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Stability of high-pressure phases in II-VI semiconductors by a density functional lattice dynamics approach

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Stability of the rocksalt structure with respect to the high-pressure *Cmcm* structure was investigated for several II-VI semiconductors (ZnS, ZnSe, CdS, and CdSe). The lattice dynamics calculations reveal that the rocksalt structure is unstable with respect to the transversal acoustic mode at the Brillouin zone boundary. The phase transition is of the second order and is associated with cell doubling in the high-pressure *Cmcm* phase with frozen deformation. The present calculation gives the transition pressure more accurately than the classical method, which uses the common tangent. Since the volume change at the transition is very small or zero in all studied crystals, transitions were estimated from the pressure at which the frequency of the zone boundary transversal acoustic mode goes to zero. The observed pressures of the phase transitions in structural measurements were reproduced more accurately than in previous calculations and the difference between observed and calculated transition pressure is of the order of 1% to 8%.

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I. INTRODUCTION

The study of pressure induced phase transitions has been a rapidly expanding field of research during the past few decades.[1] Recently, due to the development of the high-pressure experimental techniques, our knowledge of phase transitions at high pressures is considerably improved. The use of a diamond anvil cell (DAC) and x-ray image plates in experiments at synchrotron sources became a standard experimental technique during the last decade.[2,3] In such a way we are obtaining accurate structural information at pressures not accessible before. Enormous improvement in computational power and development of a number of new, efficient *ab initio* program packages, mainly based on density functional theory (DFT), considerably expanded our ability to predict new phases and understand the mechanism of pressure-induced phase transitions even in complex systems.

It was discovered that many semiconductors have a rich phase diagram, as a function of pressure and temperature, with a number of phases, which were not known before. The recent high-pressure experiments revealed that even simple semiconductors such as Si and Ge have a number of new and unexpected structures at high pressures.[1,4]

The standard method for the calculation of relative stability of high-pressure phases is usually based on the examination of energy as a function of pressure for different phases (for review see Ref. 1). Using such a procedure, it is not certain that all studied crystal structures are stable.

The stability of crystal lattice is determined by three stability conditions[5] which all must be fulfilled simultaneously for a given crystal. The first condition is that the crystal lattice is free from forces, i.e., that the total force on each atom is zero. The second condition is that the crystal lattice is stable against macroscopic displacement such as compression (expansion) or shear.[5] The third stability condition is that the crystal lattice is stable against any small displacement. This means that for any displacement there is a restoring force bringing atoms back to the equilibrium. This condition is equivalent to the statement that all phonon frequencies are real.[6] The well-known soft-mode theory[7] of structural phase transitions is based on the idea that the frequency of a certain phonon mode is approaching zero as we change some external parameter (temperature, pressure, electric or magnetic field, etc.), thus leading to the crystal instability, resulting with a new crystal structure.

The motivation for the present calculations was the fact that there is small or zero volume change between cubic ($Fm3m$) and orthorhombic ($Cmcm$) high-pressure structures for ZnS, ZnSe, CdS, and CdSe crystals and the fact that all previous calculations gave relatively large discrepancy between observed and calculated values of transition pressures and volume changes. Also, some calculated volume changes were extremely small (Table I in Ref. 24 and Fig. 1 in Ref. 26), so the question of possible phase transition of the second order came to the focus of our interest.

II. METHOD

Ab initio lattice dynamics calculations were performed using the ABINIT program package,[8] which is based on DFT method[9] and the use of pseudopotentials. We calculated lattice dynamics using the local density approximation (LDA) for ZnS and CdS crystals. The exchange-correlation interaction is evaluated using the Perdew-Wang[10] parametrization of the Ceperly-Alder's[11] electron gas data in the LDA approximation. The generalized gradient approximation (GGA)[10] was used for ZnSe and CdSe crystals, using the Perdew-Burke-Ernzerhof parametrization of the exchange correlation functional.[12] The phonon frequencies were calculated using the perturbative method.[13,14]

The pseudopotentials used in the present calculations were the soft potentials of the Troullier-Martins[15] type, avail-

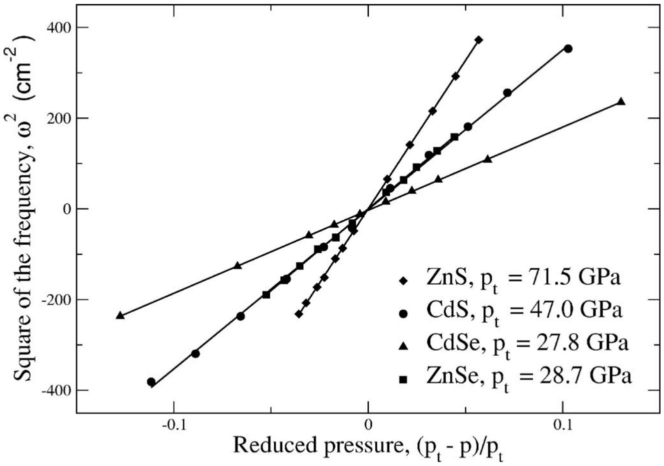

FIG. 1. The pressure dependence of the square of the TA phonon frequency in cubic NaCl structure. The pressure is the reduced pressure, i.e., $(p_{\mathrm{trans}}-p)/p_{\mathrm{trans}}$.

