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Electronic Properties of Surface Vacancies in CdS Nanocrystals

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Structural and electronic characteristics of neutral and charged vacancies of cadmium and sulfur in CdS nanocrystals have been studied using the density functional method with hybrid exchange-correlation functional. Total and partial density of states, formation energies and the energies of thermodynamic transitions were calculated. Based on these theoretical findings and available experimental data, we can confirm the assumption, that the singly charged vacancies of cadmium are the centers of radiative recombination in such the structures.

Key words: Cadmium sulfide, nanocrystal, photoluminescence, vacancy, density functional method.

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Introduction

Cadmium sulfide (CdS) is a classic direct gap $A^{II}B^{VI}$ semiconductor with a band gap of 2.42 eV (515 nm) at room temperature, but remains an interesting material during the long time [1, 2]. However, in recent years, this interest has grown significantly due to possible application of CdS nanocrystals (NCs) in micro- and optoelectronics and, particularly, in light-emitting diodes, lasers, sensors, photoelectrical devices, solar cells, memory cells etc. [3-7].

Bulk CdS is a non-stoichiometric semiconductor of *n*-type, provided by the presence of intrinsic defects, such as sulfur vacancies and interstitial cadmium [8]. However, at the nanoscale, the recombination processes are expected to be affected by the presence of the surface defects due to the smallness of NCs size, resulting mainly in the luminescence characteristics of NCs. In the most of cases, PL spectra of such the nanocrystals, are determined by the inter-band transitions only, as widely described in the literature [9-11]. Nevertheless, the defect-associated luminescence may be observed in PL spectra of cadmium chalcogenides [12] as well. It is noteworthy to note, that the formation of one or other kind of defects in crystal structure depends significantly on the NC manufacturing method. Due to the presence of defects, the local states appear near the conducting band bottom or valence band top. This, in turn, affects significantly the optic properties of the systems under study, since with a decreasing the system size and, consequently, the currents localization, the contribution of fundamental absorption is also decreasing, while the contribution from the localized states becomes significant. Such low-energy electron excitations and the mechanism of their localization are responsible for the radiative, optic and luminescent properties of the semiconductors [13].

There is a set of works [14-19] dedicated to the problem of the photoluminescence properties and establishing the mechanism of radiative recombination in CdS nanocrystals. However, many factors remain undefined, particularly, the nature of the recombination centers have still not been clarified. There are the assumptions made in many works that the radiation occurs through the V_{Cd}-V_S [15, 19] centers, acceptor centers V_{Cd} [16-18] or through the surface defects of unknown nature.

In the present work, we perform the density of states calculations of the neutral and charged vacancies of cadmium and sulfur in CdS NCs, in order to make a conclusion which kind of these defects are the most probable center of radiative recombination.

I. Numerical method

The cadmium vacancy can be found in V_{Cd}^{0}, V_{Cd}^{1-} and V_{Cd}^{2-} charge states, while sulfur vacancy in V_S^{0}, V_S^{1+} and V_S^{2+}, respectively. For isolated nanocrystal, V_X vacancy formation energy for given charge state at zero temperature is defined by expression [20]:

$$E(x,q) = E_{CdS}(x,q) - E_{CdS} + \mu_x + E_F^q \qquad (1)$$

where x — Cd or S atom, $q = 0$, ±1, ±2 — vacancy charge state, μ_x – cadmium or sulfur chemical potential, which could be taken as a total energy of a corresponding separate atom. $E_{CdS}(x,q)$ and E_{CdS} – total energy of a system with vacancy V_x^q and defect-free system at zero temperature — when all of atoms are located in the equilibrium positions. E_F^q – electrochemical potential of electrons at zero temperature, which serves as a Fermi level in our case. All the energies are accounting with respect to the top of VB, which is set to zero for the convenience. However, due to the small size of the system, an adding or removing even a single electron leads to significant redistribution of the charge density. Therefore, during the calculations of charged defects formation energies, the Fermi level is defined as a total energy difference between charged (with a given q) and neutral (q=0) defect-free systems. Basically, this is the energy, necessary to add q electrons to the system without the changes in atomic geometry positions. If we allow the charged defect-free system to relax, the system might arrive to the new equilibrium atomic positions, leading to the changes in total energy by the value, known as Franck-Condon shift:

$$E_r^q = E_{CdS}(q) - E_{CdS} - E_F^q \qquad (2)$$

An important characteristic of the structures with defects is the thermodynamic transitions energies, also known as defects ionization energies. The energy of a such transition is defined in terms of formation energies $E(x,q_0)$ of corresponding defect charge states:

$$\varepsilon\left(x, {}^{q_0}/_{q}\right) = \frac{E(x,q_0) - E(x,q)}{q_0 - q} \qquad (3)$$

