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Journal of Molecular Structure: THEOCHEM 807 (2007) 153–158

THEO CHEM

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A density-functional study of nickel/aluminum microclusters

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Received 8 September 2006; accepted 12 December 2006

Abstract

The geometric structures and electronic properties of Al_mNi_n (m+n = 2–4) microclusters have been investigated using a hybrid density-functional method (B3PW91) within the effective core potential level. Al and Ni system have been studied in their ground states. The ground-state geometric and electronic structures are obtained, which are in good agreement with experimental results available. In addition, the corresponding total energies, binding energies, possible dissociation channels, are also presented and discussed.

Keywords: Bimetallic clusters; AlNi; DFT; Electronic properties

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1. Introduction

The physics and chemistry of metal clusters continues to be a subject of intensive studies [1–5]. Clusters often possess unique properties different from both the extended bulk and the atomic states. Consequently, the study of the size evolution of various cluster properties, such as equilibrium geometries, stability, ionization potentials, etc. is an interesting and challenging problem. In the context, the transition-metal (TM) clusters, which have obvious economical importance, have been extensively studied. Due to the existence of d electrons, however, physical and chemical properties of TM clusters show remarkable size-dependent variations that cannot be explained using the shell model of s valence electrons. It presents a challenge to both experimental and theoretical investigations on TM clusters.

Recently, some meaningful improvements have been achieved in the studies of mixed clusters including TM atoms. Thomas et al., reported that the magic numbers appear at $n = 6$, 13, 19, and 23 by observing the mass spectrum of $CuAl_n^-$ clusters [6]. More recently, under anion photo-detachment photoelectron spectroscopy at 4.66 eV photo energy, Axel Pramann et al. [7] observed photoelectron spectra of $Co_{n-1}V_1^-$ (n = 4–14) and $Co_{n-2}V_2^-$ (n = 9–14) clusters. Theoretically, some attempts have been done on Cu–Co clusters [8], Ni–Cu clusters [9], Al–Ti clusters [10], and so on. Such investigations provide a state-of-the-art tool to gain insights into chemical and physical properties of binuclear TM complexes on a microscopic scale as a function of size and distribution.

The microclusters of aluminum, nickel and their mixture have been considered in the article. From the metallurgical point of view, the bimetallic nanoclusters have become very popular [11–14]. Their crystal structures, phase diagram data, electronic structures, optical properties, have been investigated intensely. The intense interest in these elements is due partly to their shape–memory–allay properties that render them industrially important.

In the present paper, structural and electronic properties of 12 different microclusters of the type Al_mNi_n ($m + n = 2$–4) have been investigated. The dimers (Al_2, Ni_2, AlNi), trimers (Al_3, Ni_3, Al_2Ni, Ni_2Al), and ternary (Al_4, Ni_4, Al_2Ni_2 Al_3Ni, $NiAl_3$) have been studied in their ground-state. The density-functional theory calculations have been performed within the small-core pseudopotential level. All calculations are performed using the GAUSSIAN 98 program package [15].

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doi:10.1016/j.theochem.2006.12.015

2. Method of calculation

In the present study, Al_mNi_n ($m + n = 2$–4) microclusters have been investigated theoretically by applying B3PW91 [16–19] as the hybrid Hartree–Fock(HF)-density-functional theory (DFT) exchange-correlation functionals within LANL2DZ pseudopotential and basis set. The combination is the most effective level of theory available for the analysis of metallic systems; several applications have already been reported [20]. The B3PW91 is fully nonlocal functional consisting of the generalized gradient approximation (GGA) of Becke for exchange functional mixed with a contribution calculated Hatree–Fock. The correlation contribution is calculated using the ab initio GGA PW91 correlation functional.

The small-core pseudopotentials (LANL2DZ) given by Hay and Wadt [21–23] are used to describe valence electrons. The effective core potentials include relativistic mass–velocity term and the Darvvin term for Al and Ni atoms in the LANL2DZ. In the present calculations, LANL2DZ basis set and the number of primitive Gaussians used in LANL2DZ vary from atom to atom, depending on the valence structure of atoms considered. In the paper, the optimized ground-state structures, electronic properties, and vibrational spectra of Al_mNi_n ($n + m = 2$–4) microclusters for 12 different species have been calculated.

