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Structural stabilities and electronic structures of Ti atomic chains

Ai-Yu Li, Ren-Quan Li, Zi-Zhong Zhu*, Yu-Hua Wen

Department of Physics, Xiamen University, Xiamen 361005, P.R. China

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Abstract

The present first principles density-functional calculations reveal that titanium can form one-dimensional chains in linear, dimer, zigzag and ladder structures. The most stable structure is a zigzag chain with a unit cell rather close to an equilateral triangular geometry with four nearest neighbors. Two intermediary chains between the linear and zigzag ones have the ladder and dimer structure, respectively. Titanium can also form a metastable zigzag structure with an obtuse bond angle. It is important and interesting to find that during the elongation of the zigzag chain, the bond angle will shift abruptly from a sharp angle to an obtuse one at a critical point, and the bonding character also transforms from mainly metallic to more covalent. This is the first time that such a structural transition is discussed in the atomic chain system. The electronic structures of these one-dimensional titanium chains are also discussed.

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Keywords: Titanium; Atomic chains; Structures; Ab initio calculations

1. Introduction

The advances made in the last two decades in materials processing and measurement techniques have allowed the production and investigation of nanoscale structures. Single chains of suspended gold atoms with a length of four or more atoms have been produced between two gold electrodes [1,2], which have been considered as one of the milestones in nanosceince. The stability of finite and infinite atomic chains and their atomic and electronic structures have been studied extensively since then [3–13], including various 1D structures of noble metals (mainly gold) [3–9], transition metals [8–10], alkali metals [4,11], simple metals [4,12], and alloy wires [13]. One of the puzzling observations in the experimental studies [1,2] is that a linear strand of Au atoms has much larger atomic spacing than that of bulk. A consistent and acceptable explanation presented by Portal et al. [3] is that the chains in fact are not linear but possess a zigzag structure, so that the observed interatomic distances correspond to the second nearest but not the nearest bond lengths. In their following comparative studies [4], Au, Cu, Ca and K infinite chains were found to form planar zigzag structures with equilateral triangular geometry. The calculations on Au and Al chains show a second stable zigzag structure with a bond angle of $\alpha = 131^\circ$ for gold [4] and $\alpha = 139^\circ$ for aluminum [12], respectively. Besides the Au and Al chains, Rh [9] and Zr [10] are also found to have two stable zigzag equilibrium configurations. The theoretical study of these one-dimensional atomic systems can contribute to apprehending of the process of nanowires stretched to atomic chains. Also, one-dimensional chains are the testing ground for well-established theories of three-dimensional systems, and of fundamental importance for understanding the atomic structures, mechanical and electronic characters of metal nanowires.

Motivated by the fundamentally importance and experimental findings on atomic chains, we have performed a systematic study on the infinite atomic wires made of titanium. Titanium, as a transition metal with a $3d^2 4s^2$ valence state, may be considered to be more complicated than Au which has only s-type outermost valence electrons and Al which has s, p-type valence orbitals. Studies by

*Corresponding author. Fax: +86 592 218 9426.
E-mail address: zzhu@xmu.edu.cn (Z.-Z. Zhu).

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Yang [14] show that titanium atoms have a relatively high nucleation and low diffusion rate so that it is more favored energetically over Au and Al to form continuous chains on a variety of single wall nanotubes. Other experiments [15,16] also offered definitive evidence that titanium atoms deposited on a single wall carbon nanotube were capable of forming continuous wires. In this paper, we concentrate on the structural stabilities and the electronic properties of the one-dimensional Ti chains. Our results show that titanium can form one-dimensional chains in linear, dimer, zigzag and ladder structures. The most stable structure is the zigzag chain with a unit cell rather close to an equilateral triangular geometry. We found that during the elongation of the zigzag chain, the bond angle will shift abruptly from a sharp angle to an obtuse one at a critical point. The bonding also transforms from mainly metallic to that with more covalent character. This is a new phenomenon that has not been found in other atomic chains studied.

