CdS Microclusters in Sodalite Frameworks of Different Composition: A Density Functional Study

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We present a local density functional study of Cd_4S and Cd_4S_4 clusters inside sodalite cages of different compositions (Al:Si ratios). The composition of the framework determines the cluster → cage charge transfer and strongly affects the atomic structure of the inclusion. The energy gap and the character of the highest occupied (HOMO) and lowest unoccupied (LUMO) electronic states depend on the size and stoichiometry of the included clusters, as well as on the overall stoichiometry of the composite. The calculated gap for Cd_4S inclusions in aluminosilicate and aluminate sodalite (at half and full packing respectively) is ~2.5 eV (i.e., about twice the calculated gap of bulk CdS), while for Cd_4S_4 in aluminosilicate and pure silica sodalite (at half packing) it is 1.7-1.9 eV (i.e., about 1.5 times the gap of bulk CdS). Our results indicate that simple confinement arguments are usually insufficient to predict the behavior of semiconductor−zeolite composites.

I. Introduction

The creation of novel materials by insertion of molecules and/or clusters into the cages and channels of zeolitic frameworks is a subject of intensive research and continuing interest.[1,2] In particular zeolites are considered as ideal templates for growing three-dimensional "quantum-dot crystals", with several potential applications in the field of optoelectronic devices. So far, the possibility of incorporating small semiconductor clusters[3] into various zeolite hosts has been demonstrated by several experimental studies. An important issue which has emerged concerns the structure of the semiconductor−zeolite composites and how this is related to the fundamental gap of these systems.

Some aspects of this issue have been analyzed in a few recent theoretical investigations. The structure and stability of M_4X_4 (M = Cd or Zn; X = O or S) clusters in siliceous faujasite has been investigated using atomistic simulation methods.[4] These calculations found significant distortions of both the host lattice and the cubic clusters and predict that half packing of the lattice (i.e., in which only alternate sodalite cages are occupied by the clusters) is preferred to full packing. In a Local Density Functional (LDF) study by two of us,[5] the structure and electronic properties of different microclusters of III−V compound semiconductors (GaP, InAs, and GaN) in aluminosilicate sodalite have been examined. Structures are found to be characterized by a strong bonding of the group III atoms to the oxygens of the cage. The clusters introduce optically active electronic states in the energy gap of the zeolite, and the overall gap of the semiconductor-zeolite composite is determined by the chemical nature of the cluster. LDF calculations have been carried out also for Si_n (n = 2−7) clusters in silicasodalite,[6] a system for which no charge transfer between cluster and

framework should occur. For sufficiently small aggregates (n < 5), both the atomic and the electronic structures of the embedded clusters are close to those of the clusters in free space. For larger n's, the volume of the sodalite cage becomes too small, the cluster is "squeezed" inside the cage, and the interaction between the framework and the embedded cluster becomes repulsive.

In this work, we again use first principles LDF methods to investigate CdS microclusters in sodalite. The properties of CdS clusters and nanocrystals have been the subject of numerous experimental[3] and theoretical investigations (see, for example, refs 7 and 8) over the last years. Morever, several experimental studies have dealt with II−VI semiconductor inclusions in the sodalitic cages of zeolites of different composition (for a recent review, see ref 2). In most of these experiments the clusters which are believed to occur are II_4VI and II_4VI_4. In our study we shall thus consider Cd_4S and Cd_4S_4 inclusions and study how the atomic and electronic structures depend on the composition and charge of the sodalitic framework. Although density functional theory is known to severely underestimate the HOMO−LUMO (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital) band gap,[9] so that calculated gaps are not immediately comparable to experiment, in this work we are mostly interested in trends, which are widely believed to be quite well described by this approach.

II. Computations

A. Geometry. The sodalite structure can be described as a body-centered cubic arrangement of β cages, or sodalitic cages.[10] The β cage is the building block of several zeolites, including sodalite, zeolite A, as well as zeolites X and Y. This cage has the shape of a truncated octahedron, with eight hexagonal and six square faces. In the sodalite structure, cages are joined through the square faces. The vertices of the cage correspond to tetrahedrally coordinated (T) Si or Al atoms. Each of these

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TABLE 1: Structural Parameters of the Sodalite Framework in the Presence of Different Included Clusters[a]

