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THEORETICAL MODELING OF THE ELECTRONIC PROPERTIES CORE AND SURFACE OF $CdSe_{1-x}Te_x$ CHALCOGENIDE NANOCRYSTALS VIA DFT CALCULATION

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II-VI zinc-blende $CdSe_{1-x}Te_x$ ternary semiconductor alloy nanocrystals core and oxidized surface are investigated using Ab- initio Density functional theory (Ab-initio-DFT) at the generalized-gradient approximation (GGA) level with STO-3G basis set coupled with large unit cell method(LUC). Calculations include only 8 core atoms for concentration (x=0, 0.5, 1) with 3D periodic boundary condition (PBC) and using 2D (PBC) with particular regard to the oxygenated (001)-(1x1) slab geometry surface. Many properties included total energy , cohesive energy , energy gap , valence and conduction band width and density of states for core and surface part have been investigated. The results obtained show that the lattice constant of $CdSe_{1-x}Te_x$ nanocrystal increases with increasing the Te concentration, and the lattice constant for the surface part is smaller than of core part. Results for CdSe and CdTe core part for 8 atoms show the value of energy gap are equal to (1.774 , 3.330)eV respectively, while the energy gap for Cd_8Se_8- O_4 and Cd_8Te_8-O_4 at the same core part are equal to (0.010, 0.054)eV respectively. The energy gap for alloying composition $CdSe_{0.5}Te_{0.5}$ for 8 core atoms is equal to (2.545 eV) its between that for CdSe and CdTe , while the energy gap for $Cd_8Se_4Te_4$-O_4 at the same core part is equal to (0.032) eV.

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1. Introduction

II–VI semiconducting materials are very interesting and potential candidate for this ever-advancing technological fields ,as they show a high efficiency of radiative recombination, high absorption coefficients, and direct band gaps corresponding to a wide spectrum of wavelengths from the UV to IR region, recently ternary alloys of semiconducting materials have received much attention in the fields of optoelectronic devices and solar energy conversion owing to their properties of band gap and lattice constant modulation by composition and other growth parameters[1-3]. CdSe and CdTe semiconductors form a solid solution throughout the entire composition in the compound $CdSe_xTe_{1-x}$. Cadmium Selenid Tellurium films with ‘x’ varying in between 0 and 1 exhibit very interesting semiconducting properties such as direct transition, not very large band gap width (1.35–1.75 eV), and short penetration length of the light.

These materials can be advantageously used for various technological applications in particular for the conversion of solar energy in photoelectrochemical devices and this compound can also be used for the photo-assisted decomposition of water[4]. For best solar energy conversion, the band gap of the semiconductor should be very close to the maximum energy in the visible spectrum to utilize the solar spectrum efficiently. These materials are characterized by different degrees of covalent, ionic, and metallic bonding, and they crystallize in different crystal structures, CdTe compounds have cubic (zinc-blende) structure [5,6], whereas CdSe compounds depending on the growth condition may have both zinc-blende and wurtzite (hexagonal) structures at normal conditions. The main advantage of the $CdSe_xTe_{1-x}$ alloys is its crystal structure and at

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normal conditions. The main advantage of the $CdSe_xTe_{1-x}$ alloys is its crystal structure and tailoring of band gap by changing the concentration of selenium and tellurium, so that solar energy can be effectively harnessed for maximum conversion to electrical energy.

The present work will be involved in calculating electronic properties of $CdSe_{1-x}Te_x$ ternary nanocrystals with concentration for (x=0, 0.5 , 1) for 8 core atoms only.