able at the ABINIT web site,[8] without any further adjustment. As it was pointed out before,[16] it is essential to include the *d* electrons in pseudopotentials in order to get more accurate results. The energy cutoff was 40 Ha and Brillouin zone summation was performed on a $12\times12\times12$ Monkhorst-Pack grid[17] for CdS and ZnSe and on a $16\times16\times16$ grid for ZnS and CdSe. Since the NaCl phase of semiconductors often shows metallic character,[4] due to the sixfold coordination, we used metallic "cold smearing"[18] with the smearing parameter of 0.01 Ha.

According to the available experimental data, all studied crystal have very small or zero volume change[1] and the standard method for the estimation of phase change is very difficult to apply.

The main part of the present calculation was to monitor the pressure dependence of the phonon frequencies, i.e., the stability of the crystal lattice with respect to small displacements. The Landau theory of phase transition[19] establishes certain restrictions on the possible low symmetry group (high-pressure phase) with respect to the parent high symmetry NaCl phase with space group *Fm*3*m*.[20] Particularly, the phonon frequency at the *X* point on the Brillouin zone boundary was monitored, since according to Landau theory, there is one *q* point at which transition could take place.

In the case of NaCl → *Cmcm* phase transition there is a possible instability toward the transversal doubly degenerated acoustic mode (TA) at *X* point in the high symmetry NaCl (*Fm*3*m*) phase (Fig. 1). It leads to the freezing of the phonon amplitude at the transition pressure and to the cell doubling with two formula units in the high-pressure (low symmetry) orthorhombic *Cmcm* phase, observed in experiments.[2,3] The present calculations reveal that the pressure-induced phase transition is of the displacive type and is driven by a TA soft mode at the *X* point on the boundary of the Brillouin zone (Figs. 2 and 3).

In order to make a further check on the stability of the NaCl phase, we calculated phonon frequencies for various symmetry directions in the Brillouin zone at the pressures close to transition pressures. We found that all phonon frequencies are real at the pressures of few GPa below the transition pressure (Fig. 3).

III. RESULTS

A. ZnS crystal

The stable low pressure structure of ZnS is zinc-blende (zb) which under the pressure of 15 GPa (Refs. 21 and 22) undergoes a transition to the NaCl type of structure. The NaCl structure is stable in a broad pressure range. This structure undergoes a phase transition to orthorhombic *Cmcm* structure with space group *Cmcm* at the pressure of 69 GPa.[2] The high-pressure crystal structure of ZnS crystal was studied experimentally[2,23] and theoretically.[24] In the recent theoretical study,[24] the authors came to the conclusion that phase transition is around ~60 GPa. Also, they found extremely small volume change of the order of 0.03%. The present calculation gives the phase transition pressure of 71.5 GPa

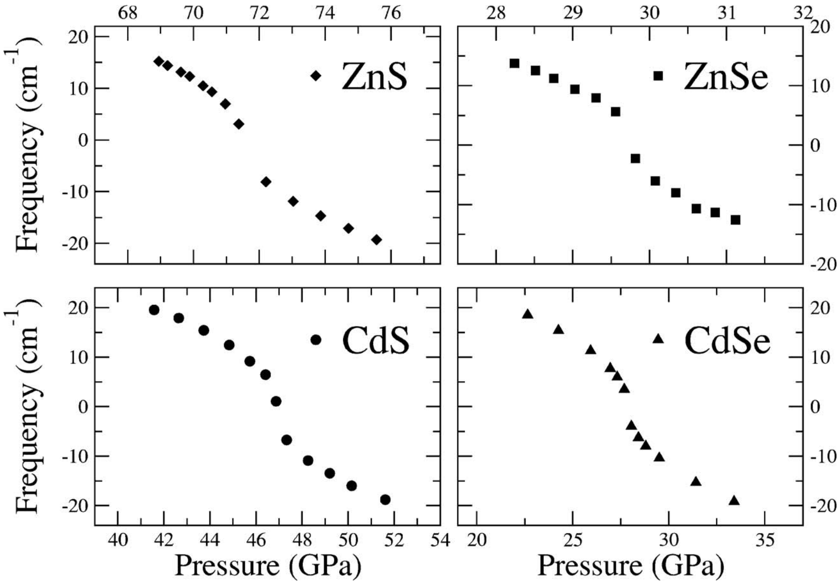

FIG. 2. The pressure dependence of TA phonon frequency at *X* point of the BZ for ZnS, ZnSe, CdS, and CdSe crystals in NaCl structure.

