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Ordered oxygen arrangement in titanium nanoparticles: Ab initio study

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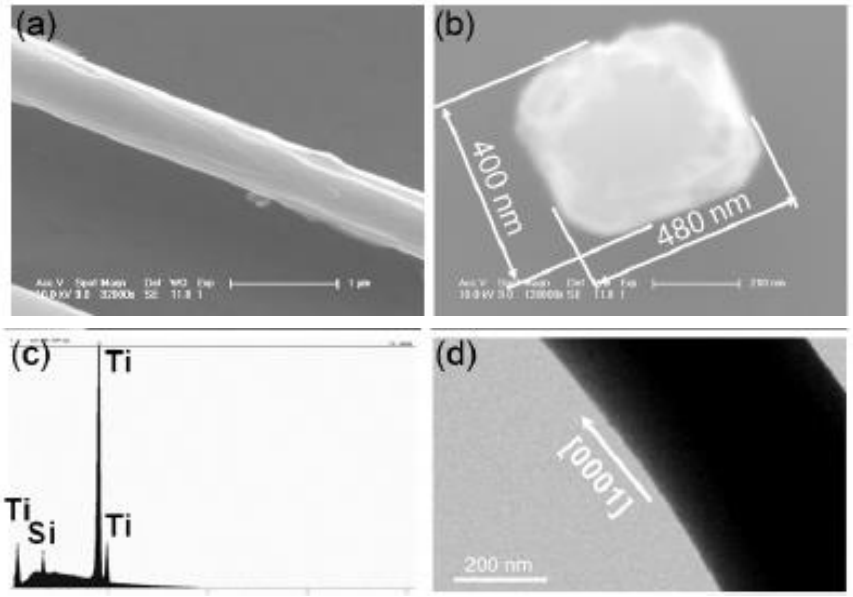
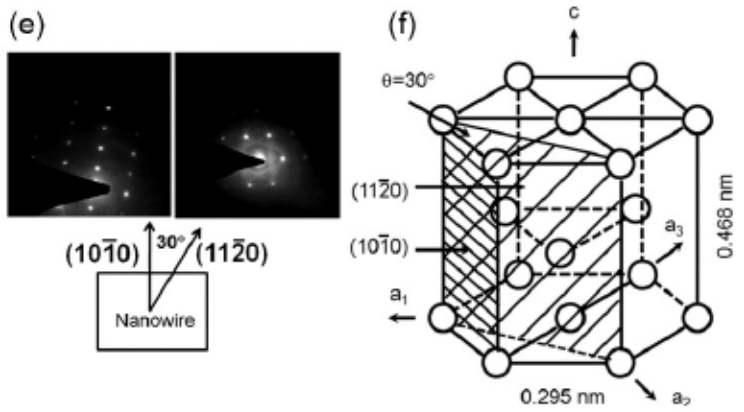
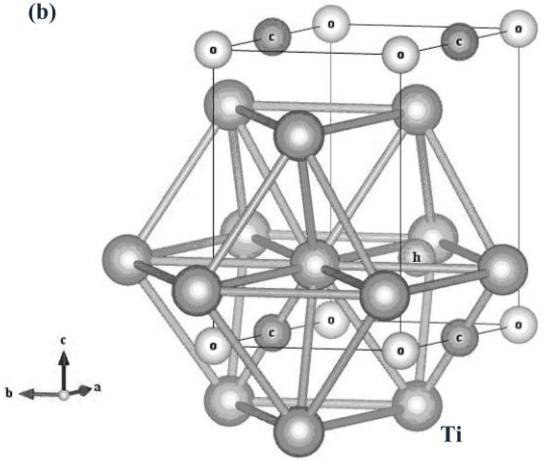
1. # Titanium nanowires





X. Huang et al. Nanotechnology. 23. (2012). 125601.

2.