2. Theory

Density functional theory (DFT) coupled with the large unit cell (LUC) were used in the evaluation of the electronic structure of $CdSe_{1-x}Te_x$ nanocrystals using Hartree-Fock ab-initio method. The Large unit cell (LUC) gives the profits gained from cyclic boundary in simulating the solid . The LUC alters the shape and the size of the primitive unit cell so that the symmetry points in the original Brillion zone at a wave vector k become equivalent to the central symmetry point in the new reduced zone [7, 8]. In this method, the number of atoms in the central cell (at k=0) is increased to match the real number of nanocrystal atoms. The large unit cell method is a supercell method that was suggested and first applied for the investigation of the electronic band structure of semiconductors [9-11]. This method differs from other supercell methods. Instead of adding additional k points to the reciprocal space, the number of atoms in the central cell (k=0) is increased and a larger central unit cell is formed [9]. k=0 is an essential part of the theory of LUC because it uses only one point in the reciprocal space that means only one cluster of atoms exist which is the features of quantum dots [12]. The periodic boundary condition (PBC) method available in Gaussian 03 program is used to perform the present tasks [13].

In the large unit cell method, only the lattice constant is optimized for the core part. However, the surface part bond lengths and angles still need to be optimized because of surface reconstruction. The oxidized surface contains the surface oxygen and outer four layers of $CdSe_{1-x}Te_x$ atoms whereas the core includes the remaining $CdSe_{1-x}Te_x$ atoms.

Gaussian 03 program is used to perform the core LUC and the oxygenated (001)-(1 × 1) surface that can be added to obtain a complete electronic structure view. [14].

We shall use the density functional theory at the generalized gradient approximation (GGA) method level.

Kohn-Sham density theory [15] is widely used for self consistent – field electronic structure calculations of the ground state properties of atoms, molecules, and solids. In this theory, only exchange – correlation energy $E_{XC} = E_X + E_C$ as a functional of the electron spin densities $n_{\uparrow}(\vec{r})$ *and* $n_{\downarrow}(\vec{r})$ must be approximated. the generalized gradient approximation (GGA) [16,17]:

$$E_{XC}^{GGA}[n_{\uparrow}, n_{\downarrow}] = \int \in_{XC} (n_{\uparrow}, n_{\downarrow}, \vec{\nabla} n_{\uparrow}, \vec{\nabla} n_{\downarrow}) n(\vec{r}) d^3 r \tag{1}$$

where $n = n_{\uparrow} + n_{\downarrow}$, $\in_{XC} (n_{\uparrow}, n_{\downarrow})$ is the exchange-correlation energy per electron of an electron gas with uniform spin densities $n_{\uparrow}(\vec{r})$ *and* $n_{\downarrow}(\vec{r})$, using the latter (GGA) very good results for molecular geometries and ground-state energies have been achieved [18].

3. Calculations and results

The nanocrystal core 3D periodic boundary condition (PBC) of $CdSe_{1-x}Te_x$ nanocrystalls calculations has been studied and using 2D (PBC) with particular regard to the oxygenated (001)-(1 × 1) surface is added to obtain a complete electronic structure view. Fig. 1(a) shows the total energy as a function of the lattice constant optimization of 8 atom core part LUC for CdSe, (b) the optimized geometrical structure of CdSe 8 atom core , Fig. 2(a) shows the total energy as a function of the lattice constant optimization of 8 atom core part LUC for Cd_8Se_8- O_4 , (b) the optimized geometrical structure of Cd_8Se_8- O_4 8 atom core. While for CdTe and Cd_8Te_8-O_4 are shown in figs. 3(a , b) and 4(a , b) respectively. However, for $CdSe_{0.5}Te_{0.5}$ and $Cd_8Se_4Te_4$-O_4 are shown in figs. 5 (a , b) and 6 (a , b) respectively.

Stability of the nanocrystal is at equilibrium when lattice constant is equal to (0.587, 0.620, 0.645)nm for core part ,while it is equal (0.585, 0.608, 0.627) nm of the surface part for concentration (x=0, 0.5, 1) respectively, which the attraction and repulsion forces between atoms are equal such as previous studied[10,19].

Fig. 2 shows the total energy as a function of lattice constant and the optimized geometrical structure for the stoichiometry (Cd_8Se_8-O_4) atoms. The optimized bond length (Cd-O) is (1.71 A˚) while that of (Se-O) is (1.67 A˚). However these values in other studies are (2.0A˚) for (Cd-O) and (1.53A˚) for (Se-O) [20] .

