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Transferable pair potentials for CdS and ZnS crystals

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A set of interatomic pair potentials is developed for CdS and ZnS crystals. We show that a simple energy function, which has been used to describe the properties of CdSe [E. Rabani, *J. Chem. Phys.* **116**, 258 (2002)], can be parametrized to accurately describe the lattice and elastic constants, and phonon dispersion relations of bulk CdS and ZnS in the wurtzite and rocksalt crystal structures. The predicted coexistence pressure of the wurtzite and rocksalt structures as well as the equation of state are in good agreement with experimental observations. These new pair potentials enable the study of a wide range of processes in bulk and nanocrystalline II–VI semiconductor materials.

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I. INTRODUCTION

Many important processes in solid state materials, such as the melting transition,^{1,2} structural transformations,^{3,4} or diffusion of impurities and defects⁵ require atomistic resolution in space and time for a comprehensive understanding of the underlying mechanism. Despite major advances in electron microscopy,⁶ experiments can only provide a coarse-grained view of such processes. Molecular dynamics computer simulations can in principle provide the necessary microscopic perspective, but their predictive power depends on the reliability and feasibility of available models.

Methods based on first principles that retain a description of the electronic state of the system potentially offer the highest accuracy. Because of their high computational demand, however, they are not currently suited for in-depth studies of systems involving more than a few hundred atoms, or time scales longer than a few tens of picoseconds. Classical interaction potentials, parameterized to reproduce emergent properties of the modeled material, offer a compromise between accuracy and computational speed. Potentials of different functional form and complexity have been developed for materials with widely disparate chemical and physical properties, ranging from water⁷ to gold⁸ and biopolymers.⁹ Depending on the properties studied, agreement with experiment can be very good, in some cases rivaling or even besting that of affordable *ab initio* methods.

Sparked by a comprehensive experimental study of the structural changes occurring in CdSe nanocrystals under pressure,^{3,10–15} a simple pair potential has been developed¹⁶ and successfully applied to reveal the mechanisms of structural rearrangements in both bulk and nanocrystalline CdSe.^{4,17–24} Recently, a pair potential for PbSe that uses the same functional form has been applied in a simulation study of shape change and fusion of PbSe nanocrystals.²⁵ However, simulation studies of processes in many other semiconductor

materials, or in multi-component systems such as core/shell crystals or seeded nanorods, have been precluded by the lack of available models. Here we present a set of model potentials for crystalline CdS and ZnS, two semiconductors with potential use in various light harvesting and opto-catalytic devices.²⁶ The potentials are designed to reproduce the bulk lattice and elastic constants of the relevant crystal structures, as well as phonon dispersion relations. They are specifically constructed to be compatible with each other and with the existing model for CdSe (Ref. 16) and therefore also enable simulations of mixtures of the three compounds.

The paper is organized as follows: In Sec. II, we discuss the construction of the pair potentials and specify their parameters. In Sec. III, we apply the models to calculate bulk enthalpies as a function of pressure and the equations of state for CdSe, CdS, and ZnS and compare the predictions to experimental results. To ascertain the transferability of the potentials, we also calculate structural properties of crystals with impurities and compare them to values obtained with *ab initio* methods. Discussion and conclusions are given in Sec. IV.

II. THE PAIR POTENTIAL

We use the simple model developed for CdSe (Ref. 16) as a template to also describe CdS and ZnS. The two-body interatomic potential consists of a long range Coulomb part and a short range part which is represented by a Lennard-Jones (LJ) form:

$$V_{ij} = \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\}, \quad (1)$$

where the indexes i and j refer to Cd, Zn, S, and Se atoms. To facilitate transferability and reduce the number of parameters, we use standard combining rules for interactions of unlike atom types, namely, $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ and $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$.

TABLE I. Potential parameters defining the interatomic interactions in ZnS, CdS, and CdSe.

	q_i (e)	σ (Å)	ϵ/k_B (K)
Zn	1.18	0.02	17998.4
S	-1.18	4.90	16.5
Cd	1.18	1.98	16.8
Se	-1.18	5.24	14.9

The parameters q_i , ϵ_i , and σ_i were obtained by fitting the lattice and elastic constants, and phonon dispersion relations of bulk CdS and ZnS in three crystal structures: wurtzite, zinc-blende, and rocksalt. As an additional constraint, the energy difference between the wurtzite and rocksalt structure at zero pressure was fitted to *ab initio* calculations.^{27,28} This was done to ensure that the wurtzite structure is the more stable structure at low pressures. The fitting calculations were performed at 0 K, although the experimental data were obtained at finite temperatures.

