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Atomic Scale Models for Grain Boundary Potentials in Perovskites

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Polycrystalline perovskite oxides exhibit a wide variety of properties, such as ferro-electricity, mixed conductivity and high-T_c superconductivity (HTS). In this study, a nominally undoped 58° [001] grain boundary in $SrTiO_3$ is used as a simple model system to estimate the changes in atomic structure and composition that occur at perovskite grain boundaries. Using the results from extensive analytical scanning transmission electron microscope (STEM) analyses, the intrinsic electrostatic potential at the $SrTiO_3$ grain boundary has been estimated and is in excellent agreement with the transport properties reported in the literature. Theoretical calculations based on these results for the similarly structured HTS material, $YBa_2Cu_3O_7$ (YBCO), show that the presence of this potential can naturally explain the widely observed transport properties of HTS grain boundaries.

The $SrTiO_3$ grain boundary described above was investigated by atomic resolution Z-contrast imaging and EELS using a 200 kV STEM/TEM JEOL2010F. The combination of these techniques [1] allows us to obtain direct images of the atomic structure (spatial resolution ~0.2 nm) of the bulk sample and to correlate this with the atomically resolved spectroscopic information (3s acquisition per spectrum with ~1.2 eV resolution). [2] Figure 1a shows the Z-contrast image of the high angle grain boundary, with the dislocation cores clearly visible in the boundary plane. The boundary appears darker in the image due to the lower concentration of material (i.e. it contains half occupied columns of Sr), and the induced strain at the boundary. Ti and O core-loss spectra taken directly from the dislocation-core centers and the adjacent columns are used to calculate the oxygen vacancy concentration. Figure 1b shows the estimated uncompensated vacancy concentration profile as a function of distance from the boundary plane. This profile is consistent with recent ab-initio calculations that have determined it to be energetically favorable for grain boundaries in $SrTiO_3$ to be non-stoichiometric. [3] From standard models for the charge at grain boundaries, the grain boundary potential can be estimated from this to be 5.4±0.7 V.

$SrTiO_3$ grain boundary structures (and properties) have been shown to be similar to other perovskite grain boundaries, such as the HTS material, YBCO. [4] With knowledge of the atomic arrangement of the boundary plane, the density of excess electrons due to the non-stoichiometry of the structure can again be estimated. Theoretical calculations for the grain boundary potential in undoped $YBa_2Cu_3O_7$ use the Thomas-Fermi screening formalism for the screened electric potential at the dislocation cores (figure 2a). Treating the grain boundary as a linear array of dislocation cores (for which the spacing as a function of misorientation angle is well known), the grain boundary potential at higher misorientation angles is a superposition of the individual cores. As the misorientation angle increases from low to high angles, the individual cores begin to overlap, creating a potential barrier along the entire grain-boundary plane (figure 2b). Considering the tunneling of superconducting charge carriers across this potential barrier leads to an accurate estimation of the observed transport properties of YBCO grain boundaries. [5]

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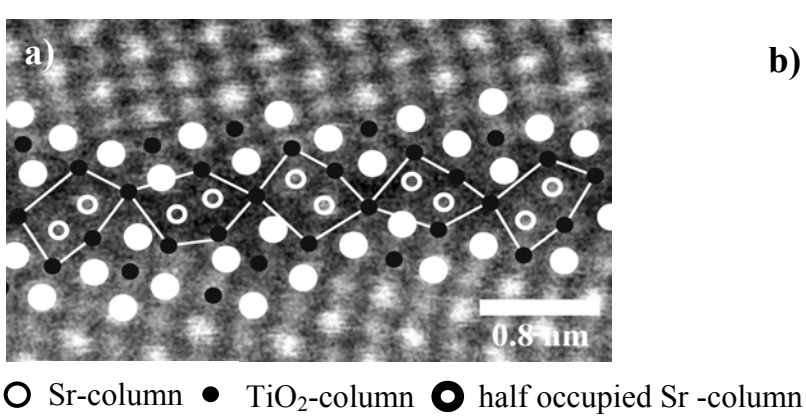

Figure 1: a) Z-contrast image of the 58° [001] tilt grain boundary at room temperature overlaid the structure of the grain boundary

b) Oxygen vacancy concentration across the boundary, acquired from EELS

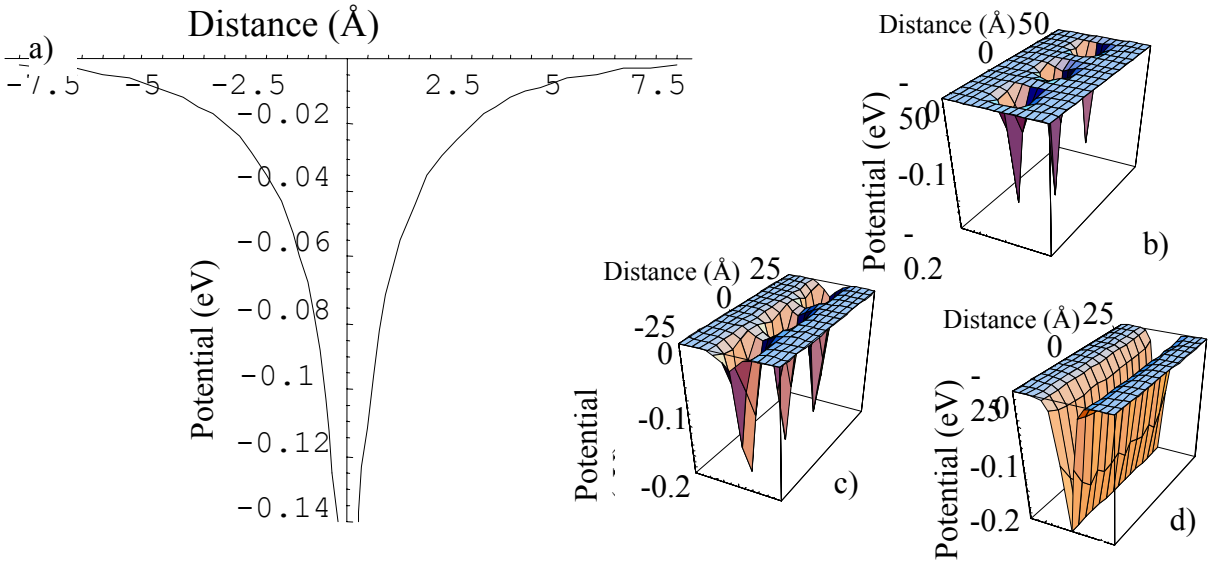

Figure 2: a) Calculated potential of a single dislocation core in YBCO

3-D plots of the potentials of b) a 5º low-angle grain boundary, c) an 11 intermediate-angle grain boundary, and a 36º high-angle grain boundary.

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