit the results of the first-principles calculations to carefully constructed model descriptions, and use these models to understand such questions as the finite-temperature phase transition sequences or the dependence of polarization and piezoelectric response upon composition and structure.

Accomplishments

Domain walls in corundum-derivative ferroelectrics. Domain walls are the topological defects that mediate polarization reversal in ferroelectrics, and they may exhibit quite different geometric and electronic structures compared to the bulk. Therefore, a detailed atomic-scale understanding of the static and dynamic properties of domain walls is of pressing interest. In this work, we used first-principles methods to study the structures of 180-degree domain walls, both in their relaxed state and along the ferroelectric reversal pathway, in ferroelectrics belonging to the family of corundum derivatives. Our calculations predicted the orientation, formation energy, and migration energy of domain walls, and also identified important couplings between polarization, magnetization, and chirality at the domain walls. We

also pointed out a strong empirical correlation between the height of the domain-wall mediated polarization reversal barrier and the local bonding environment of the mobile cations as measured by bond valence sums. Our results thus provide both theoretical and empirical guidance to future searches for ferroelectric candidates in materials of the corundum derivative family.

Electric-field induced Raman shifts in GaN. In a collaboration with experimental colleagues, we used density-functional theory to calculate the shifts of Raman vibrational modes resulting from an electric field applied along the c-axis in wurtzite GaN. Our results provided an explanation for experimental work showing that these shifts are an order of magnitude larger than those that would be expected based on the inverse piezoelectric effect, by separating out the effects of internal distortions and lattice strains. This work was done in collaboration with the experimental group of Evelyn Wang at MIT.

Theory of flexoelectricity. In previous work, we developed methods for computing the flexoelectric responses of bulk materials, i.e., the electric polarization arising in response to a strain gradient. Because crystal periodicity is not preserved in the presence of a strain gradient, the problem is quite subtle and new ways of formulating the problem and carrying out calculations need to be developed. Previous methods developed by us and others relied either on supercell or slab calculations, requiring cumbersome computation of artificial unit cells that are much larger than the primitive one. We have carried out the theoretical formulation, computational implementation, and testing of a new approach based on linear-response methods for determining the first-order polarization wave arising from a long-wave strain perturbation, all in the context of a single-unit-cell bulk calculations. This required overcoming several obstacles, such as the treatment of induced currents in the context of nonlocal pseudopotentials. Moreover, we have extended this work by demonstrating an improved implementation based on a "metric wave" framework, consisting in the reformulation of an acoustic phonon perturbation in the curvilinear frame that is comoving with the atoms. Essentially, the perturbation effects are encoded in the first-order variation of the real-space metric, while the atomic positions remain fixed. This greatly facilitates the calculation of advanced electromechanical couplings such as the flexoelectric tensor. This work was done in collaboration with the group of Massimiliano Stengel in Barcelona, Spain, and Prof. Cyrus Dreyer (former postdoc on this grant) at Stony Brook University. An open-source implementation of our computational methodology is included in Versions 9.0 and above of the ABINIT software package.

Antiferroelectric topological insulators. We introduced the concept of this new class of functional materials in which an electric field can be used to control topological order and induce topological phase transitions. Using first principles methods, we predicted that several alkali-MgBi orthorhombic members of an ABC family of compounds are antiferroelectric topological insulators. We estimated the electric field necessary to switch between polarization states, and also showed that epitaxial strain and hydrostatic pressure can be used to tune the topological order and the band gap of these ABC compounds. Antiferroelectric topological insulators could enable precise control of topology using electric fields, enhancing the applicability of topological materials in electronics and spintronics.

