ABSTRACT

Experimental and Theoretical Studies on Flexoelectricity

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This dissertation explores the fundamental science of flexoelectricity and its implications using a combined experimental and theoretical approach. I begin by introducing the flexoelectric effect and formalizing the basics of strain gradients, polarization, and flexoelectric coefficients. Next, I describe the development of a flexoelectric characterization system based upon three-point bending and demonstrate the tenets of measuring flexoelectric coefficients with experiments on single crystals of $SrTiO_3$. After deriving expressions for these measured flexoelectric coefficients for crystals of arbitrary symmetry and orientation in terms of flexoelectric tensor components, elastic constants, and geometric factors, I address anticlastic bending suppression effects in three-point bending and assess the use of Euler-Bernoulli beam theory.

Having established how to measure and interpret flexoelectric coefficients with three-point bending, I characterize the flexoelectric response of a range of commercially available single crystal oxides including $SrTiO_3$, $KTaO_3$, $LaAlO_3$, TiO_2, $YAlO_3$, and $DyScO_3$.

These measurements help address the issue of data deficiency in flexoelectricity by significantly increasing the number of systems in which flexoelectricity has been studied. They also indicate low dielectric constant materials have large flexocoupling voltages exceeding nominal expectations.

To explore the structural origins of these measured flexoelectric responses, I perform ab initio calculations of bulk flexoelectric coefficients. After benchmarking the bulk flexoelectric coefficients computed with an all-electron code and examining the impact of the exchange and correlation functional, I calculate the bulk flexoelectric coefficients of the (pseudo) cubic perovskites I characterized experimentally. I find the predicted flexoelectric coefficients differ in both size and magnitude from the measured values. To address this difference, I investigate the role of surfaces in flexoelectricity and demonstrate the importance of the strain derivative of the mean-inner potential to the total flexoelectric response of a finite sample. I then perform density functional theory calculations on many low energy surfaces to explore the role of surface chemistry, structure, and adsorbates on the strain derivative of the mean-inner potential. I also show how this flexoelectric contribution can be estimated from electron scattering factors. Ultimately, combining the mean-inner potential contribution to the total flexoelectric response with the first principles bulk flexoelectric coefficients yields good agreement with the $SrTiO_3$ and $KTaO_3$ measurements.

Moving beyond single crystals, I explore how the total flexoelectric response is impacted by defects. First, I show $LaAlO_3$ twin boundaries have flexoelectric coefficients $\sim$10 μC/m and dictate the flexoelectric response of twinned $LaAlO_3$ samples. Next, I demonstrate the flexoelectric response of Nb-doped $SrTiO_3$ is 10^3 times that of undoped

$SrTiO_3$. Lastly, I find MgO has an anomalously large flexoelectric response which greatly surpasses ab initio expectations. Collectively, these experiments demonstrate extrinsic contributions to flexoelectricity can often overshadow intrinsic contributions and dictate the total flexoelectric response.

Next, I explain why large charging occurs in the lanthanide scandates and its connection to large flexoelectric bending at the nanoscale. In doing so, I address the role of the 4f states in the bulk valence band of $GdScO_3$, $DyScO_3$, and $TbScO_3$ through a combination of photoelectron spectroscopy and ab initio simulations, and discuss determining a surface structure on the (110) surface of $DyScO_3$. I also provide some methods to overcome charging effects in X-ray photoelectron spectroscopy and electron energy loss spectroscopy.

Lastly, I argue triboelectricity is driven by contact deformation-induced band bending which arises through the flexoelectric effect. After developing a simplified flexoelectric model for triboelectricity based upon Hertzian contact, I generalize the model to incorporate band structure and treat contact deformation-induced band bending for two arbitrary materials in contact. I explore this model in some specific contact cases to demonstrate its connection to well-known charge transfer mechanisms and its ability to explain numerous experimental triboelectric observations which have been historically unexplained.