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Calculated structural and electronic properties of CdSe under pressure

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Pseudopotential total-energy calculations are presented for four phases of CdSe in the zinc-blende, wurtzite, rocksalt, and CsCl structures, and the pressure-induced structural transitions are studied. The band structure of the high-pressure rocksalt phase of CdSe, calculated using the *ab initio* pseudopotential method within the local-density approximation is given along with a calculation of the quasiparticle excitation energies at symmetry points. The effects of the Cd 4*d* electrons are discussed and are shown to have a major influence on the pressure dependence of the band gap in the rocksalt phase. The results are in good agreement with available experimental data and a high-pressure CsCl phase of CdSe is predicted.

I. INTRODUCTION

Because of the potential technological applications of II-VI compounds, they have recently received considerable attention from experimentalists and theorists.[1] In a previous paper[2] we presented the results of *ab initio* quasiparticle band structure calculations for six II-VI compounds at atmospheric pressure. In this paper we concentrate on CdSe and examine its electronic and structural properties.

Cadmium selenide is a semiconducting compound which under atmospheric conditions occurs in two modifications, one having the hexagonal wurtzite structure and the other having the cubic zinc-blende structure. Usually the cubic modification exists in thin layers, while bulk CdSe has the hexagonal structure. Under pressure CdSe undergoes a structural transformation into the rocksalt structure, and previous experimental estimates for the transition pressure are 2.7–3.7 GPa,[3] 3.3 GPa,[4] 3.0 GPa.[5] It was also determined that CdSe in the rocksalt structure has an indirect gap of 0.6 eV at 3 GPa.[3,6] Recent experiments[7] demonstrated that CdSe remains a semiconductor up to a pressure of 50 GPa, although there are indications of a structural phase transition at around 40 GPa.

Using the pseudopotential method for total-energy calculations,[8] we estimate the transition pressure for the wurtzite to rocksalt transformation to be 3.0 Gpa in a good agreement with the experimental results. Although our electronic band structure calculations based on the local density approximation (LDA)[9] result in semimetallic behavior with zero gap for the rocksalt phase, the quasiparticle calculations employing the *GW* approximation[10–12] for the self-energy operator give an indirect gap of 0.7 eV at the transition pressure. We also find a transition from the rocksalt to the CsCl phase at a pressure of 94 GPa, but some unknown intermediate structures between the rocksalt and CsCl phases are possible.

Recently, a number of interesting experiments have been done[13,14] on structural and electronic properties of CdSe nanoclusters. Although we deal here with the properties of bulk CdSe, our calculations can be considered as a starting point for future theoretical studies of the size-dependent properties of CdSe nanocrystals.

This paper is organized as follows. Section II briefly describes the theoretical method. In Sec. III the results of the LDA total energy calculations for different phases of CdSe are presented. The quasiparticle band structures for the rocksalt high-pressure phase of CdSe are also presented in this section. Some conclusions are given in Sec. IV.

II. METHOD

The pseudopotential total-energy scheme[8] with the plane-wave basis set is used to compute the energies of different phases of CdSe. The ionic pseudopotentials for Cd and Se are generated according to the Hamann-Schlüter-Chiang scheme.[15] To describe some of the influence of the *d* electrons on the valence complex, partial core corrections for exchange and correlation[16] are included into the Cd pseudopotential. Core corrections are shown[17] to be important for obtaining good agreement with the experimental data for the structural properties of systems with *d* electrons in the valence band. We use a cutoff energy of 35 Ry for the zinc-blende, wurtzite, and rocksalt structures. The ideal values for the c/a ratio (1.633) and the internal parameter u (0.375) are used for the wurtzite phase.

To study the influence of the *d* electrons on structural and electronic properties of high-pressure phases of CdSe, the total-energy calculations are also done with a Cd^{12+} pseudopotential generated using the method of Troullier and Martins.[18] A cutoff energy of 60 Ry is used for the rocksalt and CsCl phases in these calculations.

