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The Effect of Substitution of a Zn Atom in $Cd_{n-1}Te_n$Clusters (n=1-10)

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Abstract

In this research, structural and electronic properties of $ZnCd_{n-1}Te_n$ clusters (n=1-10) have been studied by formalism of density functional theory and using the projector augmented wave within local density approximation. The structural properties (such as bond length/angle and coordination number), electronic and optical properties (such as binding energy, Kohn-Sham spectrum and partial charge density, absorption spectrum) of ZnCdTe clusters were investigated and compared to these of CdTe clusters. A transition from Two-dimensional (2D) to Three-dimensional (3D) structures is observed from n=5→n=6. Results obtained for the most stable geometrics of the ZnCdTe clusters show that a Zn atom increases binding energy and consequently stability of CdTe clusters. It also decreases (increases) bond lengths (angles) for it’s nearest neighbor atoms. An analysis of partial charge density and eigenvalue spectrum for $ZnCd_{n-1}Te_n$ clusters reveals that there are Te-*s* and Cd-*d* hybridizations for low energy levels.

1. Introduction

During the last decade, noticeable difference of nano-scale clusters from their molecular and bulk counterpartshave attracted attention of researchers in varied areas like medicine, catalyst and nano-device fabrications, apart from physics and chemistry. Material scientists and engineers are interested in cluster studies due to their unique physical and chemical properties which depended strongly on their size. The structural and electronic properties of clusters can be dramatically different from those of the bulk due to the high surface area to volume rate [1-4]. The substitution or addition of a few atoms to a cluster can also result in structural rearrangement. A critical role in dictating the properties of a material can be attributed to relation between the geometry and electronic structures.

Although CdTe single crystal with band gap of 1.45eV is a good candidate for detecting X-ray and γ-ray [5-6] , it makes low leakage current and high stopping power of radiation in devices. A small mole fraction of zinc can reduce these defects without significantly changing the stopping power of radiation [5]. The results reported by Rodri´guez*et al*. show that structural, thermal and optical properties of CdZnTe are strongly dependent on the Zn distribution [7]. Prías-Barragán*et al*. have determined the energy band gap of CdZnTe as a function of the Zn concentration by photoacoustic absorption and optical analysis of $Cd_{1-n}Zn_nTe$ for low zinc concentration [8]. Photoluminescence and absorption studies of defects carried out by C.B. Davis *et al*. on CdTe and $Zn_xCd_{1-x}Te$ crystals show that there are three regions on their PL spectrum; near-band-gap region, the defect band and the deep-level. This band gap increases from 1.4 eV for CdTe to 1.67 eV for Zn-doped CdTe crystal(x=0.09), while the defect band is attributed to tellurium vacancies and the deep level is related to a bulk rather than a surface effects[9]. The studies of G. G. RUSU on the influence of Zn doping on the electrical conductivity and temperature dependence and optical absorption spectra of CdTe thin films show that depending upon Zn content, the electrical conductivity at room temperature for the deposed films is about of six to ten orders of magnitude higher than that of non-doped CdTe films. It is observed an increase of the optical band gap from 1.49 eV (for non-doped) to 1.67 eV (for Zn-doped CdTe) [10].

Cadmium zinc telluride ($Cd_{1-n}Zn_nTe$), a ternary II-VI compound semiconductor has a direct band gap between 1.45eV to 2.26eV (near infrared to visible) that can be tuned by controlling the Zn dopant in the grown crystals. It is a suitable candidate for opto-electronic devices like solar cells, light emitting diodes, X-ray and γ-ray radiation detectors [11-13]. However, less attentions has been given to the study of CdZnTe clusters, though we need an understanding of the physical and chemical properties of the clusters for the given applications. Theoretical studies on the CdTe clusters have been previously performed by Bhottachoya and Kshirsager[14-15], but no work has been done on Zn-doped CdTe clusters.