The optimized average surface lattice constant of Cd_8Se_8-O_4 is (0.585nm), While its value for 8 atoms for core part (0.587nm) . The energy gap of this stoichiometry is (0.010eV), while in core part is equal (1.774 eV).

From comparing the energy gap of LUC of core with the energy gap of oxygenated (001)-(1×1) surface, we can note that the energy gap at the surface is much less than that at the core. Energy gap has been calculated using the following equation:

Eg = | (LUMO) - (HOMO) | [21]. As a consequence, the energy gap is controlled by the surface of nanocrystals.

Fig. 4 shows the total energy as a function of lattice constant and the optimized geometrical structure for the stoichiometry Cd_8Te_8-O_4 atoms. The optimized bond length Cd-O is 1.7 Å while that of Te-O is 2.0 Å. However, these values in other studies are 1.90 Å of Cd-O and 2.31 Å of Te-O [22]. The optimized average surface lattice constant of Cd_8Te_{8}-O_4 is 0.627 nm, while its value for 8 core atoms part is 0.645 nm. The energy gap of this stoichiometry is 0.054 eV, which in core part is equal to 3.330eV.

Fig. 6 shows the total energy as a function of lattice constant for the stoichiometry $Cd_8Se_4Te_4$-O_4 atoms. The optimized average surface lattice constant of is 0.608 nm, while its value for 8 core atoms part is 0.620 nm .The energy gap of this stoichiometry is 0.032 eV, which in core part is equal to 2.545eV.

The results show that the core states larger energy gap and smaller valence and conduction bands. Owing to perfect symmetry of the core, the core states are more density of states. This reflects the broken symmetry and discontinuity at the surface and existence of new kind of atoms (oxygen atoms), and the variation of bond lengths and angles as well as lattice constant [7,9].

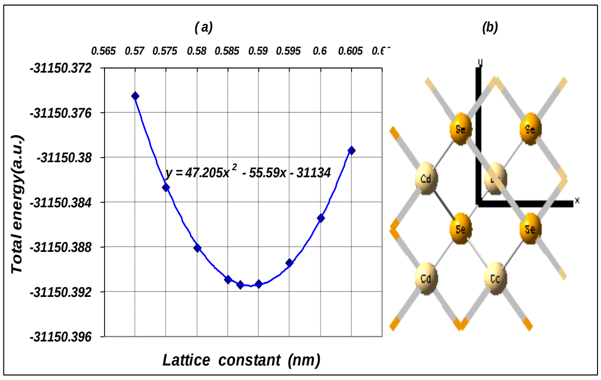

Fig.1 (a) Total energy as a function of lattice constant of CdSe for 8 core atoms per LUC (b) The optimized geometrical structure of 8 atom core

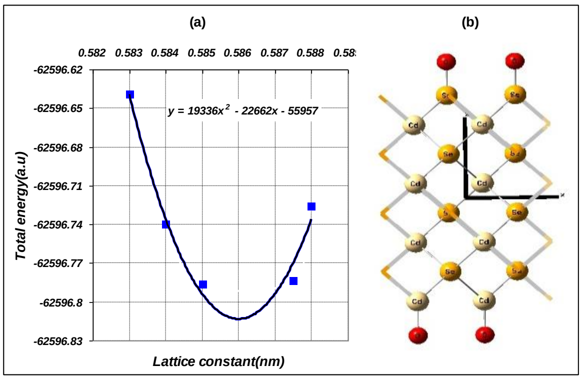

Fig.2 (a) Total energy for 8 core atoms oxygenated (001)-(1×1) Cd_8Se_8- O_4 surface as a function of lattice constant (b) The optimized geometrical structure of 8 atom core