All the pseudopotentials are generated with semirelativistic corrections. Ten special $\mathbf{k}$ points[19] are chosen in the irreducible part of the Brillouin zone for the zinc-blende, rocksalt, and CsCl structures using the Monkhorst-Pack scheme.[20] Four special **k** points[19] are used for the wurtzite structure. The Ceperley-Adler interpolation formula[21] for the exchange-correlation energy is used.

The quasiparticle calculations are based on the Hybertsen-Louie approach[11,12] to the *GW* approximation.[10] In the quasiparticle calculations the 4*d* electrons of Cd are treated as a part of the core complex. The discussion of the validity of this approximation for quasiparticle calculations can be found in Ref. 2. The quasiparticle energies are calculated for the rocksalt phase at the critical volume obtained from the total-energy calculations for four high symmetry **k** points (L, X, Γ, and the **k** point in the middle of the Σ line). The LDA eigenvalues are used as a first approximation for the quasiparticle energies. The LDA eigenfunctions are considered to be an excellent approximation for the quasiparticle wave functions. To screen the Coulomb interaction, a generalized form of the Levine-Louie model dielectric matrix[22] extended to finite frequencies by a generalized plasmon-pole model is used. This dielectric function requires only the dielectric constant ϵ_∞ as an input. The experimental value[23] of 5.8 for the dielectric constant has been used in our calculations. Although this is the dielectric constant for the wurtzite phase of CdSe, we can use it for CdSe in the rocksalt structure since the results of these calculations are not very sensitive to the choice of ϵ_∞, which is responsible mostly for long-range screening.[24]

A number of numerical cutoffs are involved in the quasiparticle calculations. The dielectric matrix is truncated at $|\mathbf{q}+\mathbf{G}| = 3.1$ (a.u.)$^{-1}$. Ten special **k** points[19] in the irreducible part of the Brillouin zone have been chosen to perform the integration, and 100 bands are taken into account in the calculations of the matrix elements of the self-energy operator.

III. RESULTS

The results of the LDA total-energy calculations for four phases of CdSe are summarized in Tables I and II. We use the equation of state proposed by Murnaghan[25] to fit the calculated total energies. From the total-energy versus volume curves, the equilibrium lattice parameters and the bulk moduli are computed.

From Table I we see that the calculated lattice parameters for the zinc-blende and wurtzite structures are less than the experimental values by 2–3%. This is a consequence of the fact that we do not allow for the relaxation of the Cd 4*d* electrons and thus overestimate their screening of the ion. The partial core corrections improve the results by taking into account the overlap of the core and valence charge densities but cannot reproduce the results of such relaxation. Table II shows that the inclusions of the *d* electrons into the valence complex results in increasing of the lattice parameters by 1.3% and slightly larger bulk moduli. These changes are in agreement with the general trends expected from an inclusion of *p*-*d* mixing.[26]

TABLE I. Calculated and experimental (see Ref. 23) equilibrium lattice parameters and bulk moduli for the zinc-blende and wurtzite phases of CdSe. The ideal values of the c/a ratio and the internal parameter u are used in our calculations for the wurtzite structure. The numbers in parentheses give the percentage difference from the experimental values.

	Zinc-blende		Wurtzite	
	Calc.	Expt.	Calc.	Expt.
a (Å)	5.929 (-2.0%)	6.052	4.200 (-2.3%)	4.299
c (Å)			6.804 (-2.9%)	7.010
B_0 (GPa)	53.8		53.5 (-2.7%)	55

The total-energy versus volume curves are given in Figs. 1 and 2. The curves in Fig. 1 are obtained by fitting the results of our calculations with the Cd^{2+} pseudopotential to the Murnaghan equation of state. Within the accuracy of our total-energy calculations (1 mRy) we are not able to distinguish between the cubic zinc-blende and hexagonal wurtzite structures, which indicates that these two phases are very close in energy. This agrees with the fact that both phases are found at normal pressure. The estimated transition pressure of the wurtzite to rocksalt structural transition is 3 GPa. This value lies within the range of the experimental values for the transition pressure (2.7–3.7 Gpa).[27] According to the calculation with the Cd^{2+} pseudopotential, the total energy of the rocksalt phase remains lower than the total energy of the CsCl phase up to a pressure of 180 GPa.