	SOD−2(Na$_4$Cl)	SOD−Cd$_4$S	SOD−2(Cd$_4$S)	SOD−Cd$_4$S$_4$
		Angles (deg)		
$\widehat{SiOAl}$	138.2	12 × 138.7	140.3 ± 6.1	144.8 ± 5.2
		12 × 141.9		
τ_{Si}	24 × 107.7	12 × 103.2		
		12 × 112.3		
	12 × 113.0	6 × 109.7		
		6 × 116.2		
average	109.5	109.5	109.5 ± 3.3	109.5 ± 4.4
τ_{Al}	24 × 108.7	12 × 104.0		
		12 × 113.0		
	12 × 111.0	6 × 107.6		
		6 × 115.3		
average	109.5	109.5	109.4 ± 3.4	109.5 ± 3.7
ϕ_{Si}	23.9	6 × 18.6	21.5 ± 1.6	6 × 15.7 ± 2.0
		6 × 24.8		6 × 18.8 ± 0.6
ϕ_{Al}	22.4	6 × 17.5	20.3 ± 1.6	6 × 15.0 ± 1.3
		6 × 23.8		6 × 17.9 ± 1.0
		Distances (Å)		
$\overline{SiO}$	1.62	12 × 1.652	1.631	12 × 1.627
		12 × 1.605		12 × 1.593
$\overline{AlO}$	1.74	12 × 1.744	1.728	12 × 1.716
		12 × 1.705		12 × 1.688

[a] Values for natural sodalite (second column) are from experiment (ref 13), while all other values are from calculations in this work. τ denote $\widehat{OTO}$ angles, where T = (Al and Si); ϕ are the collapse angles for the TO$_4$ tetrahedra. Average values together with their dispersion (standard deviation) are reported. When not explicitly given, the dispersion should be considered very small or negligible. For some parameters inequivalent sets of values are distinguished.

is connected via oxygen bridges to four other T-atoms in the first coordination shell. In sodalite, only one type of T-site is present.

The sodalite structure can be prepared with a variety of framework compositions and charges, from a neutral silica framework [Si$_{12}$O$_{24}$]^0,[11] to pure aluminate sodalite [Al$_{12}$O$_{24}$]$^{-12}$,[12] to the most frequent aluminosilicate sodalite [Al$_6$Si$_6$O$_{24}$]$^{-6}$ (formulas refer to a unit cell). The negative charges are provided by counterions inside the sodalite cages. The counterions usually consist of M$_4$X clusters, where M = cation and X = anion. In natural sodalite, for instance, a Na$_4$Cl cluster is present inside each cage, so that the unit cell content is [Al$_6$Si$_6$O$_{24}$] −2(Na$_4$Cl).

In the following, CdS microclusters embedded in [Al$_6$Si$_6$O$_{24}$] (SOD), [Si$_{12}$O$_{24}$] (SiSOD), and [Al$_{12}$O$_{24}$] (AlSOD) frameworks are considered. For the SOD framework, we use the lattice constant of natural sodalite, a = 8.92 Å, which has been obtained in a previous LDF study.[13] For SiSOD and AlSOD, lattice constants of 8.836[11] and 8.818 Å,[12] respectively, are used.

B. Technical Details. Calculations have been carried out using LDF theory within the framework of the Car−Parrinello method.[14,15] The electronic valence wavefunctions are expanded in plane waves and are calculated only at the Γ point of the Brillouin zone. For Si, Al, Cd, and S, electron−core interactions are described by norm-conserving pseudopotentials[16] in a Kleinman and Bylander form,[17] whereas for oxygen an "ultra-soft" pseudopotential[18] is used. For Cd, only 5s electrons are treated explicitly as valence electrons, whereas nonlinear core corrections are used to take care of the filled 4d shell.[19,20] A kinetic energy cutoff $E_{cut,1}$ = 16 Ry, is used for the smooth part of the electronic wave functions, while the cutoff for the augmented electron density is $E_{cut,2}$ = 200 Ry.[21] The parametrisation of Perdew−Zunger[22] is employed for the functional of local exchange correlation. A preconditioned algorithm[23] is used in the electronic minimization procedure. With a preconditioning cutoff E_p = 2 Ry and an electronic fictitious mass μ = 500 au, our time step is Δt = 9 au. The atom positions are relaxed using a damped second-order dynamics algorithm until residual forces are less than 0.0003 au.

C. Preliminary Test: Bulk CdS. Most of the ingredients of our calculations have already been tested in our previous studies of sodalite and offretite zeolites.[5,13,24] As a further test for the present study, we have calculated the lattice parameter of bulk CdS in the zincblende structure using a cubic supercell containing 64 atoms and sampling the Γ-point only of the corresponding Brillouin zone. The resulting value is a = 5.92 Å (corresponding to a nearest neighbor CdS distance of ∼2.57 Å), to be compared to an experimental value of ∼5.82 Å. The difference between theory and experiment is less than 2%. The calculated band gap for bulk CdS is E_{gap}^{bulk} = 1.3 eV, to be compared to the experimental gap of 2.5 eV. As mentioned previously, the strong underestimate of energy gaps is a well-known feature of density functional calculations.

III. Results

A. Cd$_4$S Clusters in Aluminosilicate (Al:Si = 1) and Pure Aluminate Sodalite. *1. SOD−2(Cd$_4$S) and SOD−Cd$_4$S.* In order to illustrate the influence of the cluster → framework charge transfer on the structure and band gap of the composite, it is interesting to compare the behavior of SOD−2(Cd$_4$S), in which each sodalite cage contains a Cd$_4$S cluster, with that of SOD−Cd$_4$S, in which only one every two cages contains a cluster. SOD−Cd$_4$S is a stoichiometric composite, where the six electrons that Cd$_4$S can donate perfectly compensate the missing charge of the sodalitic framework. For SOD−2(Cd$_4$S), instead, the charge that the clusters may donate to the framework is twice the missing charge on the sodalitic cage. This may make the practical realization of such structure difficult (see also below).