To obtain transferable potentials and ensure neutrality of the modeled materials, we fixed the magnitude of all ion charges to that of the original CdSe model, i.e., $|q_i| = 1.18$ e. We then proceeded in the following way. To obtain a model for CdS compatible with that of CdSe, we relaxed the LJ parameters for S, keeping parameters for Cd fixed. In the second step, to arrive at a model for ZnS, we likewise relaxed the LJ parameters for Zn, keeping S fixed. Thus, a total of four parameters (σ_{Zn} , σ_S , ϵ_{Zn} , and ϵ_S) was determined with the fitting.

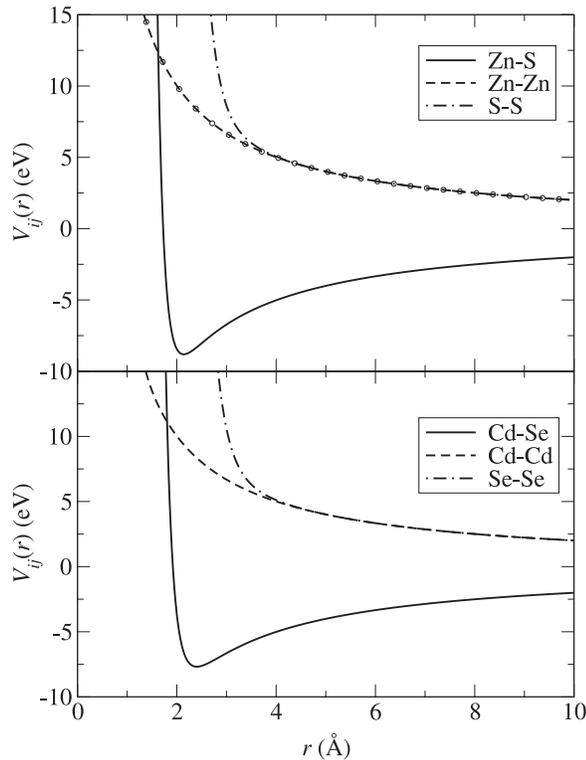


FIG. 1. Interatomic pair potentials for Zn-Zn, S-S, and Zn-S (top panel) and Cd-Cd, Se-Se, and Cd-Se (bottom panel). Open circles in the upper panel show the pure Coulomb repulsion term.

We used a relaxed fitting procedure similar to the one discussed in Refs. 29 and 30. This procedure is substantially more expensive computationally than the conventional fitting. However, it allows a much higher quality of fitting which is required to properly reproduce the structural properties of CdSe. In the relaxed fitting procedure, the error was defined on the residual of the structural and dynamical properties of the optimized configurations of the different crystal phases rather than on the experimental observed structures. Namely, the configurations and the lattice constants of each crystal phase were quenched using the conjugate gradient algorithm, and the aforementioned properties were calculated and compared to the experimental values for the quenched structures. In all the results reported here we have used Ewald sums to evaluate the electrostatic interactions,³¹ with a partitioning parameter between the two spaces chosen to minimize the computational effort.³² The Lennard-Jones part of the potential was cut at half the box length (≈ 10 Å).

The final parameter values resulting from the fit (including those for CdSe from Ref. 16) are summarized in Table I. A plot of the interatomic pair potentials is shown in Fig. 1. The van der Waals (vdW) radii of the negatively charged S and Se anions are significantly larger than those of the cations. In agreement with the corresponding ionic radii, the vdW radius of S is smaller than that of Se and the radius of Zn is smaller than that of Cd. For Zn we find that the best fit is obtained for a nearly vanishing vdW radius and a large value of ϵ_{Zn} . These