In this letter, we perform a first principle study of $ZnCd_{n-1}Te_n$ clusters (n=1-10) to explore the effect of a Zn atom on the structural and electronic and optical properties of Cd_nTe_n clusters. The next section briefly describes our computational details, the third section shows the results and discussion and final section concludes this work.

2. Computational method

The calculations are done using the Born-Oppenheimer approximation[16]and theHohenberg-Kohn density functional theory (DFT) [17]. The single particle equations for electronic structure are solved self-consistently within Kohn-Sham formalism of density functional theory [18] with Vienna *ab initio* Simulation Package (VASP) [19], using the projector augmented wave (PAW) method [20]. The calculations employ local density approximation (LDA) in the Ceperley and Alder (CA) form, as approximated by Perdew and Zunger [21].

Clusters are placed at the center of a cubic supercell with side 20Å which periodic boundary conditions are also imposed on that. We do not any symmetry constraints on initial geometries for their relaxations. Initial geometries optimizations are implemented using conjugate gradient (CG) method until all forces components are less than 0.005eV/Å with a convergence in total energy of $1.0\times10^{-4}\,eV$. The wave functions are expanded in a plane wave basis set with the kinetic energy cutoff 276.7eV and calculations have been performed at the Γ-point only. For calculations presented here, only *s*(2) and *d*(10) electrons of zinc and cadmium and *s*(2) and *p*(4) electrons of tellurium are treated as valence electrons.

3. Results and discussion

In order to study $ZnCd_{n-1}Te_n$ clusters, first we obtained the lowest energy structure of Cd_nTe_n clusters. The Cd and Te atoms characteristics mentioned in the previous section are employed for the calculation of the Cd_nTe_n clusters [22]. For small clusters, the initial structures are guessed by using some chemical and/or symmetry related considerations. Increasing number of atoms and their freedom to interact with each other leads to many structures. Therefore, finding ground state structures of large clusters is a hard task, and low energy structures may be missed if the starting configurations of the search are not set appropriately. In order to avoid this, we perform *ab initio* calculations starting with several (up to 200 depending upon the size) initial two-dimensional (2D) and three-dimensional (3D) structures, for each neutral cluster.The results explored from solving Schrodinger equation show the ground state geometries of the Cd_nTe_n clusters are in agreement with the previous work done (for n=1-6) by Bhottachoya*et al.* [14].

The smallest CdTe cluster is CdTe dimer with bond length of 2.56Å belongs to $C_{\infty v}$ point symmetry group. This bond is 0.1Å less than what reported by Bhottachoya*et al*. This difference may be related to differences in pseudopotentials and exchange-correlations of GGA and LDA which have been used for calculations. A rhombus-shaped structure is predicted as the lowest energy structure (LES) of Cd_2Te_2 (like $ZnCdTe_2$ as shown in Figure 1). Among small CdTe clusters, it is observed only Cd-Cd bond in this geometry which is 0.23Å less than that in Cd_2 dimer. This can be attributed to more tendency of Cd atoms to increase coordination number in order to get more stability. The measured Cd-Te bonds are equal to 2.76Å and smaller than those of Cd_2Te_2 in previous work as expected. The Cd-Te bond lengths of the Cd_nTe_n clusters in our work are summarized in Table 2. The LESs obtained for Cd_nTe_n with n=3,4 and 5 are 2D structures, as triangular, rectangular and pentagonal structures with stoichiometry configurations for Cd and Te atoms respectively. These geometries also reported by Bhottachoya. For larger clusters, $n \geq 6$, the average bond length (in Table 2) shows a tendency to increase, indicating the cluster always tends to have the highest dimension for longer bond length.

The substitution of a single Zn atom at the Cdatom sites in the CdTe cluster can reveal changesin its structural and electronic properties, such as bond length and angle, binding energy, HOMO-LUMO gap and symmetry reduction or elimination. Hence, we need to find and analyze the most stable structures of $ZnCd_{n-1}Te_n$ clusters out of all possible cases. The results show that these changes can be large for the nearest neighbors of impurity atom and slight for other atoms. Figure 1 shows the most stable structures of the Zn doped CdTe clusters. Blue (red) and grey colours denote Zn (Cd) and Te atoms.

