

**Project Title:**
**Numerical study on new functionality of spin-heat crosses effect**

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Strontium titanate ( $\text{SrTiO}_3$ ) is often used as substrate for growth of new materials. Bulk  $\text{SrTiO}_3$  is an insulator with band gap 3.3 eV. We are now interested on the magnetic and electronic properties on bulk  $\text{SrTiO}_3$  on occasions of intrinsic defects.

In this study, first principles plane-wave based calculations with the generalized gradient approximation (GGA) were performed using *VASP* code. We also consider the on-site coulomb interaction on titanium d orbitals and effective U is taken as 4.36 eV. We use  $3 \times 3 \times 2$  supercell to simulate defect effect on cubic perovskite structure of  $\text{SrTiO}_3$ . For a single O (Sr or Ti) vacancy, one oxygen (Sr or Ti) atom is removed out of supercell. All the atoms in these defective supercells were full relaxed until the atomic forces were below 0.01 eV/Å.

The formation energies of vacancies in  $\text{SrTiO}_3$  were calculated from total energies of the supercells, based on the standard formalism by Zhang. For a vacancy with a charge state q, the formation energy is given by

$$E_f = E_T(\text{defect}:q) - \{E_T(\text{perfect}) - n_{\text{Sr}}\mu_{\text{Sr}} - n_{\text{Ti}}\mu_{\text{Ti}} - n_{\text{O}}\mu_{\text{O}}\} + q(\epsilon_F + E_{\text{VBM}}) \quad (1)$$

Here  $E_T(\text{defect}:q)$  is the total energy of the supercell containing a vacancy with a charge state q;  $n_{\text{Sr}}$ ,  $n_{\text{Ti}}$  and  $n_{\text{O}}$  are the number of Sr, Ti and O atoms vacancies;  $\mu_{\text{Sr}}$ ,  $\mu_{\text{Ti}}$  and  $\mu_{\text{O}}$  are the atomic chemical potential; and  $\epsilon_F$  is the Fermi energy measured from the valence band maximum(VBM).

As we known, formation energies of vacancies in  $\text{SrTiO}_3$  depend on atomic chemical potentials  $\mu_{\text{Sr}}$ ,  $\mu_{\text{Ti}}$  and  $\mu_{\text{O}}$ . In the case of the ternary  $\text{SrTiO}_3$  system, the atomic chemical potential are determined from equilibrium conditions of various phases containing Sr, Ti, and O. In general we assume  $\text{SrTiO}_3$  is stable

and the chemical potential of three elements satisfy the following condition:

$$\mu_{\text{Sr}} + \mu_{\text{Ti}} + 3\mu_{\text{O}} = \mu_{\text{SrTiO}_3}(\text{bulk}) \quad (2)$$

In this work we considered both oxidation (Case a and b) and reduction (Case c, Case d and Case e) conditions. In case a,  $\text{SrTiO}_3$  is in the equilibrium with O and SrO, then

$$\mu_{\text{Sr}} + \mu_{\text{O}} = \mu_{\text{SrO}}(\text{bulk}), \mu_{\text{O}} = \mu_{\text{O}}(\text{bulk}) \quad (3)$$

In case b,  $\text{SrTiO}_3$  is in the equilibrium with O and  $\text{TiO}_2$ , then

$$\mu_{\text{Ti}} + 2\mu_{\text{O}} = \mu_{\text{TiO}_2}(\text{bulk}), \mu_{\text{O}} = \mu_{\text{O}}(\text{bulk}) \quad (4)$$

In case c,  $\text{SrTiO}_3$  is in the equilibrium with Ti and TiO, then

$$\mu_{\text{Ti}} + \mu_{\text{O}} = \mu_{\text{TiO}}(\text{bulk}), \mu_{\text{Ti}} = \mu_{\text{Ti}}(\text{bulk}) \quad (5)$$

In case d,  $\text{SrTiO}_3$  is in the equilibrium with Sr and SrO, then

$$\mu_{\text{Sr}} + \mu_{\text{O}} = \mu_{\text{SrO}}(\text{bulk}), \mu_{\text{Sr}} = \mu_{\text{Sr}}(\text{bulk}) \quad (6)$$

In case e,  $\text{SrTiO}_3$  is in the equilibrium with Sr and Ti, then

$$\mu_{\text{Ti}} = \mu_{\text{Ti}}(\text{bulk}), \mu_{\text{Sr}} = \mu_{\text{Sr}}(\text{bulk}) \quad (7)$$

In order to determine the atomic chemical potentials, we also calculated total energies of the bulk states of Sr(fcc), Ti(hcp), SrO(Fm3m),  $\text{TiO}_2$ (P42/mmm) and TiO(Fm3m) at their equilibrium states.  $\mu_{\text{O}}$  is obtained from the total energy of  $\text{O}_2$  molecule using a cubic supercell  $15 \times 15 \times 15 \text{Å}^3$ .

