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Physics Letters A 348 (2006) 416–423
PHYSICS LETTERS A
www.elsevier.com/locate/pla

Study of GaAs cluster ions using FP-LMTO MD method

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Received 3 March 2005; received in revised form 25 August 2005; accepted 25 August 2005

Available online 1 September 2005

Communicated by R. Wu

Abstract

Using full-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method, we have investigated the electronic and geometric structures of Ga_nAs_n ($n = 4, 5, 6$) cluster ions in detail. Their lowest energy structures are found. We have also investigated the evolution of some Ga_4As_4, Ga_5As_5 and Ga_6As_6 clusters as a function of charging. Our calculations suggest that some of the lowest energy structures for the cluster ions are different from those of the corresponding neutral clusters. Upon charging, the structures will undergo structural distortion because of the electrostatic repulsion among the charged atoms. Gallium atoms are more easily on capped atomic positions than arsenic atoms in the negative Ga_nAs_n clusters.

PACS: 36.40.-c; 71.10.-b; 37.15.-p

Keywords: Cluster ions; Ground-state structure; Binding energy

1. Introduction

The study of semiconductor clusters, including their ions, has become one of the most exciting research areas over the past several decades. With theoretical methods, systematic study on their physical and chemical properties is challenging. In particular, for the mixed clusters like GaAs, the theoretical investigation on them is comparatively difficult because of the computational difficulties associated with the structural and permutational variations resulting from the presence of more than one element even though they contain a few atoms. However, due to their scientific and technological applications [1], a great effort has been devoted to the investigation on their properties. Up to now, some development has already been obtained both experimentally and theoretically.

Experimentally, laser vaporization followed by supersonic expansion was used to produce GaAs clusters and their positive and negative ions [2–4]. Theoret-

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0375-9601/$ – see front matter
doi:10.1016/j.physleta.2005.08.071

ically, a few reports about the GaAs clusters could be found [5–16]. For the neutral Ga_4As_4 cluster, Mohammad et al. considered three structures (T_d, C_i, D_{2d}) using an ab initio molecular-orbital method [9], and Song et al. examined six structures, which are a rhombic prism structure, a planar octahedron structure, an edge-capped pentagonal pyramid structure, an edge-tricapped rhombus structure, a double bicapped rhombus structure, and a double rhombus structure, using ab initio method [10]. Vasiliev et al. studied the absorption spectra of two Ga_4As_4 clusters using a time-dependent density-functional formalism within the local density approximation [11]. In Song's report, the rhombic prism symmetry structure was regarded as the ground-state structure for a Ga_4As_4 cluster [10]. Other authors thought of the C_i structure as the lowest energy structure [5,6,8,9,11]. Wei Zhao et al. calculated the Ga_4As_4 cluster using the FP-LMTO MD method [13]. They found a new edge-capped pentagonal bipyramid structure as its ground-state structure. Its binding energy is much larger than that of the C_i symmetry structure [13]. For a Ga_5As_5 cluster, Lou et al. presented two structures using the Dmol method. Their binding energies were comparatively low. The ground-state energy structure is a tetracapped trigonal prism (TTP) structure [5]. Andreoni considered three structures [7], while Yi considered one structure (a cube-based structure) using cp method [16]. Vasiliev et al. also studied the absorption spectra of two Ga_5As_5 structures [11]. Zhao et al. also studied the Ga_5As_5 cluster using FP-LMTO MD method [14]. They presented 27 stable structures for the neutral Ga_5As_5 cluster. A two-capped cube structure was regarded as its ground-state structure [15]. They also investigated 9 stable structures for neutral Ga_6As_6 cluster [16]. Among those studies, the calculations are confined to the neutral Ga_nAs_n clusters. In fact, on charging the neutral clusters, their structures and properties change significantly. However, to our best knowledge, no reports on the ionic Ga_nAs_n clusters have been found up to now. Therefore, it is necessary to investigate the ionic Ga_nAs_n clusters.

In this Letter, we investigate the ionic Ga_nAs_n ($n = 4$–6) clusters using full-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method. Our main aim is to search their ground state structures and investigate the influence of charging on the neutral clusters.

2. Method

The full-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method is a self-consistent implementation of the Kohn–Sham equations in the local-density approximation [17–20]. During the molecular-dynamics calculations, space is divided into two parts: non-overlapping muffin-tin (MT) spheres centered at the nuclei, and the remaining interstitial region. LMTOs are augmented Hankel functions inside the MT spheres, but not in the interstitial region [21–24]. Self-consistent calculations are carried out with a convergence criteria of 10^{-5} a.u. on the total energy and 10^{-3} a.u. on the force. The details of how the molecular dynamics method can be performed are described in references [21–24]. We have investigated Si_n cluster and Ge_n clusters using the method [25–28]. The calculated results from the method are in good agreement with those obtained by some other advanced molecular dynamics methods [29,30]. In this Letter, we obtain a number of new isomers by means of FP-LMTO-MD method. But, only some representative structures are presented below in order to stress the essentials of the clusters.

3. Structures and discussions

In order to systematize the search for the equilibrium structures of the Ga_nAs_n clusters, we need many initial geometric configurations as seeds. There are hundreds of possibilities of arranging two kinds of atoms to form a Ga_nAs_n ($n = 4$–6) cluster. In our calculations, the main initial atomic configurations are set up by random selections of atomic positions in three-dimensional space. The separation of the atoms is confined in some range. In addition, some initial configurations are selected from the stable structures of their corresponding neutral clusters. A series of final stable structures are obtained after hundreds of initial geometric configurations were relaxed. In some cases, the geometrical optimization of several different initial configurations is found to give one and the same structure upon optimization. Because we adopt enough initial geometric configurations including almost all the arrangement of two kinds of atoms, we have good reason to say that the structures with largest binding energies in this Letter are the ground state structures