The structure of SOD−2(Cd$_4$S) was calculated starting from natural sodalite, SOD−2(Na$_4$Cl), and replacing each Na$_4$Cl tetrahedral unit by a Cd$_4$S cluster. Upon relaxation, a very different behavior of the two non-equivalent Cd$_4$S clusters in the unit cell is observed (see Table 3). This is at variance with the results for SOD−2(III$_4$V) composites, where the two nonequivalent clusters have the same structure also after relaxation.[5] In the present case, one Cd$_4$S maintains a tetrahedral

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TABLE 2: Structural Parameters of the Silica− and Alumina−Sodalite Frameworks[a]

| | SiSOD−Cd$_4$S$_4$ | | AlSOD−2(Cd$_4$S) | |
			(experimental)	(simulation)
		Angles (deg)		
$\widehat{SiOSi}$	12 × 147.8	$\widehat{AlOAl}$	24 × 126.1	24 × 130.6
	12 × 157.4			
τ_{Si}	12 × 105.0	τ_{Al}	48 × 108.1	48 × 107.8
	24 × 106.9		24 × 112.5	24 × 113.0
	12 × 110.8			
	24 × 113.6			
ϕ_{Si}	12 × 11.30	ϕ_{Al}		12 × 28.506
	12 × 16.11			12 × 28.518
		Distances (Å)		
$\overline{SiO}$	24 × 1.626	$\overline{AlO}$	48 × 1.750	24 × 1.716
	24 × 1.594			24 × 1.717

[a] Symbols and notations are as in Table 1. For AlSOD−2(Cd$_4$S) both theoretical and experimental results from ref 12 are presented. For these systems, dispersions of the data are negligible.

TABLE 3: Geometrical Parameters of Cd$_4$S Clusters Included in Sodalitic Frameworks[a]

| | SOD−2(Cd$_4$S) | | AlSOD−2(Cd$_4$S) | |
		SOD−Cd$_4$S	(experimental)	(simulation)
$\overline{CdO}$	2.488 2.445		2.386	2.198	2.285
	3.044		2.989	3.297	3.213
$\overline{CdS}$	2.634 2.487		2.668	2.535	2.528
$\overline{CdCd}$	2.718				
	2.733				
$\widehat{CdSCd}$	109.4		109.5		109.5

[a] For SOD−2(Cd$_4$S), the parameters of the two clusters in the unit cell are separately reported. For the split-up cluster (right column), the bond length of the CdS fragment and the distances in the Cd$_3$ fragment are reported. For AlSOD−2(Cd$_4$S), the calculations are compared to the experimental values reported in ref 12.

symmetry, with the Cd atoms located at the center of the 6-ring faces of the cage, whereas the other cluster is strongly deformed. Two fragments may be distinguished: a Cd−S strongly bonded pair (Cd−S = 2.487 Å), with the cadmium atom still interacting with the cage, and an L-shaped Cd$_3$ fragment. Relaxed structural parameters for the framework are given in Table 1, together with corresponding results for other sodalite composites. We can remark that the framework geometry does not change substantially from one composite to the other.

In the relaxed configuration of the stoichiometric SOD−Cd$_4$S composite, the tetrahedral symmetry of the Cd$_4$S cluster is conserved, with a Cd−S bond length of 2.668 Å, slightly longer than the calculated bulk bond length of 2.57 Å (see Table 3). Nearest-neighbor and next-nearest-neighbor oxygens around each Cd are at distances 2.386 and 2.989 Å, respectively. The optimized structures of the filled and unfilled cages are different: the filled cages are wider than the unfilled ones, and the oxygen atoms are more collapsed in the void cells (as shown by the collapse angles ϕ, in Table 1). The final configuration for both cages shows a very little dispersion of the geometrical parameters around their average values.

To get insight into the energetics of cluster incorporation, we have calculated the embedding energy E_{emb}, which we define as the difference between the total energy per unit cell (E_{tot}) of the sodalite framework with the encapsulated cluster(s), and the sum of the energies of the *non-interacting, neutral* framework (E_{frame}), and cluster(s) (E_{clus}). In this case for E_{clus} we take the total energy of neutral Cd$_4$S frozen in the structure attained within the sodalite cage. For SOD−Cd$_4$S, the resulting value is E_{emb} = 4.619 hartrees. Such a large energy can be

TABLE 4: Structural Parameters for Cd$_4$S$_4$ Clusters Embedded in Sodalite and Silicasodalite Frameworks at Half Packing[a]

	SOD−Cd$_4$S$_4$	SiSOD−Cd$_4$S$_4$	Cd$_4$S$_4$
$\overline{CdO}$	2.336	2.913	
	2.849	3.201	
$\overline{SO}$		2.796	
		3.425	
$\overline{CdS}$	2.487	2.539	2.582
$\widehat{CdSCd}$		79.3	73.0
$\widehat{SCdS}$		99.8	104.7

[a] For comparison, the corresponding values for an isolated Cd$_4$S$_4$ cluster are also reported (last column). Notice that both the cluster embedded in silicasodalite and the "free" Cd$_4$S$_4$ have S atoms on their outer shell.

