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Theory and Simulation of Defects in Oxide Materials

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OBJECTIVES

Transition metal oxides span a wide range of structural and electronic properties. Some are insulating and brittle; others are malleable and conducting or even superconducting at low temperatures. In fact, perovskite-based copper oxides form arguable the most important class of high-temperature superconductors. Oxides also crystallize in a wide range of crystal structures, e.g., NaCl, perovskite, pyrochlore, fluorite, and spinel to name a few, and exhibit a wide range of interesting physical properties ranging from simple ferroelectricity to correlated electron effects such as magnetism. Recently, a class of oxide materials known as multiferroics (where several order parameters co-exist), has attracted significant attention. Oxide materials find numerous applications as passivating agents, dielectrics, actuators, switches, magnetic field sensors and new types of electronic memory devices.

In all these applications, *defects* play an important role. From basic thermodynamics, defects are unavoidable. We know that if the energy cost of creating a point defect is not very high, the associated increase in entropy with defect formation will decrease the free energy and stabilize the defect. Every crystal at finite temperature contains an equilibrium concentration of point defects. In particular, oxides of transition metals are known to exhibit unusually high concentrations of defects owing to the variable valence or oxidation state of a metal with a partially filled *d*-shell. Elementary point defects include vacancies and interstitials, as well as dopant impurities, which may be either substitutional or interstitial. The electro-neutrality rule dictates more complex defects, i.e., charge defects appear in balancing pairs such as Frenkel-type (vacancy plus same type interstitial) or Schottky type (pairs of vacancies) defects.

In addition, many metal oxide surfaces and interfaces are technologically important: it is often said that the ``interface" is the device. Elemental transition metal oxides, e.g., HfO_2, ZrO_2, TiO_2, have recently found applications in complementary metal oxide semiconductor (CMOS) technology. Used as gate dielectrics instead of SiO_2 they enable continuing scaling of CMOS in accordance with the Moore's law. One of the major problems with using these materials (so called high-k dielectrics owing to their large dielectric constant k) is related to the complicated electrochemistry of oxygen vacancies in the bulk of the oxide film as well as at its interface with Si and gate metal. Another important aspect in all these electronic materials is the role of quantum confinement at small length scales. As the electronics industry strides toward small and smaller devices, it is important to understand the how the macroscopic behavior of these materials, with and without defects, will change as one approaches the nanoscale.

More recently, the possibility of building all-oxide electron devices has been suggested as a consequence of the discovery of the high mobility two dimensional electron gas (2DEG) at the $LaAlO_3/SrTiO_3$. Though the electron mobility is not as high as in 2DEG in GaAs quantum wells, it is sufficient to build transistors, provided the defect scattering can be reduced. This will be a remarkable achievement given the fact that both materials are wide gap perovskite oxides!

ACCOMPLISHMENTS

Our work spans four years, including a no cost one year extension. During this period, we explored a wide variety of oxide materials and related problems, including materials at the nanoscale and generic problems associated with oxide materials such as the development of more efficient computational tools to examine these materials. We wrote 34 papers, all published in refereed journals. Most of work was published in Physical Review or Applied Physics Letter. Several of our papers were published in high impact journals such as Physical Review or Reports in Physics. Below we highlight some of our notable accomplishments. A full list of our publications is appended at the end of this report.

Predicting optical and structural properties of materials, oxides, and highly correlated systems

We developed and implemented methods to understand the optical and structural properties of oxides. For ground state properties, our work is predominantly based on pseudopotentials and density functional theory (DFT), including new functionals and going beyond the local density approximation (LDA): LDA+U. To study excited state properties (quasiparticle and optical excitations), we use time dependent density functional theory, the GW approach, and GW plus Bethe-Salpeter equation (GW-BSE) methods based on a many-body Green function approaches. Our work focused on the structural, electronic, optical and magnetic properties of defects (such as oxygen vacancies) in hafnium oxide, titanium oxide (both bulk and clusters) and related materials.

Hybrid Functionals. Different hybrid functionals mix in differing amount of nonlocal exchange, depending on the particular functional, to the exchange-correlation functional in a generalized Kohn-Sham formulation of density functional theory. The orbital energies based on such hybrid functionals have been reported to yield good band gaps for semiconductors. We found that contrary to previous beliefs, existing hybrid functionals do not in general give reliable band gaps. Even in cases where a particular functional may yield a good bulk band gap, the same functional in general does not provide accurate gap values for the same material in different structural configurations such at surfaces or in nanostructures. We illustrated this point by examining the Si surface and the graphene nanoribbons. The Si (111) 2x1 surface possesses two distinct band gaps, the bulk-state gap and surface-state gap, that have been measured by photoemission and optical experiments. We find that none of the popular hybrid functionals adequately describe the surface-state gap, even though some hybrid functionals describe the bulk gap well. For the semiconducting graphene nanoribbons, some hybrid functionals describe the optical band gaps well (although the known strong excitonic nature of the optical excitations is absent in these studies), but not the quasiparticle gap. In both examples, there is a large variability in the results from different hybrid functionals.