The calculations carried out on the smallest ZnTecluster, show that its bond length (BL) and binding energy per atom (E_b) are 2.37Å and 0.86-eV/atom respectively. The E_b for the lowest energy structure of X_nY_n clusters is defined as

$$E_b=(nE[X]+nE[Y]-E[X_nY_n])/(n_X+n_Y) \qquad (1)$$

which E[X] is total energy of system X. Table1 summarizes the binding energies per atom and bond lengths for Zn_2, Cd_2, CdTe and ZnTe dimers. The E_b of Zn_2 is 0.01eV/atom more than that of Cd_2, while their bonding are predominantly van der Waals but with slight covalent character. These results show that Zn_2 is more stable than Cd_2. Also as seen in Table 1, heteroatomic dimers have more the E_b and less BL than homoatomic dimers which can be referred to the charge transfer from cation to anion which can be revealed as a variation in their bonding characters, from van der Waals-covalent character to ionic-covalent character.

A comparison of the E_b and BL of ZnTe dimer with those of CdTe dimer shows that the E_b of ZnTe dimer is 0.09eV more than that of CdTe dimer, while its BL is 0.19Å less than that of CdTe dimer. Such characteristics may be attributed to stronger interaction of Te atom with Zn as compared to Cd atom which arising from the difference between their electronegativity and covalent radius values. Therefore, it can be deduced that Zn atom can stabilizes Te atom more than Cd atom.

Table 1. Binding energies and bond lengths of Zn_2, Cd_2, CdTe and ZnTe clusters**.**

Cluster name	**Binding energy($\frac{eV}{atom}$)**	**Bond length(Å)**
Zn2	0.03	3.12
Cd2	0.02	3.11
CdTe	0.77	2.56
ZnTe	0.86	2.37

The predicted structure for the LES of $ZnCdTe_2$ is a 2D structure similar to a distorted rhombus. The Zn atom reduces Zn_{Cd}-Te bond from 2.76Å to 2.55Å and Zn_{Cd}-Cd bond from 2.88Å to 2.7Å. The Zn_{Cd} denotes the Zn atom which has been replaced at site of the Cd atom.These changes are also accompanied by a decrease at $\hat{Te}$ angles from 62.8° to 60.9° and an increase at Zn_{Cd} from 58.6° to 63.5° as compared to those of Cd_2Te_2.

The equilibrium geometry predicted for $ZnCd_2Te_3$ looks like a triangle (Fig. 1). The Zn dopant reduces the nearest Zn_{Cd}-Te bonds more by 0.2Å and about 0.01Å other bonds of Cd_3Te_3. With increasing constructive unit (CdTe) of the ZnCdTe clusters up to n=4-5, the LESs are revealed as 2D structures with stoichiometry configurations of Cd/Zn-Te atoms similar to smaller clusters. These structures seem like a distorted rectangular and a pentagonal structures respectively. In general, existence of the Zn atom in the CdTe clusters is caused that their structural symmetry to be reduced or lost. There is a decrease in bond length of the Zn_{Cd}-Te by 0.01Å as compared to that of the Cd_3Te_3 cluster, whereas it is observed an increase of 2°-3° for $\hat{Te}$ and Zn_{Cd} angles. The LESs of the $ZnCd_{n-1}Te_n$ clusters, n≤5, retain their stoichiometry configurations in 2D closed rings. Each cation(anion) is bonded by anion (cation), except for the Zn cation in $ZnCdTe_2$ that has been connected to all atoms.