**TABLE 5: Electronic Gap Widths and Spatial Localization of HOMOs and LUMOs for the Composite Samples**

	E_{gap}(eV)	HOMO	LUMO
SOD−2(Cd$_4$S)	0.91	cluster (S of CdS)	cluster (Cd$_4$S)
SOD−Cd$_4$S	2.42	mixed (S and O)	cluster
AlSOD−2(Cd$_4$S)	2.55	cage (O)	cage (O)
SOD−Cd$_4$S$_4$	1.93	mixed	cage (O)
SiSOD−Cd$_4$S$_4$	1.66	cluster	cluster

rationalized by taking into account the transfer of six electronic charges from the cluster to the cage and the resulting electrostatic interactions between [Cd$_4$S]$^{6+}$ and the [Al$_6$Si$_6$O$_{24}$]$^{6-}$ framework. For the SOD−2(Cd$_4$S), the calculated E_{emb} is 8.626 hartrees, (i.e., substantially less than twice the embedding energy for SOD-Cd$_4$S), indicating that half packing of the lattice is preferred to full packing.

In Figures 1a,b the electronic densities of states (DOS) of SOD−2(Cd$_4$S) and SOD−Cd$_4$S are compared to that of the negatively charged empty framework [SOD]$^{6-}$. For the latter we find an HOMO−LUMO gap of 3.94 eV, which is close to the gap of 4.39 eV that Filippone et al.[13] calculated for SOD−2(Na$_4$Cl) (for which the experimental gap is ∼6.1 eV). For SOD−2(Cd$_4$S) system, the band gap is rather small, 0.91 eV, even smaller than the calculated gap for bulk CdS, whereas the electronic gap of SOD-Cd$_4$S is 2.42 eV, (i.e. almost twice the gap for bulk CdS). We remark that both these gaps are quite different with respect to the calculated gap of GaP−sodalite systems,[5] in spite of the fact that the experimental gaps of bulk CdS and bulk GaP are very similar. Analysis of the electronic charge distributions of the HOMOs and LUMOs, shows that for SOD−2(Cd$_4$S) both the HOMO and the LUMO are associated with states of the included clusters, whereas for SOD−Cd$_4$S the HOMO has mixed cluster−framework character and the LUMO is localized on the cluster (see Table 5). It may be also interesting to point out that for SOD−2(Na$_4$Cl) both the HOMO and the LUMO have been found to be localized on the framework's oxygen atoms,[13] while for III−V infilled clusters the HOMO arises from the inclusions and the LUMO has a mixed cluster−cage character.[5]

2. AlSOD−2(Cd$_4$S). Al$_{12}$O$_{24}$−2(Cd$_4$S) has been synthesized and experimentally characterized by X-ray diffraction, infrared spectroscopy, and ultraviolet reflectance.[12] This combination of alumina-sodalite cage and Cd$_4$S inclusions has again a stoichiometric composition.

Comparison between experimentally determined and calculated structural parameters of the included clusters is presented in Table 3. The agreement is good, differences between the two sets of data being smaller than 5%. Our calculations show that upon relaxation the included clusters fully preserve the tetrahedral symmetry. Moreover, the relaxed configurations of

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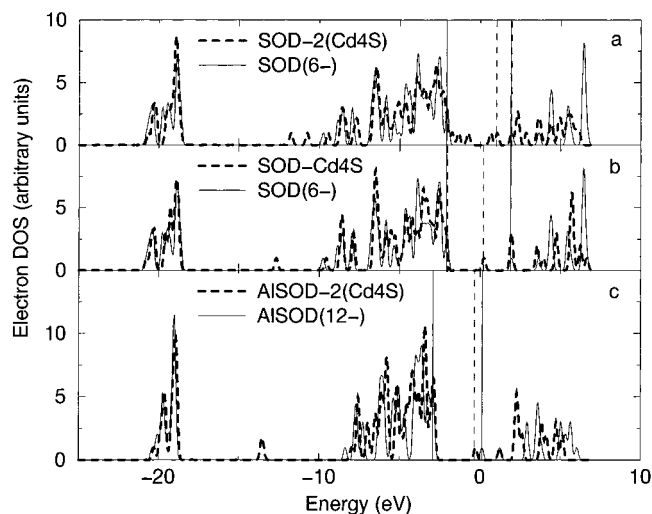
Figure 1. DOS for aluminosilicate— and alumino—sodalite with Cd_4S included clusters. For each case both the DOS for the framework—cluster composite (dashed line) and the bare charged framework (thin full line) are shown. The vertical dashed (full) lines indicate the gap for the cluster-cage composite (bare framework). Note that in part c the HOMOs for the composite and the framework coincide. Different densities are aligned at the main peak of the deepest bands (at ~ -20 eV) and are normalized to the number of valence states of the corresponding sample. The calculated eigenvalue spectrum has been broadened with a gaussian of width 0.14 eV.

