

Study The Effect Of Sulfur Atoms On The Electronic Structure For The Gallium Arsenide Nanocrystals Of Eight Atoms

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Abstract:

Ab initio restricted Hartree-Fock (RHF) method coupled with the large unit cell method (LUC) is used to simulate 8 atoms GaAs nanocrystals. To determine the electronic structure and some physical properties (total energy- the degeneracy of energy levels- the ionicity). The present work has been divided into two parts core part and surface part where in core part we used eight GaAs nanocrystal atoms while we used four sulfur atoms in the surface in one direction Z-axis. We reached that the best value to the lattice constant to GaAs nanocrystal is 5.18 Å and the surface is readused the energy gap.

الخلاصة

تم استخدام طريقة المبادئ الأساسية المحددة لهارتري-فوك وتقريب خلية الوحدة الكبيرة لدراسة ثمان ذرات من بلورة الغاليوم ارسنايد النانوية حيث تم دراسة التركيب الالكتروني وبعض الخصائص الفيزيائية (الطاقة الكلية-درجة الانحلالية- الايونية) ولقد تم تقسيم العمل الى جزئين الاول هو الجزء الخاص بالقلب و الثاني الجزء الخاص بوجود سطح للبلورة ولقد استخدمت ذرات الكبريت S لتكون سطح هذه البلورة. وقد اظهرت النتائج ان قيمة افضل ثابت شبكي لهذه البلورة ٥.١٨ انكستروم والتأثير الواضح للسطح على فجوة الطاقة اي بوجود ذرات الكبريت عنما بعدم وجودها وايونية البلورة حيث نلاحظ نقصان فجوة الطاقة كذلك التغير في تركيز الشحنة لكل من ذرات Ga و As.

Introduction

GaAs is a III-V compound semiconductor composed of the element gallium (Ga) From column III and the element arsenic (As) from column V of the periodic table of the elements. GaAs was first created by Goldschmidt and reported in 1929, but the first reported electronic properties of III-V compounds as semiconductors did not appear until 1952 [Nayak et al. , (2006)]. It consists of two F.C.C. lattice overlapping with each other and from the other one is shifted by a quarter, shown in figure 1.

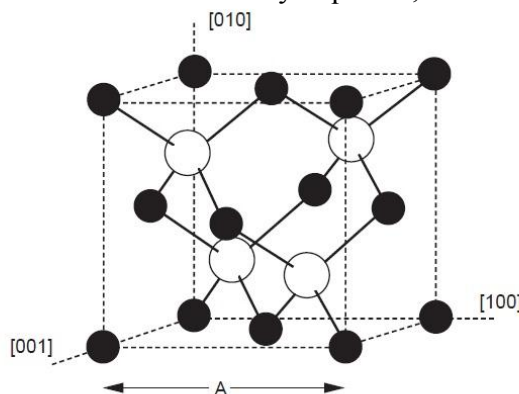


Fig.1 Unit cube of GaAs crystal lattice [Nayak et al., (2006)]

GaAs is a direct band gap semiconductor, which means that the minimum of the conduction band is directly over the maximum of the valence band (For undoped GaAs, the energy band gap at room temperature is 1.42 eV [Nayak et al. , (2006); Chiang, 1975]. Transitions between the valence band and the conduction band require only a change in energy, and no change in momentum, unlike indirect band-gap semiconductors such as silicon (Si). This property makes GaAs a very useful material for the manufacture of light emitting diodes and semiconductor lasers, since a photon is emitted when an electron changes energy levels from the conduction band to the valence band. Alternatively, an incident photon can excite an electron from the valence band to the conduction band, allowing GaAs to be used in photo detectors. Electronic structure of GaAs has been studied extensively because it is widely used in electronic products [Nayak et al. , (2006); Chiang, 1975].

Theory:

The most rigorous approach to the problems of condensed matter physics is the first principles methods (ab initio). They don't employ any empirical parameters in the calculations. The results are based on quantum mechanics and well controlled approximations. The most employed methods using first principles methods are the Hartree-Fock method which divided into restricted and unrestricted [Stevenson, 2005]. To be able to perform ab initio calculations for large molecules in acceptable time, we must accept further approximations either in the wavefunctions or in the Hamiltonian. The wavefunctions are expanded as linear combinations of suitably chosen basis functions (which favors the use of Gaussian functions because they allow an easy computation of overlap and exchange integrals). In the Hamiltonian, the electron-electron interaction terms provide the most difficult part, because they act between all pairs of electrons in the molecule or crystal system so that a change in one electron coordinate affects all other electrons. The HF method is the basis for the most accurate calculations which can be performed today on fast computers for small to medium sized molecules [Grotendorst *et al.*, 2000]. For a given molecular system the Schrodinger equation, the most important equation in modern science, is:

$$\hat{H}\Psi = E\Psi$$

Where H is the Hamiltonian operator, Ψ is the total wave function, and E is the energy eigen value. The time independent Hamiltonian operator of concern in most ab initio computations is given as:

