Thermodynamics of Oxygen Defective Magnéli Phases in Rutile: A First Principles Study

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Abstract

Ab initio thermodynamics has been used to calculate the formation energies, in different environmental conditions, for a number of oxygen defective structures in rutile. In addition to the Ti_nO_{2n-1} ($3 \le n \le 5$) Magnéli phases the two fundamental point defects, Ti interstitial and neutral oxygen vacancies, were considered. The predicted phase stability was compared to available experimental data: there is reasonable agreement between the calculated phase boundaries and those observed experimentally. These results were used to discuss a mechanism that has been proposed as an explanation for the formation of the crystallographic shear planes in rutile.

Introduction

TiO_{2-x} rutile only exists in non-stoichiometric form and has a complicated defect structure[1, 2] . For low *x*, the point defects that dominate are neutral oxygen vacancies and titanium interstitials[3]. As the sample is reduced, defect structures with long range order form: the Magnéli phases.

Figure 1 gives an idea of the complexity of the defect structure in the titanium-oxygen system. The figure shows a region of the experimental temperature-composition phase diagram of the Ti-O system. The cascade of equilibriums in the oxygen mole fraction's range of 0.64 to 0.66 are the Magnéli phases.

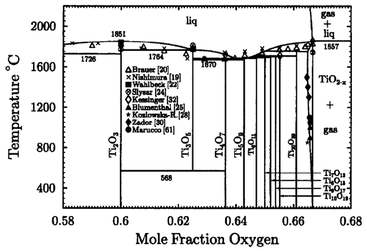


Figure 1: Reproduced with permission form Waldner et al (Ref. 1).

Figure 2a shows a rutile bulk supercell viewed along the x axis. Oxygen are grey and titanium are black. Figure 2b shows a Ti_4O_7 Magnéli phase viewed from the same point of view: the black line indicates the {121} planes cutting trough that section.

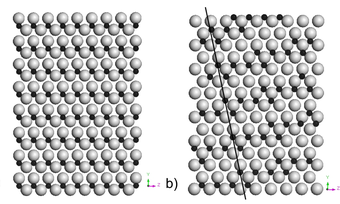


Figure 2

- They have a Ti_nO_{2n-1} stoichiometry.
- For $4 \le n \le 9$ the oxygen defects accommodate in {121} planes.
- They have a laminar structure which consist of parallel-sided slabs of rutile piled up in the {121} direction and separated by oxygen defective planes.
- Ti_4O_7 is the most studied. At 154 K it suffers a metal semiconductor transition[4] and acquires a 0.29 eV band gap[5].

Theory

- Formalism designed to compare the relative stability of different oxygen defective structures which are assumed to be in equilibrium.
- Vacancies are created in an ideal bulk rutile.
- The system has two degrees of freedom oxygen partial pressure (P_{O2}) and temperature (T).
- The system's stability is analysed through the Gibbs formation energy of the oxygen defects. The expression for this energy is:

$$\Delta G_f^{Def}(T, p_{O_2}) = \frac{1}{n_{TiO_2}}\left(E^{supcell}(0K) - n_{TiO_2}E_{TiO_2}^{bulk}(0K)\right) + \frac{n_O^{Def}}{n_{TiO_2}}\mu_O^{ref}(T, p_{O_2})$$

- The defect formation energy depends on T and P_{O2} through the oxygen chemical potential.
- The temperature and pressure dependence of the free energies and chemical potentials of all condensed phases has been neglected.

Results and Discussion

QUESTION: Given a particular concentration of oxygen defects, would they prefer to be isolated or to form a Magnéli phase?

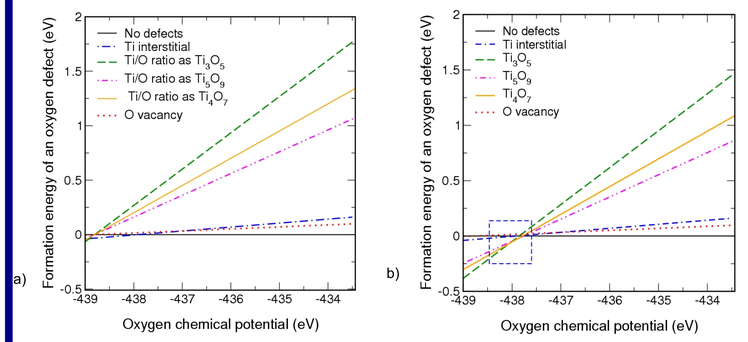


Figure 3: Defect formation energies for the studied systems as a function of the oxygen chemical potential. (a) systems of non-interacting oxygen defects where the O/Ti ratio is equivalent to the one in Ti3O5, Ti4O7 and Ti5O9. (b) the Ti_3O_5, Ti_4O_7 and Ti_5O_9 Magnéli phases.