The inclusion of the *d*-electron relaxation changes this picture at high pressure. The results of the total-energy calculations for the high pressure rocksalt and CsCl phases of CdSe with the Cd^{12+} pseudopotential are reproduced in Fig. 2. The calculated pressure of the rocksalt to CsCl structural transition is 94 GPa. A number of intermediate phases may exist between the rocksalt and CsCl structures. This means that the structural transition to CsCl phase does not necessarily occur in nature at a pressure of 94 GPa.

Good agreement with experiment for the calculated wurtzite to rocksalt transition pressure values, and the

TABLE II. Calculated equilibrium lattice parameters and bulk moduli for the rocksalt and CsCl phases of CdSe with and without valence *d* electrons. The numbers in parentheses show the percentage increase of the calculated lattice constant with valence *d* electrons.

	Rocksalt		CsCl	
	without *d* el.	with *d* el.	without *d* el.	with *d* el.
a (Å)	5.514	5.586 (+1.3%)	3.430	3.474 (+1.3%)
B_0 (GPa)	74	78	78	79

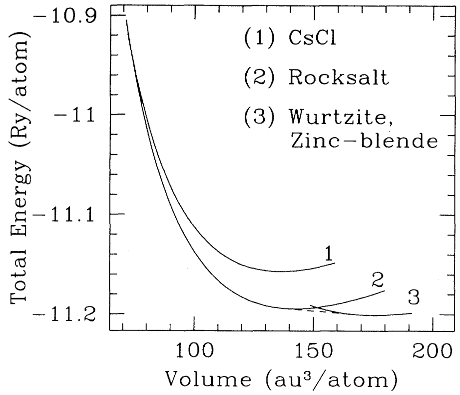

FIG. 1. Total-energy versus volume curves for the zinc-blende, wurtzite, rocksalt, and CsCl phases of CdSe with *d* electrons kept in the core. The broken line corresponds to the zinc-blende to rocksalt structural phase transition. The wurtzite and zinc-blende energies lie on the same curve within the accuracy of our calculations.

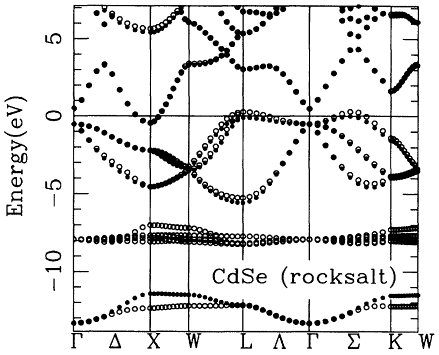

FIG. 3. Calculated LDA band structures for CdSe in the rocksalt structure at the calculated equilibrium volume. Solid circles correspond to the calculation with *d* electrons in the core, open circles to the calculation with valence *d* electrons. Since we are interested only in the relative position of the bands, we have arbitrarily chosen the energy of the upper conduction bands at the Γ point to be the same for both band structures.

large difference between the transition pressures calculated with and without *d*-electron relaxation for the rocksalt to CsCl transition indicate that the *d*-electron effects become more important at higher pressure where the interatomic distances get smaller.

The LDA band structures for the rocksalt phase of CdSe at the transition pressure of 3 GPa calculated with Cd^{2+} and Cd^{12+} pseudopotentials are given in Fig. 3. Because of the usual underestimation of the fundamental gap in the LDA calculations the calculated band structures are semimetallic. As we will show later, the quasiparticle calculation opens the gap reproducing the correct insulating behavior for the rocksalt phase of CdSe.

