BRIEF NOTE

Ab initio Phonons in Kesterite and Stannite-Type Cu₂ZnSnSe₄

Andrei Postnikov* and Narjes Beigom Mortazavi Amiri

Laboratoire de Physique des Milieux Denses, Institute Jean Barriol and Paul Verlaine University — Metz, 1 Boulevard Arago, F-57078 Metz, France

On the basis of density functional calculations of electronic structure by the Siesta method in the local density approximation, the zone-center vibrational spectra for two crystallographic modifications of Cu₂ZnSnSe₄ are constructed. The difference of frequencies, between kesterite and stannite phases, of some characteristic modes is discussed. It is suggested to use some of these modes (notably the Zn-related one at 239–254 cm^{-1}) as a vibrational signature of the kesterite structure, e.g., for samples characterization. © 2011 The Japan Society of Applied Physics

Cu₂ZnSnSe₄ (CZTSe), a promising indium-free material for photovoltaic applications, has a body-centered tetragonal crystal structure derived from CuInSe₂ chalcopyrite via double substitution of indium atoms, in an ordered manner, by zinc and tin. This can be done, e.g., producing the sequence of (001) cation planes …/Cu+Zn/Cu+Sn/… and hence the kesterite (KS) structure, or …/Cu+Cu/Zn+Sn/… and hence stannite (ST). In both structures, a given atom species has the same nearest coordination, dictated by the need to satisfy the octet rule, but at longer ranges the connectivity patterns differ. This affects electronic structure, e.g., optical properties, but also lattice dynamics, that might become useful for characterizing, or recognizing, the structures of these materials. The identification of phonon modes is rarely straightforward, and usually is much helped by having first-principles calculation results as a benchmark.

In the following, from first-principle calculations done in the framework of the density functional theory, we calculate and compare vibration frequencies and eigenvectors in KS and ST phases of CZTSe. The method technically used for electronic structure calculations is Siesta,[1] which relies on norm-conserving pseudopotentials and atom-centered numerical basis functions with finite confinement radii; the force constants are collected from applying small finite displacements of all atoms, whereupon the phonon frequencies and eigenvectors follow from diagonalizing the dynamical matrix by an auxiliary code. The details of calculation are explained elsewhere.[2] Exchange–correlation was treated in the local density approximation. From a number of previous studies on similar systems[3–7] it is known that the band structure obtained this way is not good for analyzing optical properties, since the calculated band gap is (wrongly) negative. However, the phonons, being a ground-state property, can be reasonably well calculated.

The zone-center projected density of vibration modes, 21 in total, resolved into contributions from individual constituents, is shown in Fig. 1, after calculations done for the single CZTSe unit cell. Similarly to the case of CuInSe₂ chalcopyrite studied earlier,[8] we found transversal optical phonons to be arranged into three groups, at 60–90, 174–187, and 209–254 cm^{-1}. "Zone-center projected" above implies that the vibration eigenvectors, before being taken to square for yielding the weights of spectral lines, are first summed up over the like atoms in the unit cell (see Postnikov *et al.*[9] for details). This suppresses those contributions of Cu and Se which include opposite move-
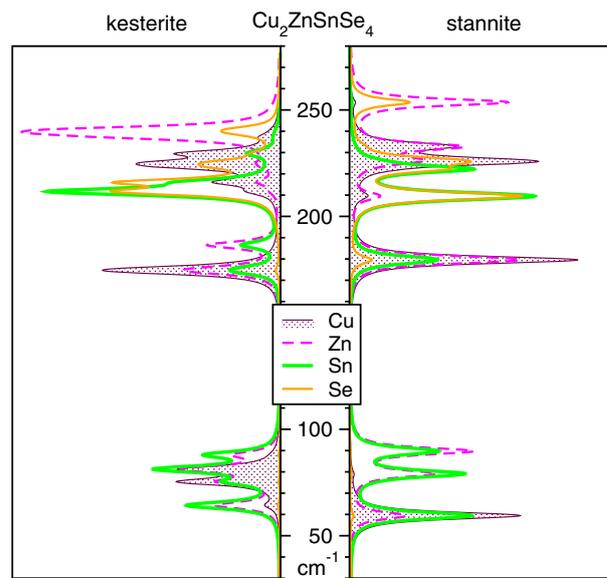

