First principle study of structural stability and electronic structure of CdS nanoclusters

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Using first-principles density functional calculations, we have studied the structural stability of stoichiometric as well as non-stoichiometric CdS nanoclusters at ambient pressure with diameters ranging up to about 2.5 nm. Our study reveals that the relative stability of the two available structures for CdS, namely zinc blende and wurtzite, depends sensitively on the details like surface geometry and/or surface chemistry. The associated band gap also exhibits non-monotonic behavior as a function of cluster size. Our findings may shed light on reports of experimentally observed structures and associated electronic structures of CdS nanoclusters found in the literature.

I. INTRODUCTION

The study of physical properties of systems with reduced dimensionality, such as nanoclusters, has become one of the challenging field of research in recent years. For semiconductor nanoclusters, there is a remarkable increase in the band gap compared to the bulk value, as the size of the cluster decreases. This has opened up immense technological possibilities in diverse fields such as solar cells,[1] electronic devices,[2] and possible electronic devices. Among various semiconductor nanoclusters, II-VI semiconductor CdS has received a lot of attention, primarily due to the following facts, (i) CdS is a direct gap semiconductor with rather large band gap of about 2.5 eV,[3] (ii) quantum confinement effect can be reached quite easily because of the large excitonic Bohr radius \( \approx 3 \text{nm} \),[3] (iii) CdS can be synthesized experimentally rather easily in the size range required for quantum confinement. The situation, however, is complicated by the fact that the reduction in particle size seems to influence the structural stability of one phase over the other[4] in a way that is very little understood so far.

Bulk CdS stabilizes in hexagonal wurtzite (WZ) structure. Two other crystal structures, cubic zincblende (ZB) and rocksalt structures, in addition to the WZ one or even simultaneous presence of several crystallographic phases, have been reported in literature[2,5] for nanoclusters. The formation of rocksalt structure is reported only at a high pressure[5] which we exclude from our present discussion, focusing only on the relative stability of WZ and ZB crystal structures at ambient pressure condition. This is an important issue since not only the band gap depends on the crystallographic structure of the nanocrystal[2] all physical properties such as the effective masses depend on the underlying crystal structure. However, the structural similarity between WZ and ZB and the associated small differences in cohesive energies of the order of few tens of meV/atom make the situation complex. While such an interesting issue has drawn attention in past and have lead to theoretical analysis based on parametrized tight-binding models[6,7] to our knowledge no rigorous first-principles study exist to address this issue. Very little is also known about the details of the experimental situation, e.g. the stability of non-stoichiometric versus stoichiometric clusters, the role of passivator and their influence on structural stability. In absence of detail knowledge of the experimental scenario which may also vary in different experimental condition like synthesis route, we considered in the following the \textit{ab-initio} theoretical study of stability of both stoichiometric and non-stoichiometric clusters, naked as well as passivated. Our study shows that the relative stability between WZ-structured and ZB-structured clusters are governed by the details of surface geometry and surface chemistry. In case of passivated clusters, we have also studied the associated band gap as a function of cluster size which depending on specific case also shows highly nonmonotonous behavior.

II. BUILDING UP OF CLUSTERS

The WZ to ZB transformation involves change in symmetry from hexagonal to cubic, while keeping the nearest neighbor atomic co-ordination fixed at four. The ZB lattice consists of two interpenetrating face centered cubic lattices of Cd and S, displaced from each other along the body diagonal by \( a_{ZB}/4 \), \( a_{ZB} \) being the cubic lattice constant. On the other hand, WZ lattice consists of two interpenetrating hexagonal closed packed lattices, one displaced from another by 3\( c/16 \) along the \( c \)-axis. These result into two different stacking sequences: ABAB... along [0001] direction for WZ and ABCABC... along [111] direction for ZB (see Fig.1).