In going from n=5 to 10, we observe a transition from 2D→3D structure and a decrease in the cluster symmetry which enhances its flexibility with increasing the ring size. The most probable reason can be a strong tendency to have 3D structure in order to get more stability. Base on DFT calculations, the geometries predicted for large clusters, $n \geq 6$, seem similar to cages including connected small rings. While stoichiometry configurations are observed in some cages, the coordination number of all anions (or cations) increases with respect to those in small clusters. The maximum coordination number obtained for Zn (4), Cd (4) and Te (3) atoms are observed in the $ZnCd_5Te_6$, $ZnCd_6Te_7$ and $ZnCd_9Te_{10}$ clusters respectively.

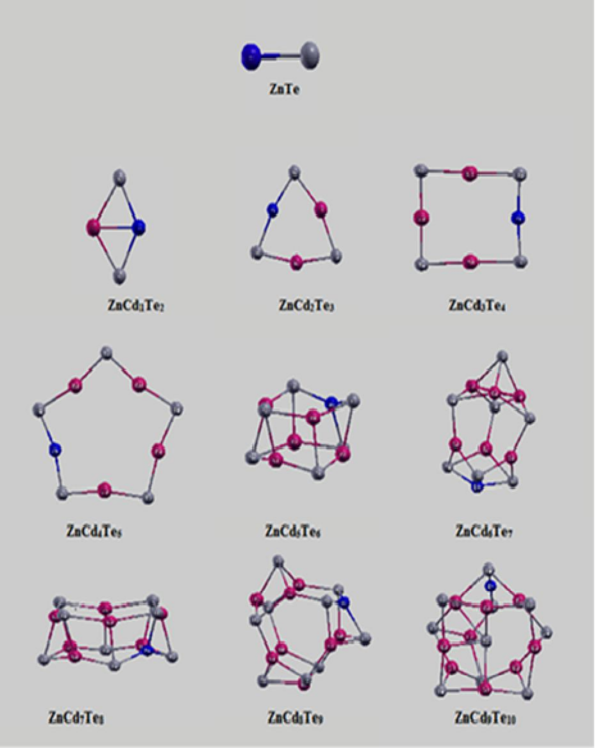

Fig.1. (Color online) The most stable structures of $ZnCd_{n-1}Te_n$ clusters (n=1-10).

Average bond lengths of Cd-Te and Zn-Te for the Cd_nTe_n and $ZnCd_{n-1}Te_n$ clusters are given in Table2. As seen, there is an increasing trend accompanied by oscillatory behavior in bond lengths for both Cd_nTe_n and $ZnCd_{n-1}Te_n$. The shortest bonds are found for CdTe and ZnTe dimer which are 0.25 and 0.27Å smaller than the nearest neighbor distance in bulk [23].

The most reasons for bond-length (angle) decrease (increase) at the Zn site may be attributed to less covalent radius and more electronegativity of the Zn atom as compared to those of the Cd atom. The notable point for the most stable structures is that we have never observed configuration for the Te and Cd atoms similar to those of bulk phase. This can be attributed to Coulomb repulsion between the lone-pair electrons in chalcogenide atoms that reveals dangling bonds in their clusters and consequently, movement toward outer sites in clusters.

Table 2. Average bond lengths of Cd-Te and Zn-Te for the LES of Cd_nTe_n and $ZnCd_{n-1}Te_n$clusters (n=1-10).

(Cd_nTe_n)/n	**BL(Cd-Te)(Å)**	**($ZnCd_{n-1}Te_n$)/n**	**BL(Zn-Te)(Å)**
1	2.56	1	2.32
2	2.76	2	2.49
3	2.69	3	2.44
4	2.67	4	2.43
5	2.66	5	2.42
6	2.84	6	2.59
7	2.84	7	2.59
8	2.85	8	2.59
9	2.82	9	2.58
10	2.92	10	2.64

By increasing the size of cluster, one can observe chemical and physical properties which can be different from those of the bulk. In a crystal, one can observe energy bands constructed from quasi continues levels, whereas in a small cluster it is the same as that for a molecule. As cluster size increases, the discrete levels approach a band-like limit. In this evolution, the binding energy (E_b), HOMO-LUMO gap and charge density also undergo changes. This$E_b$has been plotted for $Cd_nTe_n$and $ZnCd_{n-1}Te_n$ clusters as a function of cluster size, n, in Fig. 2.