	NM	FM	AFM
	0	-29.6	-10.0

TABLE I: energies of magnetic states related to Nonmagnetic state in Ti vacancy. The unit of energy is meV.

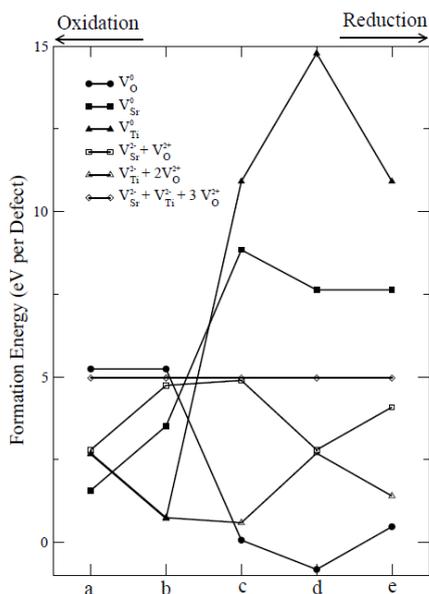


FIG. 1: Defect formation energies of isolated neutral vacancies in  $\text{SrTiO}_3$  at each equilibrium point.

The optimized lattice constant is  $3.943 \text{ \AA}$  which agree well with experimental data ( $3.905 \text{ \AA}$ ). As we known LDA or GGA calculations always underestimate the band gap, the band gap of  $\text{SrTiO}_3$  is  $1.77 \text{ eV}$  base on GGA calculation, which is almost half of experimental value. Even with GGA+U technique, it increases only up to  $2.35 \text{ eV}$ , being still significantly smaller than experimental one. We adopt the GGA+U method to deal with all defective supercell calculations below. Firstly we considered charge neutral defect samples, which are Sr Vacancy ( $V_{\text{Sr}}^0$ ), O Vacancy ( $V_{\text{O}}^0$ ), Ti Vacancy ( $V_{\text{Ti}}^0$ ), Sr partial schottky reaction ( $V_{\text{Sr}}^{2-} + V_{\text{O}}^{2+}$ ), Ti partial schottky reaction ( $V_{\text{Ti}}^{4-} + 2V_{\text{O}}^{2+}$ ) and full schottky reaction ( $V_{\text{Sr}}^{2-} + V_{\text{Ti}}^{4-} + 3V_{\text{O}}^{2+}$ ). The formation energies of various defect samples are compared in Fig. 1. We found that at high oxygen partial pressure Sr (Ti) vacancy is more stable (Case a and b), but O vacancy will be energetically favorable in reduction condition (case c, d and e).

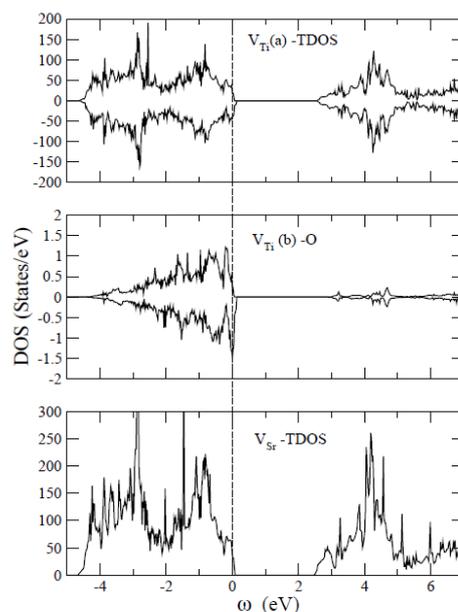


FIG. 2: Density of states for Ti vacancy and Sr vacancy.

In order to check the magnetic properties of defects states, we double the supercell and consider the Ferromagnetic states and Antiferromagnetic states. It was found that spin polarized state is most stable for Ti vacancy system (Tab. I), but for Sr vacancy the nonmagnetic state is kept. We also plot the total density of states for Ti vacancy and Sr Vacancy (Fig.2). We found that magnetism in Ti vacancy is from the oxygen atoms which are located as nearest neighbor of Ti vacancy.

In the following year, we will study the oxygen vacancies on  $\text{LaAlO}_3/\text{SrTiO}_3$  interface and demonstrate the transport properties on different oxygen pressure.