- At low oxygen chemical potential, rutile with interstitionally dissolved titanium is predicted to be stable.
- Non-interacting oxygen defects have formation energies which are almost always positive
- Interacting oxygen defects -forming as Magnéli phases- have lower formation energies than isolated defects and, at low oxygen chemical potentials, these formation energies are negative.

ANSWER: Oxygen defects in rutile prefer to aggregate to form Magnéli phases, in agreement with experiments.

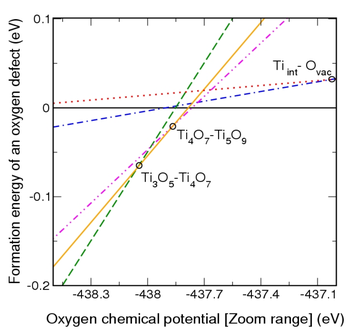


Figure 4: Large scale display of the region enclosed in a blue box in figure 3b.

Equilibrium point Ti_4O_7-Ti_5O_9:

$$\Delta G_{Ti_4O_7}^{Def}(\mu_O) = \Delta G_{Ti_5O_9}^{Def}(\mu_O) \Rightarrow \mu_{Ti_4O_7-Ti_5O_9}^{eq}$$

$$\mu_{Ti_4O_7-Ti_5O_9}^{eq} = E_0 + (\mu_{O_2}^0 - E_0)\frac{T}{T^0} - \frac{5k}{2}T\ln\left(\frac{T}{T^0}\right) + kT\ln\left(\frac{P_{O_2}}{P_{O_2}^0}\right)$$

Relationship between T and P_{O2} at equilibrium

Results and Discussion

Experimental and theoretical P_{O2} and T relationships at the Ti_3O_5-Ti_4O_7 and Ti_4O_7-Ti_5O_9 equilibrium points are depicted in figures 4a, b, c, and d.

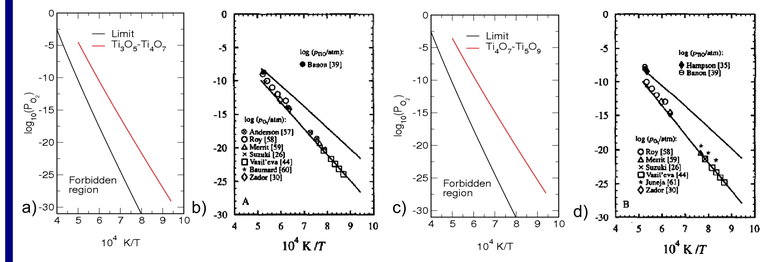
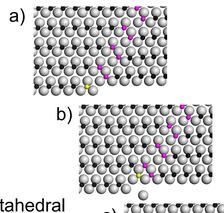


Figure 5: figures (b) and (d) reproduced with permission from Waldner et al (Ref. 1)

From rutile to the Magneli phases

- One of the proposed mechanisms for the formation of the Magnéli phases involves migration of titanium atoms[7].
- Titanium's chemical potential is enhanced at the surface: there is a chemical potential's gradient favoring Ti's diffusion towards the interior (See figure 6).



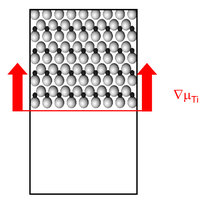


Figure 6

- Ti "jump" between octahedral sites, diffusing away from the surface (See figures 7a, b,c, and d).
- Non-bonded oxygen detach from the surface and enter the gas phase (See figure 7b).

Figure 7

Computational Method

Total energy calculations were performed using the CASTEP code, which implements DFT within the plane wave pseudopotential approximation. Ultrasoft pseudopotentials were used and the electronic exchange and correlation were described using LDA. More detailed information in: L. Liborio and N. Harrison, PRB 77, 104104, (2008).

Conclusions

- The thermodynamics of rutile's higher oxides has been investigated by first principles calculations.
- First principles thermodynamics reproduce the experimental observations reasonably well.
- At a high concentration of oxygen defects and low oxygen chemical potential, oxygen defects prefer to form Magneli phases.
- These results support the mechanism proposed by Andersson and Waldsey for the production the Magneli phases in rutile.

References

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Acknowledgements

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