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Original Scientific Paper

High-pressure Phase Transition in CdTe by a Density Functional Lattice Dynamics Approach*

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Abstract. An investigation of the stability of the metallic rocksalt structure with respect to the high pressure *Cmcm* structure for II-VI semiconductor CdTe was performed. The lattice dynamics calculations, based on density functional perturbation theory (DFPT), reveal that the rocksalt structure is unstable with respect to transversal acoustic mode at the Brillouin zone boundary. The phase transition is of the second order (zero volume change), associated with cell doubling in the high pressure *Cmcm* phase with frozen in deformation. The present calculations give the transition pressure more accurately than classical common tangent method. Since the volume change at the transition is very small or zero, the transition was estimated from the pressure at which the frequency of zone boundary transversal acoustic mode goes to zero. The observed pressure of the phase transition in structural measurements, reproduced more accurately than in previous experiments, differs from calculated transition pressure by about 15 %.

Keywords: lattice dynamics, DFT, metals, phase transitions

INTRODUCTION

The study of pressure induced phase transitions has been a rapidly expanding field of research during the past few decades.[1] Improvements in the resolution of powder X-ray diffraction experiments, with synchrotron sources, at high pressures made in diamond anvil cells (DAC) and more sophisticated methods of data analysis, have revealed the existence of many new and unexpected high-pressure phases.[2,3] At the same time, enormous advances in the accuracy and efficiency of first-principles electronic structure calculations have allowed detailed studies of the energetics and structural systematics of materials under high pressure. These first-principles calculations, based mainly on density functional theory (DFT), have features that make them complementary to experimental studies. They are approximate and have a number of limitations, of which one has to be very aware, but they give information which is not available from experiments. Furthermore, one has a precise control over the physical conditions and chemical composition of the system, thus excluding all the uncertainties about the structures present. Also, it is easy to perform calculations at very high pressures, although the corresponding experiments may be very difficult to perform. The calculations can therefore, also, be used to predict new high-pressure phases.

The stability of crystal lattice is determined by three stability conditions, which must all be fulfilled simultaneously for a given crystal:[4] first, crystal lattice must be free from forces; second, crystal lattice must be stable against macroscopic displacement such as compression (expansion) or shear; third, crystal lattice must be stable against any small displacement. The third condition is equivalent to the statement that all phonon frequencies have real values.[5] The soft-mode theory of structural phase transitions is based on the idea that the frequency of a certain phonon mode is approaching zero as one changes some external parameter (temperature, pressure, electric or magnetic field, *etc*.), thus leading to the crystal instability and resulting with a new more stable crystal structure.

The standard method for the calculations of relative stability of high-pressure phases is usually based upon the examination of a total energy as a function of pressure for different phases. Using such a procedure, it is not always easy to determine the relative stability of studied crystal structures. Likewise, in certain cases, transition pressures are very difficult to obtain.

At ambient pressure the stable structure of CdTe crystal is zinc-blende (zb). With increasing pressure, zb phase undergoes a transition to a cinnabar (cinn)

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Dedicated to Professor Boran Leontić on the occasion of his 80th birthday.

** Author to whom correspondence should be addressed. (E-mail: ilukacevic@fizika.unios.hr) phase at 3.5 GPa,[6,7] which is stable only in a short pressure interval before it changes to the rocksalt (NaCl) phase at 3.8 GPa[6] and subsequently to *Cmcm* phase at 10.1 GPa:[8,9]

$$\text{zb} \rightarrow \text{cinn} \rightarrow \text{NaCl} \rightarrow Cmcm.$$

All experiments[6–9] used an ADX (Angle Dispersive X-ray diffraction) method for monitoring the sample and DAC for simulating pressures up to 28 GPa. Experimental results confuted up to that time results that NaCl structure first undergoes the transition to a β-tin phase at the pressure of 10 GPa,[10] and then to an orthorhombic structure with space group *Pmm*2 above 12 GPa,[11] which were obtained because of the continuous nature of the NaCl → *Cmcm* transition, coupled with the limited resolution and lower sensitivity of previous studies.[8] Furthermore, they observed the continuous onset of the distortion of the cubic NaCl phase, with no signficant discontinuity in either the lattice parameters or the unit-cell volume in the region of the transition.[8] On the other hand, the volume change during the zb → cinn and cinn → NaCl transitions has a discontinuity, $\Delta V_{\text{zb} \rightarrow \text{cinn}}$ = 13.3 % [6,7] and $\Delta V_{\text{cinn} \rightarrow \text{NaCl}}$ = 3.7 %,[6] which is a property of the first order transitions.