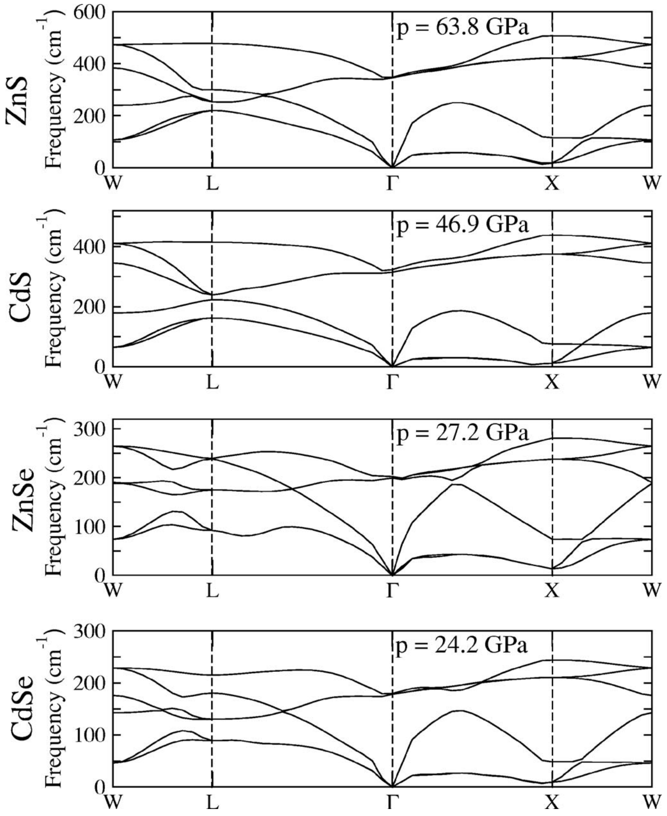

FIG. 3. The phonon dispersion curves of ZnS, CdS, ZnSe, and CdSe crystals in cubic NaCl structure. The pressure is close to the transition pressure but below the transition pressure, i.e., few GPa below the pressure of NaCl→*Cmcm* transition.

(Fig. 2 and Table I), which is very close to the observed one of 69 GPa.[2]

B. ZnSe crystal

The high-pressure properties of the ZnSe crystal were studied both experimentally[3,25] and theoretically.[26] The sequence of high-pressure phases is the same as for the other studied semiconductors zb→NaCl→*Cmcm*.

The calculated[26] transition pressure for NaCl→*Cmcm* transition is 35 GPa, while the present calculation gives the pressure of the phase transition NaCl→*Cmcm* to be 29.8 GPa (Fig. 2 and Table I), so the difference is of the order of less than 1%.

TABLE I. Observed and calculated pressures of phase transitions and equilibrium lattice constants (zero pressure zinc-blende structure) of ZnS, ZnSe, CdS, and CdSe crystals.

Compound	p_t^{calc} (GPa)	p_t^{expt} (GPa)	a_0^{calc} (Å)	a_0^{expt} (Å)
ZnS	71.5	~69	5.32	5.41
ZnSe	29.8	30	5.67	5.63
CdS	47.0	51	5.83	5.81
CdSe	27.8	27	6.05	6.09

C. CdS crystal

The structure of high-pressure phases of CdS crystal were studied experimentally[2] and the transition pressure for NaCl→*Cmcm* transition was found to be 51 GPa. The present calculation gives the pressure of the phase transition NaCl→*Cmcm* to be 47.0 GPa (Fig. 2 and Table I), which is lower than the experimental pressure for about 8%. The authors[2] were not able to distinguish if high-pressure space group was *Cmcm* or *Pmmn*. The present calculation supports *Cmcm* space group as the high-pressure one.

D. CdSe crystal

The high-pressure sequence of phase structures in CdSe crystal follows the usual zb→NaCl→*Cmcm* pattern of high-pressure phases and was studied experimentally[2] and theoretically.[26] The present calculation gives the phase transition pressure of 27.8 GPa (Table I and Fig. 2), which is very close to the observed pressure[3] at 27 GPa.

The above results imply that phase transition, i.e., the pressure at which phonon frequency is equal to zero, is well reproduced within DFT calculations, using the standard "of the shelf" pseudopotentials, not specially tailored for the present calculation.

IV. DISCUSSION

In summary, according to the results of the present calculations, the transition pressure is reproduced very well using the DFT lattice dynamics approach. The phase transitions, in all studied II-VI semiconductors, are structural phase transition of displacive type, driven by a soft transversal acoustic phonon mode at *X* point on the Brillouin zone boundary. This leads to the cell doubling in the low symmetry (high-pressure) orthorhombic phase with space group *Cmcm*.

It means that the second derivative of the total energy with respect to the displacements is described well with available pseudopotentials and that dynamical properties are quite accurately reproduced, at least for the phase transitions which are close to the second order.[19]

The differences between calculated and observed phase transitions in ZnS, CdS, ZnSe, and CdSe crystals are small and are in the range from 1% to 8%. This is more accurate than previous results,[26,24] where the differences were between 10% and 20%.

Furthermore, our results show that the calculation of the lattice dynamics can be a reliable way to predict transition pressure by monitoring the pressure dependence of phonon frequencies. Of course, it is applicable to the cases where Landau theory of the phase transition is valid, i.e., group subgroup relation is determined by the theory.

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