Defects in Hafnia. We calculated the quasiparticle defect states and charge transition levels of oxygen vacancies in monoclinic hafnia. The charge transition levels, although they are thermodynamic quantities, can be critically dependent on the band gap owing to localized defect states. These quasiparticle defect level effects are treated using the first principle GW approximation to the self-energy. We showed that the quality and reliability of the results may be evaluated by calculating the same transition level via two physical paths and that it is important to include the necessary electrostatic corrections in a supercell calculation. Contrary to many previous reports, the oxygen vacancies in monoclinic hafnia are found to be a positive U center, where U is the defect electron addition energy. We identified a physical partitioning of U in terms of an electronic and structural relaxation part.

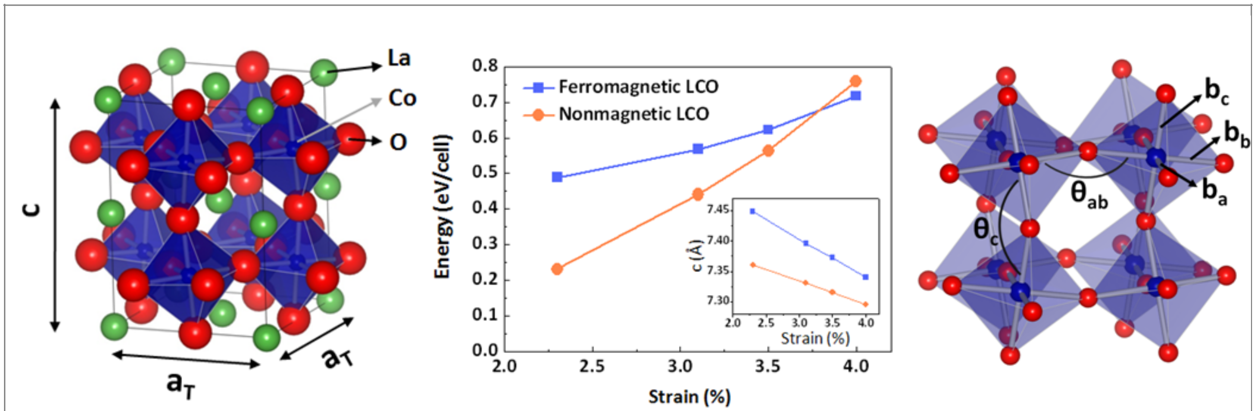
Dye Sensitized TiO_2 Clusters. The development of new types of solar cells is driven by the need for clean, sustainable energy. Dye sensitized solar cells are considered as a promising route for departing from the traditional solid state cells. In this context, we presented a milestone G0W0 study of two of the crystalline phases of dye-sensitized TiO_2 clusters, reported by Benedict and Coppens [J Am Chem Soc 132 (9), 2938 (2010)]. We discussed in detail the issues pertaining to G0W0 calculations, namely: (i) convergence with respect to the number of empty states, (ii) sensitivity to the mean field starting point, and (iii) the validity of the assumption that the DFT wave-function is a good approximation to the QP wave-function. We showed how these issues are manifested for dye molecules and for dye-sensitized TiO_2 clusters. In addition, we demonstrated that even when DFT gives a qualitatively correct picture, G0W0 calculations can give more valuable quantitative information regarding the fundamental gaps and level alignment between the dye molecule and the TiO_2 cluster.

Hybrid density functional study of oligothiophene/ZnO for photovoltaics. Organic-inorganic donor-acceptor interfaces are gaining growing attention in organic photovoltaic applications as each component of the interface offers unique attributes. We employed hybrid density functional theory to examine the electronic structure of sexithiophene/ZnO interfaces. We find that interfacial molecular orientations strongly influence the adsorption energy, the energy level alignment, and the open-circuit voltage. We attributed the orientation dependence to the varied strength of electronic coupling between the molecule and the substrate. Our study suggests that controlling the interfacial design of molecular orientations can optimize photovoltaic performance.

Defects in complex oxides. A chief focus of our work is to understand the energetics ofneutral and charged oxygen vacancies in cubic $SrTiO_3$ (STO) and rhombohedral $LaAlO_3$ (LAO). The formation energy of the defects is rather sensitive to the exact energy position of the defect level, therefore we used a hybrid functional approach. These are compared with computationally less expensive LDA+U calculations and with the quasiparticle calculations at the GW level. We found that charged oxygen vacancies are important defects in perovskite oxides, and in addition they are often linked to the electronic properties of the LAO/STO interface where a two-dimensional electron gas has been reported and is currently under intense investigation worldwide.

We have also investigated the influence of surface vacancies on the surface stability of a stoichiometric freestanding $LaAlO_3$ (001) thin film. Defect-free three and five unit cell thick $LaAlO_3$ (001) thin films show macroscopic electric fields of 0.28 V/ and 0.22 V/, respectively. The built-in electric field is sufficiently strong for a thick film of five unit cells to undergo a dielectric breakdown in the local density approximation. We showed that the electric field can be effectively compensated by La vacancies on the LaO surface, O vacancies on the AlO2 surface, or both types of vacancy present at the same time. Comparing surface Gibbs free energies we show that several surface vacancy structures are thermodynamically stable.