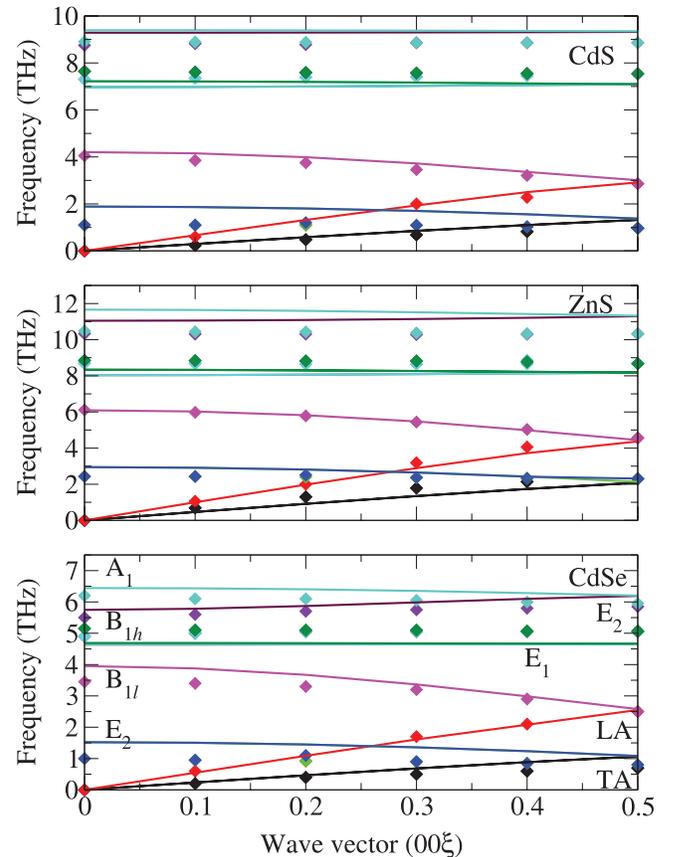


FIG. 2. Phonon dispersion relations of wurtzite CdS (upper panel), ZnS (middle panel), and CdSe (lower panel) along the ΓA direction. The filled diamonds represent literature results.³³⁻³⁵

TABLE II. Calculated lattice constants (in Å), elastic constants (in GPa), and bulk modulus (in GPa) of CdS, ZnS, and CdSe for three crystal structures. Experimental results are given in parenthesis when available. (Elastic constants and bulk moduli were taken from Refs. 43 and 45–47.)

CdS	Wurtzite	Zinc-blende	Rocksalt
<i>a</i>	4.16 (4.13) (Refs. 39 and 40)	5.83 (5.82) (Ref. 41)	5.43 (5.44) (Ref. 42)
<i>c</i>	6.61 (6.70) (Refs. 39 and 40)		
<i>C</i> ₁₁	107.3 (90.7)	99.6	96.9
<i>C</i> ₁₂	35.8 (52.1)	32.9	53.7
<i>C</i> ₁₃	15.9 (51.0)		
<i>C</i> ₃₃	144.3 (93.8)		
<i>C</i> ₄₄	19.1 (15.0)	41.3	53.8
<i>C</i> ₆₆	20.1 (16.3)		
<i>B</i>	54.0 (65.0)	55.1 (55.0)	68.1
ZnS			
<i>a</i>	3.89 (3.85) (Refs. 27 and 43)	5.48 (5.41) (Refs. 27 and 43)	5.20 (5.06) (Refs. 27 and 43)
<i>c</i>	6.26 (6.29) (Refs. 27 and 43)		
<i>C</i> ₁₁	161.4 (131.2)	150.1 (94.2)	109.7
<i>C</i> ₁₂	53.8 (66.3)	51.4 (56.8)	88.0
<i>C</i> ₁₃	28.2 (50.9)		
<i>C</i> ₃₃	213.1 (140.8)		
<i>C</i> ₄₄	32.4 (28.6)	62.2 (43.6)	88.1
<i>C</i> ₆₆	53.8 (32.4)		
<i>B</i>	82.3 (82.1)	84.3 (69.3)	94.6
CdSe			
<i>a</i>	4.37 (4.30) (Ref. 44)	6.13 (6.08) (Ref. 44)	5.74 (5.71) (Ref. 13)
<i>c</i>	6.97 (7.01) (Ref. 44)		
<i>C</i> ₁₁	87.2 (74.6)	82.4	73.2
<i>C</i> ₁₂	29.1 (46.1)	26.6	45.3
<i>C</i> ₁₃	13.3 (39.4)		
<i>C</i> ₃₃	118.0 (81.7)		
<i>C</i> ₄₄	15.9 (13.0)	33.4	45.3
<i>C</i> ₆₆	29.1 (14.3)		
<i>B</i>	44.1 (53.4)	45.1	54.6