As seenin this figure,theE_b of Cd_nTe_nclustersshow the increasing trend as cluster size increases. In the range of n=l-4, there is a steep increase in the E_b for n=2 with respect to its neighbors, corresponding to Cd_2Te_2 being a more stable structure. A less steep rise in binding energy per atom from n=5 to 6 corresponds to the transition from 2D to 3D. The binding energy per atom saturates at n=6 and does not shows much vibration for n>6 so that this variation is less than 0.3eV/atom. The binding energy per atom of the $ZnCd_{n-1}Te_n$ clusters shows more increasing trend similar to that of the $Cd_{n-1}Te_n$ clusters. The minimum binding energy difference occurs for their respective smallest clusters and this difference increases remarkablely for large clusters.

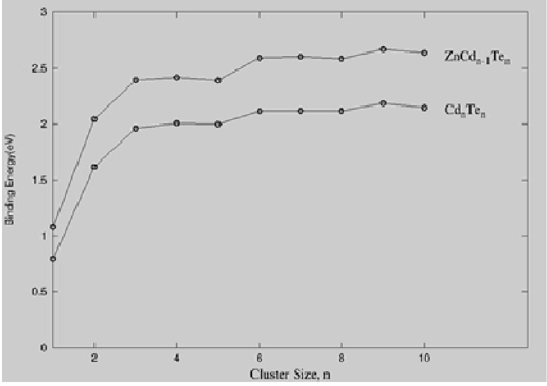

Fig. 2.(color online) Binding energy per atom (in eV/atom) for the lowest energy structures of $Cd_nTe_n$and $ZnCd_{n-1}Te_n$ clusters (n=1-10) as a function of cluster size.

This may be related to an increase in coordination number of Zn atom (such as $ZnCdTe_2$) or an strong overlap between the Zn-*d* orbital and the Cd-d/Te-*p* orbitals of its nearestneighbors.Then, one can conclude that doping of the Zn atom can improve significantly the binding energies of the CdTe clusters, and consequently their stabilities.

A perfect description of the electronic structure can be based on eigenvalues of the Kohn-Sham equation and the occupation number of atomic levels. We have plotted the atomic spectrum of Te and Zn atoms and $ZnCd_{n-1}Te_n$ clusters in Fig. 3. The Fermi energy level has been shifted to zero value. A comparison of the Te and Zn energy levels with that of Cd-*d* level (-6.20eV) shows the Cd-*d* level lies between the Te-*s* (-9.12eV,down) level and Zn-*d* (-4.35eV,up) level which latteralsolies below the Te-*p* (-0.01). Then, it is expected that the Te and Zn orbitals to be hybridized in the levels close to the highest occupied molecular orbital (HOMO). As the clusters size increases, the lowest unoccupied molecular orbital (LUMO) and HOMO level move to up-ward and down-ward respectively. This movement is slight for the HOMO levels. A comparison of HOMO-LUMO gap of the ZnCdTe with those of the CdTe clusters shows that the Zn dopant increases typically this gap about 0.2 and 0.3eV more for ZnTe and $ZnCdTe_2$ with respect to those of CdTe and Cd_2Te_2 respectively. These results are also in consistent with the experimental results reported by Prías-Barragán*et al*. that the low Znconcentration (for <0.08) increases the band gap of the CdTe single crystal.Accordingly, the Zn substitution in the CdTe clusters may be considered as an important factorfor red/blue shift of nanoparticles in nano-regime.