Previous theoretical research of the high-pressure phases of CdTe crystal by Côté *et al.*[12] gave only qualitative agreement with experimental results for the dependences of internal parameters and lattice constant ratios on pressure in *Cmcm* phase. Also, they calculated the volume change during the NaCl → *Cmcm* transition to be 1.8 %. Nevertheless, they used the, obviously inappropriate, common tangent method for predicting the transition pressure. Despite that, the calculated transition pressure was found to be 12 GPa, in a good agreement with the experimental value of 10.1 GPa. Theoretical research done by Benkhettou *et al.*[28] found NaCl phase not to be stable at any pressure interval.

The motivations for the present calculations were the existence of a reliable experimental results for the CdTe crystal at high pressures,[6–9] which also serve as verification points, and the fact that there is a very small volume change during the transition between NaCl and *Cmcm* phases of CdTe crystal, indicating that the transition is of the second order. The latter questions the usability of so far used common tangent method[12] for structural systematics and phase transition pressure determination. Furthermore, dynamical instability of the TA phonon mode in the NaCl phase occurs before the transition to the *Cmcm* phase,[13] so that lattice dynamics calculations of the softening of the certain phonon mode came into the focus of our interest.

METHOD

Ab initio lattice dynamics calculations were performed using the ABINIT program package,[14] based on DFT[15] and the use of pseudopotentials and the plane wave basis sets. Lattice dynamics calculations were done using the local density approximation (LDA). The exchange-correlation interaction is evaluated using the Perdew-Wang[16] parametrization of the Ceperley-Alder's[17] electron gas data. The phonon frequencies were calculated using the density functional perturbation theory (DFTP),[18] as implemented in the ABINIT package.

The pseudopotentials used in the present calculations were Troullier-Martins[19] type pseudopotentials, available at the ABINIT web site,[14] without any further adjustments. As it was pointed out before,[20] it is essential to include the cation species d electrons in pseudopotentials in order to get more accurate results, for they are energetically very close to valence s electrons. The energy cutoffs were 40 E_h (1 E_h = 27.21138 eV) for the ground state (GS) calculations in zb and NaCl phases and response function (RF) calculations in NaCl phase and 44 E_h for the ground state calculations in cinn phase. Brillouin zone summation was performed on a 18 × 18 × 18 (22 × 22 × 22) and 12 × 12 × 12 Monkhorst-Pack grid[21] for the GS and RF calculations respectively in zb (cinn) and NaCl phases. These parameters ensured the convergence of the structural properties of the studied phases and the phonon frequencies in the NaCl phase: total energies are converged under 5×10^{-4} E_h (0.014 eV) and phonon frequencies under 1 cm^{-1}. Since high-pressure phases of semiconductors like CdTe often show metallic character,[22] we used metallic "cold smearing"[23] with the smearing factor of 0.04 E_h and 0.01 E_h for the ground state and response function calculations respectively.

The main part of the present calculations was to monitor the pressure dependence of the phonon frequencies, *i.e.* the stability of the crystal lattice with respect to small displacements (for example, see Ref. 24). The Landau theory of phase transitions[25] establishes certain restrictions on the possible low symmetry group (high-pressure phase) with respect to the high symmetry NaCl phase (space group *Fm*3*m*). Particularly, the phonon frequency at the X point on the Brillouin zone boundary was monitored, since, according to Landau theory,[26] there is one q point at which transition could take place.

In the case of the NaCl → *Cmcm* phase transition, there is a possible instability toward the transversal doubly degenerate acoustic mode (TA) at X point in the high symmetry NaCl phase.[13] 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 orthorhombic *Cmcm* phase. 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.

RESULTS

Experimental results suggest that the NaCl → *Cmcm* phase transition occurs at the pressure of 10.1 GPa.[8,9] Previous theoretical calculation, using the above discussed and for this type of phase transitions inapplicable common tangent method, obtains the phase transition pressure of 12 GPa.[12] Interestingly, the authors themselves question the reliability of the used common tangent method, for the reasons mentioned: energetic indistinguishability of the NaCl and *Cmcm* phases in the pressure interval around the phase transition and very small volume change during the phase transition, when studying structural systematics and calculating the phase transition pressures (see Figure 1 in Ref. 12). For the same reasons, the authors do not obtain the stability of the experimentally observed cinn phase in any pressure interval.

Present calculations included the ground state (GS) calculations for obtaining the structural parameters of different phases of CdTe crystal (Table 1) and response function (RF) calculations for obtaining the phonon frequencies at different pressures in the NaCl phase of CdTe crystal (Table 2). GS calculations gave a good agreement with the experimental data with errors consistent with the use of LDA approximation. These results confirmed the applicability of the used pseudopotentials. RF calculations were done for a series of pressures in the pressure range between 8 GPa and 15 GPa (Figure 1). Transition pressure was obtained at 11.6 GPa.

