

Analytical Model for the Effect of Pressure on the Electronic Structure of Germanium Nanocrystals

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Abstract

The electronic structure modification of germanium nanocrystals under the condition of external pressure has been investigated, in order to gain a better understanding of their relevant properties. In this paper, an atomistic insight into the effect of size-pressure variation on the electronic structure of germanium nanocrystals (of 8, 16, 54 atoms) is performed. The effect of pressure on the structural and electronic properties of germanium nanocrystals has been investigated using the large unit cell within the framework of ab initio restricted Hartree-Fock theory and the linear combination of atomic orbital approximation included in Gaussian03 software by considering the effects of size and pressure. Cohesive energy, indirect band gap, valence bandwidth and bulk modulus are all obtained, which is consistent with understanding the interdependence of these quantities and their common atomistic origin originates with size- and pressure-induced change, leading to a variation of the crystal potential. Theoretical results are compared with the experimental measurements. The calculations show an agreement of the calculated lattice constant at equilibrium point, cohesive energy, valence bandwidth, and bulk modulus with the experimental data. Computed band gap is greater than the experimental value. That is what expected from Hartree-Fock method. Band gap shows a good trend compared to theoretical values. The calculations of the effect of pressure on the aforementioned properties are investigated. It is found that the valence bandwidth decrease with the increase of pressure, and cohesive energy decrease with the increase of tensile pressure in 8 atoms while it increase in both 16 and 54 atoms. Lattice constant increase with pressure in three crystals, and energy gap decrease with pressure in both 8, and 16 atoms crystals and increase with pressure in 54 atoms nanocrystal. The maximum value of pressure is taken to be 7.6 GPa, because beyond this value, the phase of Ge transforms from nanocrystals to another phase.

II. Introduction

In recent years, the pressure investigations of semiconductor nanostructures such as nanocrystals, nanowires, and nanotubes have become a focus area in condensed matter physics and material science because of their tunable optical properties for applications in optoelectronics, quantum dot lasers, high density memory, bioengineering [1], etc.

Because the electronic structure of semiconductors plays a fundamental role in electrical and optical properties [2], it is important and necessary to investigate the electronic structure change in order to gain a better understanding of their relevant properties. It is difficult to compute static and dynamical properties of crystals such as cohesive energy, bulk modulus and lattice vibrations experimentally.

Thus, it is a significant way to understand the modification of electronic structure of semiconductor nanocrystals under the condition of external stimuli such as pressure, temperature, etc. In this paper, we establish an analytical model and present an atomistic insight into the size effect of the pressure-electronic structure variable of semiconductor nanocrystals under hydrostatic pressure.

IV. Computational details:

We shall perform the core part using the large unit cell (LUC) method[3-6]. The (LUC), which is a kind of supercell methods, was suggested and first applied for the investigation of electronic band structure of bulk materials and in particularly elemental semiconductors in the 70s of the last century [7]. After its success in describing the electronic structure of bulk semiconductors, the method was also applied to a variety of systems. The method was usually coupled with semiempirical methods to overcome ab initio computational difficulties of large scale and deformed systems [6, 7]. The periodic boundary condition (PBC) method available in Gaussian03 program [8] is used to perform the present tasks. The restricted Hartree-Fock (RHF) method (in which the solution is restricted so that the spatial wave functions for paired electrons are the same) is used for molecules in which all the electrons are paired [9].