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN}$$

Where T_N and T_e are the kinetic energy operators for the nuclei and electrons respectively. V_{ee} , V_{eN} , and V_{NN} are the potential energy operators between electron-electron, electron-nucleus and nucleus-nucleus respectively. Hamiltonian operator for a closed-shell system in which molecular orbitals MOs must contain two or zero electrons (sometimes called restricted Hartree-Fock) can be expressed as:

$$H = -\frac{1}{2} \sum_i^{2n} \nabla_i^2 - \frac{1}{2} \sum_A^N \frac{1}{M_A} \nabla_A^2 - \sum_i^{2n} \sum_A^N \frac{Z_A}{r_{iA}} + \sum_{i>j}^{2n} \frac{1}{r_{ij}} + \sum_{A>B}^N \frac{Z_A Z_B}{R_{AB}}$$

For 2n electrons and N nuclei, ∇_i^2 is the Laplacian operator for the ith electron, ∇_A^2 is the Laplacian operator for the nucleus A, M_A is the mass of nucleus A, Z_A is the atomic

number of nucleus A, r_{iA} is the distance between the i th electrons and nucleus A, r_{ij} is the distance between nuclei i th and j th electrons, and R_{AB} is the distance between nuclei A, B. The indices $i > j$ and $A > B$ in the fourth and fifth terms are necessary to prevent counting the same interaction twice. Where we have used Hartree's atomic units ($\hbar = m_e = e = 1$) [Hegre et al., 1986; Sodergren, 2004].

The equations below are commonly known as the Hartree-Fock equations which state that the best molecular orbitals are all eigen functions of the Fock operator, Where 1, 2 refers to the first and the second electrons respectively. [Atkins *et al.*, 1997; Hassan, 2011]

$$\left[H^{core} + \sum_j (2J_{ij} - K_{ij}) \right] \psi_i = \sum_j \epsilon_{ij} \psi_i$$

Where J_{ij} , K_{ij} are the Coulomb and exchange operator respectively which are defined by [Atkins et al., 1997; Hassan, 2011]:

$$J_{ij} = \iint \psi_i(1) \psi_j(2) \frac{e^2}{r_{ij}} \psi_i(1) \psi_j(2) d\tau_1 d\tau_2$$

$$K_{ij} = \iint \psi_i(1) \psi_j(2) \frac{e^2}{r_{ij}} \psi_i(2) \psi_j(1) d\tau_1 d\tau_2$$

Equation (2-32) can be written in the form [Hassan, 2011],

$$F\psi_i = \sum_j \epsilon_{ij} \psi_j$$

In which F refers to the Fock-Hamilton operator, ϵ_{ij} is the eigen value of the F operator. Large unit cell method (LUC) calculations were performed previously for GaAs nanocrystals with smaller number of atoms. This method uses ($k = 0$) approximation, that is one point in the wave vector space. The LUC method is one kind of supercell methods with the above $k = 0$ restriction. In this method, and instead of adding more k points, the single central cell is expanded to contain more atoms, which are now called core atoms in the present work. We found this method very suitable for describing the core of a nanocrystal since it still has the outer dangling bonds that are saturated by surface atoms.

Results and discussion:

We will perform the core part calculations using 3-D large unit cell method (LUC). The 2-D calculation for the sulfur surface is added to obtain a complete electronic structure view. The periodic boundary condition (PBC) method, available in GAUSSIAN 03 program [Frisch et al., 2003] is used to perform the present tasks. In figure (2) total energy of 8 atoms GaAs nanocrystal core as a function of lattice constant is plotted we can see that the total energy decreases with increasing the lattice constant till it reaches the equilibrium lattice constant, after the equilibrium lattice constant the total energy increases with increasing lattice constant the behavior of total energy as a function of lattice constant is due to the attraction forces that happened at the large distance between atoms. Decreasing the distance between atoms leads to decreasing the total energy, at shorter distance between atoms the repulsion forces become dominant and happened to

cause the increase of the total energy. The stability of the GaAs nanocrystal at the equilibrium lattice is due to the equality of attraction and repulsion forces at this point where in the present work it equal to -447595.715 eV and the best lattice constant is $5.18\text{\AA}$ while its experimental value is $5.65\text{\AA}$ in the bulk model [Madelong, 1982].