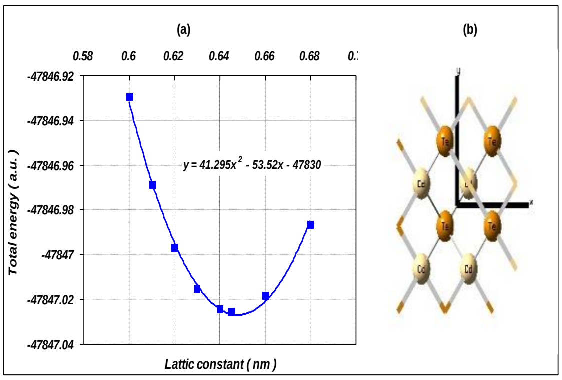

Fig.3 (a) Total energy as a function of lattice constant of CdTe for 8 core atoms per LUC (b) The optimized geometrical structure of 8 atom core

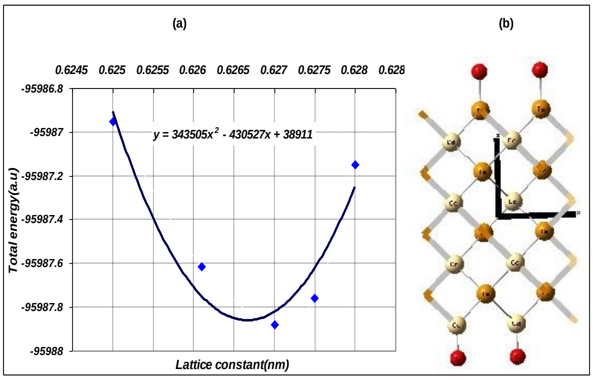

Fig.4 (a) Total energy for 8 core atoms oxygenated (001)-(1×1) Cd_8Te_8-O_4 surface as a function of lattice constant (b) The optimized geometrical structure of 8 atom core

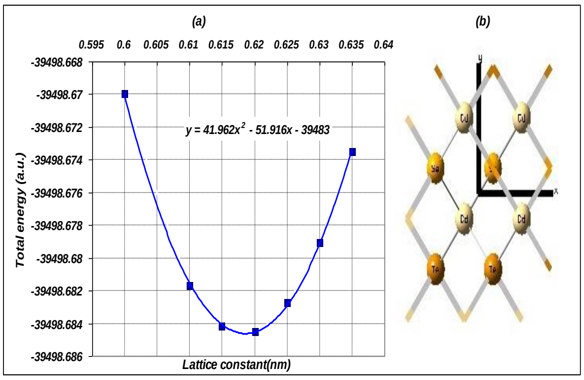

Fig.5 (a) Total energy as a function of lattice constant of CdSe$_{0.5}$*Te*$_{0.5}$ *for 8 core atoms per LUC (b) The optimized geometrical structure of 8 atom core*

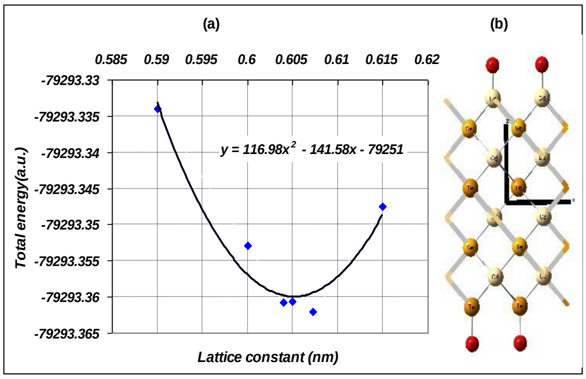

Fig.6 (a) Total energy for 8 core atoms oxygenated (001)-(1×1) $Cd_8Se_4Te_4$-O_4 *surface as a function of lattice constant (b) The optimized geometrical structure of 8 atom core*

Fig. 7 shows variation between Te % concentration (x = 0, 0.5, 1) and lattice constant for core and surface, which appear linear increasing but values surface part are less than core part.