III. Theory

We used the framework of large unit cell coupled with restricted Hartree – Fock method (LUC- RHF). The

Restricted Hartree – Fock (RHF) method uses the linear combination of atomic orbitals (LCAO)[10] :

$$\psi_i = \sum_u^m C_{ui} \phi_u \quad \dots\dots\dots(1)$$

Here, $C_{\mu i}$ are the combination coefficients. The determination of the combination coefficients is based on the variational methods in quantum mechanics. The variation of these coefficients leads to a set of algebraic equations which are called Roothan –Hall equations [3].

$$\sum_v (F_{\mu\nu} - \epsilon_i S_{\mu\nu}) C_{vi} = 0. \quad \dots\dots\dots(2)$$

In the above equation $S_{\mu\nu}$ is the overlap integral defined by

$$S_{\mu\nu} = \int \phi_\mu(1) \phi_\nu(1) d\tau_1. \quad \dots\dots\dots(3)$$

$F_{\mu\nu}$ is the fock operator matrix given by [6]

$$F_{\mu\nu} = H_{\mu\nu} + \sum P_{\lambda\sigma} [(\mu\nu / \lambda\sigma) - \frac{1}{2}(\mu\lambda / \nu\sigma)]. \quad \dots\dots\dots(4)$$

$H_{\mu\nu}$ is the matrix elements of the core Hamiltonian of a single electron in the field of the nuclei. Its operator representation is given by [11]

$$H_{\mu\nu} = \int \phi_\mu(1) \left[-\frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{r} \right] \phi_\nu(1) d\tau_1. \quad \dots\dots\dots(5)$$

Here Z_A is the charge of nucleus A and the summation is overall nuclei. The density matrix is defined by

$$P_{\mu\nu} = 2 \sum_i^{occ} C_{\mu i}^* C_{\nu i}. \quad \dots\dots\dots(6)$$

The summation is over occupied orbitals only for closed shell systems which are the case in the present work. Two-electron integrals are the most time expensive in the above equations, are defined by [6,11]

$$(\mu\nu / \lambda\sigma) = \int \int \phi_\mu(1) \phi_\nu(1) \frac{1}{r_{12}} \phi_\lambda(2) \phi_\sigma(2) d\tau_1 d\tau_2. \quad \dots\dots\dots(7)$$

The total energy E^T is defined as [6]

$$E^T = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu} \sum_{\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} [(\mu\nu / \lambda\sigma) - \frac{1}{2}(\mu\lambda / \nu\sigma)] + V_{NN} \quad \dots\dots\dots(8)$$

Where the last term of the right side of Eq. (8) represents the inter-nuclear potential energy. All the above integrals are evaluated using Gaussian program [8].

The effect of pressure on the electronic structure and other properties can be calculated from the present theory computational procedure. By the use of our calculated values of the bulk modulus B and its derivative B'_0 , the volume change (V) with applied pressure was calculated using the following equation [12]:

$$P = \frac{B_0}{B'_0} \left[\left(\frac{V_0}{V} \right)^{B'_0} - 1 \right] \quad \dots\dots\dots(9)$$

P is pressure and V_0 is the equilibrium volume at zero pressure.

IV. Calculations and Results

A LUC of 8, 16, and 54 atoms is investigated for Ge nanocrystals. Although these LUCs are used typically to simulate bulk materials, we shall investigate the use of these cells to simulate the interior of nanoclusters. The building blocks of these cells are the Bravais unit cells, so that 8 atom LUC refers to one Bravais or conventional diamond unit cell cube with side a (a is the Bravais lattice constant) surrounded by other lattices to passivate outer bond we calculate the bulk modulus to be 1.191×10^{11} , 1.195×10^{11} , 1.231×10^{11} N/m² for three crystals respectively and this result agrees with experimental value [13].

Table 1: The electronic structure of 8 atoms Ge nanocrystals

(Cohesive energy eV)	Energy gap (eV)	Valance bandwidth (eV)	Stress (Gpa)	Lattice constant (m)
-11.8552	2.6367459	15.84224	-0.000910654	5.30E-10
-11.8544	2.6340248	15.56333	-0.055904961	5.35E-10
-11.8514	2.4272212	14.79952	-0.183609875	5.5E-10
-11.8471	1.8176948	14.31299	-0.557986641	5.6E-10
-11.8412	1.00517434	13.58101	-0.634223908	5.74E-10