Figure (3) shows that the total energy with the surface has the same behavior for the core with decreasing the values of total energy for surface compared with core the lowering of total energy for surface is caused by broken bonds and discontinuity at the surface leading to decrease in lattice constant, where we found that when lattice constant is $5.18\text{\AA}$ the total energy is -817738.9958 eV [Ye et al., 2008; Hassan, 2011].

The density of states of (8 atoms core LUC) GaAs nanocrystal as a function of the energy levels was calculated for both core and surface parts in figures (4,5) respectively, high density of states can be seen in the core compared with the density of states of the surface that is shown in figure(5) causes by the broken symmetry and the discontinuity at the surface and the existence of new kind of atoms (sulfur atoms) that lead to varying the bond and then changing the geometry of the structure .

The levels are set relative to the highest occupied molecular orbital (HOMO) in the two cases [Sigg et al., 2002; Buttermann et al., 2004]. The atomic charge of sulfurated (001)-(1x1) surface calculated for (8) atoms are drawn as a function of layers, as shown in figures (6,7). The change of atomic charge for GaAs nanocrystal by the effect of sulfur atoms is obvious from the figure (7). The adding of the sulfur atoms decreases the ionicity of the crystal surface. As we see, through the first few layers, the surface with existing sulfur atoms is much affected. After these layers, the surface effect may be neglected and the results reach to the bulk. Sulfur atoms drag less charge from gallium atoms than arsenide atoms because of the high affinity of gallium atoms. Figures (8,9) refers to the structure of 8 atoms GaAs in LUC and 2D slab calculations of (001) sulfurated of GaAs nanocrystal respectively.