Site	Wyckoff pos.	R_{nn} [Å]	Z	ΔE [eV]
octahedral	$2a$ (0, 0, 0)	2.09	6	+0.00
hexahedral	$2d$ ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{4}$)	1.92	5	+1.19
crowdion	$6g$ ($\frac{1}{2}$, 0, 0)	2.00	6	+1.88

H.H. Wu, D.R. Trinkle, Phys. Rev. Lett. 107 (2011) 045504.

Purpose:

1. Investigate oxygen adsorption on titanium nanoclusters;
2. Calculate the binding energy as a function of oxygen concentration.

Methods and approaches

The first-principles calculations were performed with the generalized gradient approximation and spin polarization of density functional theory in the ABINIT software package. Pseudopotentials for Ti and O atoms were constructed using the program fhi98PP. A special $1\times1\times1$ G-point in the Monkhorst-Pack grid with a cutoff energy of 816.34 eV was used to simulate the Ti clusters. The simulation clusters were placed in a very large cubic cell, which had a size of approximately 19 Å. During the course of the calculations, the atomic structure was relaxed until the interatomic forces were less than 0.005 eV/Å.

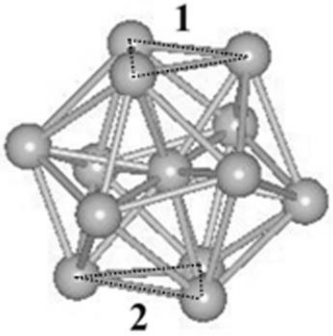
Calculations were performed using

A computer cluster at the Moscow State University in Moscow (Russia).

A cluster at the Computational Center in Khabarovsk (Russia)

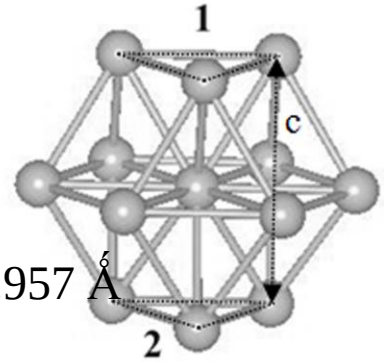
1. Titanium clusters model

c = 3.7 Å



a

a = 2.957 Å



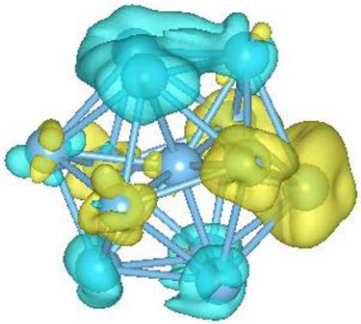
b

$P6_3/mmc$

c = 4.676 Å

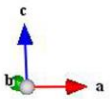
Atomic structures of (a) the icosahedral isolated Ti_{13} cluster, and (b) the Ti_{13} cluster with hexagonal structure, which is cut from the bulk titanium lattice

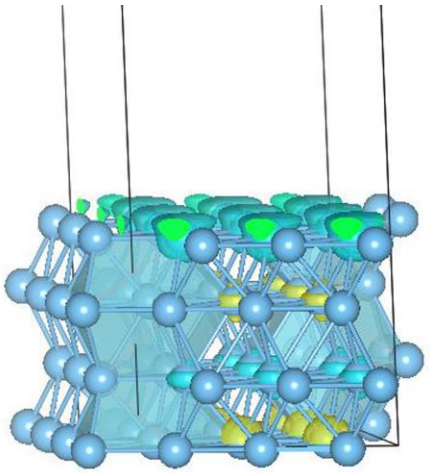
• To determine the crystallographic growth direction of the titanium nanoparticles, it is necessary to calculate the spin charge density distribution Δρ:



$$\Delta\rho = \rho_{up}^{spin} - \rho_{down}^{spin}$$

The excess electron density for the spin-down orientation is colored dark gray and the excess electron density for the spin-up orientation is colored light gray.

