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The effects of germanium on the configurations and magnetic moments of nickel clusters

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ABSTRACT

We report *ab initio* calculations of the structures, binding energy and total spin moment of Ni_nGe (n = 2–12) clusters using all electron density-functional method. Our results show that the doped Ge makes the stability of Ni_nGe clusters weakened as compared with pure Ni_{n+1} clusters. The Ni_6Ge and Ni_9Ge clusters possess relatively higher stability. Compared with the magnetism of pure Ni_{n+1} clusters, the magnetism of Ni_nGe (n = 2–10) clusters is reduced, which is attributed mainly to the nor-magnetism Ge element and the weakening of spin polarization of the Ni atoms. For $Ni_{11}Ge$ and $Ni_{12}Ge$, the spin polarization of Ni atoms is enhanced. Furthermore, it can be interpreted that the size effect which should contribute to the increase of the magnetic moment for $Ni_{12}Ge$, and the surface enhance effect should be responsible for the increase of the magnetic moment of $Ni_{11}Ge$.

1. Introduction

Structural stability, electronic structure and magnetic properties are three important linked problems in cluster research, since the magnetic moment depends on the electronic structure which in turn depends on the geometry. In recent years, extensive studies of transition-metal clusters have been conducted [1–6]. As a result, a number of associations between the structure and attribute of magnetism have been revealed. Nickel clusters are the primary target of many research groups because of their extensive catalytic and important magnetic properties [7–15]. Consequently, it is of interest to investigate changes to the structure of clusters in order to improve the magnetism of clusters by, for example, doping or mixing the clusters with other species.

Reuse and Khanna [16] carried out the first systematic study of the geometries of Ni_n (n = 2–6, 8, 13) clusters using an approach based on a linear combination of atomic molecular-orbitals within the density functional formalism. They obtained calculated geometries, and the total spin magnetic moments for these nickel clusters. Xie et al. [17] have studied the structural and magnetic properties of the Ni_n (n = 2–13) clusters using DFT calculations. They found that from n = 6–13, the total spin moment is $8\mu_B$. The electronic properties including static polarizability and anisotropy of small Ni_n ($n \leqslant 5$) clusters have been studied using a newly developed first-order polarized basis set for DFT calculations [18]. Rey et al. [19] using the SIEFA code within the DFT and nonlocal pseudopotential approach for the core electrons have found the ground-state geometries of small Ni_mC_n ($m + n \leqslant 8$) clusters. Deshpande et al. [20] have investigated equilibrium structures and the electronic and magnetic properties of small Ni_nB clusters with n = 1–8, 12 within the framework of density functional theory. The calculated results showed that doping with a boron atom enhances the stability and the energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO–LUMO) but reduces the magnetic moment of Ni clusters. Ni_nN clusters [21] were investigated within the DFT calculations and it was found that the nitrogen atom prefers surface sites and the stability were enhanced by doping a nitrogen atom compared with that of the corresponding pure clusters.

In this article, we have calculated the lowest energy geometric structures and magnetic properties for Ni_nGe (n = 2–12) clusters and also Ni_n (n = 2–13) clusters for the comparison using all-electron density functional theory. The rest of this paper is arranged as follows. Section 2 gives a brief description of the theoretical method used in this work. In Section 3, it presents the lowest-energy structures and some low-lying isomers for Ni_{n+1} and Ni_nGe (n = 2–12) clusters. The electronic structures and the magnetic properties of these ground-state clusters are also discussed in Section 3. Finally, Section 4 summarizes the main conclusions of our computational results.

2. Computational details

All calculations have been carried out using DFT provided by the Dmol package [22,23] in the Materials Studio. First of all, using

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Table 1
Calculated the binding energy E_b (in eV) and atomic bond lengths d (in Å) and experimental data of the lowest energy structure of Ni_2 dimmer.