the two nonequivalent clusters are practically identical. The little dispersions around the average values of the geometrical parameters of the clusters (see Table 3) and of the cage (see Table 2) suggest that the structure has a great stability. From Table 3 we can see that the Cd—O distances, 2.285 Å, are shorter than in any other zeolite composite we have considered. This may be an effect of both the narrower size of the aluminasodalite cage and the strong interaction between cage and inclusions which is caused by the huge charge transfer. The Cd—S distance (2.528 Å) is comparable with the bulk distance.

In Figure 1c, we compare the electronic DOS of AlSOD—$2(Cd_4S)$ to that of the negatively charged empty framework $[AlSOD]^{12-}$. For the latter the calculated gap is 2.98 eV, while for the composite it is 2.55 eV (i.e., almost twice the calculated gap of bulk CdS). This appears to be at variance with experiment, where the adsorption edge for $Al_{12}O_{24}—2(Cd_4S)$ is blue-shifted by only a few tenths of an eV with respect to bulk CdS.[12] However it is not unlikely that the experimental adsorption edges are related to different kinds of impurities and/or defects rather than to the band edges. Figure 1c suggests that the HOMO of AlSOD—$2(Cd_4S)$ arises from states of the framework, whereas the LUMO appears as a state of the framework down-shifted by the interaction with the clusters. Analysis of the electronic charge distributions confirms this suggestion, showing that both the HOMO and the LUMO are mostly localized on the oxygens of the framework, with a small contribution from the cluster S atoms. The different character of the LUMO for SOD—Cd_4S and AlSOD—$2(Cd_4S)$ can be related to the narrower gap of $[AlSOD]^{-12}$ with respect to $[SOD]^{6-}$.

B. Cd_4S_4 Clusters in Aluminosilicate (Al:Si = 1) and Silica Sodalite. *1. The "Free" Cd_4S_4 Cluster.* We have calculated the atomic structure of Cd_4S_4 starting from an initial cubic geometry in which S and Cd atoms form two interpenetrating tetrahedra (cubane). The cluster was placed in a cubic box of size equal to the unit cell of sodalite, and periodic boundary conditions were used. Upon relaxation, S (Cd) atoms
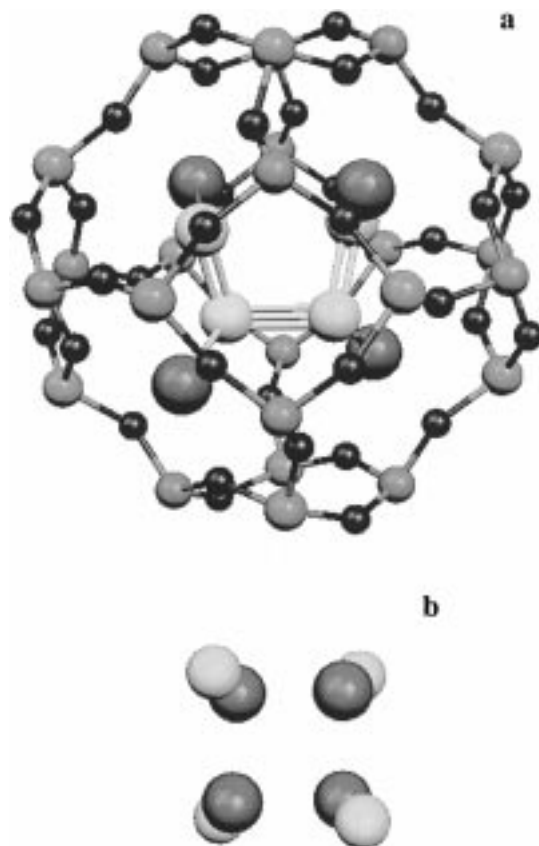

Figure 2. Ball-and-stick representation of the atomic structure of SOD-Cd_4S_4 (part a) and of "free" Cd_4S_4 (part b). Oxygen atoms are black, aluminum, and silicon are medium grey, sulphur is light grey, and cadmium is dark grey.

move outward (inward), so that in the final geometry the internal and external tetrahedra are made up of Cd and S atoms respectively. This relaxation pattern is reminiscent of the "buckling" reconstruction which takes place at the nonpolar surfaces of II—VI and III—V materials: the anions (cations) relax outward (inward), so as to give rise to fully occupied and empty dangling bond states on the anions and cations, respectively.[25] For our Cd_4S_4 cluster, Cd—S, Cd—Cd, and S—S distances are 2.58, 3.07, and 4.04 Å respectively, with Cd—S—Cd and S—Cd—S angles of ~73° and 104.7° (see Table 4). The calculated electronic energy gap between the filled S-3p and Cd-5s states is 2.09 eV.