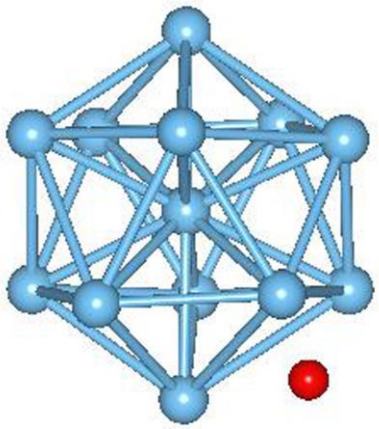




Ti(0001) surface

2. The interaction of the Ti_{13} cluster with oxygen

• To study the interaction of the Ti_{13} cluster with oxygen we considered two oxygen coverages, 0.05 and 1 ML. The 0.05 ML coverage corresponds to one O atom on the Ti_{13} surface, whereas 1 ML corresponds to 20 oxygen atoms.



1. Θ = 0.05 oxygen monolayer
2. Ih → C_{3v}(3m)
3. E_g = 0.23 ↑↓ - band gap energy.
4. The average binding energy E_b of an O atom on the Ti_{13} surface is 12.01 eV.

Fig. 1. The positions one oxygen atom adsorption on Ti_{13} cluster.

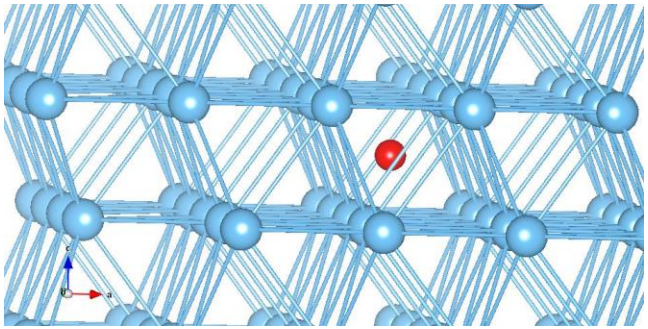
*Чибисов А.Н., Житенёв А.Н. / Химическая физика и мезоскопия. 2012. Т. 14, № 3. С. 467-470.

*A.N. Chibisov / Computational Materials Science 82 (2014) 131–133

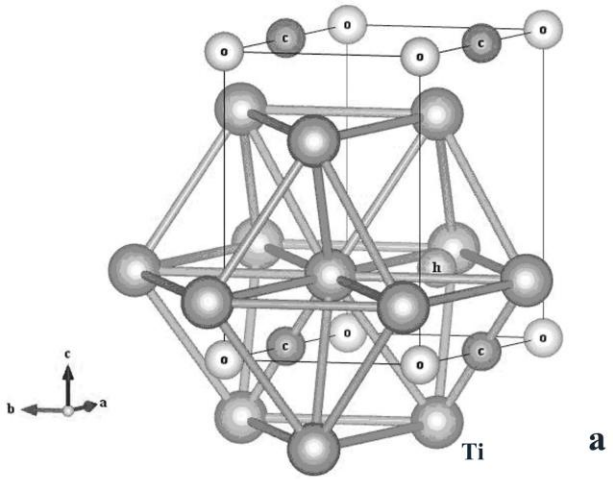
- The average binding energy E_b of an O atom on the Ti_{13} surface is given by:

$$E_b = -\frac{1}{N_O}\left[E^{O/Ti} - \left(E^{Ti} + N_O E^{O}\right)\right]$$

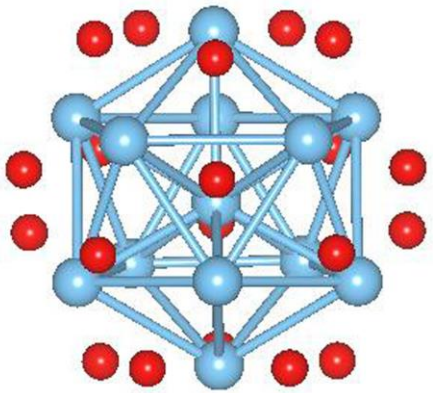
Where N_O is the number of O atoms on the surface,
$E^{O/Ti}$ is the total energy of the adsorbate-substrate system,
E^{Ti} is the total energy of the clean Ti_{13} cluster,
E^{O} is the total energy of the O atom.