The stable phase also seems to depend on the shape of the nanocrystal[12] with majority of the experimental results being for spherical nanoclusters. To generate nanocluster of geometry closest to spherical shape, we have built up the cluster shell by shell. To generate non-stoichiometric clusters, we have taken the cluster center on a Cd atom or S atom. In both ZB and WZ structures, each Cd(S) atom is tetrahedrally surrounded by...
S(Cd) atoms in its immediate neighborhood. Therefore, the surface of a non-stoichiometric cluster, generated via above-mentioned prescription contains only single species of atoms: a non-stoichiometric nanocluster of even number of shells has same kind of atoms at the surface and at the center, while a non-stoichiometric nanocrystal with an odd number of shells has two dissimilar types of atoms at the center and at the surface. On the other hand, stoichiometric clusters are generated by putting the center of the sphere on the midpoint of Cd-S bond. In this case, each shell contains equal number of Cd atoms and S atoms. Assuming spherical shapes, the bond. In this case, each shell contains equal number of Cd-S stacking of atoms along [111] direction.

The kinetic energy cut-off of the plane waves used in the calculations is 280 eV which gives convergence of total energy sufficient to discuss the relative stability of various phases. To check the validity of our calculations, we computed the cohesive energy of bulk WZ and ZB CdS. Our computed values of -2.653 eV/atom for the cohesive energy of WZ CdS and 9.7 meV/atom for ZB-WZ energy difference agree well with published results. Finite size cluster calculations were carried out using the supercell technique where a finite sized cluster is positioned within a cubic supercell. The cell dimension is set by the condition that each repeated cluster in the periodic lattice is separated by a vacuum layer of at least 12 Å, large enough so as to avoid the interaction between the clusters. To check the effect of optimization of geometry in certain specific cases, we relaxed the surface atoms keeping the core of the cluster fixed at ZB or WZ symmetry. This is a reasonable approach, considering the fact that previous studies where relaxation has been carried out for the entire cluster showed that the structural relaxation was mostly confined to the surface layer. Relaxations are performed using conjugate gradient and quasi-Newtonian methods until all the force components are less than a threshold value 0.01 eV/Å. The reciprocal space integration in all cases have been carried out with Γ point which is justified by the large dimension of the cubic supercell.

In order to study the role of passivator on the structural stability problem and the band gap problem we have also considered ab-initio calculations in presence of passivators. The surface of a naked semiconductor nanoparticle often contains electronically active states because of unsaturated surface bonds or dangling bond states. Surface passivation aims to rebond these dangling bonds with some passivating agent while maintaining the local charge neutrality of the whole system. In experiment, organic molecules are often used to passivate nanoclusters. Owing to the complexities and the numerous degrees of freedom of these passivation agents, it is not easy to do calculation with such passivators. To mimic the role of passivator in ab-initio calculation, several simpler atomistic models have been proposed. We will follow the recipe by Chelikowsky et al. which is applicable for both stoichiometric as well as non-stoichiometric clusters.

### III. COMPUTATIONAL DETAILS

We have carried out first principles electronic structure calculation within the framework of density functional theory for the constructed nanoclusters. We have used projector augmented wave (PAW) basis and local density approximation (LDA) for the exchange-correlation functional as implemented in the Vienna Ab-initio Simulation Package. The kinetic energy cut-off of the plane waves used in the calculations is 280 eV which gives convergence of total energy sufficient to discuss the relative stability of various phases. To check the validity of our calculations, we computed the cohesive energy of bulk WZ and ZB CdS. Our computed values of -2.653 eV/atom for the cohesive energy of WZ CdS and 9.7 meV/atom for ZB-WZ energy difference agree well with published results. Finite size cluster calculations were carried out using the supercell technique where a finite sized cluster is positioned within a cubic supercell. The cell dimension is set by the condition that each repeated cluster in the periodic lattice is separated by a vacuum layer of at least 12 Å, large enough so as to avoid the interaction between the clusters. To check the effect of optimization of geometry in certain specific cases, we relaxed the surface atoms keeping the core of the cluster fixed at ZB or WZ symmetry. This is a reasonable approach, considering the fact that previous studies where relaxation has been carried out for the entire cluster showed that the structural relaxation was mostly confined to the surface layer. Relaxations are performed using conjugate gradient and quasi-Newtonian methods until all the force components are less than a threshold value 0.01 eV/Å. The reciprocal space integration in all cases have been carried out with Γ point which is justified by the large dimension of the cubic supercell.