2. SOD—Cd_4S_4. Experimentally, results referring to various concentrations of Cd_4S_4 and mixed $Cd_4O_nS_{(4-n)}$ clusters within the sodalitic cages of different zeolites have been reported.[1,2] Although several of these results are still under debate,[2] it seems established that at low loading levels of CdS in zeolite Y, isolated cluster Cd_4S_4 inside the sodalite cages of Z—Y are present, with an adsorption peak at about 4.3 eV (i.e., an energy ~1.7 times the experimental gap of bulk CdS). With increasing loadings, the adsorption peak shifts to lower energies (down to about 3.5 eV), which has been interpreted as an indication of interactions between clusters. Here we restrict our study to Cd_4S_4 clusters inside sodalite at half packing.

The initial position of the cubic Cd_4S_4 cluster was chosen with the corners symmetrically pointing towards the centers of the eight 6-rings of the occupied cage. After relaxation, besides the usual splitting in the geometrical sizes of filled and unfilled cages (see Table 1), a strong deformation of the infilled Cd_4S_4 cluster is observed (see Figure 2 and Table 4). On the outer shell, Cd atoms are located in proximity of the center of the

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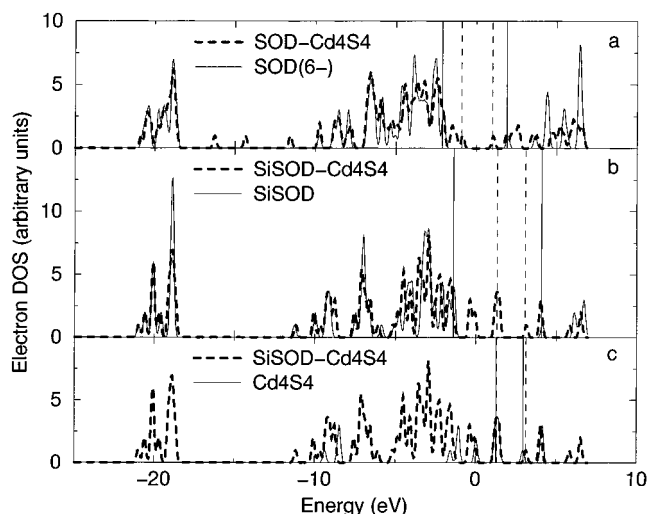
Figure 3. DOS for SOD-Cd_4S_4 and SiSOD-Cd_4S_4. For each case both the DOS for the framework−cluster composite (dashed line) and the bare framework or free cluster (thin full line) are shown. The vertical dashed (full) lines indicate the gap for the cluster-cage composite (bare framework or free cluster). In the bottom panel, the HOMO of the free cluster and of the cluster-framework composite have been aligned. Other details are as in Figure 1.

6-rings of the sodalite cage, with rather short Cd−O distances (∼2.34 and 2.85 Å). Inside this shell, the S atoms form a covalently bonded chain structure, with S−S bondlengths of 2.168 and 2.046 Å for the central and two outer bonds respectively. In addition, each S atom is bonded also to one Cd atom (Cd−S = 2.487 Å). The shape of the S-chain is reminiscent of one of the low-energy isomers of gas-phase S_4 clusters.[26] However, unlike the free clusters, the chain of sulphur atoms inside the sodalite cage is nonplanar, resembling a twisted trapezoid. It is also interesting to remark the difference between the open chain structure formed by the sulphurs of the Cd_4S_4 cluster and the P_4 ring structure which was found for the analogous Ga_4P_4 cluster infilled in sodalite.[5]

We calculated the embedding energy using for E_{clus} the energy of the optimized structure of Cd_4S_4 in free-space. The resulting value is $E_{emb} = 1.081$ hartrees, which is considerably less than the embedding energy for SOD−Cd_4S. This difference suggests that for the present system the cluster → framework charge transfer is either smaller or has a much higher energy cost, which may be related to the higher ionization potential of Cd_4S_4 with respect to Cd_4S. In fact, the Cd_4S_4 cluster must undergo a major structural rearrangement to make this charge transfer possible.

The DOS of the SOD−Cd_4S_4 structure is displayed in Figure 3a, where it is compared to the DOS of the bare framework, $[SOD]^{6-}$. In spite of the large deformation of the infilled cluster with respect to "free" Cd_4S_4, the energy gap of the composite (1.93 eV) is close to the HOMO−LUMO separation of the free cluster, while it is ∼1.5 larger than the calculated gap of bulk CdS. Analysis of the electronic charge distributions shows that both the HOMO and the LUMO have mixed character, the HOMO being however mostly localized on the S atoms of the clusters, while the LUMO is mostly localized on the oxygens of the cage (see Table 5).