Piezoelectric response of van der Waals layered bismuth tellurohalides. In contrast to conventional ferroelectric materials having reversible ferroelectric polarization associated with unstable atomic displacements, BiTeX (X=Cl, Br, I) exhibit a polarization associated with the asymmetric atomic stacking sequence in the triple atomic layers. The triple layers are weakly bonded to each other by van der Waals interactions, suggesting a soft mechanical response to external uniaxial strain while the intra-triple-layer charge distribution is hardly affected. We employed density-functional theory calculations to investigate the polarization and the piezoelectric response of the BiTeX materials. Our results show that an approximation in which each triple-layer is treated as a rigid unit, with the spacing between triple layers being modulated by external strain, gives a surprisingly good description of the piezoelectric stress tensor element e33. This is essentially a new mechanism for piezoelectricity, and we argue that this mechanism ought to apply to polar van der Walls bonded layered materials more generally. In our tested materials, although e33, at ~0.5C/m2, is smaller than for PbTiO3 or PZT by one order of magnitude, it is still

comparable to that of wurtzite semiconductors. However, because of the soft interlayer van der Waals interactions, the piezoelectric strain coefficient, d33 ~ 25pm/V, it is comparable to that reported for some thin-film PZT samples, although still one order of magnitude smaller than for thick-film PZT. Our results indicated that the BiTeX (X = I, Br, Cl) class of materials could provide an alternative material system for use as a basis for microactuator and other specialized applications.

Modulation doping in LaNiO3/SrIrO3 superlattices from first principles. Doping is commonly used to tune and optimize material properties such as conductivity and optical properties. Doping at extremely high concentrations, at the level of an electron per formula unit, can stabilize novel phases. We have studied lanthanum nickelate (LaNiO3)/strontium iridate (SrIrO3) superlattices using the first-principles density functional theory (DFT) +U method, focusing on the 1/1 superlattice. For this superlattice we find that there is a modulation doping in which approximately one electron per formula unit is transferred from the SrIrO3 layers to the LaNiO3 layers, converting all nickels from Ni3+ to Ni2− in the electron-doped LaNiO3 layers and and all iridiums from Ir4+ to Ir5+ in the hole-doped SrIrO3 layers. We also determined the low energy structures and orbital occupations as well as the electronic and magnetic structures.

Piezoelectricity and optoelectronic effects in AlN/ScN superlattices. We carried out first-principles calculations to investigate the effect of epitaxial strain on energetic, structural, electrical, electronic and optical properties of 1x1 AlN/ScN superlattices. This system is predicted to adopt four different strain regions, in each of which different physical responses are optimized, including piezoelectricity, electro-optic coefficients, elasto-optic conversion, and elasticity. Varying the strain between these four different regions also allows to create an electrical polarization. These properties are found to arise in a nominally paraelectric material as a result of a softening of the lowest optical polar mode, with giant responses shortly after this polar mode sets in. Furthermore, the electronic band gap not only changes its nature (direct versus indirect), but also covers a wide range of the electromagnetic spectrum from the cyan, though blue, violet, and the near ultraviolet, to the middle ultraviolet. The present findings demonstrate the potential of assembling two different materials in a short-period superlattice heterostructure as a means to design multifunctionality including striking piezoelectric and optoelectronic phenomena. This work was done in collaboration with the group of Laurent Bellaiche at U. Arkansas.

Polarity from stacking order in semimetallic MoTe2. Polar semimetals are of growing interest, especially those exhibiting a ferroelectric-like structural transition from a high-symmetry phase as the temperature is reduced. Here we explored the van der Waals layered material MoTe2, which has also attracted attention because type-II Weyl nodes appear in the vicinity of the Fermi level in the polar phase. We uncovered an unusual dependence of the polarity upon the stacking sequence of the two dimensional layers, and showed that our results can be captured in a simple model that can describe domain walls and their dynamics in this unusual system.

Berry flux diagonalization calculation of switching polarization. The switching polarization of a ferroelectric is a characterization of the current that flows due to changes in polarization when the system is switched between two states. Computation of this change in polarization in crystal systems has been enabled by the modern theory of polarization, where it is expressed in terms of a change in Berry phase as the material switches. It is straightforward to compute this change of phase, but only modulo 2pi, requiring a branch choice from among a lattice of values separated by 2pi. The measured switching polarization depends on the actual path along which the material switches, which in general involves nucleation and growth of domains and is therefore quite complex. In this work we presented a first principles approach that allows the switching polarization to be determined using a knowledge of only the initial and final states. It selects a branch choice corresponding to the polarization change that would occur along a minimal path connecting the states, but without the need to construct such a path.