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The proposed recipe requires use of two different kind of fictitious hydrogen atoms, $H^*$, to passivate the dangling bonds of CdS nanoclusters. To keep the passivated cluster neutral, one species of the fictitious atoms is chosen to have a nuclear charge of $1+\eta$ and valence electron charge of $-(1+\eta)$, where $\eta$ is a positive number. These atoms are bonded with Cd atoms. The other species of atoms is chosen to have a nuclear charge of $1-\eta$ and a valance electron charge of $-(1-\eta)$. These atoms are bonded to the S atoms. The value of $\eta$ for which gap is maximum in the curve of gap vs $\eta$, is found to be 0.5 for II-VI semiconductor nanoparticles.\(^\text{10}\) The bond lengths of $H^*$-Cd and $H^*$-S were determined from two model systems, Cd$H_4^*$ and SH$H_4^*$, in which bond length are fully optimized. The orientation of $H^*$ around Cd and S is fixed in the same tetrahedral orientation as it is in ZB or WZ structure.

IV. RESULTS

A. Energy stability

1. Unpassivated stoichiometric clusters

Fig.2 shows the plot of the computed cohesive energy for unpassivated stoichiometric clusters as a function of growing cluster size, where we define the cohesive energy per atom as $E_c = \frac{E_{\text{tot}} - \sum \beta n_\beta E_\beta}{\sum \beta n_\beta}$, $E_{\text{tot}}$ being the total energy of the cluster, $E_\beta$ being the energy of an isolated $\beta$ atom ($\beta =$ Cd, S) and $n_\beta$ = number of either type of atoms in the cluster. The cohesive energy shows an overall decrease with the increase of cluster size for both the ZB and WZ structures due to the reduction in the ratio of surface atoms to bulk atoms upon increasing cluster size. However, the variation of cohesive energy is found to be non-monotonic with increasing size. Connecting the cohesive energies of all the even shell clusters and that of odd shell clusters separately, we find that the even shell clusters show higher binding (and therefore lower cohesive energy) than the odd shell clusters. Further to study the relative stability between the ZB and WZ symmetry, we show in Fig.3, the cohesive energy difference between ZB and WZ structures at each shell size. Whenever the quantity plotted is negative, it implies that the cubic structure is more stable, while a positive value signals the hexagonal structure as the stable phase. Our results, as plotted in Fig.3, show a general trend that from 3 shell onwards, the odd shell clusters stabilize in cubic ZB structure, while all even shell clusters prefer to form in hexagonal WZ structure. To check the robustness of our result with respect to structural relaxations of the surface atoms, we have also carried out structural relaxation of the surface atoms for 3-shell and 4-shell stoichiometric nanoclusters, keeping the position of core atoms fixed in ZB or WZ geometry, as explained in section III. Although the quantitative values change somewhat (by about 4-10 meV), the trend remains the same, i.e. cluster with odd number of shells like 3-shell stabilizes in cubic ZB structure and with even number of shells like 4-shell stabilizes in WZ structure. This is in accordance with the finding by Joswig et al.\(^\text{10}\) that total energy upon relaxation of such clusters reduces only little. In order to understand the oscillating stability of the WZ and ZB structures and also the higher stability of the even shell clusters compared to odd shell clusters in general, we have analyzed the different contributions to the total energy. For finite sized cluster, surface effect is important and the surface energy contribution to the total free energy plays the

![Figure 2](image2.png)

**FIG. 2:** Variation of cohesive energy with size for unpassivated stoichiometric clusters shown by solid dots in ZB structure and by open triangles in WZ structure. For a particular shell number, the diameter of the ZB and WZ structured cluster differ a bit (cf. Table I), therefore the average diameter is shown in the $x$-axis of the plot. Same convention is followed in all the following plots wherever applicable. Chemical formula for each shell is given both in ZB (upper) and WZ (lower) structures.