3. SiSOD−Cd_4S_4. To further investigate the influence of the cage composition on the structure of the inclusion, we have considered Cd_4S_4 clusters embedded within the charge-neutral cages of silicasodalite (SiSOD), with a filling factor of 1:2. For this case, we expect to see a weakening of the forces between cage and inclusion, which would result in a purely geometric confinement of the cluster. In fact the relaxed structure of the

cluster (see Table 4) shows the S anions in the outer shell of the cluster and the Cd cations in the inner shell, just like the isolated cluster. Moreover, the distances between Cd and S atoms remain rather short (2.539 Å), while the Cd−O distances are significantly greater than the corresponding distances in all other sodalite composites that we have considered. As a result of the confinement, the "buckling" is smaller than that of free Cd_4S_4, as indicated by the fact the $\widehat{CdSCd}$ and $\widehat{SCdS}$ bonding angles are closer to 90°. The embedding energy is $E_{emb} = 0.451$ hartrees, (i.e. less than half the embedding energy for SOD−Cd_4S_4).

The DOS for SiSOD−Cd_4S_4 and for the bare SiSOD framework are presented in Figure 3b. For the bare SiSOD structure we find a wide gap of 5.45 eV, while that for the SiSOD-Cd_4S_4 composite is 1.66 eV, which is smaller than the calculated gap for the "free" Cd_4S_4 cluster (2.09 eV). This is surprising since the electronic structure of the cluster is expected to be influenced only by the confinement of the framework, without the formation of any bonding state or any charge transfer. However, if we compare the gap of SiSOD−Cd_4S_4 with that of isolated Cd_4S_4 *frozen* in the atomic configuration within the SiSOD cage (1.48 eV), a slight increase can be observed. This increase can be interpreted as an indication of a quantum confinement effect. On the other hand, the fact that the gap of the "frozen" cluster (1.48 eV) is smaller than that of free Cd_4S_4 (2.09 eV) can be related to the smaller "buckling" of the former, which, somewhat paradoxically, is also a confinement effect. A direct comparison of the electronic DOS for SiSOD-Cd_4S_4 and for the isolated frozen Cd_4S_4 cluster (see Figure 3c) shows a nearly perfect overlap of the states around the gap. This indicates that these states are pertinent to the cluster only, and that the semiconductive nature of the material is determined by the CdS inclusion.

IV. Summary and Conclusions

We have studied several combinations of sodalitic cages and CdS clusters by first principles LDF methods. Our results show that the composition of the sodalite framework, which determines the electronic charge transfer from the cluster to the cage, strongly affects the atomic structure of the infilled cluster. A case for which there is particular evidence of these deformations of the clusters is for SOD−Cd_4S_4. Free Cd_4S_4 consists of two interpenetrating tetrahedra, with the S (Cd) atoms on the outer (inner) shell, and the electronic structure is characterized by a relatively wide gap between filled S-3p and empty Cd-5s states. Once inside the sodalite cage, the cluster undergoes a major rearrangement in order to facilitate the cluster → framework charge transfer: the S atoms migrate to the interior of the cluster, where they form a covalently bonded chain structure, while the Cd, on the outer shell, can easily donate electrons to the cage. In the case of Cd_4S_4 inside silica-sodalite, instead, the deformations of the infilled cluster with respect to its structure in free space, are very small. In fact, in this kind of sodalite there are no missing electrons that have to be transferred to the cage, and the only effect is a spatial confinement of the CdS cluster. However, this confinement, by reducing the "buckling", has the peculiar effect of reducing the energy gap with respect to that of free Cd_4S_4.

If we compare the CdS−sodalite structures of this work with the corresponding geometries of III−V inclusions in sodalite of ref 5, some interesting features emerge. While Cd_4S_4 and Ga_4P_4 inclusions show comparable geometries, the structures of the Cd_4S inclusions are typically less distorted than those of the analogous III_4V clusters and usually keep a tetrahedral symmetry, similar to that of the Na_4Cl inclusions of natural

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sodalite. For all CdS−sodalite composites the cage is less collapsed than in the case of III−V inclusions, and the calculated structural parameters of the framework are quite similar to the experimentally determined parameteres of natural sodalite.

All the systems that we have studied show semiconductive properties, their gaps varying in a range 0.91−2.55 eV. We can distinguish between Cd_4S and Cd_4S_4 inclusions, as well as between stoichiometric (SOD−Cd_4S, AlSOD−2(Cd_4S), and SiSOD−Cd_4S_4) and nonstoichiometric composites (SOD−2(Cd_4S) and SOD−Cd_4S_4). For stochiometric SOD−Cd_4S and AlSOD−2(Cd_4S), the gaps are ∼2.5 eV (i.e., twice the calculated gap of bulk CdS), both HOMOs have a large contribution from the framework, while the LUMOs have a different character in the two cases. For the nonstochiometric SOD−2(Cd_4S) composite, the gap is only ∼0.9 eV (i.e., smaller than bulk CdS), and both the HOMO and the LUMO belong to the cluster. (We recall, however, that this composite is probably unstable, as for Cd_4S inclusions in alumino-silicate sodalite half filling is preferred to full filling.) For the two Cd_4S_4−sodalite structures, the gaps are similar, 1.7−1.9 eV (i.e., about 1.5 times larger than that of bulk CdS), in spite of the different localizations of the HOMOs and LUMOs and very different geometries of the included clusters.