Weyl phases and nonlinear Hall effects in Td MoTe2. MoTe2 has recently attracted much attention due to the observation of pressure-induced superconductivity, exotic topological phase transitions, and nonlinear quantum effects. However, there has been debate on the intriguing structural phase transitions among various observed phases of MoTe2, and their connection to the underlying topological electronic properties. In this work, by means of density-functional theory (DFT+U) calculations, we investigated the structural phase transition between the polar Td and nonpolar 1T' phases of MoTe2 in reference to a hypothetical high-symmetry T0 phase that exhibits higher-order topological features. In the Td phase we obtained a total of 12 Weyl points, which can be created/annihilated, dynamically manipulated, and switched by tuning a polar phonon mode. We also reported the existence of a tunable nonlinear Hall effect in Td-MoTe2, and proposed the use of this effect as a probe for the detection of polarity orientation in polar (semi)metals. By studying the role of dimensionality, we identified a configuration in which a nonlinear surface response current emerges. The potential technological applications of the tunable Weyl phase and the nonlinear Hall effect were discussed.

A-type order and spin-flop transition on the surface of MnBi2Te4. In a collaboration with the experimental group of Weida Wu at Rutgers, we have provided modeling and computational support of microscopic evidence for the persistence of uniaxial A-type antiferromagnetic (AFM) order at the surface layers of MnBi2Te4 single crystals using magnetic force microscopy. Our results reveal termination-dependent magnetic contrast across both surface step edges and domain walls, which can be screened by thin layers of soft magnetism. The robust surface A-type order is further corroborated by the observation of termination-dependent surface spin-flop transitions, which have been theoretically proposed decades ago. Our results not only provide key ingredients for understanding the electronic properties of the AFM topological insulator MnBi2Te4, but also open a new paradigm for exploring intrinsic surface metamagnetic transitions in natural antiferromagnets.

Magnetic order and proximate spin-liquid state in CoCr2O4. We provided theoretical calculations as part of a collaboration with the experimental group of Jak Chakhalian at Rutgers. In this work, we reported on the emergent magnetic state of (111)-oriented CoCr2O4 ultrathin films sandwiched between Al2O3 spacer layers in a quantum confined geometry. At the two-dimensional crossover, polarized neutron reflectometry reveals an anomalous enhancement of the total magnetization compared to the bulk value. Synchrotron x-ray magnetic circular dichroism (XMCD) measurements demonstrate the appearance of a long-range ferromagnetic ordering of spins on both Co and Cr sublattices. Brillouin function analyses and ab-initio density functional theory calculations further corroborate that the observed phenomena are due to the strongly altered magnetic frustration invoked by quantum confinement effects, manifested by the onset of a Yafet-Kittel type ordering as the magnetic ground state in the ultrathin limit, which is unattainable in the bulk. We also applied first-principles density-functional theory calculations and classical Monte-Carlo simulations to study an ultrathin geometry composed of three triangle and one kagome cation planes, where the absence of a spin ordering transition is demonstrated down to 0.03 K. Our calculatons reveal that, although a definite magnetic ground state can be stabilized in bulk CoCr2O4 due to the availability of sufficient second-neighbor ferromagnetic exchange interactions that tend to counterbalance the magnetic frustration introduced by the first-neighbor AFM exchange interactions, this is not the case for the ultrathin films. Instead, there exists numerous competing magnetic degenerate states arising due to the uncompensated magnetic frustration in the (111)-oriented ultrathin film, which prevents the 2D system from reaching to a classical magnetic order at zero-temperature limit. We also unveil the interlink among magnetic frustration, dimensionality, and ordering temperature.

Summary of publications supported by ONR Grant 14-16-1-2951

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