In this expression the formation energies are calculated for the fully relaxed systems in corresponding charge states. If the process of charging the defect is fast, such as an electron-hole recombination, the corresponding transition energy will be nothing more than the energy of optical transition.

All the calculation have been carried out within the density functional theory, as implemented in GAMESS-US software package [21]. As a model, we use spherical $Cd_{33}S_{33}$ cluster with a center at the middle of Cd-S bond. An initial structure was hexagonal, and we kept only the atoms having no less than two nearest neighbors. Such a cluster is stoichiometric, and consists of “magic number” atoms. Moreover, there are experimental works, particularly [22], demonstrating by the use of mass-spectral analysis that colloidal nanoparticles $(CdSe)_{33}$ and $(CdSe)_{34}$ are especially stable and dominant during the growth in the simple solution method. Similar calculation of the CdTe and CdSe NCs properties have been performed in the work [23], which showed good results with the use of hybrid exchange-correlation functional B3LYP [24-27] and the Hay-Wadt set of basis functions and effective core potentials, known as LANL2DZ basis set [28-30]. We performed few test runs with different basis sets on the $(Cd_{15}S_{15})$ cluster and found that the basis LANL2DZ works well also for a CdS, providing adequate crystal structure and the Cd-S bond length. Therefore, all the calculations here were performed using this basis set.

In the present work, we perform the geometry structure and the electronic density of states calculations of the defect-free $Cd_{33}S_{33}$ NC in the charge states q = -2..2, as well as of cluster containing the cadmium vacancy V_{Cd}^q with q = 0..-2 or sulfur vacancy V_S^q with q = 0..2. The vacancies were simulated by removing the single atoms of the corresponding sort - cadmium or sulfur from the NC surface, leading to the general study the properties of $Cd_{32}S_{33}$ and $Cd_{33}S_{32}$ clusters.

II. Structural relaxations of vacancy

During the defect formation, the geometry modification of a nanocrystal takes a place. Table 1 shows in details the displacement of (S_1, S_2, S_3) and (Cd_1, Cd_2, Cd_3) atoms in vicinity of the cadmium and sulfur vacancy, respectively, with respect to their position in optimized defect-free nanocrystal or, in the case of charged defects, to their positions in defect with a lower charge. Particularly, for the neutral cadmium vacancy, root-mean square (RMS) displacement of atoms from their equilibrium positions in defect-free system is D_{RMS} = 0.3Å, and the largest displacement is found to be 1.1Å for the atoms, which had the bonds with the cadmium atom removed, while the smallest displacement in NC is of hundredths of Angstrom. For the charged cadmium vacancy V_{Cd}^{1-}, displacements are somewhat smaller: for the same sulfur atoms they do not exceed 0.8Å, and in general all the system relaxes with D_{RMS} = 0.23Å. With respect to the neutral vacancy, during the (0/-) recharging, the nearest atoms displacements are larger than for direct formation: in this case RMS displacement is D_{RMS} ~ 0.4 Å. The largest modifications in NC geometry occur for the vacancy V_{Cd}^{2-}, both for direct formation and for recharging from V_{Cd}^{2-} state. The nearest atoms displacements are found within 0.3-1.4 Å, but more serious changes occur with geometry of all the NC: the largest displacement of atoms is 2.7Å, and in overage the system relaxation is D_{RMS} ~ 0.5 Å.