particular values are a result of the constraints imposed on the charge of the ions and the sequence of fitting steps. Because of the small value of σ_{Zn} , the Zn–Zn and Zn–Cd forces at relevant distances are governed by the Coulomb term only (see top of Fig. 1). The parameters of the Zn–S and Zn–Se interactions, obtained via the standard mixing rules, have reasonable values of $\sigma \approx 2.5$ Å and $\epsilon \approx 4$ kJ/mol.

The accuracy of the model in reproducing the phonon dispersion relations of wurtzite ZnS, CdS, and CdSe along the Γ A direction is shown in Fig. 2. The experimental results were obtained from inelastic neutron scattering³⁴ on ¹¹⁶CdSe and Raman scattering for ZnS.³³ For CdS, we have compared our results with calculations providing good agreement with infrared absorption.³⁵ The split between the E_2 and B_{1l} at the Γ -point indicates the ionic nature of the material.³⁶ The overall frequencies in ZnS are higher due to the lighter masses of the atoms compared to CdS and CdSe. The transverse acoustic (TA) and longitudinal acoustic (LA) branches are back-folded into the lower E_2 and B_{1l} branches, respectively. Similar back-folding occurs for the A_1 , B_{1h} , and the upper E_2 and E_1 branches. As can be clearly seen in the figure, our simplified model captures the back-folding in all branches. The overall agreement between the calculations and the experimental results is reasonable given the simple form of the potential (cf.

Eq. (1)). The model performs slightly better for ZnS and is more accurate for the lower frequency branches. The agreement can likely be improved using a polarizable model, as is well known for alkali halides.^{35,37} We note that even better agreement with experiment has been achieved with *ab initio* methods.^{34,38}

In Table II we compare the lattice and elastic constants calculated using our model with the corresponding experimental values. Note that the results for CdSe differ slightly from our original report.¹⁶ This deviation is a consequence of using a smaller tolerance for the minimization, which was considered excessively cumbersome at the time the CdSe parameters were generated. The calculated lattice constants are within 1% of the experimental values, except for the case of the rocksalt structure in ZnS, where the error is 3%. The agreement between the calculated elastic constants and the experimental values is qualitative; the highest accuracy is achieved for C_{11} and C_{44} .

To compare the bulk modulus obtained from our model with experimental results we have used the well known relation between the bulk modulus and the elastic constants:

$$B = \frac{C_{33}(C_{11} + C_{12}) - 2C_{13}^2}{C_{11} + C_{12} + 2C_{33} - 4C_{13}}, \quad (2)$$

for hexagonal symmetry and

$$B = [(C_{11} + C_{22} + C_{33})/3 + 2C_{12}]/3, \quad (3)$$

for cubic symmetry. The calculated bulk moduli for wurtzite ZnS, CdS, and CdSe are in reasonable agreement with the experimental values (which show some spread from one report to the other). Moreover, the values of the bulk modulus are comparable in accuracy to those obtained by *ab initio* methods.^{27,28}

III. PHASE DIAGRAM, EQUATION OF STATE, AND CRYSTALS WITH IMPURITIES

To test the accuracy of our models on quantities not directly used in the fitting procedure, we calculated coexistence pressures for the wurtzite and rocksalt structures at $T = 300$ K, as well as equations of state for all three crystal structures. To further validate the potentials, we compared structural properties they predict for several low-temperature crystals with those obtained from *ab initio* methods.

In Fig. 3 we plot the enthalpy as a function of pressure for bulk ZnS, CdS, and CdSe. The pressure was varied between 0 and 15 GPa using the constant pressure Monte Carlo simulation technique.³¹ For each crystal structure, we have used a periodically replicated simulation box of more than 400 atoms, and averaged the results over 50 000 Monte Carlo cycles. Each cycle on average consisted of one attempted displacement move for all atoms, and one attempted change of the simulation box volume.