The energy of dissolved oxygen in bulk titanium is 11.85 eV.



Θ = 1 ML O



The Ti_{13} cluster structure with 20 adsorbed oxygen atoms.

1. Θ = 1 ML O
2. E_g = 0.23 ↑↓
3. The average binding energy E_b of an O atom on the Ti_{13} surface is 10.49 eV.

- The reduced binding energy indicates increased repulsive forces between the adsorbed oxygen atoms.

Conclusions

1. We have used first-principles calculations to investigate the oxygen adsorption process on the stable Ti_{13} nanocluster.
2. The atomic structure of the oxidized titanium clusters and the oxygen adsorption energy were studied in detail, for low and high O coverages on the Ti_{13} surface.
3. The results indicate that titanium, during its interaction with oxygen, and for both its bulk and nanoscale states, has O atoms advantageously located in the positions which correspond to "bulk" interstitial sites.

1. Чибисов А.Н., Житенёв А.Н. Взаимодействие наночастиц титана с кислородом: Квантово-механические расчеты // **Химическая физика и мезоскопия**. 2012. Т. 14, № 3. С. 467-470.

ВЗАИМОДЕЙСТВИЕ НАНОЧАСТИЦ ТИТАНА С КИСЛОРОДОМ: КВАНТОВО-МЕХАНИЧЕСКИЕ РАСЧЕТЫ

УДК 544.225.22

ВЗАИМОДЕЙСТВИЕ НАНОЧАСТИЦ ТИТАНА С КИСЛОРОДОМ: КВАНТОВО-МЕХАНИЧЕСКИЕ РАСЧЕТЫ

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АННОТАЦИЯ. Методом функционала электронной плотности и теории псевдопотенциалов исследована атомная и электронная структура наноразмерного икосаэдрического кластера Ti_{13}, а также его взаимодействия с кислородом. Показано, что электронная структура Ti_{13} значительно отличается от объемного титана. Кислород препятствует появлению спиновой поляризации в окружении уровня Ферми, однако он наводит дополнительные электронные уровни (со спином вверх) в валентной зоне.

КЛЮЧЕВЫЕ СЛОВА: титан, ширина запрещенной зоны, структура, адсорбция кислорода

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First principles calculations of the agglomeration of Ti nanoparticles

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ABSTRACT

We have used molecular dynamics and first-principles calculations to investigate the structure, electronic properties, and agglomeration of Ti nanoparticles. The results indicate that cluster agglomeration leads to a decrease in the band gap compared with the isolated Ti_{13} cluster. In addition, we found that titanium nanocluster growth occurred along the [0001] direction. The difference of the atomic structures of the icosahedral Ti_{13} cluster and the bulk phase of titanium was also studied. The results show that spin polarization disappears when nanoparticles agglomerate.

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Oxygen adsorption on small Ti clusters: A first-principles study

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ABSTRACT

We have used density functional theory calculations to investigate the interaction of titanium (Ti) nanoparticles with oxygen. We found the energy-favorable site for oxygen atoms on a Ti_{13} cluster surface and investigated the atomic structure of the oxidized cluster. Our results showed that during oxidation, the oxygen atoms advantageously occupied positions on the titanium clusters that are similar to "bulk" interstitial sites.

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Phase transformation in titanium nanoparticles from first principles

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Keywords: first-principles calculation, agglomeration, phase transition, nanocluster growth, titanium.

Abstract. We have used molecular dynamics and first-principles calculations to investigate the structure and agglomeration of Ti nanoparticles. The results indicate that Ti nanoclusters undergo a phase transition with a change of point group symmetry. In addition, we found that titanium nanocluster growth occurred along the [0001] direction.

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A computer cluster at the Moscow State University in Moscow