3. Results and discussion

3.1. Geometry optimization

The ground-state geometric structures of the Al_mNi_n ($m + n = 2$–4) clusters are determined by full geometric optimization. For each different composition, a number of stable structures are obtained. The structure corresponding to the lowest total energy is presented in Fig. 1 for each composition. Table 1 presents the ground-state symmetries, structural parameters along with the total energies and spin multiplicity for the Al_mNi_n ($m + n = 2$–4) clusters. To asses the accuracy of our calculations, we have compared some properties of the small clusters with available experimental value also shown in Table 1. For these ground-state structures obtained, the harmonic corresponding vibrational frequencies are given in Table 2.

3.1.1. Dimers

The ground-state of Al_2 is predicted to be triplet with a bond length of 2.57 Å. The bond length is comparable to with the experimental value $R = 2.466$ Å [24]. The spin of $S = 1$ is consistent with earlier matrix isolation measurement [25]. Recently, N. E. Schultz et al., found the group state of Al_2 [26], to have $R = 2.71$ Å and $S = 1$; the R value agree with the experimental data less well than ours (Table 1). Geometrical parameters and multiplicity of Ni_2 have been obtained by microwave spectroscopy method [27]. The ground-state $^3\Sigma_g^-$ of Ni_2 with $R = 2.20$ Å is determined using DFT method [28]. Recently, Michelini et al. [29,37] reported the ground-state and low-lying excited states of Ni_2 at the spin local density approximation (LSDA) level of theory. Our results indicate that the computed R (2.27 Å) and Multiplicity are in good agreement with the available experimental and theoretical values. For AlNi cluster, there are no experimental and theoretical data to compare in the literature. The calculated bond length and multiplicity are the first for the species.

3.1.2. Trimers

The ground-state of Al_3 are obtained, which has an equilateral triangle structure with a bond length of 2.75 Å. Recently, El-Bayyari and Erkoç [31], using the molecular-dynamics (MD) technique, found the triangular form of Al_3 with C_{2v} symmetry as the energetically most stable structure. However, Yang et al. [32] found an equilateral triangular structure for the ground-state of Al_3, which is well accord with our results. The optimized geometry of Ni_3 has a C_{2v} symmetry with $S = 2$, where the distance to apex atom is shorter than the base length. Moskovits and Dilella et al., in their electron-spin resonance spectroscopy experiment observed that the equilateral triangle geometry of Ni_3 has lowest energy [33]. However, Reuse and Khanna with a DFT calculation, found a triangle form with an apex angle 61° being most stable [28], which is comparable to our result. It is interesting that our bond length of 2.33 Å for Ni_3 is significant larger than that for Ni_2 dimer (2.27 Å), which have the same tendency with other theoretical results [29,30]. For heteronuclear trimers, we have not some experimental and theoretical results to compare; however, an interesting feature is that the optimized minimum energy structure of AlNiNi is linear in the given order, whereas Al_2Ni cluster with C_{2v} symmetry.

3.1.3. Tetramers

In our study, we find the most stable structure of Al_4 to be a planar rhombus and not a three dimensional tetrahedron. Erkoç et al. [5] found that the tetrahedron form of Al_4 was ground-state with a PEF method, however, Deshpande and Kanhere [34] using the time-dependent LSDA method found that rhombic Al_4 was energetically most favorable, which is consisted with our result. Experimental observation of Parks et al. [35] showed that the structure of Ni_4 is not certain; it was probably two dimensional such as rhombic. In the work, we also find the most stable geometry of Ni_4 to be a planar rhombus with the bond length of $R = 2.44$ Å. The spin double is good accord with the theoretical result [29]. For heteronuclear tetramers, we find that Al_3Ni and $AlNi_3$ have both three dimensional ground-state structures. Especially, Al_2Ni_2 and $AlNi_3$ have both high Multiplicities, which may be due to a significant change in the geometry of these clusters. We find $AlNi_3$ have a C_S symmetry, corresponding to a distorted tetrahedron.