![Figure 3](image3.png)

**FIG. 3:** Solid dots represent the cohesive energy difference between ZB and WZ structures for each shell size in case of unpassivated stoichiometric clusters. Solid line through them is guide to eye.
Surface energy (eV/atom) of the even shelled clusters, but also explains the relative stability between ZB and WZ structures. While nonmonotonic behavior of cohesive energy and hence larger surface states for odd shell clusters, giving rise to increased surface states that the average number of dangling bonds are larger for all surface atoms for a particular cluster size. We find even shell clusters have lower surface energy and hence more binding compared to odd shell clusters. The inset of Fig. [1] shows the surface energy difference between ZB and WZ structures for each shell size. The positive (negative) value of surface energy difference means ZB structure has higher (lower) surface energy contribution than WZ structure and therefore ZB structure is less (more) stable. This trend in surface energy variation and that of its difference is in accordance with the trend found in the cohesive energy and its difference.

Furthermore, to understand the nonmonotonic behavior in surface energy or cohesive energy as a function of cluster size, we calculated the average number of dangling bonds per surface atom. The number of dangling bonds are the total number of unsaturated bonds, defined as \( \sum_i (4 - z_i) \), where \( z_i \) is the coordination of \( i \)-th surface atom and the summation over \( i \) involves summation over all surface atoms for a particular cluster size. We find that the average number of dangling bonds are larger for odd shell clusters, giving rise to increased surface states and hence larger surface energy contribution, thereby explaining the nonmonotonic behavior of cohesive energy. While nonmonotonic behavior of cohesive energy has been reported in theoretical calculations in past [10], such systematic behavior and its analysis by application of accurate first-principles calculations, to our knowledge has not been demonstrated before. The analysis in terms of dangling bonds not only explains the higher stability of the even shelled clusters, but also explains the relative stability of WZ and ZB structured clusters since the difference of average number of dangling bonds per surface atom between ZB and WZ structured clusters oscillates between positive and negative values, being positive for even shelled clusters and negative for odd shelled clusters. The difference is zero for 1 and 2-shelled clusters since the local co-ordination of immediate neighbors is identical between ZB and WZ clusters and the difference shows up only beyond 2nd nearest neighbor.