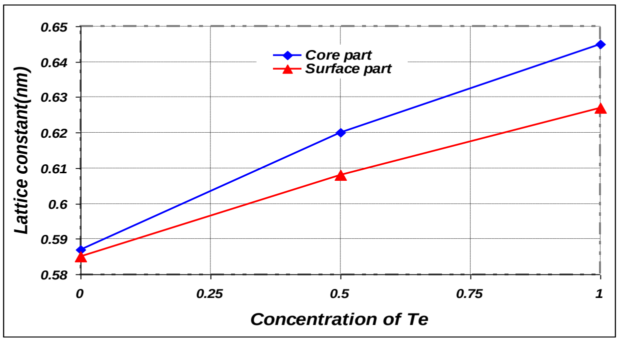

Fig. 7 Lattice constant for CdSe$_{1-x}$*Te*$_x$ *8 core atoms as a function Te % concentration (x = 0, 0.5, 1) for core and surface part*

Figs. 8,9 and 10 show the density of states of $CdSe_{1-x}Te_x$ for three tellurium concentrations x=0, 0.5, and 1 for 8 core atoms and surface respectively , which exhibits a lower density of states and higher degenerate state of surface part compared with core part. This lower density of states in surface part is caused by the broken symmetry at the discontinuity of the surface, and the existing of oxygen atoms leads to varying the bond length, angle and lattice constant[23].

The discontinuity of surface imposes level splitting on the higher degenerate state. The splitting of energy level does not affect the number of degenerate state only but also the conduction and valence band widths [24]. Also, the splitting of states and additional states have an effect on the band gap. The energy gap is shown between the two bands and equals to (0.010 eV).

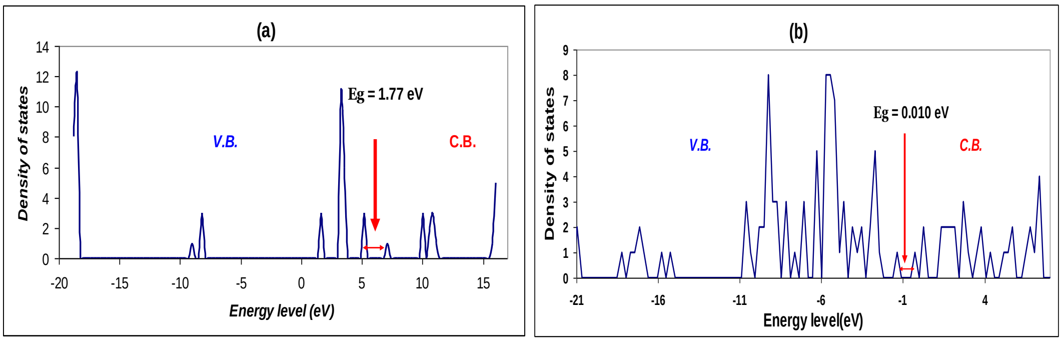

Fig.8 Density of states as a function of energy levels of (a) CdSe for 8 core atoms per LUC. (b) for Cd_8Se_8*-* O_4 *for surface oxygenated (001)-(1×1) slab having* a^2 *area*

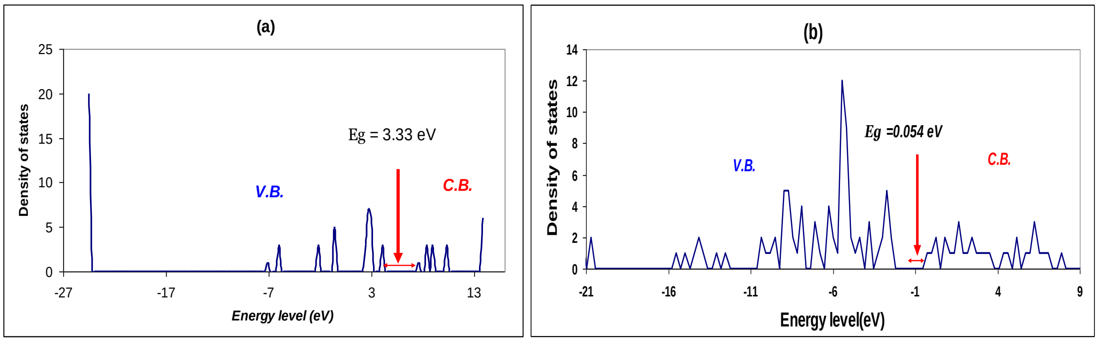

Fig.9 Density of states as a function of energy levels of (a) CdTe for 8 core atoms per LUC. (b) for Cd_8Te_8*-*O_4 *for surface oxygenated (001)-(1×1) slab having* a^2 *area.*