2. Method of calculations

Our calculations were performed within the framework of density-functional theory using the Vienna ab initio simulation package (VASP) [17,18] in a projector augmented wave (PAW) representation [19]. Ti chains were treated with the supercell geometry. The distances between the chains were taken to be 15 Å, which had been proved enough to minimize the inter-chain interactions. The wave functions were expressed by plane waves with the cut-off energy of 178.4 eV. The Brillouin zone (BZ) integration was performed with the Monkhorst–Pack scheme [20] using $(1 \times 1 \times 35)$ **k** mesh points. The total energy convergences with respect to the energy cut-off and the number of **k** points had been tested. Exchange and correlation effects were described by the Perdew–Wang 1991 generalized gradient approximation (GGA) [21]. Preconditioned conjugate gradient method was used for the wave function optimization. The optimized (full-relaxed) structures obtained in this study were achieved by using the calculated Hellmann–Feynman (H–F) forces as a guide in the processes of adjustment of the atomic configurations, until the H–F forces on each atom was less than 0.01 eV/Å. Calculations on the HCP bulk titanium gave the equilibrium lattice constants of $a = 2.93$ Å, $c = 4.61$ Å and a cohesive energy $E_c = 5.27$ eV/atom, in good agreements with the experimental results [22]; see also Table 1.

3. Results and discussions

The variation of the cohesive energies E_c of the titanium atomic chains calculated for the fully relaxed linear, dimer, zigzag and ladder structures are shown in Fig. 1 ($E_c = -E_T$ in the figure). The geometries of these structures and their relevant structural parameters are also shown by insets in the Fig. 1. The optimized structural parameters and cohesive energies of the studied 1D structures as well as those of Ti bulk are listed in Table 1. The present

Table 1
Calculated structural parameters and cohesive energies of one-dimensional Ti atomic chains and bulk Ti. The structural parameters (s, d, h, α) are explained in Fig. 1

Structures	s (Å)	d (Å)	α (deg)	E_c (eV/atom)	Coordination numbers
L		2.10		1.82	2
Z_1	1.29	2.41	64.6	2.98	~4
Z_2	1.65	1.94	116	2.49	~2
D	1.93	4.87		1.99	~2
H (ladder)	$h = 2.13$	2.63		2.48	~3
Bulk (HCP)	$a = 2.93$	$c = 4.61$		5.27	12
Bulk (expt) [22]	$a = 2.95$	$c = 4.61$		4.85	12

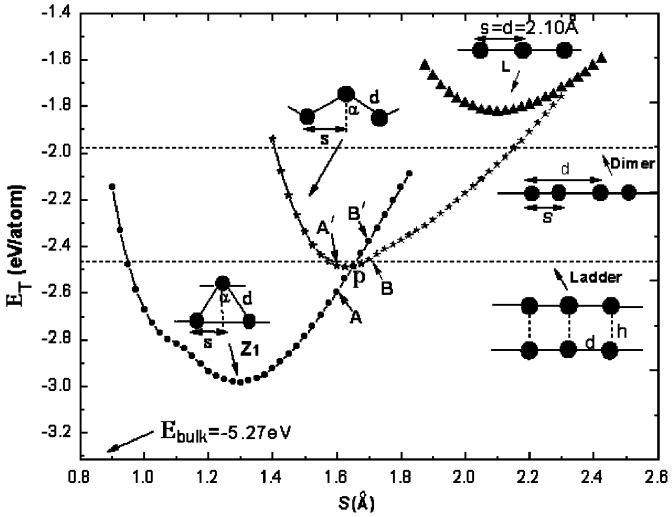

Fig. 1. Calculated cohesive energies ($E_c = -E_T$) of infinite titanium atomic chains in linear, dimer, zigzag and ladder structures. The cohesive energies of the dimer and ladder chains are indicated by dash lines, and that of the bulk is indicated by an arrow. Relevant structural parameters: bond length d, bond angle α, parameters s and h are shown by insets. The point P is the intersection point of the two zigzag chains with sharp and obtuse bond angles, respectively.

calculations indicate that titanium can form planar chains in linear, dimer, zigzag and ladder structures. The most stable geometry, i.e., with maximum cohesive energy, is a zigzag structure (specified as Z_1 structure): the energy minimum occurs at $s = 1.29$ Å (the parameter s are shown by insets in Fig. 1) and cohesive energy $E_c = 2.98$ eV/atom. The bond length of this zigzag geometry is $d = 2.41$ Å and the bond angle is $\alpha = 64.6^\circ$ which is close to an equilateral triangle of $\alpha = 60^\circ$. The cohesive energy of the truly linear structure ($\alpha = 180^\circ$, specified as L structure) is the lowest one, $E_c = 1.82$ eV/atom, which implies that it is the most unstable structure among the chains studied. The cohesive energy of the Z_1 structure is 1.16 eV/atom larger than that of the L structure. Besides the Z_1 and L structures, there are two intermediary chains having the dimer and ladder