Table 1

Displacement of (S_1, S_2, S_3) and (Cd_1, Cd_2, Cd_3) atoms in vicinity of the cadmium and sulfur vacancy

	S_1	S_2	S_3	D_{RMS}		Cd_1	Cd_2	Cd_3	D_{RMS}
V_{Cd}^0/Bare	0.314	1.016	0.603	0.312	V_S^0/Bare	1.073	0.833	0.425	0.305
V_{Cd}^{1-}/Bare	0.351	0.237	0.806	0.230	V_S^{1+}/Bare	1.278	0.717	0.333	0.395
V_{Cd}^{1-}/V_{Cd}^0	0.178	1.054	1.088	0.388	V_S^{1+}/V_S^0	0.235	0.225	0.320	0.156
V_{Cd}^{2-}/Bare	0.326	0.603	0.962	0.471	V_S^{2+}/Bare	1.413	1.327	1.149	0.561
V_{Cd}^{1-}/V_{Cd}^{1-}	0.524	0.100	1.395	0.465	V_S^{2+}/V_S^{1+}	0.152	1.744	1.423	0.386

Similar NC relaxations accompany also the process of sulfur vacancy formation. In the case of neutral vacancy V_S^0, the nearest cadmium atoms displacements are significant, 0.4 - 1.1 Å, and the total relaxation is D_{RMS} = 0.3 Å, i.e. the system relaxation is of the same order as in cadmium vacancy V_{Cd}^0. During the formation of positively charged sulfur vacancy V_S^{1+}, all the atoms of system participate in the relaxation: the largest displacement is 1.3 Å and overage D_{RMS} = 0.4 Å, while the nearest atoms are shifted on 1.2Å. If this vacancy is formed by V_S(0/1+) recharging, the relaxation is smaller — of order 0.2-0.3 Å, and the total relaxation is D_{RMS} = 0.16 Å. The largest changes in the nearest atoms geometry is observed for the vacancy V_S^{2+}: the nearest atoms displacement here is 1.1 - 1.4 Å, and D_{RMS} = 0.56 Å for the all of system. At the V_S(1+/2+) recharging, the system is being relaxed significantly as well, the largest displacement is 1.7 Å, although RMS here is D_{RMS} = 0.39 Å, what is somewhat smaller than the corresponding value for the direct formation of this kind of vacancy.

III. Electronic characteristics of vacancies

The formation energies E_{form} of neutral and charged vacancies of cadmium and sulfur, obtained by expression (1), ionization energies of defect-free system E_F^q and relaxation energies (Franck-Condon shifts) E_r^q for charged systems are listed in the Table 2.

The formation energies have been calculated for the vacancies, created directly from the defect-free nanocrystal. It is seen, that the largest energy is needed to form the neutral vacancy of sulfur, although all the values of formation energy are positive. It is noteworthy to note, that formation energies of charged vacancies are significantly smaller than for neutral ones: with the increase of ionization energy, the system relaxation becomes larger, leading to increase in Franck-Condone shift. This is especially concerned to sulfur vacancy, for which even ionization energy is in few times larger than for vacancy of cadmium. Obviously, for the stoichiometric Ncs CdS, the formation of sulfur neutral vacancy is rather unlikely, since the lowest formation energy belongs to the vacancy V_S^{2+}. However, for the large NCs, which already have the well-formed faces containing the certain sort of atoms - metal or chalcogenide, the vacancies of sulfur are considered to be the most probable kind of defects, which creates corresponding energy levels in a gap, and, consequently, participates in the photoluminescence [31]. In our case, an appearance of cadmium vacancy is more probable, although formation energy of V_S^{2+} vacancy is close to one of cadmium.

Table 2

Formation energies E_{form} of neutral and charged vacancies of cadmium and sulfur, ionization energies E_F^q and relaxation energies (Franck-Condon shifts) E_r^q.

E, eV	*q* = -2	*q* = -1	*q* = 0	*q* = 1	*q* = 2
E_F^q, eV	-4.283	-3.130	-	7.392	16.965
E_r^q, eV	-1.441	-0.089	-	-0.889	-1.872
E_{form} V_{Cd}^q, eV	1.064	2.237	3.727	-	-
E_{form} V_S^q, eV	-	-	5.992	4.523	1.877

The energies of thermodynamic transitions for the cadmium and sulfur vacancies, calculated with expression (3), are listed in Table 3. The definition “Thermal” means the energies, obtained for the case when the process is slow and the final states of defect has another, relaxed geometry structure, i.e. this energy accounts the Franck-Condon effect. “Optic” energy corresponds to the fast, “optical” transition, when the final atomic geometry structure remains the same as at the beginning. There are also reverse transitions calculated, i.e. both “charging” and “discharging” processes are considered. It is noteworthy to note here, that the reverse processes have the negative energies, and, therefore, do not produce any levels in a gap.

