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Structures of small NixTiy ($x + y \leqslant 5$) clusters: A DFT study

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Dedicated to Professor Yoshiyuki Kawazoe on the occasion of his 60th birthday.

Abstract

A density functional method BPBE with pseudo-potential basis set CEP-121G is selected to study NixTiy ($x + y \leqslant 5$) clusters. The ground state geometry, spin states, vibrational frequencies and electronic properties calculated are in good agreement with the experimental results for the homometallic clusters. The bimetallic clusters have shorter bond lengths and higher band gaps, gathering increased stability for them compared to the homometallic clusters. Segregation was found to occur in the bimetallic systems and the geometry and shape depends on the Titanium composition. NBO analysis indicates 4s orbital of Ni atom hybridizes with 3d orbital of Ti atom.

Keywords: Bimetallic clusters; DFT methods; Structures; Nitinol; Vibrational frequencies; Electronic properties

1. Introduction

The study on bimetallic clusters have been received great attention as their chemical and physical properties, which may be tuned by varying the composition and atomic ordering, as well as the size of the clusters [1]. Their surface structures, compositions, and segregation properties are of interest as they are important in determining chemical reactivity and have led to widespread applications in electronics, engineering and catalysis [2]. Though large advances have been made in experimental physics to produce measurable quantities of size selected clusters, it lacks the ability to directly explore and assign cluster geometries and discriminate between possible isomers [3].

Of particular interest was Nickel–Titanium bimetallic clusters due to their unique mechanical properties associated with reversible martensitic transformation [4]. Henceforth the alloy found a great application as Shape-Memory alloys (SMAs) and is commercially called NiTinol [5]. To understand the martensitic transformation, it is essential to know the crystal-structure of the martensitic and parent phases as precisely as possible. However, nitinol crystal-structure has been controversial as precise crystal-structure analyses were very difficult to obtain in the martensitic phase. Very recently efforts have been made to understand their crystal-structures in bulk face using DFT methods [6–8].

Studies on small metal clusters are important as they provide a link between the molecular state and the solid state. Moreover such study will provide a clear insight into its structure stability and its growth mechanism [9]. However, theoretical studies of Transition metal (TM) clusters have been difficult due to the presence of d electrons, with complicated electronic ground states structure and with different spin multiplicities [10]. Especially for Ti clusters, the energies between different spin multiplicities states are so close that determining the ground state structures is always complicated and a challengeable work [11]. In addition study of Ni clusters are complicated by their ferromagnetic nature and there exits several spin states to be investigated [12].

A number of DFT calculations to predict the geometries and spin states of small Ti and Ni clusters containing up to

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several hundred atoms have been reported [13–16]. However, the ground states structures are not determined conformably all the while, due to the lack in the choice of exchange-correlation functional. Recently several theoretical studies using empirical much body potential and Monte Carlo investigation have been done on Nickel containing bimetallic clusters [17]. Calculation based on semi-empirical molecular orbital methods and density functional theory, have also been reported for the study of Nickel containing bimetallic clusters [18–21]. Recently Oymak et al. reported on the structural and electronic properties of Alk Ti$_l$ Nim using B3LYP method [22].

In the view of understanding the structure and properties, we have made a theoretical investigation on the small bimetallic clusters of the type NixTiy ($x + y \leqslant 5$) over the complete composition range from pure Nickel to pure Titanium cluster. We present the results obtained according to the composition of the clusters and have compared their properties with monometallic clusters.

2. Computational method

One of the primary considerations involved in these calculations is the determination of the methodology, specifically the form of the exchange-correlation potential and the type of basis set to be used. Since experimental results on bond length, and vibrational frequencies for Ni and Ti dimers are available, we tested our theoretical results (Table 1) using various forms of exchange-correlation functionals, denoted as BP86, B3LYP, B3LYP, BPW91, mPWP86, B3PW91 and SVWN, using the two valance basis sets LANL2DZ and CEP-121G. Local spin density approximation method predicts shorter bond lengths and higher frequency for Ni and Ti dimers. Methods using hybrid exchanged functional overestimates bond lengths and frequency for Ni and Ti dimer, respectively. A comparison with the experimental results shows that BPBE is the most optimal method. In this method, the exchange functional was suggested by Becke's 1988 functional [23], which includes the Slater exchange along with corrections involving the gradient of the density, and the correlation functional was suggested by the 1996 functional of Perdew, Burke and Ernzerhof [24,25]. In addition the CEP-121G (compact effective potential), in which the dependence of spin–orbit effects was averaged out, was selected by us [26].