Table 1. Lattice parameters expressed in a_0 (bohr)[(a)] for three phases of CdTe crystal: zinc-blende (zb), cinnabar (cinn) and rocksalt (NaCl)[(b)]

	Experimental	Previous theoretical	Present theoretical
a_{zb}	12.25[(c)]	12.15[(f)]	11.97
a_{cinn}	8.11[(d)]	8.17[(g)]	8.12
c_{cinn}	19.34[(d)]	19.51[(g)]	19.30
u_{cinn}	0.64[(d)]	0.65[(g)]	0.61
v_{cinn}	0.57[(d)]	0.56[(g)]	0.56
a_{NaCl}	11.22[(e)]	11.19[(g)]	11.00

[(a)] 1 bohr (a_0) = 0.529177 Å = 5.29177×10^{-11} m.

[(b)] Agreement of the theoretical studies is within the LDA approximation used. Experimental data for cinn phase were obtained at 3.6 GPa.

[(c)] Ref. 11, [(d)] Ref. 9, [(e)] Ref. 2, [(f)] Ref. 12, [(g)] Ref. 28.

Table 2. Comparison of the experimental and theoretical NaCl → *Cmcm* phase transition pressures, p_{t}, in CdTe crystal[(a)]

	Experimental	Previous theoretical	Present theoretical
$\frac{p_{\mathrm{t}}}{\mathrm{GPa}}$	10.1[(b)]	12.0[(c)]	11.6

[(a)] Previous theoretical pressure was obtained with the common tangent method, while present transition pressure was obtained with lattice dynamics calculations.

[(b)] Refs. 8, 9, [(c)] Ref. 12.

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

DISCUSSION

According to the results of the present calculations, the transition pressure is reproduced very well using the DFT lattice dynamics approach. The high-pressure NaCl → *Cmcm* phase transition in CdTe is the structural phase transition of displacive type, driven by the 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.[25]

The difference between calculated and observed phase transition pressure in CdTe crystal is about 15 %.

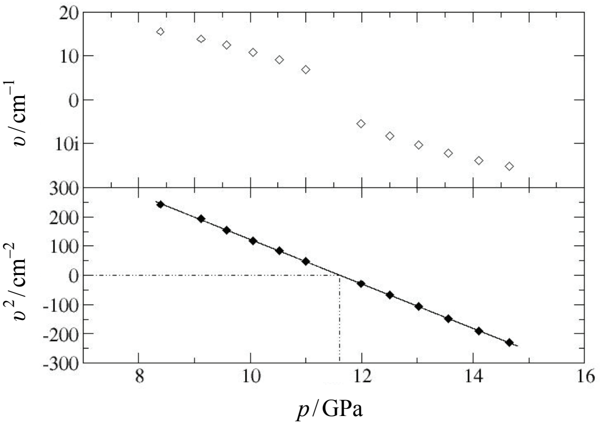

Figure 1. Pressure dependence of the transversal acoustic soft mode frequency (up) and square of the frequency (down) in the NaCl phase of CdTe crystal. A dash-dotted line serves as an eye guide.

This is a little more accurate then the previous theoretical results obtained with the common tangent method, which gave the error of 19 %. Nevertheless, common tangent method can, applied to these kinds of phase transitions accompanied by the zero volume change, give errors up to 60 %.[1]

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

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SAŽETAK

Istraživanje faznog prijelaza pod visokim tlakom u CdTe pomoću dinamike funkcionalne gustoće na rešetki

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Istraživana je stabilnost metalne NaCl strukture obzirom na visokotlačnu *Cmcm* strukturu poluvodiča II-VI grupe CdTe. Računi dinamike rešetke, zasnovani na perturbacijskoj teoriji funkcionala gustoće (DFPT, engl. *density functional perturbation theory*), otkrivaju da je NaCl struktura nestabilna obzirom na transverzalni akustički mod na rubu Brillouinove zone. Fazni prijelaz je drugog reda (promjena volumena je nula), kod kojega pri smrzavanju deformacije dolazi do udvostručenja jedinične ćelije u visokotlačnoj *Cmcm* fazi. Predstavljeni računi daju tlak prijelaza točnije nego klasična metoda zajedničke tangente. Budući da je promjena volumena u točki prijelaza vrlo mala ili nula, prijelaz je ocjenjen iz tlaka na kojemu frekvencija transverzalnog akustičkog moda na rubu zone postaje nula. Ekperimentalna vrijednost tlaka faznog prijelaza, dobivena točnije nego u prethodnim eksperimentalnim istraživanjima, se razlikuje od izračunatog tlaka prijelaza za oko 15 %.