Fig. 1. (Color online) Density of zone-center vibration modes, resolved in atomic contributions, for KS and ST-type CZTSe. For convenience, discrete peaks are artificially broadened with halfwidth parameter 2 cm^{-1}. The magnitudes of peaks are in arbitrary, but identical, units, attributed to one atom of each type.

ment of multiple atoms within a given type, and enhances overall cation vs anion vibrations on the underlying zincblende-type lattice. Notably the Se vibrations, which are in fact substantial throughout the whole frequency spectrum, become pronouncedly phase-matched only as it comes to harder modes (from 211 cm^{-1} in KS, 209 cm^{-1} in ST).

An interesting observation that certain modes in KS and ST have very close frequency yet different composition, can be traced down to the fact that, whereas the cations have similar grouping around the Se anions, over longer range they assemble into chain-like structures, exhibiting their characteristic vibration modes, in a different way. KS contains zigzag (yet planar) Zn–Se–Cu–Se–Zn chains which transverse the structure in, say, [110] direction (the other family of identical chains runs in the [1$\bar{1}$0] direction; within one or another of those chain systems, the cations are connected by Se atoms correspondingly situated either above, or below, of the Cu+Zn plane of the KS structure). One characteristic vibration in such chain, occuring at 81 cm^{-1}, is a longitudinal (along-the-chain) movement of Zn, in opposite to Cu. The resulting bending of the Zn–Se–Cu bonds induces a $\pm z$ movement of those (two out of four,

*E-mail address: postnikov@univ-metz.fr

© 2011 The Japan Society of Applied Physics

per unit cell) Se atoms which belong to the chain in question. Such vertical pulsation of Se, in its turn, pushes Sn and Cu atoms apart and back along "their" chain running perpendicular to the Zn–Se–Cu–Se–Zn one. Together, this is a coordinated movement along mutually perpendicular Zn–Se–Cu–Se–Zn and Sn–Se–Cu–Se–Sn chains, mediated by $\pm z$ pulsations of Se atoms knitting the both. This (doubly degenerate, due to tetragonal symmetry) mode at $81 \, cm^{-1}$ has substantial and roughly equal fraction of Cu, Zn, and Sn, whereas the net contribution of Se (two atoms moving oppositely and two others silent) is nearly zero, as is well seen in Fig. 1.

A close mode of comparable nature in ST, also doubly degenerate, is that at $90 \, cm^{-1}$; it involves similarly (x, y)-planar movement of the Zn atom, but now the chain it belongs to is Zn–Se–Sn–Se–Zn. The Sn atom moves in the opposite, similar to Cu in the KS structure above; the bending of the Zn–Se–Sn bonds shifts in-the-chain Se atoms alternatively along $\pm z$, transmitting the movement into the perpendicular Cu–Se–Cu–Se–Cu chain. Due to such symmetric setting of the latter chain, the net Cu contribution averages out to exact zero.

An important difference of the discussed ST mode from the previous KS one is that the cation movements are now *not* coplanar with the chains running at $[1\pm10]$, but run along the basal vectors of the tetragonal structure, i.e., at $45°$ to the chain direction. This means that any movement of Zn, Sn, or Cu affects *both* perpendicular chains in which this atom participates. Correspondingly, all four (and not just two, as in KS) Se atoms are equally involved in each of two degenerate modes. In spite of fairly different organization of phonon mode, the frequency shift is merely $9 \, cm^{-1}$ with respect to KS. One can expect, however, quite different intensities of spectral lines, which were not calculated in the present study.