2. Unpassivated non-stoichiometric clusters

Most experimental condition favors synthesis of clusters of non-stoichiometric nature. It is therefore important to consider clusters having non-stoichiometric composition. This however leads to complication due to the fact that different cluster sizes have very different Cd to S ratio, making the comparison of corresponding total energies a difficult task for which no obvious way exists. However, for a given shell, the Cd to S ratio between ZB and WZ structured clusters remains almost same [20] making the comparison of their cohesive energy meaningful. In Fig. [5] we plot the difference in cohesive energy between the ZB and WZ structured non-stoichiometric clusters as a function of increasing cluster size. The plot in the upper panel exhibits the cohesive energy differences for Cd centered clusters. The plot in the lower panel exhibits the same but for S centered clusters. We note that unlike the case of stoichiometric clusters where the surface composition always consists of equal number of S and Cd, for non-stoichiometric clusters the surface is formed exclusively by either S or Cd atoms. For Cd-centered clusters, the even(odd) shell clusters are Cd (S) terminated, while it is reversed for S-centered clusters. From the plot in Fig. [5] we find that nonmonotonic behavior of the relative stability between ZB and WZ phase persists, on top it shows additional interesting aspect in the sense...
that whether an even or odd shell cluster is formed in WZ or ZB symmetry depends on the terminating layer. Focusing on clusters with shell numbers 4 and 5 in upper pannel of Fig[6], 4 shell cluster is found to be WZ structured and 5 shell clusters is found to be ZB structured for Cd-centered cluster while moving to the lower panel of Fig[6] the reverse trend is found for the S-terminated clusters. We note that a 4 (5) shell cluster is Cd (S) terminated in the former cases and S (Cd) terminated in the latter cases. As expected this is driven by the oscillating behavior of the surface energy difference between ZB and WZ structures (shown in Fig[7]), which shows the similar trend as observed in case of the cohesive energy difference. However unlike in case of stoichiometric clusters, this trend is not explained by the difference in the average number of dangling bonds per surface atom between ZB and WZ structured clusters (shown in Fig[5]). The difference in average number of dangling bonds predicts that the surface energy of a 4-shell ZB structured cluster to be higher than that of a WZ structured cluster, hence a 4 shell cluster must form in WZ structure which is indeed the case for 4 shell Cd-centered cluster but not for 4 shell S-centered cluster. We therefore conclude that an additional effect is operative in case of non-stoichiometric clusters. The surface chemistry effect adds on the surface geometry effect in case of Cd centered clusters, while it acts in opposite way to that of surface geometry effect in case of S centered clusters, thereby reversing the trend in the sense odd shell clusters are now stabilized in WZ structure and even shell clusters are stabilized in ZB structure. The relative stability between ZB and WZ structures in case of non-stoichiometric clusters, is driven dominantly by the surface chemistry rather than the surface geometry as has been found in case of stoichiometric clusters.

In order to investigate the microscopic reasons associated with the surface that drives this effect, we have computed the average charge enclosed within a sphere around a Cd atom and that around an S atom within a given cluster. There is no unique way to divide space in an AB compound into A and B regions. Therefore, two choices of sphere radius have been made: in one case, the spheres were taken to be equal sized with radius as half the Cd-S bondlength, in another case the choice of sphere radius was guided by the Hartree plot of the potential. We carried out calculations for Cd-terminated nanoclusters and S-terminated nanoclusters as well as for that of the bulk with both ZB and WZ structures in every case. The following results emerge from these calculations independent of the structure type. While the Cd-terminated clusters show similar charge distributions as those of bulk, S-terminated clusters show about 0.2 fraction of less electronic charge enclosed within the spheres. This is found to be true for both choices of sphere radii. This, in turn, would indicate covalency to be stronger in case of S-terminated clusters resulting into significant amount of charge residing in the interstitial region between Cd and S-centered spheres. This is illustrated in Fig[6], which shows the charge density distribution (\(\delta \rho\)) around a surface S atom, and that around a surface Cd atom for a 4-shell non-stoichiometric cluster, after subtracting the charge density of the isolated atom (\(\rho_s\)) and that of the system without the chosen atom (\(\rho_t\)) from the actual system (\(\rho_t\)). While Cd terminated cluster shows

![FIG. 6: Cohesive energy difference between ZB and WZ structures for each shell size in case of unpassivated non-stoichiometric clusters. Solid dots in the upper panel represent the results for Cd-centered clusters while the solid triangles in the lower panel correspond to results for S-centered clusters. Note, by construction even shell Cd(S)-centered cluster is Cd(S) terminated and odd shell Cd(S)-centered cluster is S(Cd) terminated (see text).](image6.png)

![FIG. 7: Variation of surface energy difference (SED) between ZB and WZ structures, with increasing shell sizes in Cd-centered (represented by solid dots in (a)) and S-centered (represented by solid triangles in (b)) non-stoichiometric clusters.](image7.png)
hardly any change in the region of Cd-S bond, there is a significant accumulation of charge around the Cd-S bond in case of S-terminated cluster. This provides a clear evidence for an enhanced covalency and, therefore, reduced ionicity in case of S-terminated cluster resulting into increased stability of ZB phase over the WZ phase. In this context, it is interesting to note that the stability of the two competing crystal phases, namely ZB and WZ, changes systematically for the bulk systems, CdS, CdSe and CdTe. While CdS has the WZ structure, CdTe is known to have the ZB form which has indeed been explained in terms of increased covalency. This is consistent with the present observation of ZB structure for CdS nanocrystal being stabilized in presence of a S-terminating layer which is also substantially more covalent.