For the thermodynamic processes of the defect charging, the situation is somewhat other. In the case of cadmium vacancy, almost all the possible transitions (0/-1), (0/-2) and (-1/-2) could be observed in a gap, and this is concerned both optic and Franck-Condon transitions. For the vacancy of sulfur, all the optic transitions are possible - (0/+1), (0/+2) and (+1/+2), but the Franck-Condon transitions are limited by only two of them - (0/+1) та (0/+2), since the (+1/+2) transition has the energy exceeding the width of NCs gap.

Fig. 1 shows the total and partial density of states (PDOS), calculated for neutral and charges vacancies of cadmium and sulfur. PDOS is formed with the states of the nearest atoms, participating in the corresponding

Table 3

Energies of thermodynamic transitions for the cadmium and sulfur vacancies
(See definitions in the text)

V_{Cd}	Thermal *ε*, eV			Optic *ε*, eV				V_S	Thermal *ε*, eV			Optic *ε*, eV		
q_0/q	0	-1	-2	0	-1	-2		q_0/q	0	1	2	0	1	2
0	0.0	1.49	1.33	0.0	0.1	0.11		0	0.0	1.47	2.06	0.0	0.76	0.46
-1	-1.49	0.0	1.17	-2.71	0.0	0.47		1	-1.47	0.0	2.65	-1.95	0.0	0.94
-2	-1.33	-1.17	0.0	-2.16	-1.54	0.0		2	-2.06	-2.65	0.0	-2.43	-2.44	0.0

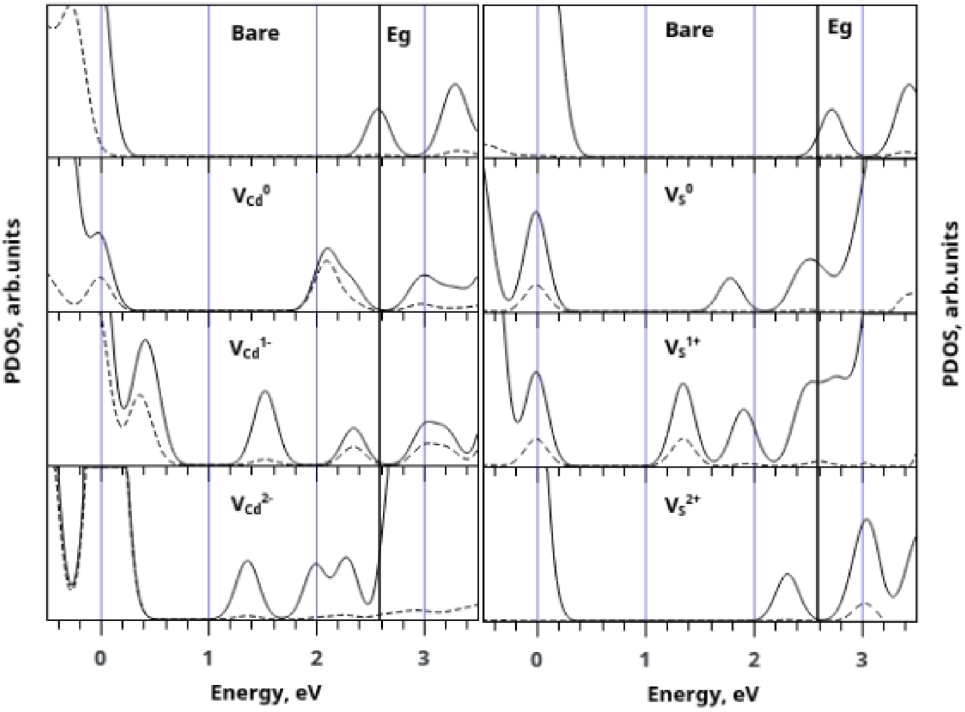

Fig. 1. Total (continuous line) and partial (dashed line) density of states of neutral and charged vacancies of cadmium and sulfur.