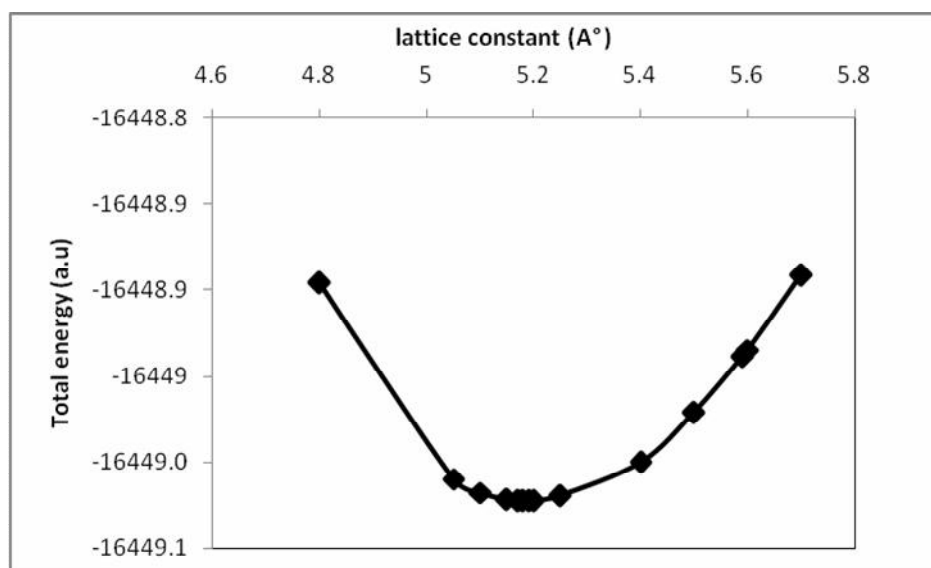


Fig.2 Total energy of 8 atoms GaAs core LUC as a function of lattice constant

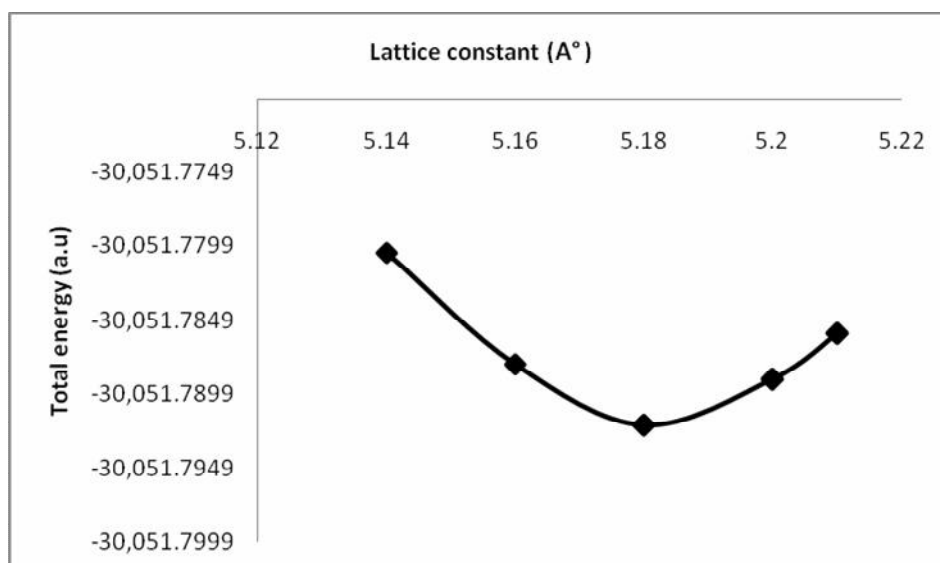


Fig.3 Total energy of surface S on GaAs core LUC As-S as a function of lattice constant