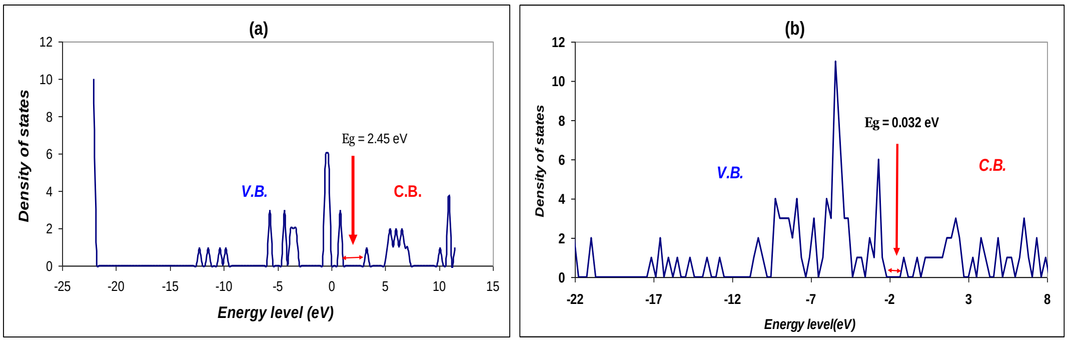

Fig. 10 Density of states as a function of energy levels of (a) $CdSe_{0.5}Te_{0.5}$ *for 8 core atoms per LUC . (b) for* $Cd_8Se_4Te_4$*-*O_4 *for surface oxygenated (001)-(1×1) slab having* a^2 *area*

Fig. 11 shows energy gap as a function of fraction Te (x = 0, 0.5, 1) for core and surface parts, the values of energy gap of core part is greater than surface part.

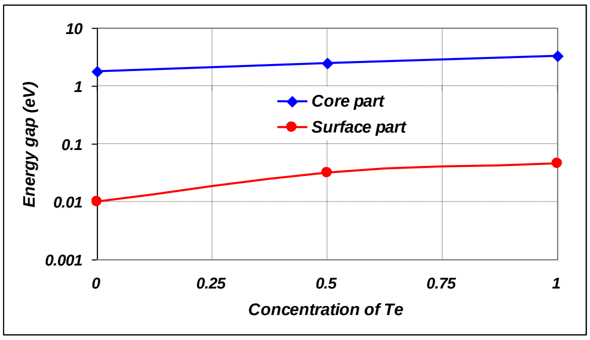

Fig. 11 Energy gap as a function Te% concentration (x = 0, 0.5, 1) of $CdSe_{1-x}Te_x$ for core and surface part.

The properties of the $CdSe_{1-x}Te_x$ nanocrystal (001)-(1×1) oxidized surface is also investigated using slab geometry of the stoichiometry $Cd_8Se_4Te_4$-O_4 LUC. This stoichiometry is repeated periodically (in 2D surface) and restricted to the actual surface size of the nanocrystal. Surface calculations are more demandable in computer time than core because of lack of symmetry which is the reason for restricting our calculations for the upper mentioned surface only. Figs. 12,13 and 14 show the surface slab atomic charges in a path that is perpendicular to the investigated surface for Cd_8Se_8- O_4 , Cd_8Te_8-O_4 and $Cd_8Se_4Te_4$-O_4 respectively.