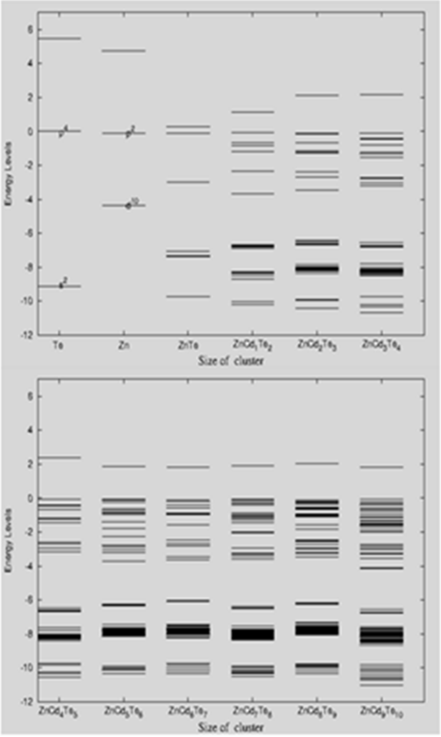

Fig. 3. Figure 3: Kohn-Sham spectrum of Te and Zn atoms and $ZnCd_{n-1}Te_n$ clusters (n=1-10). All energies are in eV.

For more accurate analysis, we have calculated the optical absorption spectra of Te_2, CdTe, ZnTe, Cd_2Te_2 and $ZnCdTe_2$ clusters (Fig.4) using time-dependent density-functional perturbation theory (TDDFPT) with the Liouville-Lanczos approach as implemented in QUANTUM ESPESSO [24-32]. As seen in Fig.4a, there is an oscillatory spectrum for Te_2 which its peak maximum lies at about 7.74 eV and may be corresponded to the transition from the occupied (HOMO) to unoccupied (LUMO) levels resembling to valence (VB) and conduction (CB) bands in crystal. Other peaks may be considered as transitions from the HOMO to upper levels than the LUMO or from lower levels than the HOMO to the LUMO or upper levels. As a Tellurium atom is replaced by a cadmium atom, the absorption intensity increases dramatically and the peak maximum also shifts toward lower energy. The Cd-Te interaction opens a gap 2.44 eV and red-shift at the spectrum peak, while the Zn-Te interaction shifts the Cd-Te peak toward higher energy (blue-shift) and reduces the gap about 0.52eV with respect to that of CdTe.

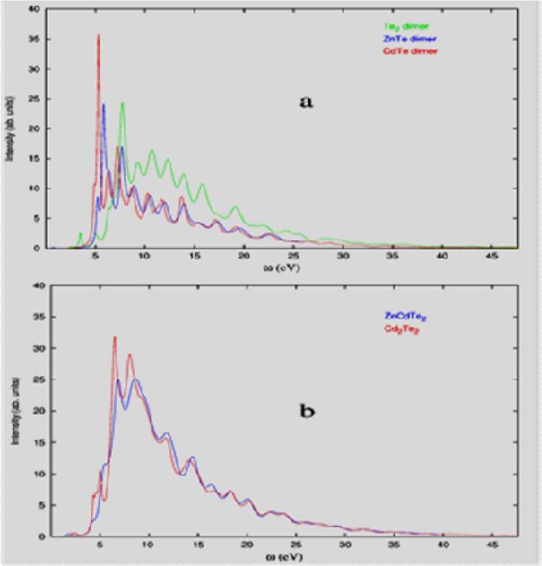

Fig. 4. (color online) Optical spectra for a; Te_2,CdTe, ZnTe and b;Cd_2Te_2 and $ZnCdTe_2$ clusters.

Also, adding a building unit of CdTe to the ZnTe dimer shifts the absorption peak from 5.82 eV for ZnTe to 6.81 eV for $ZnCdTe_2$ (Fig.4b). The red/blue shift may be attributed to larger/smaller wigner-seitz radius of Cd/Zn atom as compared to that of Te which causes less/more correlation between Cd/Zn and Te atoms respectively. The shift in peak position may be attributed to a change in the feature of a transition for these clusters which corresponding to exciton transitions in the near band gap region in their crystals.