This variety of behaviors indicates that the atomic structure and electronic properties of the material depend significantly on the size and stoichiometry of the cluster as well as on the overall stoichiometry of the composite. This finding may seem to contraddict one of the results of ref 5 (i.e., that for different GaP clusters in aluminosilicate sodalite the gap depends only marginally on the specific microcluster). However, this difference may be (at least to some extent) attributed to the fact that in that study no stoichiometric composite was considered. Moreover our results confirm the conclusion of ref 5 that in general the properties of semiconductor−sodalite composites cannot be simply interpreted in terms of a quantum confinement of the semiconductor by the zeolite framework. The present study shows that even in the case of SiSOD−Cd_4S_4 (i.e., for a system where no cluster → framework charge transfer is present) such an interpretation requires some care. In all other cases, important Cd-O interactions are present which strongly affect the properties, notably the energy gap, of the material.

References and Notes

(1) Stucky, G. D.; MacDougall, J. E., *Science* **1990**, *247*, 669.

(2) Behrens, P.; Stucky, G.D. In *Comprehensive Supra-Molecular Chemistry*; Atwood, J. L., Davies, J. E., McNicol D.D., Vogtle, F., Eds.; Pergamon Press: NY, 1996; Vol. VII, Chapter 25, p 721.

(3) For recent reviews on semiconductor clusters, nanocrystals, and quantum dots, see: Alivisatos, A. P. *Science* **1996**, *271*, 933. Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226.

(4) Jentys, A.; Grimes, R. W.; Gale, J. D.; Catlow, C. R. A. *J. Phys. Chem.* **1993**, *97*, 13535. Jentys, A.; Grimes, R. W.; *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2093.

(5) Trave, A.; Buda, F.; Fasolino, A. *Phys. Rev. Lett.* **1996** *77*, 5405.

(6) Demkov, A. A.; Sankey, O. F. In *Access in Nanoporous Materials*; Pinnavaia, T. J., Thorpe, M. F., Eds.; Plenum Press: New York, 1995; p 273.

(7) Lippens, P. E.; Lannoo, M. *Phys. Rev. B* **1989**, *39*, 10935.

(8) Tomasulo, A.; Ramakrishna, M. V. *J. Chem. Phys.* **1996**, *105*, 3612.

(9) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*, Oxford University Press: Oxford, 1989.

(10) For example, see: Dyer, A. *An Introduction to Zeolite Molecular Sieves*; John Wiley and Sons: Chichester, 1988.

(11) Bibby, D. M.; Dale, M. P. *Nature* **1985**, *317*, 157.

(12) Brenchley, M. E.; Weller, M. T. *Angew. Chem.*, **1993**, *105*, 1726.

(13) Filippone, F.; Buda, F.; Iarlori, S.; Moretti, G.; Porta, P. *J. Phys. Chem.* **1995**, *99*, 12883.

(14) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.

(15) For a review, see: Galli, G.; Pasquarello A., *Computer Simulations in Chemical Physics*; Allen, M. P., Tildesley, D. J., Eds.; Kluwer: Dordrecht, 1994; pp 261-313.

(16) Bachelet, G. B.; Hamann, D. R.; Schlüter, M. *Phys. Rev. B* **1982**, *26*, 4199.

(17) Kleinman, L.; Bylander, D.M. *Phys. Rev. Lett.* **1982**, *48*, 1425.

(18) Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892.

(19) Louie, S. G.; Froyen, S.; Cohen, M. L. *Phys. Rev. B* **1982**, *26*, 1738.

(20) Dal Corso, A.; Baroni, S.; Resta, R.; De Gironcoli, S. *Phys. Rev. B* **1993**, *47*, 3588

(21) Laasonen, K.; Pasquarello, A.; Car, R.; Lee, C.; Vanderbilt, D. *Phys. Rev. B* **1993**, *47*, 10142.

(22) Perdew, J.P.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5048.

(23) Tassone, F.; Mauri, F.; Car, R. *Phys. Rev. B* **1994**, *50*, 10561.

(24) Campana, L.; Selloni, A.; Weber, J.; Pasquarello, A.; Papai, I.; Goursot, A. *Chem. Phys. Lett.* **1994**, *226*, 245. Campana, L.; Selloni, A.; Weber, J.; Goursot, A. *J. Phys. Chem.* **1995**, *99*, 16351.

(25) Fasolino, A.; Shkrebtii; A., Selloni, A.; Surface Reconstruction and Relaxation, Landolt-Börnstein, III/24a. In *The Physics of Solid Surfaces*, Chiarotti, G., Ed.; Springer: Berlin, 1993; p 125.

(26) Hohl, D.; Jones, R. O.; Car, R.; Parrinello, M. *J. Chem. Phys.* **1988**, *89*, 6923.