In Fig.12 shows the atomic charges of oxygenated (001)-(1x1) surface calculated for stoichiometry Cd_8Se_8- O_4 atoms as a function of layer depth using the slab geometry method. The positive and negative charges are assigned to Cd and Se atoms, respectively. The Cd and Se atoms take the charges +0.331 and -0.010 arbitrary unit (a.u), respectively. While in Fig.13 which shows the atomic charges of oxygenated (001)-(1x1) surface calculated for stoichiometry Cd_8Te_8-O_4 atoms as a function of layer depth the first and the last negative charged atoms in the figure are oxygen atoms. These atoms are neighboring the outermost surface Cd atoms having positive charges 0.399 a.u. The Te atoms have negative charges -0.208 a.u.

In Fig. 14 we notes the atomic charges for $Cd_8Se_4Te_4$- O_4 which appear the negative and positive charges are assigned to Te and Cd atoms, the Te and Cd atoms take the charges -0.002 and +0.359 arbitrary unit (a.u), respectively.

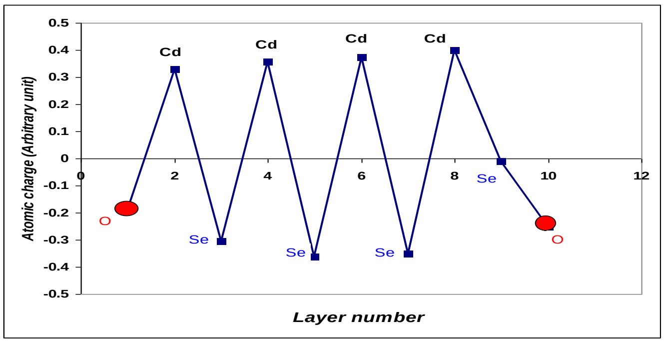

Fig.12 Atomic charges as a function of layers depth of oxygenated (001)-(1x1)surface for Cd_8Se_8- O_4 nanocrystal surface using slab geometry.

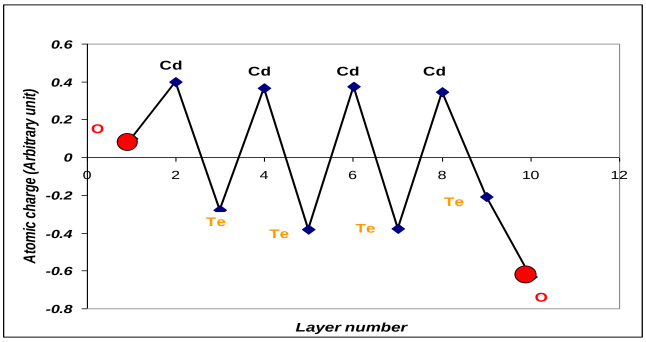

Fig.13 Atomic charges as a function of layers depth of oxygenated (001)-(1x1)surface for Cd_8Te_8-O_4 nanocrystal surface using slab geometry

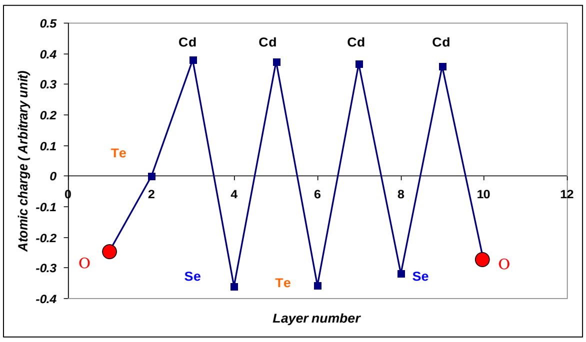

Fig.14 Atomic charges as a function of layers depth of oxygenated (001)-(1x1)surface for $Cd_8Se_4Te_4$-O_4 nanocrystal surface using slab geometry

4. Conclusions

Nanocrystal oxidized surfaces show smaller energy gaps and lattice constant, as well as the density of states of $CdSe_{1-x}Te_x$ for three tellurium concentrations x=0, 0.5, and 1 for core and surface exhibits a lower degenerate state of surface part compared with core part. This reflects the broken symmetry and discontinuity at the surface and existence of new kind of atoms (oxygen atoms), and the variation of bond lengths and angles. The energy gap for alloying composition $CdSe_{0.5}Te_{0.5}$ is between that for CdSe and CdTe .

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