At this theoretical level all possible structures were optimized with different spin multiplicity using GAUSSIAN G03 package [27]. The geometric structures with lowest energy were chosen as ground state configurations. The HOMO–LUMO gap (E_G) is computed as the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital. The Vertical Ionization potential (VIP) and Electron affinity (EA) were calculated as shown below.

$$\mathrm{VIP} = E[\mathrm{Ni}x\mathrm{Ti}y]^{+} - E[\mathrm{Ni}x\mathrm{Ti}y]$$

$$\mathrm{VEA} = E[\mathrm{Ni}x\mathrm{Ti}y] - E[\mathrm{Ni}x\mathrm{Ti}y]^{-}$$

Where $X = 1{-}5$ and $Y = 5{-}X$; $E[\mathrm{Ni}x\mathrm{Ti}y]^{+}$ is the energy of the cation; $E[\mathrm{Ni}x\mathrm{Ti}y]^{-}$ is the energy of the anion and $E[\mathrm{Ni}x\mathrm{Ti}y]$ is the energy of the neutral cluster.

Analysis of the charge distribution and charge-transfer processes was performed using the natural bond orbital (NBO) partitioning scheme [28].

3. Computational results

The ground state geometric structures of the NixTiy ($x + y \leqslant 5$) clusters are determined by full geometric optimization. For each different composition, a number of stable structures are obtained. The structures corresponding to the lowest energy is presented in Fig. 1. The optimized bond lengths, bond angle (θ), their ground state spin multiplicity (M) and structural symmetries are shown in Table 2. The Band gap (E_G) and the harmonic frequencies of the clusters are presented in Table 3. Experimental and calculated Vertical Ionization potential

Table 1

The calculated bond distance R (Å) and vibrational frequencies (cm^{-1}) of Ni and Ti dimer in different DFT methods with CEP-121G and LANL2DZ (in bracket) basis sets

Method	Pseudopotential and basis set	R (Å)		Frequency (cm^{-1})	
		Ni_2	Ti_2	Ni_2	Ti_2
SVWN	CEP-121G (LANL2DZ)	2.049 (2.056)	1.887 (1.888)	356 (385)	505 (531)
BLYP	CEP-121G (LANL2DZ)	2.151 (2.146)	1.961 (1.951)	302 (316)	444 (462)
B3LYP	CEP-121G (LANL2DZ)	2.393 (2.375)	1.945 (1.911)	228 (233)	481 (519)
BP86	CEP-121G (LANL2DZ)	2.129 (2.129)	1.943 (1.933)	314 (326)	449 (473)
mPWP86	CEP-121G (LANL2DZ)	2.127 (2.127)	1.941 (1.932)	315 (328)	451 (476)
B3P86	CEP-121G (LANL2DZ)	2.364 (2.352)	1.821 (1.895)	236 (243)	557 (533)
BPW91	CEP-121G (LANL2DZ)	2.134 (2.136)	1.944 (1.934)	311 (320)	441 (467)
B3PW91	CEP-121G (LANL2DZ)	2.379 (2.368)	1.829 (1.810)	233 (236)	539 (647)
BPBE	CEP-121G (LANL2DZ)	2.133 (2.136)	1.943 (1.934)	311 (321)	441 (467)
PBEPBE	CEP-121G (LANL2DZ)	2.135 (2.139)	1.946 (1.937)	310 (319)	444 (467)
Experiment		2.154[a]	1.943[b]	259[a]	409[b]

[a] See Ref. [30].

[b] See Ref. [29].