3. Passivated stoichiometric clusters

In realistic situation, the clusters are grown in presence of some passivating agent. Although ideally the role of the passivator is to restrict the growth of the cluster by saturating the unpassivated dangling bonds, which opens up a clear gap in the energy spectrum without supposedly changing the intrinsic properties of the clusters, it may also influence the energy stability of the cluster itself. This is however very complicated and rather unexplored issue due to the complexity of various passivating agents used in experiments. A good understanding of the atomic structure of such complex passivating agents like trictylphosphine (TOP) or trictylphosphine oxide (TOPO) in many cases is unavailable and it is almost impossible to deal with such large complexes within an accurate first-principles approach. Very often, therefore fictitious H atoms are used in theoretical calculations for the purpose of passivation. In absence of any other well-defined procedure we have therefore considered the passivation by fictitious H atoms and in the following have studied the effect of the passivation on both stoichiometric and non-stoichiometric CdS nanoclusters.

In Fig. 10, we show the computed density of states of a representative stoichiometric CdS cluster with 4 shell and ZB structure in absence and presence of passivation. We note that assumed passivation could successfully remove the states close to Fermi energy, opening up a gap of about 1.5 eV. Similar results are obtained for clusters with other different shell structures and also with WZ symmetry. Having been convinced about the proper functioning of the passivator, in Fig. 11 we show the variation of the cohesive energy differences between the ZB and WZ structured stoichiometric CdS nanoclusters as a function of increasing cluster size. Interestingly we note, that the oscillating behavior of the relative stability between ZB and WZ structured clusters observed for naked stoichiometric clusters survives even in presence of passivation, in the sense the even shelled clusters favor the WZ structure and the odd shell clusters favor the ZB structure. This presumably is driven by the fact that the difference in number of bonds with fictitious H atoms between WZ and ZB structures oscillates as a function of increasing cluster size. As already stated, we have followed in the above a simplified treatment of passivating agent, the situation in presence of realistic passivators need to be explored, which however is beyond the scope of our present study.

FIG. 8: Average number of dangling bonds per surface atom (DB) for non-stoichiometric CdS clusters in ZB and WZ structures. The inset shows the difference between ZB and WZ structures. Plot is independent of whether the clusters are Cd-centered or S-centered.

FIG. 9: (Color online) Charge density contribution (δρ = ρt − ρa − ρs) around a surface atom of 4-shell non-stoichiometric CdS nanoclusters. The isosurface is chosen at .007 e−/(Å3).
4. Passivated non-stoichiometric clusters

In this section, we focus on non-stoichiometric clusters and the role of passivation in this class of clusters. The passivation has been done following the same prescription as in case of stoichiometric clusters. Fig. 12 shows the density of states plot for a representative non-stoichiometric cluster. As found in case of stoichiometric clusters, the passivator removes the surface states appearing close to Fermi energy in the unpassivated case and shifts them away from Fermi energy, thereby opening up a clear gap at the Fermi energy. The corresponding variation in the relative stability of the ZB and WZ structures for the passivated non-stoichiometric clusters are shown in Fig. 13. The upper panel shows the data for Cd-centered clusters while the lower panel shows the data for S-centered clusters. The chosen scheme of passivation seems to have a pronounced effect for the non-stoichiometric clusters in the sense apart from very small clusters, the tendency towards formation in ZB phase seemingly is found to be higher than that in WZ phase in general, irrespective of even or odd number of shell, and terminating layer, although in some cases the energy difference is indeed tiny (within 1-2 meV) and is within the calculational accuracy. For the non-stoichiometric clusters, study of realistic passivators will be even more interesting since in many cases the passivating agent itself may have S/Cd content, giving rise to preferential S or Cd termination of the synthesized clusters.
FIG. 13: Variation of cohesive energy difference between ZB and WZ structures with size for passivated Cd-centered (upper panel) and S-centered (lower panel) non-stoichiometric clusters.