Among a number of other similar yet shifted modes, the analysis of which is sometimes difficult,[2] we discuss here one more relatively clean case, characterized by a fairly large frequency shift. We refer to the hardest modes of spectrum, exhibiting a considerable Zn contribution in both KS and ST. In KS, this is the (double degenerate) mode at $239 \, cm^{-1}$, in which Zn moves roughly along the already discussed Zn–Se–Cu–Se–Zn planar chains; however, the Se ions of this chain now move in the opposite to Zn, as in a neat zinc-blende TO mode. In the ST structure, the chains of such composition and (somehow simplifying) displacement pattern can also be found. However, they are not confined to the (Zn+Cu) (001) plane, but propel through the crystal along the z-direction, interposing the Zn atoms from consecutive (Zn+Sn) (001) planes by intermediary (Cu+Cu) ones, knitting this by Se anions. As a result of different bond bending and different Zn–Zn chain step than in the KS structure, the vibration in ST occurs at $254 \, cm^{-1}$. To this comes an additional difference in the nature of discussed modes. The highest KS mode, as any one running along the *basal* diagonal of a tetragonal structure, is double degenerate. On the contrary, the Zn vibrations in the highest ST mode come about from averaging over chains running along the *spatial* diagonals of the tetragonal cell, and hence forced to align the Zn movement parallel to [001], i.e., slightly off
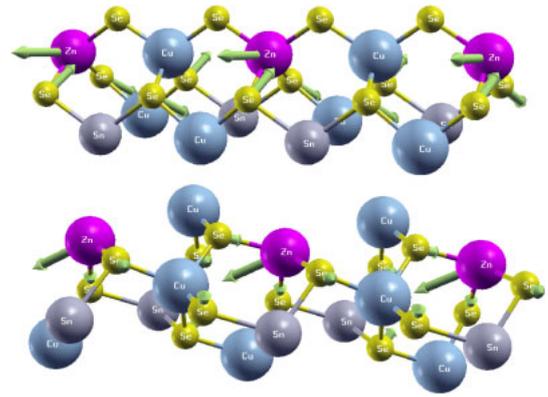

Fig. 2. (Color online) Snapshots of the hardest transversal optical mode in KS ($239 \, cm^{-1}$, top image) and ST ($254 \, cm^{-1}$, bottom image) phases of CZTSe. Arrows indicate relative displacement of ions, as follows from phonon mode eigenvectors.

the chain direction, and make this mode non-degenerate. Figure 2 shows cuts from KS and ST crystals along the direction of respective Zn–Se–Cu–Se–Zn chains, with displacement patterns shown for different atoms, as extracted from corresponding phonon eigenvectors.

The experimental evidence about phonons in CZTSe is scarce; Altosaar *et al.*[10] reported a Raman spectrum of $Cu_2Zn_{1-x}Cd_xSnSe_4$ powder, without specifying crystal structures. They emphasize that two peaks, at 173 and $196 \, cm^{-1}$, do not depend on Cd doping, whereas the position of the less intense peak in the 231–$253 \, cm^{-1}$ interval shifts with doping. This agrees with our attribution of vibration modes in kesterite, whereby the respective frequencies of the most Zn-sensitive ones seem to be at $174, 187, 239 \, cm^{-1}$ (see Fig. 1).

Summarizing, we provided a first-principle description of zone-center phonons in KS and ST structures of CZTSe, supported by available experimental information. The predicted differences in frequency of some characteristic modes may be, in our opinion, useful for identifying KS or ST phases by means of vibrational spectroscopy.

1) J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal: J. Phys.: Condens. Matter **14** (2002) 2745. Siesta homepage: [http://www.icmab.es/siesta/].
2) N. B. Mortazavi Amiri and A. Postnikov: Phys. Rev. B **82** (2010) 205204.
3) J. M. Raulot, C. Domain, and J. F. Guillemoles: J. Phys. Chem. Solids **66** (2005) 2019.
4) S. Chen, X. G. Gong, A. Walsh, and S.-H. Wei: Appl. Phys. Lett. **94** (2009) 041903.
5) J. Paier, R. Asahi, A. Nagoya, and G. Kresse: Phys. Rev. B **79** (2009) 115126.
6) S. Chen, X. G. Gong, A. Walsh, and S.-H. Wei: Phys. Rev. B **79** (2009) 165211.
7) S. Nakamura, T. Maeda, and T. Wada: Phys. Status Solidi C **6** (2009) 1261.
8) A. V. Postnikov and M. V. Yakushev: Thin Solid Films **451–452** (2004) 141.
9) A. V. Postnikov, O. Pagès, and J. Hugel: Phys. Rev. B **71** (2005) 115206.
10) M. Altosaar, J. Raudoja, K. Timmo, M. Danilson, M. Grossberg, J. Krustok, and E. Mellikov: Phys. Status Solidi A **205** (2008) 167.