

First principle study on the bonding mechanism of nanoring structure Ga_8As_8

L.Z. Sun, X.S. Chen^a, X.H. Zhou, Y.L. Sun, Zh.J. Quan, and Wei Lu

National Laboratory of Infrared Physics, Shanghai Institute for Technical Physics, Chinese Academy of Sciences, 500 Yu-Tian Road, Shanghai 200083, P.R. China

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Abstract. The stable ring structure of Ga_8As_8 has been found by the first principle calculations previously. Here we use the full-potential linearized augmented plane wave (FP-LAPW) method within the framework of the density functional approach to investigate the electronic structure and bonding mechanism of the ring structure. The stable and equilibrium ring structure is confirmed again and the relationship between the nanoring structure and the bulk materials is obtained by the comparison of the density of states (DOS) and bonding charge density of the ring structure with that of the bulk GaAs materials. The valence charge density and the bonding charge density of the ring structure are obtained, and then the bonding characteristics are analyzed. The calculations reveal that the bonding of the ring structure of Ga_8As_8 is with covalent bonding characteristic and in the same time the homo-bond Ga-Ga in the side face of the ring structure is found.

PACS. 36.40.Cg Electronic and magnetic properties of clusters – 71.15.Nc Total energy and cohesive energy calculations

1 Introduction

The electronic structure and bonding mechanism of clusters have been drawing a great deal of attentions since clusters links the gap between isolated molecule and bulk material. On the one hand, people are interested in how the structure and electronic properties of clusters approach to that of bulk materials as their sizes (atomic number of clusters) increase. On the other hand, due to the existence of isomers for a certain size clusters, the studies of clusters become more complex. In this way, experiments cannot be properly interpreted without detailed knowledge of the electronic and geometrical structure of the cluster. At present, such information can best be provided by theoretical calculation, especially with the first principle method. In the same time, the structural and electronic properties of semiconductor clusters have been extensively studied because of their fundamental interest and potential application in nano-electronics, such as small gallium arsenic clusters.

Liao et al. have computed the optimized geometries and energy separations of several electronic states of Ga_3As_2 and Ga_2As_3 clusters by using the completed active space multiconfiguration selfconsistent-field (CASSCF) followed by multireference singles + doubles configuration interaction (MRSDCI) computations which included up to 1.9 million configurations [1]. Graves et al.

have found the D_{2h} , C_1 , and C_i symmetry for the equilibrium structures for Ga_2As_2 , Ga_3As_3 , and Ga_4As_4 respectively with the self-consistent field (SCF) Hatree-Fock calculations [2]. The computational method DMol based on the local density approximation (LDA) has been used to interpret the electronic structure for the Ga_xAs_y clusters ($x + y \leq 10$) [3]. In recent years, the time-dependent density-functional formalism within the local density method [4], first-principle pseudopotential calculations [5] and FP-LMTO MD method [6] etc also have been used to investigate the electronic structure of the Ga_xAs_y clusters, and the total numbers of the atoms in the clusters increase to 12 [5]. In reference [7], the stable and most symmetrical ring structure of the Ga_8As_8 clusters has been found with the General Atomic and Molecular Electronic Structure System program. The equilibrium geometric structure, IR and Raman spectra, and the polarizabilities properties have been reported. In this paper, the electronic properties (including the bonding charge density, density of states (DOS), and charge transfer in the bonding process) of the cluster Ga_8As_8 have been studied by using the full-potential linear augmented plane wave (FP-LAPW) method within the density-functional theory (DFT) framework.

2 Computational procedure and method

The calculations are performed within the framework of the density functional theory [8] combined with the

^a e-mail: xschen@mail.sitp.ac.cn

Perdew-Burke-Ernzerhof (PBE) exchange-correlation potential [9], using the WIEN2K package [10] which is the implementation of the FP-LAPW method. In order to ensure well convergence, the muffin-tin radius and the number of k -points have been chosen after optimization. A satisfactory convergence has been achieved by considering a number of FP-LAPW basis functions up to $R_{MT}K_{max} = 6.0$ for the supercell, where the K_{max} is the maximum value of the plan wavevector which determines the so called energy cutoff for the plane wave expansion. The states treated as valence are As($3d^{10}4s^24p^3$) and Ga($3d^{10}4s^24p^1$), and the muffin-tin radii are 2.40 and 2.30 atom unit (a.u.) for As and Ga, respectively. The self-consistent iteration is considered to be converged when both the total energy and the total charge in the atomic sphere are stable within 10^{-4} eV per unit cell and 10^{-4} electron charges per atom, respectively. In order to avoid the interaction between the clusters, $15 \times 15 \times 15 \text{ \AA}^3$ super-cell has been used in present paper. The relaxation procedures are calculated following the damped Newton dynamic scheme [11,12]. The equilibrium structure is obtained by considering the forces on the ions to be below 0.05 eV/\AA . In order to interpret the bonding mechanism of the cluster, the valence charge density and bonding-charge density have been calculated with the formula [13] as below:

$$\Delta\rho(r) = \rho_{solid}(r) - \sum_{\alpha} \rho_{\alpha}(r - r_{\alpha}) \quad (1)$$

where $\rho_{solid}(r)$ is the charge density of the equilibrium structure, $\rho_{\alpha}(r - r_{\alpha})$ is the charge density of the atom α . Therefore, the bonding-charge density represents the net charge redistribution as atoms are brought together to form the ring structure. To obtain a measure of the hybridization strength between the orbitals in the system, one can examine the density of states (DOS) and its partial density of states (p -DOS) which show how the ‘‘atomic’’ levels evolve into band states. The total and partial density of states are calculated using the modified tetrahedron integration method [14] and is broadened using a Gaussian-like function with full width at half maximum (FWHM) equal to 0.1 eV.

3 Results and discussions

The relaxation calculations with the damped Newton dynamic scheme within the FP-LAPW method confirm that the four layers ring structure of Ga_8As_8 clusters is the stable and equilibrium structure again. The equilibrium ring structure of Ga_8As_8 clusters as shown in Figure 1. The atoms As(1~4), Ga(9~12), As(5~8), and Ga(13~16) form the four layers and in each layers the four arsenic and four gallium atoms form the square configuration respectively. And each atom has three nearest neighbors and form three hetero-bond. The bond length and the bond angle have some trivial changes in comparison with the results in reference [7] and the changes make the cluster closer to pure C_{4v} symmetry. The bond length of Ga-As between the neighbor layers are about $2.448 \sim 2.450 \text{ \AA}$.

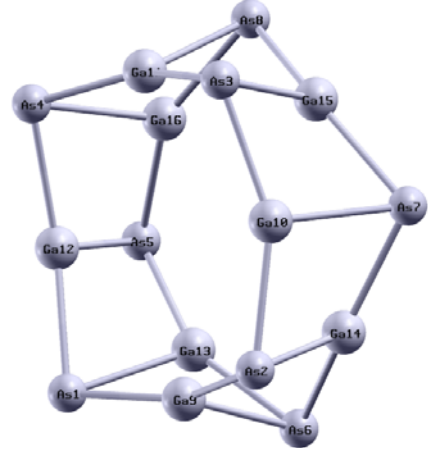


Fig. 1. The equilibrium ring structure of Ga_8As_8 clusters.

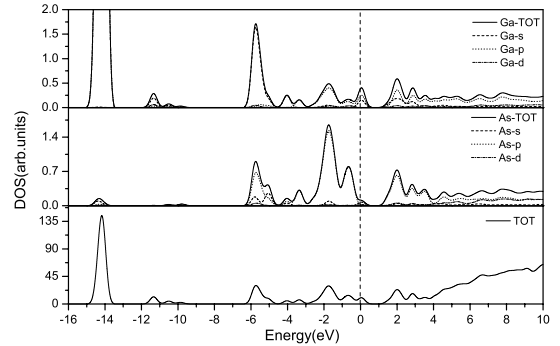


Fig. 2. The total density of state (DOS) of Ga_8As_8 and the total DOS of As and Ga in the Ga_8As_8 . The Fermi level locates zero.