Table 2: The electronic structure of 16 atoms Ge nanocrystals

Cohesive energy (eV)	Energy gap (eV)	Valance bandwidth (eV)	Stress (Gpa)	Lattice constant (m)
-11.8552	2.5496707	16.47817	0.00760246	5.2E-10
-11.8545	2.5904872	16.08469	0.000478274	5.26E-10
-11.8514	1.823137	14.32986	-0.183609875	5.6E-10
-11.8472	1.251706	13.89775	-0.423700712	5.7E-10

Table 3: The electronic structure of 54 atoms Ge nanocrystals

Cohesive energy (eV)	Energy gap (eV)	Valance bandwidth (eV)	Stress (Gpa)	Lattice constant (m)
-12.706	3.807929	17.09392	0	5.1E-10
-12.7296	3.816065	16.9969	-0.00065	5.15E-10
-12.7393	3.83939	16.87043	-0.00177	5.17E-10
-12.7363	3.842916	16.55391	-0.00513	5.2E-10

From tables above, it is clear that for optimize lattice constants the increase in tensile stress lead to the decrease in valance bandwidth because the atoms become occasional from each others and this reduce the splitting of energy levels causing reducing in valance bandwidth. Relativistic corrections reduce the gap of the considered nanocrystals by less than 0.3 eV for the Ge nanocrystals [14]. The calculated energy gap is agree with experimental value calculated by [15] This value is very close to the germanium gap calculated using the same geometry [10] and the cohesive energy decreases as the pressure increases in 8 atom crystal because the distance between atoms increased and this reduce attraction force so the nanocrystals can withstand for maximum stress at equilibrium lattice constants [16]. While cohesive energy increase in both 16 and 54 atoms crystals. One can notice from tables above that all electronic properties increase with the increase of the size of nanocrystals from 8 atoms to 54 atoms. The value of pressure we reach is agreed with experimental value (-8 Gpa) calculated by [15] Fig (1) shows the total energy as a function of atomic volume for Ge (54 atoms LUCs core part) which is the same for the others, it is used to calculate bulk modules.

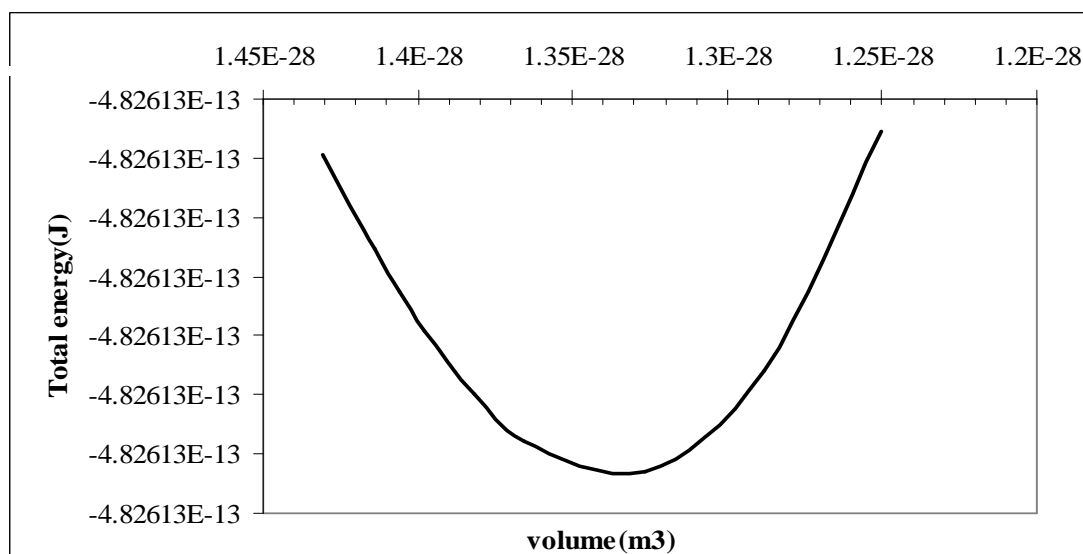


Fig 1: The variation of total energy as a function of atomic volume for (54) of Ge atoms LUC