	PBE	PW91	BP	BLYP	Exp [27]
E_b	6.04088	6.14104	6.05982	5.68926	2.042 ± 0.002
d	2.095	2.091	2.095	2.111	2.1545 ± 0.0004

several kinds of exchange correlation functionals, we have performed all-electron test calculations on the Ni_2 dimmer. The functionals used in the test include the following: the Perdew–Wang (1991) (denoted as PW91) with the Becke (B88) [24] exchange functional (denoted as BP together); the Lee–Yang–Parr (LYP) [25] correlation functional with B88 (denoted as BLYP together);

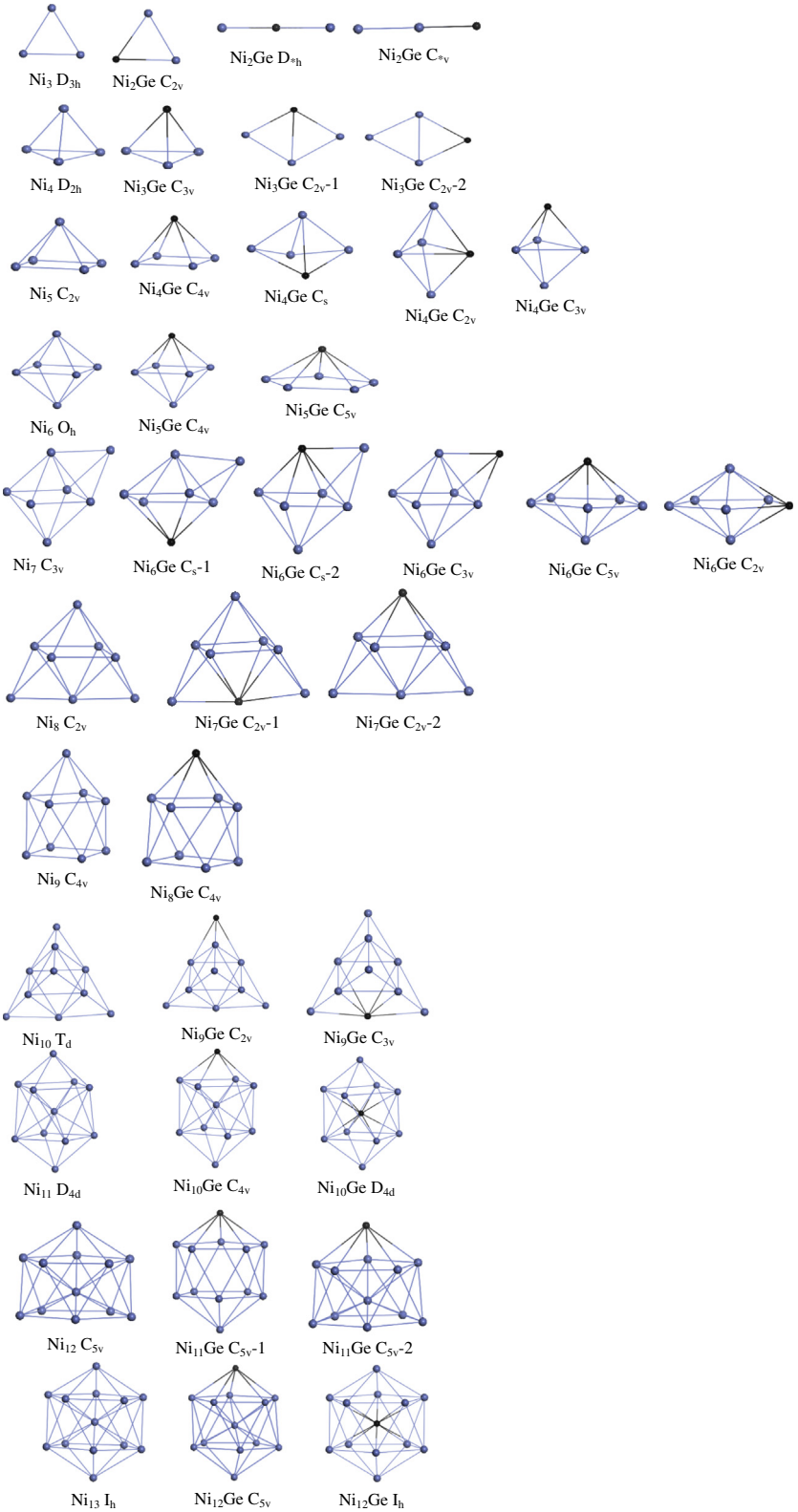

Fig. 1. The structural sketches and their symmetries of Ni_{n+1} and Ni_nGe (n = 2–12) clusters. Dark balls indicate Ge atom and light ones Ni atoms.