Because of the nonrelativistic character of our calculations, the calculated band structures do not contain spin-orbit splitting. But since the scalar relativistic corrections have been introduced into the pseudopotentials, the calculated LDA energies correspond to the position of the center of gravity of spin-orbit split energy levels.

According to our calculations, the rocksalt phase of CdSe is an indirect gap semiconductor with the fundamental gap corresponding to the energy separation from the middle of the valence band Σ line to the conduction band *X* point of the Brillouin zone. The LDA energy of the upper valence band at the *L* point is only 0.1 eV lower than the energy of the upper valence band in the middle of the Σ line.

From Fig. 3 we see that there is almost no change in the relative position of the energy levels at the Γ point after introduction of *d* electrons into the valence complex. Due to inversion symmetry, bands with *d* symmetry cannot couple to the bands with *p* symmetry at the Γ point. Hence there is no repulsion between the *d* bands and the upper valence band at Γ. The angular decomposition of the LDA wave functions at the *L* point and along the Σ directions shows that even without *d* electrons in the valence band, these states have an admixture of *d* character on Cd ions. These states can couple to the valence *d*-electron states. The level repulsion leads to a decrease of the fundamental gap by 0.4 eV.

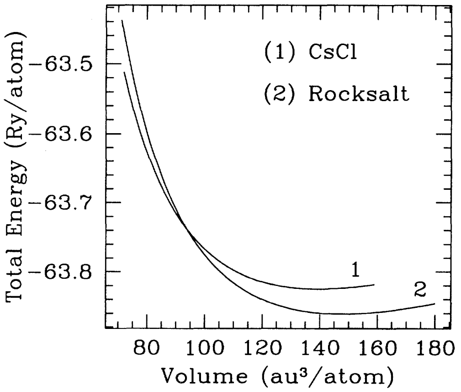

FIG. 2. Total-energy versus volume curves for the rocksalt and CsCl phases of CdSe with valence *d* electrons.

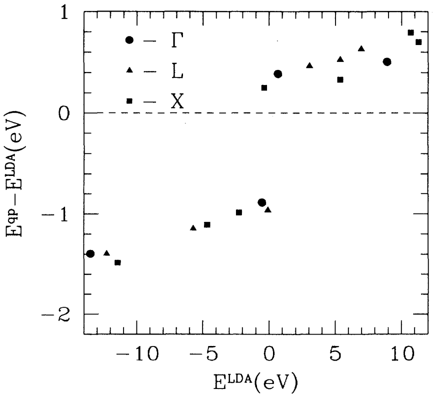

FIG. 4. The *GW* corrections to the LDA energies for CdSe in the rocksalt structure at different symmetry points (circles correspond to Γ, squares to *X*, and triangles to *L*).

TABLE III. Calculated LDA and *GW* energies (in eV) at symmetry points for the rocksalt phase of CdSe at 3 GPa. All energies are referenced to the top of the valence band.

	LDA	*GW*		LDA	*GW*		LDA	*GW*
Γ_{1v}^+	-13.76	-14.34	L_{1v}^-	-12.41	-13.00	X_{1v}^+	-11.51	-12.20
Γ_{15v}^-	-0.59	-0.66	L_{1v}^+	-5.96	-6.30	X_{3v}^+	-4.93	-5.23
Γ_{1c}^+	0.86	2.11	L_{3v}^+	-0.09	-0.24	X_{5v}^+	-2.42	-2.59
Γ_{15c}^+	8.96	10.29	L_{1c}^-	3.06	4.36	X_{1c}^-	-0.36	0.74
			L_{3c}^-	5.40	6.77	X_{3c}^-	5.33	6.45

The results of our LDA and *GW* band structure calculations for three high-symmetry points are given in Table III. The *GW* calculations open the gap and increase both the valence and conduction band widths with respect to the corresponding LDA calculations. According to our quasiparticle calculations, the self-energy corrections do not change the position of the fundamental gap (from the middle of the Σ line to X). The calculated value[28] of the fundamental gap at the calculated transition pressure is 0.7 eV in good agreement with the experimental value of 0.6 eV at 3 GPa. Because of the energy dependent character of the self-energy operator Σ, the *GW* corrections to the LDA eigenvalues are also energy dependent. This dependence is illustrated by Fig. 4.