Approximating the true coexistence pressure by points of equal enthalpy, we find that the phase transformation from wurtzite to the rocksalt structure occurs at ≈ 2.4 GPa, ≈ 1.6 GPa, and ≈ 11.4 GPa for CdSe, CdS, and ZnS, respectively. These values agree well with experimentally observed transition pressures of ≈ 2.5 GPa,^{13,48} ≈ 2.5 – 3.2 GPa,^{49–52} and ≈ 12 GPa,⁵³ for CdSe, CdS, and ZnS, respectively. In all three materials, the zinc-blende crystal structure is not stable

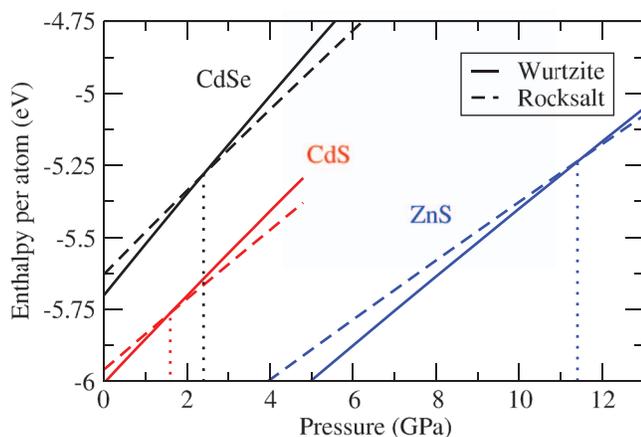


FIG. 3. Enthalpies as a function of pressure of bulk ZnS (upper panel), CdS (middle panel), and CdSe (lower panel), at a temperature of 300 K. The solid and dashed lines show results obtained for wurtzite and rocksalt crystal structures, respectively. The vertical dotted lines mark points of equal enthalpies and approximately correspond to thermodynamic wurtzite to rocksalt transition pressures in the respective materials.

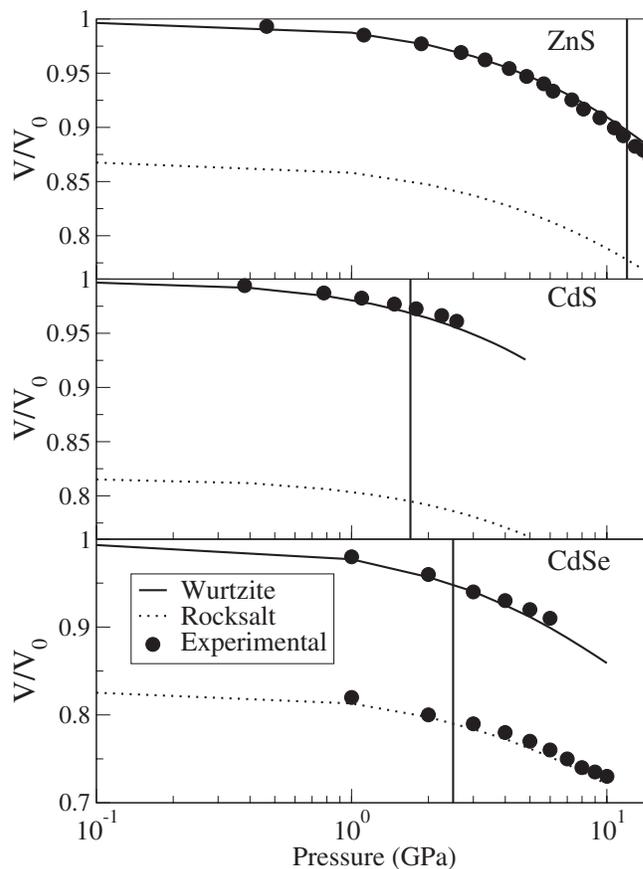


FIG. 4. Volume as a function of pressure for bulk ZnS (upper panel), CdS (middle panel), and CdSe (lower panel). The solid and dotted lines are the calculated results for wurtzite and rocksalt crystal structures, respectively. V_0 is the unit cell volume of the wurtzite structure at zero pressure. Filled circles show experimental results.^{13,53,54} (Note that the CdSe data were obtained in experiments on 45 Å diameter CdSe nanocrystals.¹³)

in the pressure range studied here; its enthalpy (not shown) is slightly higher than the corresponding wurtzite enthalpy.

