Vibrational properties of the high-pressure Cmcm phase of ZnTe

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A lattice dynamical model based on ab initio methods has been developed for the common Cmcm-type orthorhombic high-pressure phase of binary semiconductors. It is applied to ZnTe. The model supplies the zone-center phonon frequencies which are compared to experimental Raman scattering results. The complete phonon dispersion relations and the one-phonon density of states of Cmcm-ZnTe are calculated. The phonon eigenvectors at the Γ-point of the Brillouin zone are given.

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I. INTRODUCTION

Several tetrahedrally coordinated III-V and II-VI semiconductors adopt an orthorhombic crystal structure under pressure with space group Cmcm and Z=4 formula units per unit cell.1,2 The structure can be viewed as a distorted variant of the rocksalt structure (see Fig. 1). The structure type, which we denote by its space group Cmcm, the zincblende-cinnabar→Cmcm. The stability range of the Cmcm phase of ZnTe extends from 12 to about 85 GPa, where a new modification appears. In CdTe (as in other II-VI and III-V compounds) a rocksalt-type phase occurs before transformation to a Cmcm phase.1,2 Such differences in phase stability behavior have been correlated with the degree of ionicity.4,5

Given the low ionicity of ZnTe (compared to other II-VI compounds) and the relatively high atomic co-ordination of the Cnmc phase,1 this modification can be expected to be metallic. In fact, at pressures higher than ∼12 GPa metallic-like transport properties are observed.6 Furthermore, in near-infrared reflectivity measurements a Drude-like tail appears at the phase transition from semiconducting cinnabar to Cmcm.7,8

The first observation of the Cmca structure in ZnTe3 and followup experimental studies of other binaries initiated quite a number of ab initio total energy calculations; most of the theoretical work is covered in a recent review.2 Specifically for Cmcm-ZnTe, calculations were reported in Refs. 9–13. The obtained band structure of Ref. 11 is consistent with metallic behavior.

In contrast to experimental and theoretical phase stability, the lattice dynamical properties characteristic of the ubiquitous Cmcm-type structure are not well known. A few Raman data were reported for Cmcm-ZnTe,3,4 but no detailed interpretation could be given in terms of a quantitative phonon model.

Here we report lattice dynamics calculations of Cmcm-ZnTe based on ab initio pseudopotentials which allow us to obtain the dynamical matrix. The method provides frequencies and eigenvectors in the complete Brillouin zone and thus, the phonon density of states. The calculated zone-center frequencies are compared to Raman data. Of the six Raman-active modes predicted by group theory four are observed experimentally. These are assigned on the basis of the calculated results.

II. CALCULATIONS

The primitive cell of the Cnmc structure contains two formula units. In terms of the lattice vectors of the orthorhombic Bravais lattice, a possible choice of primitive lattice vectors is \( \mathbf{a}_1=(a/2,-b/2,0) \), \( \mathbf{a}_2=(a/2,b/2,0) \), \( \mathbf{a}_3=(0,0,c) \), \( abc/2 \) being the volume of the primitive unit cell. The reciprocal lattice vectors are \( \mathbf{b}_1=(1/a,-1/b,0) \), \( \mathbf{b}_2=(1/a,1/b,0) \), \( \mathbf{b}_3=(0,0,1/c) \). The angle between \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \) is 84°, i.e. the net is close to tetragonal, see Fig. 2.

A factor group analysis leads to 12 vibrational modes at the Γ-point:

\[
\Gamma = 2A_g + 2B_{1g} + 2B_{1u} + 2B_{2u} + 2B_{3g} + 2B_{3u}.
\]

The six gerade modes, \( 2A_g, 2B_{1g} \) and \( 2B_{3g} \), are Raman-active and three of the six ungerade modes, \( B_{1u}, B_{2u}, \)
and $B_{3u}$ are the acoustic ones. The remaining three are infrared-active modes. Thus, 12 phonon branches are expected for a general value of $q$.

The vibrational properties of the Cmcm phase of ZnTe have been analyzed following *ab initio* methods. The calculations use the density functional theory (DFT) with the general gradient approximation (GGA) as implemented in the VASP package,\textsuperscript{15,16} and with Vanderbilt-type ultrasoft pseudopotentials\textsuperscript{17} provided with VASP. This package solves the generalized Kohn-Sham equations by an iterative matrix diagonalization based on the minimization of the norm of the residual vector for each eigenstate and an optimized charge-density mixing routine. The pseudopotentials for the Zn and Te atoms are representing $d^{10}s^2$ and $s^2p^4$ electron configurations, respectively. A plane-wave basis set was used to expand the electronic wave functions at special $k$-points generated by a $6 \times 6 \times 6$ Monkhorst-Pack $k$-mesh.

We have used the crystallographic orthorhombic unit cell with 8 atoms to optimize the crystal structure at a pressure of 11.6 GPa. The resulting lattice parameters are $a = 5.4265$, $b = 6.0889$ and $c = 5.0009$ Å, the free positional parameters are $y_{Zn} = 0.6289$ and $y_{Te} = 0.1898$. The axial ratios and positions compare well with the experimental values given in Ref. 3. The calculated cell volume of 165.2 Å$^3$ ($V/V_0 = 0.725$, $V_0$ being the volume of the cubic phase at ambient conditions) corresponds to an experimental pressure of about 12.3 GPa (based on an interpolation of data given in Ref. 3).