The *GW* corrections to the LDA eigenvalues are almost linear in energy and **k** independent for the valence bands. The **k** dependence is more pronounced for conduction states as compared to valence states. This behavior is similar to the results for the zinc-blende and wurtzite phases of different II-VI semiconductors.[2]

The effects of *d* electrons on the gap value become especially important if we consider the pressure dependence of the gap. This dependence for two indirect gaps (Σ to X and L to X) is given in Fig. 5. Here we use the LDA values, since we expect that even though the LDA calculations underestimate the gaps, the difference of the LDA energies for different pressures should be close to the differences of the corresponding quasiparticle energies.[29]

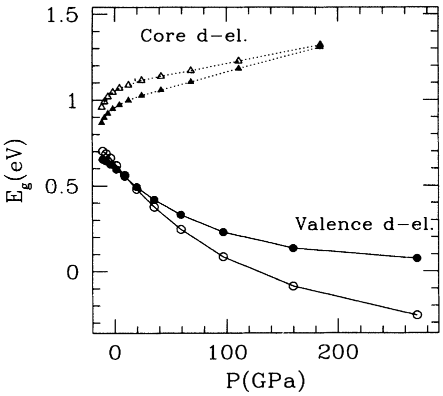

FIG. 5. Pressure dependence of the indirect (LDA) gaps for CdSe in the rocksalt structure. The solid points correspond to the "L-X", the open points to the "Σ-X" gap. The broken lines represent the calculations with *d* electrons in the core, the solid lines with *d* electrons in the valence complex. The "Σ-X" gap with valence *d* electrons is arbitrarily taken to be equal to 0.6 eV at 3 GPa.

From the calculations with the *d* electrons in the core, we find that the fundamental gap should be increasing with pressure. This conclusion agrees with the results of the analogous calculations for III-V compounds in the rocksalt structure[30] but contradicts the experimental data for the pressure derivative of the fundamental gap of the rocksalt phase of CdSe, which is found to be negative and equal to -0.015 eV/GPa.

Inclusion of the Cd 4*d* electrons into the valence band completely changes the pressure dependence of the gap. Since the *p*-*d* level repulsion becomes stronger as we increase pressure and decrease the interatomic distances, the gap now is decreasing with pressure (see Fig. 5). The "L-X" gap decreases faster, and, according to our calculations, the fundamental gap of the CdSe in the rocksalt structures is from L to X at pressures higher than 15 GPa.

The calculated pressure derivative of the fundamental gap at a pressure of 3 GPa is -0.006 eV/GPa. It reproduces the correct qualitative character of the gap pressure dependence. We do not expect very good quantitative agreement with the experimental value of the derivative, since the calculation of $\frac{\delta E}{\delta P}$ involves the calculations of the second differencies of energies and thus its precision is low.

IV. CONCLUSIONS

In this paper we studied the structural and electronic properties of CdSe under pressure. Both LDA and quasiparticle band structures for the high-pressure rocksalt phase of CdSe are calculated. The resulting structural properties and fundamental gap value are in a good agreement with the available experimental data. The effects related to the Cd 4*d* electrons are shown to be important at higher pressure. A high-pressure CsCl phase of CdSe is predicted.

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[27] We stress that the calculated transition pressures correspond to $T=0$. The finite temperature in experiments could lead to some changes in the phase transition pressure with respect to the presented results due to the entropy term in the free energy. A detailed analysis of the phase diagram is left for future work.

[28] Due to the low symmetry of the $\mathbf{k}$ point corresponding to the top of the valence band (the middle of Σ line), we performed the *GW* calculation at a close point with higher symmetry and then corrected the obtained energy using the linear correction (see Fig. 4) to the difference of the LDA eigenvalues for these two $\mathbf{k}$ points.

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