*Stabilization of ferromagnetism by strai*n. To identify the possible effect of epitaxial strain on stabilization of the ferromagnetic state of $LaCoO_3$ (LCO), we compare the total energy of the magnetic and nonmagnetic states of the strained theoretical bulk structure at four strain levels 2.3%, 3.1%, 3.5%, and 4.0%. We used density functional theory within the local spin-density approximation combined with the Hubbard U method (LSDA+U). We used a large tetragonal cell with a 20-atom basis see the figure below (left). At a given strain, we optimize the c lattice constant and fully relax all internal atomic coordinates for both nonmagnetic and magnetic configurations. In the figure (center) we plot the total energy as a function of strain for both structures, showing that the energy of the nonmagnetic configuration increases faster than that of the magnetic configuration as applied tensile strain increases. Beyond a tensile strain of 3.8%, ferromagnetic LCO becomes more stable than the nonmagnetic structure.



The tetragonal simulation cell of LaCoO
structures (middle). Octahedral configuration of ferromagnetic LaCoO

Band alignment in photocatalytic oxide heterostructures. Recent advances in oxide heteroepitaxy, have made it possible to grow high-quality, single crystal anatase-TiO_2 films on perovskite substrates such as $SrTiO_3$ (STO) or $LaAlO_3$ (LAO). This provides an excellent model system for controlled studies of the photocatalytic behavior of anatase under various conditions. While a considerable amount of experimental work can be found in the literature, a detailed theoretical understanding of the electronic structure of the anatase-TiO_2/perovskite interface is lacking. Using density functional theory (DFT), scanning transmission electron microscopy (STEM), and electron energy loss spectroscopy (EELS) we studied the interface structure and electronic properties of the anatase-TiO_2/SrTiO3(001) heterostructure epitaxially grown on Si (001) by molecular beam epitaxy (MBE). We demonstrate that charge transfer at the TiO_2/SrTiO3 interface is induced by the chemical bond formation between Ti and O. Subsequent O lattice polarization is found to be the leading screening mechanism at the interface. By comparing the theoretical local electronic structure to the O K edge electron energy loss spectra EELS taken at the interface with atomic resolution, we are able to trace the local band structure evolution in response to the change in symmetry and bonding across the interface. We uncovered the profound effect of interfacial point defects (O vacancy and F impurity) on the band alignment.

Orbital ordering in transition metal perovskites under reduced symmetry. Combining density function theory and model Hamiltonian analysis, we studied the general features induced by oxygen vacancies (OV) in prototypical perovskite oxide, $SrTiO_3$. We discover that the most important effect caused by an oxygen vacancy is the reduction of the local cubic symmetry and introduced coupling between 3d3z2y and i 4s, 4p orbitals of Ti atoms located next to the vacancy. This conclusion is quite general and holds for any transition metal perovskite under symmetry-reduced environments, such as an interface or a defect nearby. According to our analysis, the OV-induced localized state is highly one-dimensional and is mainly composed of Ti3d3z2 s mainly composed of TiTiperovskite under symmetry-reducis) and Ti 4s, 4p at the OV site.

New Computational Approaches

Computational Approaches for Excited State Properties. We have developed and optimized algorithms that enable the simulation of the excited-state properties of systems with more than a hundred atoms in a simulation cell using the GW and GW-BSE approaches. This is a significant advance over existing methods and is an essential step toward the study of defects using supercell geometry. We have extended and implemented the DFT+GW method to calculate the charge transition levels of defects in solids. We show that, for quantitatively accurate results, several important physical effects must be accounted for including: a) the accuracy of the quasiparticle wave function which can be monitored using different transition pathways, and b) Coulomb fields from replicas in neighboring supercells.

"Parallel" Eigensolvers. Solving the Kohn-Sham equation, which arises in density functional theory, is a standard procedure to determine the electronic structure of atoms, molecules, and condensed matter systems. The solution of this nonlinear eigenproblem is used to predict the spatial and energetic distribution of electronic states. However, obtaining a solution for large systems is computationally intensive because the problem scales super-linearly with the number of atoms. We have demonstrated a divide and conquer method that partitions the necessary eigenvalue spectrum into slices and computes each partial spectrum on an independent group of processors in parallel. This algorithm should have a profound effect on our ability to capitalize on the next generation of computational platforms, which will have a large number of processors, but not extensive shared memories. This architecture will result in low cost "FLOPS," but will penalize extensive communication. Contemporary computational models, discretizations, solvers, algorithms, and software have largely not been designed with processor-level massive parallelism in mind. Hardware vendors, driven in part by power consumption issues, have imposed on the computational community platforms in which future peak performance increases will come from processors capable of massive hardware multithreading.

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