An interesting phenomenon that may occur at the applied pressure is a sudden change in the arrangement of the atoms, i.e., a structural phase transition of atomic arrangement. The ultimate pressures can lead to an increment in the volume causing enormous changes in the inter-atomic bonding [17]. We notice that the valance bandwidth vary with tensile stress as shown in the figure below

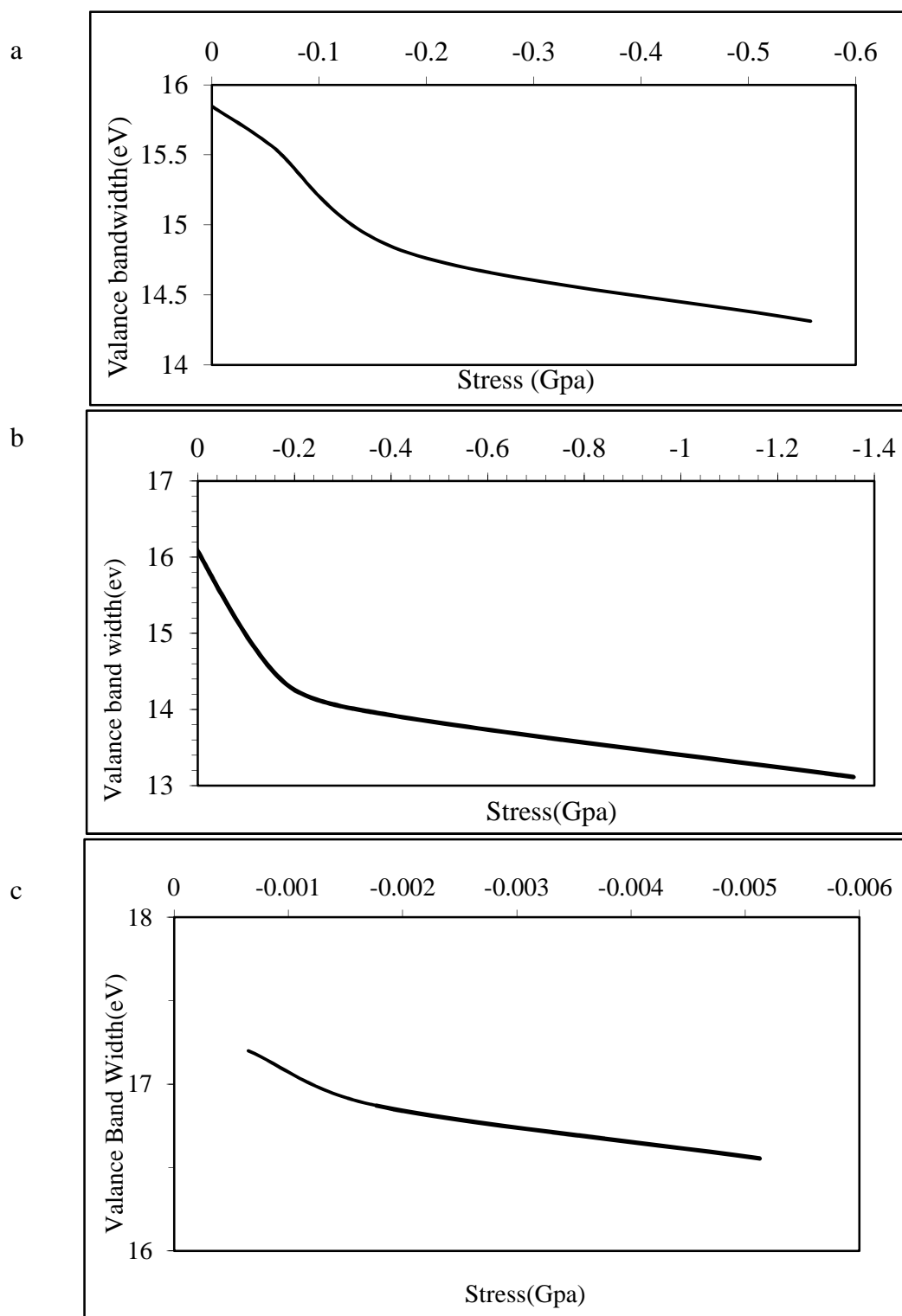


Fig. 2: The effect of pressure on the valence bandwidth for (a.8, b. 16, c. 54) of Ge atoms LUC. The predicted effect of pressure on the valence bandwidth is illustrated in Figure 2. The valence bandwidth decreases with the increases of pressure for all crystals we study this behavior is similar to [17]. The effects of pressure on the energy gaps for these crystals are shown below