defect formation: the sulfur atoms S_1-S_3 for the vacancy of cadmium and Cd_1-Cd_3 for sulfur vacancy. All spectra are obtained using the Gaussian convolution with a smearing parameter 0.25 eV and are aligned over HOMO levels, taken as zero energy for the convenience. It is seen, that the DOS of initial, defect-free NC has a clear gap (the HOMO-LUMO energy distance) of Eg = 2.6 eV. The nearest sulfur atoms produce the energy states in vicinity of the valence band top (HOMO level), while the energy levels corresponding to states of cadmium could be found far outside the gap. During the creation of the neutral cadmium vacancy, the states of S_1-S_3 are forming the peak close to LUMO level. Also, these states appear as a smooth band at the valence band top. This diffused peak becomes more pronounced in the vacancy charge state $q = -1$, which form the acceptor level and, consequently, new bands in the gap, caused by not the nearest environment only, but also are related with the relaxation of all the system, as it was described before. This “general” relaxation becomes dominant in the more delocalized states formation during the recharging the vacancy into state $q = -2$, while the states of S_1-S_3 atoms in this case form the peak close to the valence band top. The presence of such well-defined peak in the DOS during the singly charged vacancy formation means that these centers could be responsible for the radiative recombination in CdS NCs. This result is a theoretical confirmation for the assumptions made in experimental works, that surface singly charged vacancies of cadmium are the centers of luminescence. Really, the peak in DOS in this case is on about $\Delta E \approx 0.4$ eV far from the valence band top (HOMO level), and the (-1/-2) recharging energy of the cadmium vacancy (see Table 3) is close to this energy distance. There is a band at $E \approx 2.2$ eV in the experimental PL spectra, corresponding to the non-equilibrium curriers transitions from the conduction band on this level. It is noteworthy to note, that in work [7], two closely located bands in PL spectra of CdS NCs in the region 2.1 - 2.3 eV are assigned to interstitial sulfur ions. With regards to the results, obtained in this work, we can assume, that one of these bands is related with singly charged cadmium vacancies, and another — with interstitial sulfur ions. To confirm this assumption, the DOS calculation for CdS NCs containing such kind of defect should be performed. This, however, is the subject of additional work and will be published elsewhere.

Concerning the sulfur vacancy, the states of nearest Cd_1-Cd_3 atoms appear in the forbidden gap in the vacancy charge state $V_S(q = +1)$ only. Also, they form a clear peak close to the conduction band bottom (LUMO level) in the systems with neutral or $q = +1$ charged vacancy. The rest of peaks, arising in a gap, are related with the general relaxation of the system. Additionally, important is that our model of NC is relatively small, and the absence of even a single atom, obviously, leads to the notable changes of size and, consequently, in the corresponding DOS. Therefore, the most important is the information about the charged defects, since in this case we deal with the systems with the same number of atoms.

Conclusion

In the present work, we studied the cadmium and sulfur vacancies formation processes and their density of states, for both neutral and charged states. It has been found, that for the singly charged acceptor-type vacancies of cadmium, the well-defined peak in DOS appear on the energy distance of ≈ 0.4 eV far from the valence band top. This result indicates that the singly charged cadmium vacancies are the centers of radiative recombination in the CdS NCs.

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Електронні характеристики поверхневих вакансій у нанокристалах CdS

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Структурні та електронні характеристики нейтральних і заряджених вакансій кадмію та сірки у нанокристалах CdS досліджено методом функціоналу густини з використанням гібридного обмінно-кореляційного функціоналу. Розраховано повну та парціальну густину електронних станів, енергії формування та енергії термодинамічних переходів. На основі отриманих теоретичних результатів та наявних експериментальних даних, зроблено висновок, що однозарядні вакансії кадмію є центрами випромінювальної рекомбінації у таких структурах.

Ключові слова: кадмій сульфід, нанокристал, фотолюмінесценція, вакансія, метод функціоналу густини.