In Fig. 4 we plot the equation of state (volume as a function of pressure) for all three materials. We find excellent agreement with experiments on CdSe,¹³ CdS,⁵⁴ and ZnS.⁵³

Table III shows a comparison of structural properties predicted by the pair potentials and density functional theory (DFT) calculations within the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE).⁵⁵ Lattice parameters a and c and bond length d of the wurtzite compounds at zero temperature were calculated in Monte Carlo simulations of 360 periodically replicated atoms and DFT-PBE calculations of supercells containing 128 atoms. The DFT-PBE calculations were performed using the Vienna Ab-initio Simulation Package (VASP).⁵⁶ We employed projector-augmented wave potentials which treat Cd $4d10 5s2$, Zn $3d10 4s2$, S $3s2 3p4$, and Se $4s2 4p4$ states explicitly as valence electrons.^{57,58} A $2 \times 2 \times 2$ Monkhorst-Pack mesh was used for k-point sampling,⁵⁹ with convergence verified against a $4 \times 4 \times 4$ mesh. The cutoff energy of the plane-wave basis set was 400 eV. All structures were fully relaxed with respect to the volume and internal degrees of freedom. We find good agreement between the two methods.

TABLE III. Lattice parameters a and c , as well as bond length d of wurtzite CdS, ZnS, and CdSe at zero temperature. Values were obtained from the pair potentials and DFT-PBE (all values in units of Å). Experimental values are given for reference. We also compare the bond length d_i of impurity atoms i . For instance, d_{Zn} is the bond length of a Zn impurity atom in CdS.

CdS	Potential	DFT-PBE	Expt.
a	4.16	4.19	4.13 (Refs. 39 and 40)
c	6.61	6.83	6.70 (Refs. 39 and 40)
d	2.53	2.56	
d_{Zn}	2.46	2.39	
d_{Se}	2.59	2.66	
ZnS			
a	3.89	3.85	3.85 (Ref. 43)
c	6.26	6.31	6.29 (Ref. 43)
d	2.37	2.36	
d_{Cd}	2.45	2.52	
CdSe			
a	4.37	4.38	4.30 (Ref. 44)
c	6.97	7.15	7.01 (Ref. 44)
d	2.66	2.68	
d_{S}	2.59	2.51	

To validate the transferability of the pair potentials, we also compare the bond length of different impurity atoms at low concentrations of one atom per simulation cell. The methods agree well, with relative differences in bond lengths smaller than 3%.

IV. CONCLUSIONS

We have developed a set of transferable pair potentials for CdS and ZnS whose form is similar to that used for CdSe.¹⁶ The model consists of positively and negatively charged ions (Cd/Zn and S/Se, respectively) which interact via a Coulomb potential, supplemented by short-range repulsion terms and van der Waals attractive terms. In order to be able to model alloys and hetero-structures of CdSe/CdS/ZnS, we used standard combining rules for the cross terms and fixed the magnitude of the charges to the value obtained for CdSe,¹⁶ thereby reducing the total number of fitting parameters to 4. The parameters were fitted to reproduce lattice and elastic constants, and phonon dispersion relations of wurtzite, zinc-blende, and rocksalt crystals structures.

We have calculated the transition pressure of the wurtzite to rocksalt transformation, as well as equations of state at room temperature for all three materials. Our results are in good agreement with experiments, thus verifying the accuracy and practicability of the pair potential on quantities not used in the fitting procedure. As a test for the transferability of the potentials, we have compared the bond lengths of impurity atoms with DFT-PBE calculations and obtained good agreement.

As a final note, we point out that the simple functional form of the potential naturally limits the portability of our model. In particular, we have tested its accuracy in reproducing the lattice constants of ZnSe, a material whose properties were not included in the fit but which can be easily modeled using the parameters for Zn and Se. We find that deviations

from experimental values are on the order of 5%, considerably larger than for the other materials.

The current work extends our previous work on CdSe and provides a basis for the study of structural properties and dynamical processes of a larger variety of physically interesting materials. These include phase transformation in core-shell structures, alloys which are important for suppression of the Auger process,^{60,61} seeded nanorods, and more.

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