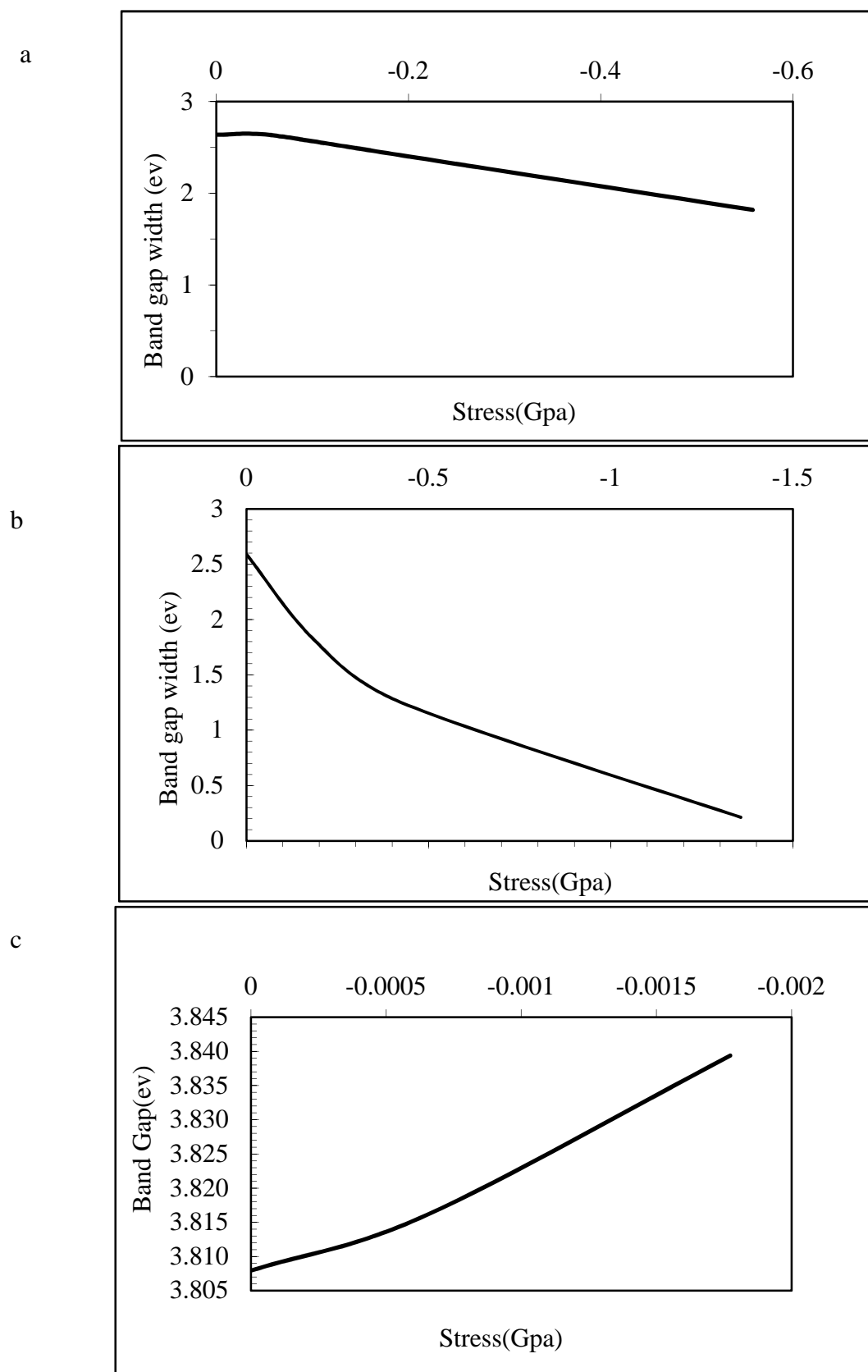


Fig. 3: The effect of pressure on the energy gaps for (a. 8, b 16, c. 54) of Ge atoms LUC

The effect of external pressure could induce band gap minimization in both 8, and 16 crystals, which is well in agreement with the related theoretical results[18] while it increase in 54 crystal which represent a

turning point of the Ge crystal behavior from semiconductor to an insulator. High pressure can lead to more far packed structures compared with those at initial situations at zero pressure[19] Thus, longer bond length results in reinforcing covalency and indicates a way to alter the electronic state of semiconductor nanocrystals. Cohesive energy varies with stress as shown below