More accurate investigation of such electronic properties may be carried out with study chargedensity for the energy levels. Therefore, we have plotted the partial charge density contour for some energy levels of $ZnCd_2Te_3$ cluster. Numbers at the bottom of each contour denote the number of the energy level. As seen in Fig. 5.(1), the most charge density contribution is related to Te-*s* orbitals which have high overlapping with their neighbor atoms. It is necessary to mention that charge distribution localized around Cd atoms is related to their *d* orbitals that is a characteristic of the *d* orbitals.

By increasing the level number, the *d* orbitals contributions increase so that they can overlap, as shown in Fig. 5.(4). For upper levels (up to level 13), we observe the slight contributions of charge density for Te-*s* and Zn-*d* orbitals in addition to those of Cd-*d* orbitals, but closing to inter-mediate levels (up to level 18), the most charge density distribution is localized around the Zn atom. For levels near to HOMO, it is observed interaction between the *d* orbital of the Zn dopant and Te-*p* orbitals (levels 20 and 22). According to the results obtained in calculations and observations in Fig. 4, one can conclude that hybridization of the Zn-*d* orbital with the orbitals close to HOMO can be the most reason for change in HOMO-LUMO gap of their clusters or an important factor for red/blue shift in their nanoparticles. Also, the HOMO and LUMO show an atomic *p* characteristic.

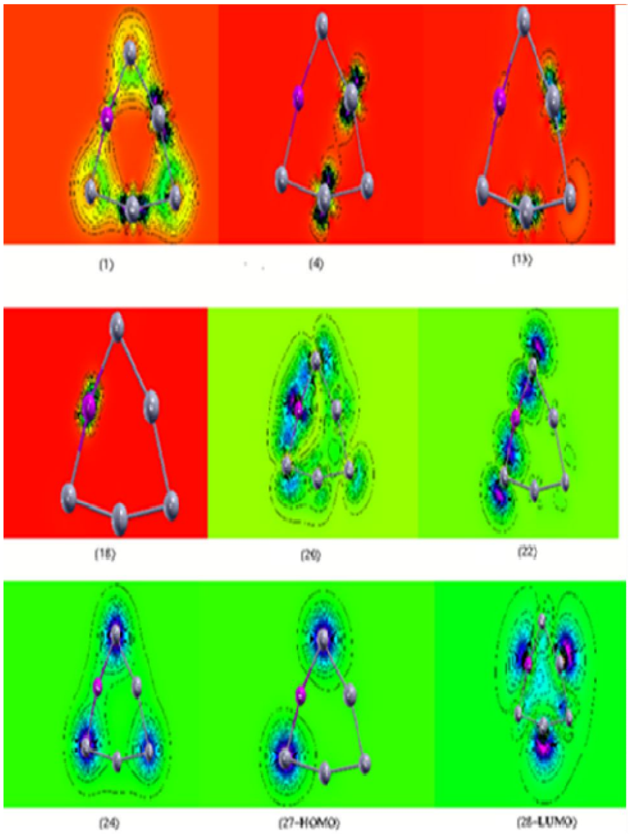
(1) (4) (13)
(18) (20) (22)
(24) (27-HOMO) (28-LUMO)

Fig. 5.(color online) Partial charge density contours for $ZnCd_2Te_3$ clusters. Numbers at the bottom of each contour denote the serial number of the molecular orbital level.

4. Conclusion

Geometries of Zn-doped CdTe clusters show that the small clusters have 2D configurations which is a direct consequence of dangling bonds of chalcogenide atoms. Transition from 2D→3D is observed in going from $ZnCd_4Te_5$ to $ZnCd_5Te_6$ that accompanied with increasing coordination number for all Zn, Cd and Te atoms. The calculations carried out based on TDDFPT show a Zn atom reveals a blue-shift in the optical transition peak of the CdTe clusters which is in agreement with experimental results for its crystal. The notable point is that we didnot observe tetragonal structure for these atoms as one can see in bulk. The results obtained based on the charge density contours show the most charge distributions are localized around the Te atoms in low energy levels, while there is a case hybridized of *s-d* or *p-d* orbitals for intermediate energy levels.

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