It is well-known that the valence band maximum (VBM) and the conduction band minimum (CBM) in general III-V semiconductors mainly derive from the p states of the group V atoms and the s states of the group III respectively. The total DOS and partial DOS results of Ga_8As_8 ring structure, as shown in Figure 2, show that the VBM and CBM mainly come from the arsenic p electronic states and both anions p states and cations s states respectively. The calculations revealed that the contribution of the As- p states in the CBM is larger than Ga- s states. In Figure 2, there is a peak about -5.8 eV at the bottom of the first region of the valence band in the total DOS in similar to that of the bulk materials, coming from the Ga- s electronic states. We can see from DOS clearly that the Fermi level lies in the valence band. There are two empty states above the Fermi level which means that the Ga_8As_8 cluster possess metallic characteristic. As mentioned above, the ring structural clusters Ga_8As_8 belong to the C_{4v} symmetry, namely the atoms in the same layer are equivalent, respectively. There are only four un-equivalent atomic sites in the ring structure. The partial density of states of the As1- p state and As8- p state (the two atoms in different layers) in Figure 3 reveal the different properties of the atomic sites projected in the same coordinate. The partial projected states p_x and p_y are the projection in the layer plane and the p_z

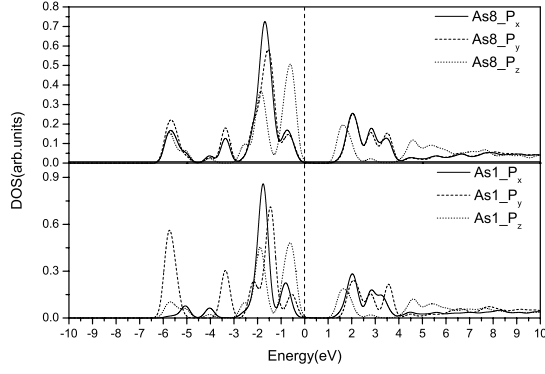


Fig. 3. The comparison of the partial DOS of p state for the two arsenic from different layers. The Fermi level locates zero.

is the projection parallel to the rotate axis of the ring structure. The partial state p_z almost shows the same electronic state distribution for both different atom layers since along the rotated axis directions two un-equivalent arsenic atoms nearly have the same bonding mechanism. For the p_y projection of As1 there is one Ga-As bond in the layer plane along the projection direction and the angle of p_x projection of As1 is smaller than that of the As8. This makes the energy position of p_x and p_y projection of As1 shift up. The different projection of p_x and p_y for the two un-equivalent atom layers give rise to different electronic splitting states in the total DOS. In Figure 3 we can see that the VBM characteristic is mainly determined by p_z partial states.

In order to interpret the bonding mechanism of the Ga₈As₈ clusters, the total charge density and the bonding-charge density have been calculated on the plane determined by three atoms in Figures 4 and 5, such as, Ga9-As1-Ga12 plane of the ring structure and Ga9-As1-Ga13 plane in the side face of the ring structure. In the DIFF figures, dash and solid lines denote negative and positive charge density relative to the atom charge density respectively. The positive (negative) charge redistribution can be identified with electronic transfer into (outward) bonding or anti-bonding electronic states. Compare of the both DIFF results, we can find that Ga9 have more anti-bonding charge density in the Ga9-As1-Ga13 plane than that in the Ga9-As1-Ga12 plane. Moreover in the Ga9-As1-Ga13 plane, there are charge accumulation and distribution between the Ga9 and Ga13. This means that the Ga-Ga homo-bond exist in the side face of the ring structure. The figures show strong covalent characteristics of the bond As-Ga in both planes. In order to reveal the characteristics clearly, the valence charge density along the bond line of As-Ga has been calculated as shown in Figure 6. The valence charge density along the As-Ga bond line of the GaAs bulk materials is also included in the figure. The results reveal that in the As-Ga bond from either the cluster Ga₈As₈ or the GaAs bulk materials, the middle region of the bonds concentrate the bonding electrons. Figure 6 also indicates that the bonding electrons more concentrate along the bonding line in the bulk materials than that of the Ga₈As₈ clusters.

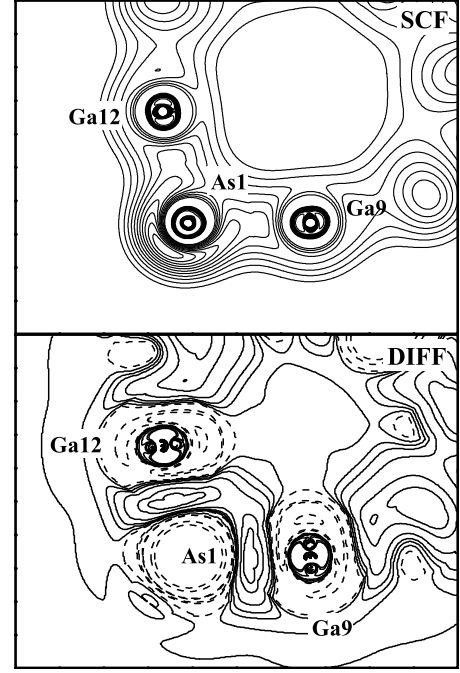


Fig. 4. The charge density (denoted by SCF) and bonding charge density (denoted by DIFF) of Ga₈As₈ clusters in the plane Ga9-As1-Ga12. The contour step size is $0.8 \times 10^{-3} \text{ e/a.u.}^3$ for the total charge density (SCF) and $0.2 \times 10^{-3} \text{ e/a.u.}^3$ for the bonding charge density (DIFF).