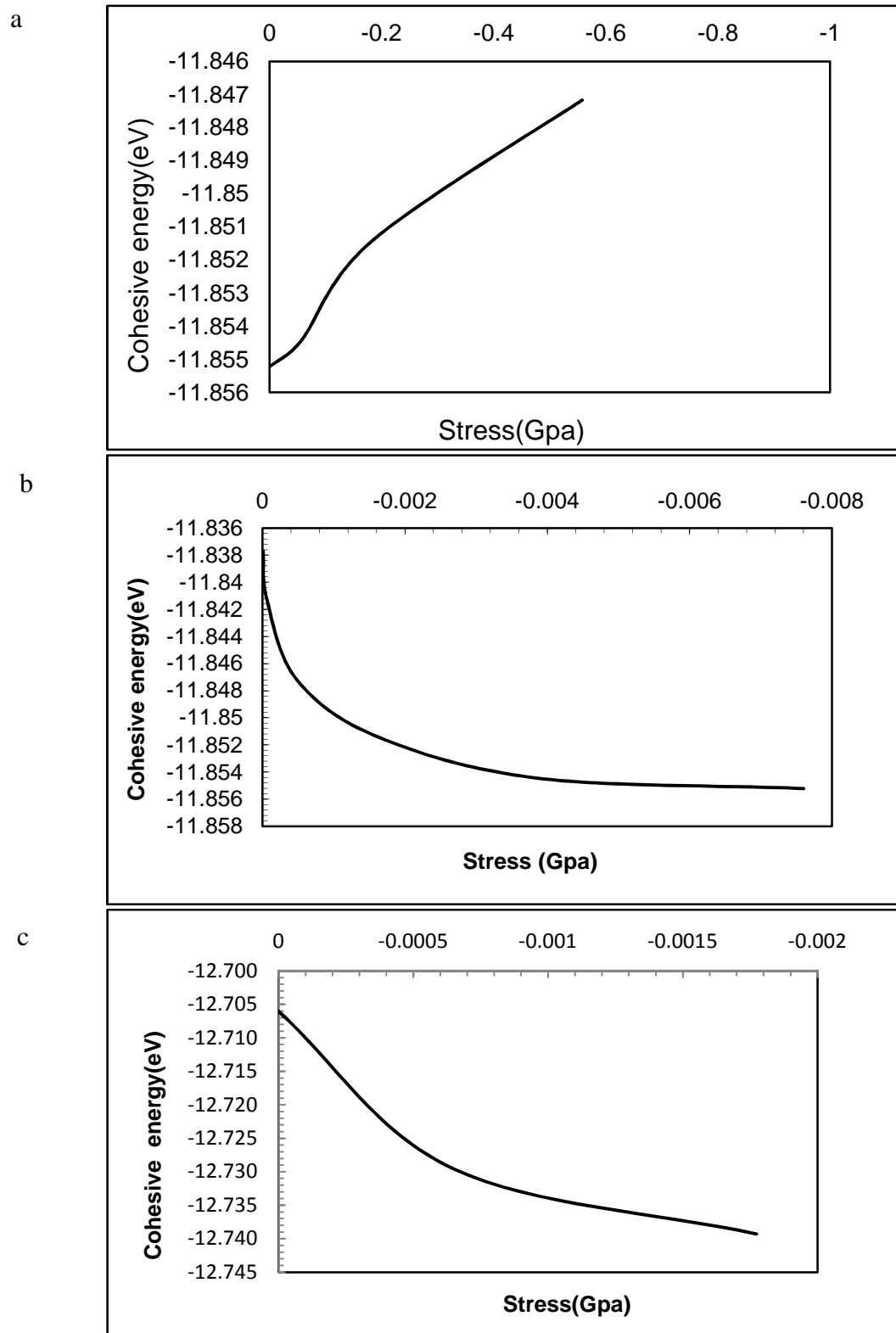


Fig. 4: The effect of pressure on the cohesive energy for (a. 8, b 16, c. 54) of Ge atoms LUC

As shown in figure, the increase in pressure leads to decrease in cohesive energy in 8 atom nanocrystals while an increase in cohesive energy occurs in both 16, and 54 atoms nanocrystals this may belong to the shape of crystal that it is cubic in 8 atom and parallelograms in 16 and 54 atoms in which the direction of applied stress enhance the cohesive energy. In accordance with above considerations, lengthen bond lengths enhance the crystal field and hence band gap energy expansion. It is consequences of the binding energy that can be enhanced. More surprisingly, these factors can strengthen each other on the electronic structures and relevant properties of nanosolids.

The band gap energy depends on the crystal field or a sum of the binding energies over the entire solid. The binding energy, or interatomic potential, depends on the atomic distance and charge quantity of the atoms. Thus, the energy gained by pressure and nanosized effect[20] can tune the band gap energy of semiconductor materials. It implies that it is possible to discover new sources for light emission with a desired wavelength by controlling the physical size or external stimuli. Likewise, the strain of nanostructures would be a more significant role for band gap variation.

Conclusions

In this paper, a study of some properties of ge nanocrystals is presented. The cohesive energy, lattice constant, and bulk modulus, its have been calculated by (Ab-Initio RHF) method. The calculated results indicate that this model gives results in good agreement with the corresponding theoretical results, and this shows the possibility of using this model in qualitative study of some materials. A reasonable agreement of the valence bandwidth is shown in comparison with the available theoretical result. However, there is a large difference between the calculated indirect band gap and the corresponding experimental value because of nano size. The effect of pressure on these properties is investigated. It is found that for optimize lattice constants the increase in tensile stress lead to the decrease in valance bandwidth because the atoms become occasional from each others and this reduce the splitting of energy levels causing reducing in valance bandwidth at the expense of energy gap and the cohesive energy decreases as the pressure increases in 8 atom crystal because the distance between atoms increases and this reduce attraction force so the nanocrystals can withstand for maximum stress at equilibrium lattice constants. While cohesive energy increase in both 16 and 54 atoms crystals that is belong to its shape. One can notice from tables above that all electronic properties increase with the increase of the size of nanocrystals from 8 atoms to 54 atoms. The maximum value of pressure is taken to be 7.6 GPa, because beyond this value of pressure, the phase of ge nanocrystals transforms to another form.

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