FIG. 14: Calculated band gaps for stoichiometric clusters plotted as a function of increasing cluster size. Inset shows the positions of HOMO (solid right triangles) and LUMO (solid left triangles) with respect to HOMO of 6th shell cluster, as a function of cluster size.

FIG. 15: Calculated band gaps for non-stoichiometric clusters plotted as a function increasing cluster size. Upper and lower panels show the Cd-centered and S-centered clusters respectively. Inset shows the positions of HOMO (solid right triangles) and LUMO (solid left triangles) with respect to HOMO of 6th shell cluster, as a function of cluster size.

B. Band Gap Variation with cluster size

The study of CdS clusters in presence of passivator also allows us to investigate the variation of the band gap as a function of increasing cluster size. In Figs. 14 and 15, we show the computed band gaps as a function of increasing shell size for both ZB and WZ phases, for stoichiometric and non-stoichiometric clusters. The insets show the individual variations of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). First of all, the band gap associated with WZ structured clusters are found to be slightly higher than that of the ZB structured clusters in most of the cases, which results due to the fact that the band gap of the WZ phase in bulk is slightly higher than that of the ZB phase in bulk. CdS being a direct gap semiconductor, the band gaps of WZ and ZB phases are expected to be similar. As expected, the calculated band gap shows an overall decrease as a function of increasing cluster size due to the well known quantum confinement effect, asymptotically approaching the bulk band gap value in the limit of the infinite cluster size. The calculated band gap for the clusters are systematically underestimated due to the overbinding problem related with LDA treatment of exchange-correlation functional. For non-stoichiometric clusters, the band gap variation is found to be highly nonmonotonic. The odd shell clusters for Cd-centered clusters and the even shell clusters for S-centered clusters show significantly higher value of band gap compared to their respective counterparts. We therefore conclude that the S-terminated clusters in general show larger band gap
comparing to Cd-terminated clusters. As is evident from the variation of HOMO and LUMO energies shown in the inset, this oscillation is primarily contributed by the oscillation in the LUMO. The origin of such a behavior lies in the density of states of the unpassivated cluster itself. Comparing the density of states of Cd-terminated and S-terminated non-stoichiometric clusters as shown in left and right panels of Fig. 12, we found that while for S-terminated DOS, there exists a well-defined gap in the unoccupied part of the spectrum, the situation is very different in case of Cd-terminated cluster. The spectrum is practically gap less or with very small gap in the unoccupied region. Inclusion of passivating atom, changes the unoccupied spectra drastically in case of Cd-terminated cluster, while the unoccupied spectra apart from the removal of the states very close to Fermi energy changes only modestly in case of S-terminated clusters.

V. SUMMARY

Using first-principles density functional based calculations employing plane wave basis set we present an extensive study of the energy stability and the band gap variation in CdS clusters. In particular, we have considered the relative stability between ZB and WZ structures. In order to explore the varied experimental conditions, we have considered non-stoichiometric as well as stoichiometric clusters, in absence and presence of passivating atoms. Our study shows that the relative stability depends crucially on the surface structure, both geometry and chemistry depending on the specific cases. This may give rise to highly nonmonotonic behavior of the relative stability as a function of the growing cluster size. The band gap variation for the non-stoichiometric clusters is also found to exhibit strong oscillation.

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