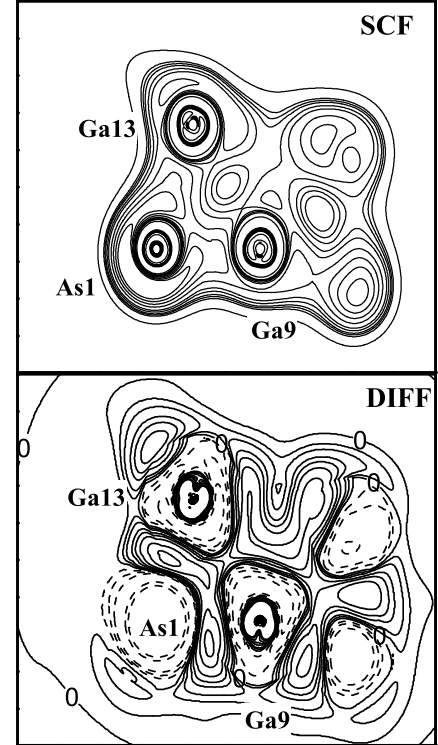


Fig. 5. The charge density (denoted by SCF) and bonding charge density (denoted by DIFF) of Ga₈As₈ clusters on the plane Ga9-As1-Ga13. The contour step size is $0.8 \times 10^{-3} \text{ e/a.u.}^3$ for the total charge density (SCF) and $0.2 \times 10^{-3} \text{ e/a.u.}^3$ for the bonding charge density (DIFF).

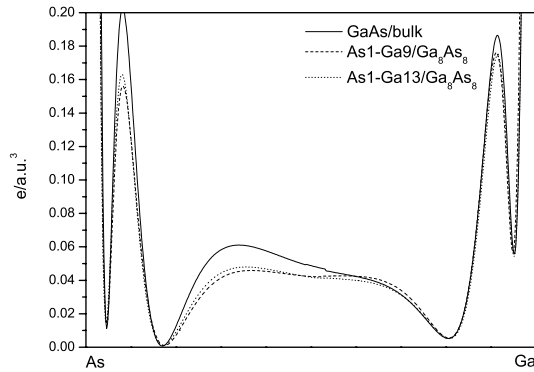


Fig. 6. The total charge density along the bond line of As1-Ga9, As1-Ga13 and As-Ga bond in GaAs bulk materials.

Table 1. Atomic charge (e^-) within the atomic basins of Ga and As (As1 and Ga9 in Ga_8As_8 clusters) are calculated according to Bader's topological analysis.

	As	Ga
As_8Ga_8	-0.75759	0.95086
GaAs-bulk	-0.71289	0.70819

It is well-known that the topological analysis [15] following Bader's "atoms in molecules" (AIM) theory is considered to be a useful tool for a quantitative description of the charge-density distribution. This method gives a unique definition of partitioning space into atomic basins by simply knowing the total charge density. The atomic basin is defined as a region of space traversed by trajectories of the density gradient termination at a given nucleus and enclosed inside a zero charge density flux surface. Table 1 contains total charges of As and Ga in GaAs bulk materials and Ga_8As_8 clusters defined as the integrated densities inside the atomic basins. The results indicate that there is more ionicity of the Ga-As bond of the cluster than that of the bulk.

4 Conclusion

The full-potential linearized augmented plane wave (FP-LAPW) method within the framework of the density functional approach has been used to investigate the electronic structure and the bonding mechanism of the ring structure cluster Ga_8As_8 . The stable Ga_8As_8 ring structure of four atomic layers with C_{4v} symmetry is confirmed again. The

bonding mechanism calculations show the Ga-Ga homobond in the side face of the ring structure. The different and common electronic structure, and the bonding mechanism for the Ga_8As_8 clusters and GaAs bulk materials have been discussed. The ionicity of the Ga-As bond in the bulk and clusters has been compared by the integrated basin charge.

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