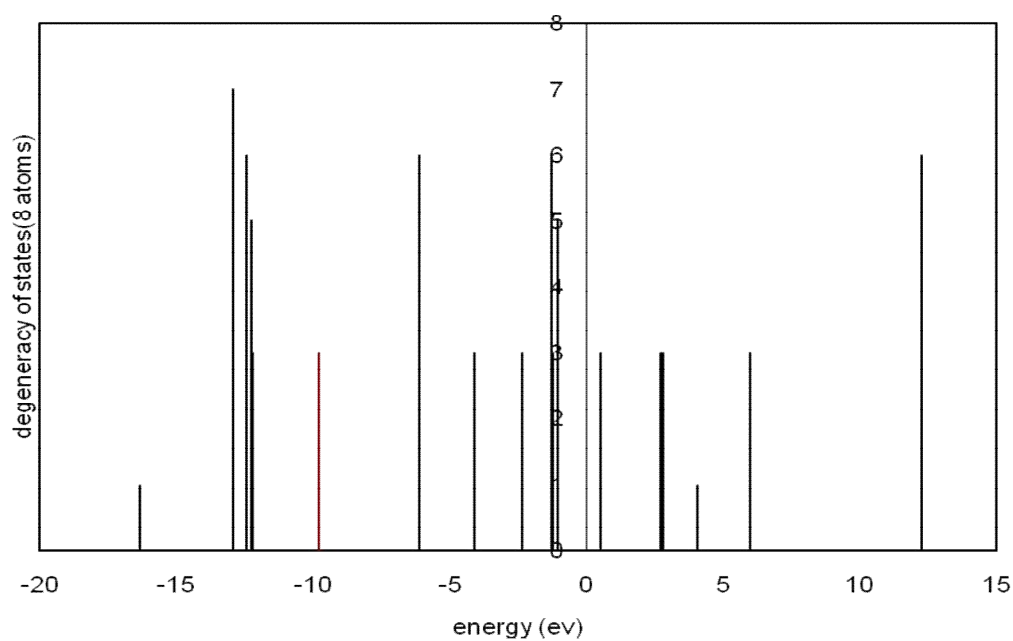


Fig.4 The Degeneracy of energy levels of 8 atoms LUC core

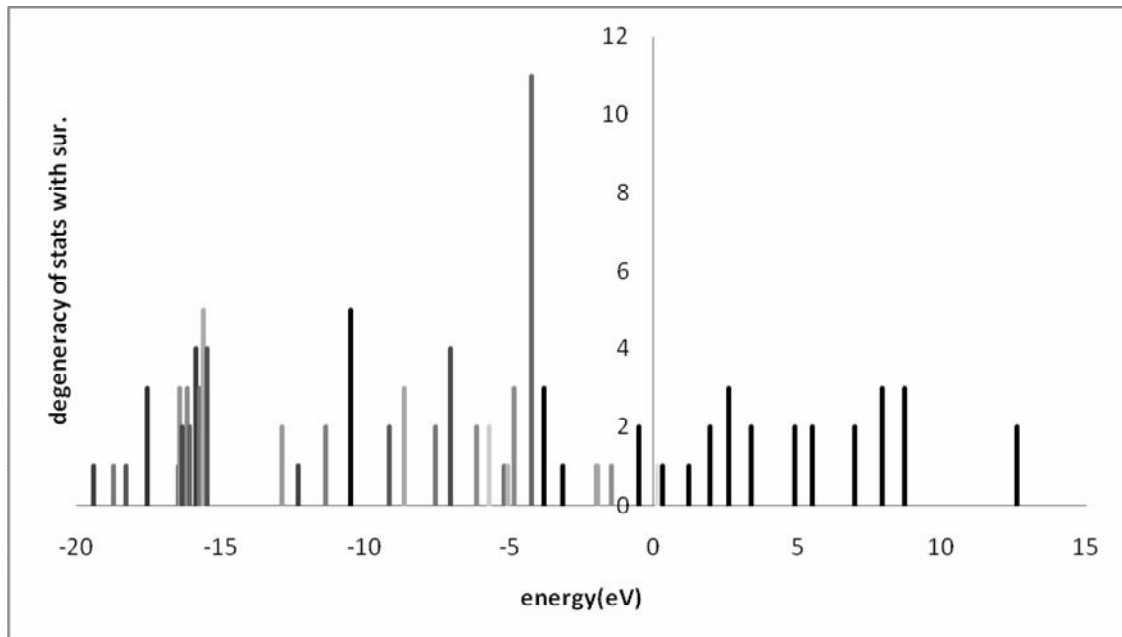


Fig.5 The Degeneracy of energy levels of 8 atoms LUC with surface

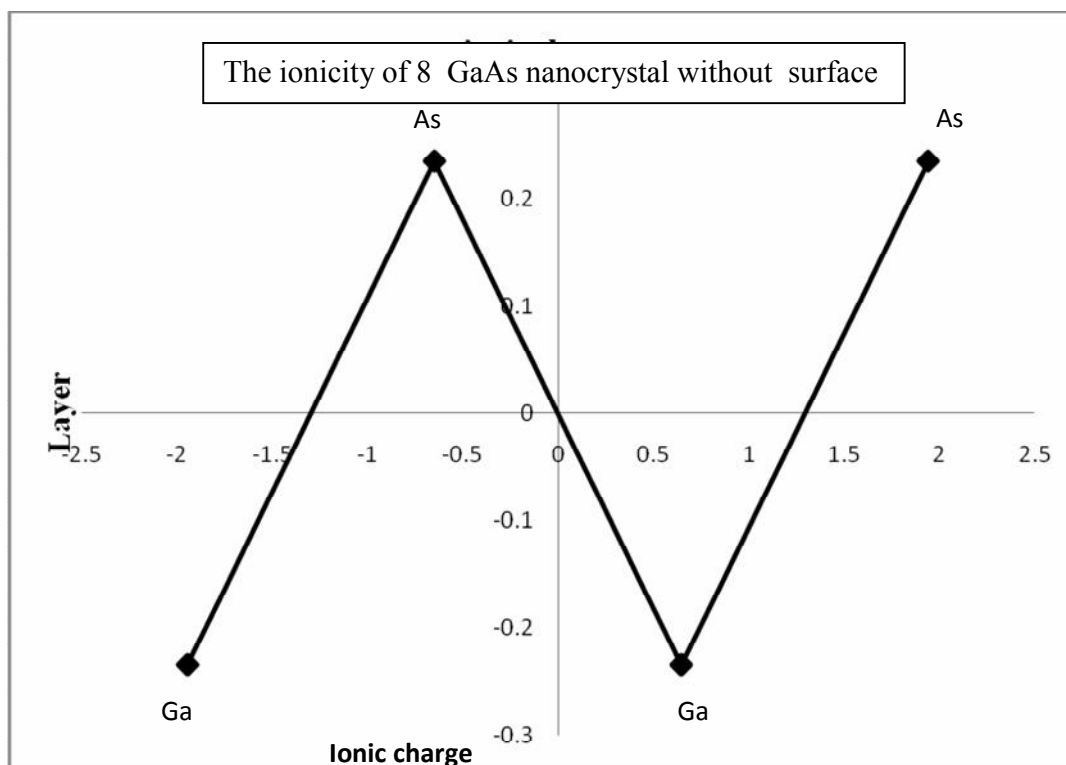


Fig.6 The ionicity of 8 GaAs nanocrystal without surface