The phonons were determined by a direct method\textsuperscript{18,19} using an optimized supercell subjected to the symmetry of the Cmcm space group. A $2 \times 2 \times 2$ supercell with 64 atoms was constructed for that purpose, the special $k$-points were generated by a $3 \times 3 \times 3$ Monkhorst-Pack scheme, and the Hellmann-Feynman forces were computed for independent displacements required by the symmetry of the unit cell. The displacement amplitudes were 0.03 Å. Positive and negative

### Table I: Zone-center phonons of the Cmcm phase of ZnTe

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\omega$ (cm$^{-1}$)</th>
<th>$d\omega$/dP (cm$^{-1}$/GPa)</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{1g}$</td>
<td>75.72</td>
<td>53(4)</td>
<td>0.93(10)</td>
</tr>
<tr>
<td>$B_{3g}$</td>
<td>86.73</td>
<td>88(1)</td>
<td>2.0(4)</td>
</tr>
<tr>
<td>$A_g$</td>
<td>103.40</td>
<td>97.9(2)</td>
<td>1.92(14)</td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td>141.76</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>168.12</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$A_g$</td>
<td>171.45</td>
<td>161.3(2)</td>
<td>1.90(6)</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>173.79</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$B_{3g}$</td>
<td>194.80</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>202.14</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
It should be noted that the effective charge is screened out due to the metallic nature of Cmcm-ZnTe.

Since we have calculated the dynamical matrix, our approach provides the complete phonon dispersion relations. They are shown in Fig. 3 along the high-symmetry directions $\Gamma-S-R-Z-T-Y-\Gamma-Z$, calculated at $11.6$ GPa. There are 12 phonon branches (four atoms in the primitive cell), all single degenerate, except the high-symmetry lines $R-Z$ and $Z-T$ along which all branches are doubly degenerate. **It should be noted that the calculations were performed by assuming that the effective charge is screened out due to the metallic nature of Cmcm-ZnTe.**

FIG. 5: Atom displacements for the zone-center vibrational modes of the Cmcm phase of ZnTe. The phonon frequencies calculated for a cell volume of $165.2 \, \text{Å}^3$ (experimental pressure $12.3 \, \text{GPa}$) are also given.

Since the calculated phonon frequencies at the $\Gamma-$point are listed in the first column of Table I. The eigenvectors corresponding to these modes are shown in Fig. 5. Only the independent atoms (two formula units) are shown in the figure. All atoms are at $x = 0.5$, Zn$_1$ and Te$_1$ at $z = 0.25$ and Zn$_2$ and Te$_2$ at $z = 0.75$. The atomic movement of the modes is along $x$, $y$ or $z$. The lowest-energy $B_{1g}$ mode is a bending mode, where the atomic movement **fold the vertical and horizontal plane around the 90 degrees equilibrium position** and thus it is expected to have the lowest frequency. The next mode, $B_{3g}$, is a combination of stretching and bending. The first $A_g$ mode is a kind of torsional mode, where the distorted rhombus is twisted by the atomic movement. The other $A_g$ mode is the only pure stretching mode. The remaining gerade modes as well as the three infrared-active ungerade ones involve combinations of stretching and bending.

**III. COMPARISON WITH EXPERIMENT**

Raman spectra of the Cmcm phase of ZnTe are displayed in Fig. 6. The description of the experiment can be found elsewhere. Although the Cmcm phase of ZnTe

![Raman Spectra](image-url)
has a metallic character, the presence of free carriers does not preclude the detection of phonon Raman signals.

In Fig. 6, the three spectra at 14.2, 14.3 and 14.8 GPa were recorded for increasing pressure, whereas the remaining spectra were obtained with releasing pressure. Some of the upstroke spectra still show Raman modes belonging to the cinnabar phase; these are marked by stars to distinguish them from the Raman modes of the Cmcm phase. The cinnabar modes are not present when the pressure is released. For increasing pressure, the Cmcm phase of ZnTe was first observed near 13.7 GPa, on downstroke it is detected down to at least 10.8 GPa.

In the Raman spectra, only four of the six expected Raman modes are observed. The Raman frequencies measured at 12.2 GPa are given in Table I. From a comparison with the calculated frequencies, the two main peaks in the spectra are the two $A_g$ modes. The $B_{1g}$ mode shows as a rather weak feature but it is clearly observed in all spectra. The $B_{3g}$ mode appears as a shoulder at the lower frequency tail of the $A_g$ feature. The higher frequency $B_{1g}$ and $B_{3g}$ modes do not show up in the experimental spectra.

In Table I we list the dependence of the experimental phonon frequencies on pressure in the range from 10.8 to 16.0 GPa and the Gr"uneisen parameters of the observed Raman modes. The Gr"uneisen parameters are comparable to those of the LO and TO modes in the zincblende structure of ZnTe. The value of the Gr"uneisen parameter of the $B_{3g}$ mode is an exception, but its larger value compared to the rest of modes can probably be attributed to the inaccuracy in the determination of the mode frequency at different pressures (cf. Fig. 6).

IV. CONCLUSIONS

We have studied the vibrational properties of the Cmcm high-pressure phase of ZnTe by means of first-principle calculations with the aim of interpreting the Raman spectra of this high-pressure phase. The observed Raman features can be assigned on the basis of the phonon frequency calculations. The phonon dispersion curves along several high symmetry directions of the Brillouin zone have been obtained. The total and partial phonon densities of states are given as well. The results obtained here could be useful for interpreting Raman spectroscopic data of high-pressure Cmca phases of other binary semiconductors.

Acknowledgments

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