Modeling of the cubic and antiferrodistortive phases of SrTiO$_3$ with screened hybrid density functional theory

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We have calculated the properties of SrTiO$_3$ (STO) using a wide array of density functionals ranging from standard semilocal functionals to modern range-separated hybrids, combined with several basis sets of varying size and quality. We show how these combinations' predictive ability varies significantly, for both STO's cubic and antiferrodistortive (AFD) phases, with the greatest variation in functional and basis set efficacy seen in modeling the AFD phase. The screened hybrid functionals we utilized predict the structural properties of both phases in very good agreement with experiment, especially if used with large (but still computationally tractable) basis sets. The most accurate results presented in this study, namely, those from HSE06 with a modified def2-TZVP basis set, stand as one of the most accurate modelings of STO to date when compared to the literature; these results agree well with experimental structural and electronic properties as well as providing insight into the band structure alteration during the phase transition.

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I. INTRODUCTION

Strontium titanate (SrTiO$_3$; STO) is a complex oxide perovskite of great technological interest for its superconductivity,[1] blue-light emission,[2] photovoltaic effect,[3] and so on. Under normal conditions, bulk SrTiO$_3$ crystallizes in a cubic perovskite structure; it subsequently undergoes a second-order phase transition at $T_c = 105$ K to a tetragonal structure with slightly rotated oxygens around the z axis, known as the antiferrodistortive (AFD) phase (see Fig. 1). Many of the interesting properties of STO, either in bulk or in superlattices formed with other metal oxides, are believed to be caused by the cubic to AFD phase transition. Examples of this attribution are STO's superlattice's high-T_c superconductivity[4–6] and its colossal magnetoresistivity.[7] First-principles calculations (see Ref. 8 and references therein) have indicated that the strain-induced competition between octahedral rotation modes and the lattice distortion in metal oxide superlattices are behind these interesting properties. Thus, there is a considerable need[9,10] for precise theoretical calculations of the structural and electronic properties of complex oxides, as well as accurate estimation of the phase transition order parameters, to understand and eventually exploit these phenomena.

The phase transition of STO is governed by two order parameters. The primary order parameter is the rotation angle of the TiO$_6$ octahedra (θ). The experimentally measured[11] octahedral rotation of AFD STO is 1.4° at 77 K and increases as the temperature drops toward the maximum measured value of 2.1° at 4.2 K. The octahedron's rotation is believed to be almost complete[12] at around 50 K, where $\theta = 2.01° \pm 0.07°$ was reported.[13] The secondary order parameter is the tetragonality of the unit cell (c/a), which increases from 1.00056 (Ref. 14) to 1.0009 (Ref. 15) as the temperature decreases from 65 to 10 K.[16] The AFD phase can also appear in thin films of STO (Refs. 17–19) at much higher T_c than the bulk, depending on

the substrate used, the thickness of deposited STO film, the strain, and the lattice mismatch. For example, 10 nm of STO deposited on LaAlO$_3$ undergoes a transition to the AFD phase at $T_c \cong 332$ K.

As the simplest metal oxide perovskite, STO has been extensively studied in recent decades with different *ab initio* schemes.[20–24] However, it is still a challenging material for theory; only a few of the previously published works have been able to accurately describe the structural and electronic properties of both phases of STO. The balance of this section will consist of a brief review of the theoretical work performed to date.

Sai and Vanderbilt[25] carried out one of the first local density approximation (LDA) calculations on STO using a plane-wave basis and ultrasoft pseudopotentials. The LDA predicted an exaggerated tetragonal AFD phase of STO, with octahedral rotation angles of 6°, significantly overestimating the 2.1° rotation measured experimentally.[11] Use of the LDA with other basis sets[26] shows similar issues, predicting rotations up 8.4°.

Wahl *et al.*[23] used a plane-wave basis while simulating STO with the LDA,[27] the Perdew-Burke-Ernzerhof (PBE) functional,[28,29] and its reparametrization for solids, PBEsol.[30,31] (See Sec. II for further descriptions of these density functionals.) The LDA underestimated experimental lattice constants, while PBE overestimated them; both methods had band gaps that were seriously underestimated compared to experiment. This underestimation is well known for these functionals; see, e.g., Ref. 32 and references therein. PBEsol was found to reproduce accurately the experimental structure, but considerably underestimated the band gaps. For the AFD phase, the octahedral angle θ was found to be very sensitive to the functional used; all three overestimate the AFD deformation, with the LDA worse than the PBE and the PBEsol splitting the difference. Rondinelli and Spaldin[33] applied the LSDA $+ U$ correction to cubic STO and found that while it corrects the band gap, the calculated octahedral