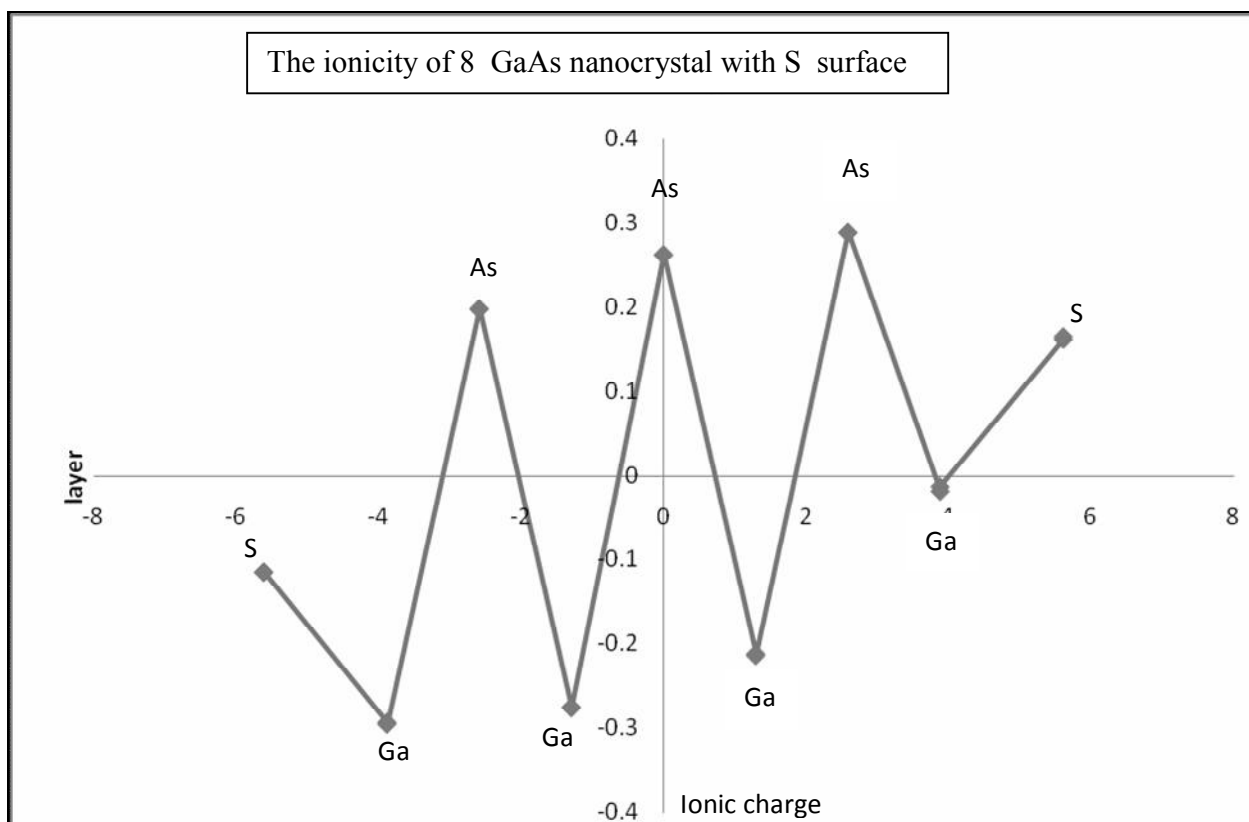


Fig. 7 The ionicity of 8 GaAs nanocrystal with surface

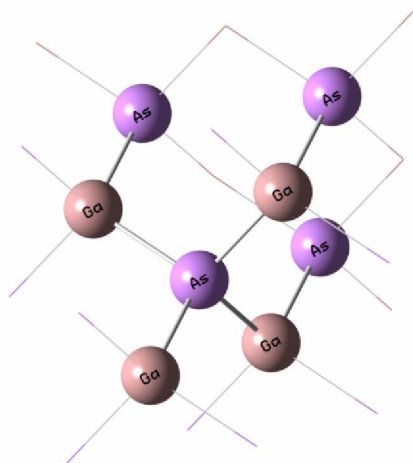


Fig.8 The structure of 8 atoms GaAs in LUC

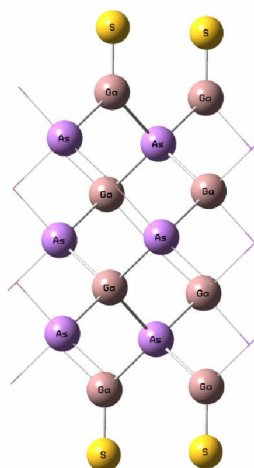


Fig .9 2D slab calculations of (001) sulfurated of GaAs nanocrystal

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