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# Soft-phonon dynamics of the thermoelectric $\beta$-SnSe at high temperatures

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ABSTRACT

Results of inelastic neutron scattering experiments on SnSe single crystals at high temperatures along with theoretical studies based on the density functional theory are reported. Our experiments reveal significant softening of the transverse acoustic branch along the $[0, \xi, 0]$ direction in the low-temperature $\alpha$-SnSe of *Pbnm* symmetry as temperature approaches $T_c = 807$ K from below. This process is followed by a condensation of the zone-boundary $Y$-phonon of the high-temperature $\beta$-SnSe with *Cmcm* symmetry at the onset of phase transition. The employed theoretical approach supports experimental observations and demonstrates that the phase change in SnSe is mediated by an unstable zone-boundary phonon with the $Y_2^+$ irreducible representation within the *Cmcm* symmetry space group of the high-temperature $\beta$-SnSe. The present work provides a detailed understanding of the soft-mode dynamics in SnSe and conclusively shows that the $\alpha \rightleftharpoons \beta$ structural transformation in this currently topical thermoelectric material is of displacive type.





## 1. Introduction

A layered-structure and narrow-gap semiconductor SnSe, which is a promising material for advanced optoelectronic devices [1] has received renewed experimental interest [2–4] stemming from its potential application in thermoelectric technology. Experimental investigations reported exceptionally good thermoelectric properties of SnSe single crystals at 923 K, indicated by the high thermoelectric figure of merit $ZT \sim 2.6$ resulting from the ultra-low lattice thermal conductivity $\kappa_L = 0.23$ $\mathrm{Wm^{-1}K^{-1}}$. On the other hand, a moderate thermoelectric performance ($ZT \sim 0.5$) was observed for a polycrystalline SnSe below 800 K. These motivated further theoretical studies [5–10] aimed at understanding a possible origin of its remarkably enhanced thermoelectric response. An unprecedented $ZT$ and $\kappa_L$ were found for the high-temperature (HT) $\beta$-SnSe phase adopting orthorhombic structure with the space group *Cmcm* (No. 63) above the phase transition temperature $T_c \sim 807$ K [11,12]. Upon cooling, $\beta$-SnSe undergoes a continuous structural transition to the low-temperature (LT) $\alpha$-SnSe structure with the *Pbnm* (*Pnma*) symmetry (space group No. 62) [13,14]. The $\alpha \rightleftharpoons \beta$ transformation has been suggested [11,12] to be the second-order phase transition of displacive type and mediated by a zone-boundary soft phonon mode of the HT $\beta$-phase which condenses at $T_c$. The recent inelastic neutron scattering (INS) experiments along with the density functional theory (DFT) simulations carried out for $\alpha$-SnSe showed strong anisotropy in softening of both acoustic and optic phonons with increasing temperature [15]. This effect was especially pronounced for the zone-center transverse optic mode with $A_g$ symmetry while approaching $T_c$.

So far, a combined experimental and theoretical studies [15,16] addressed mostly the lattice dynamics of the low-temperature $\alpha$-SnSe phase, leaving the dynamical properties of the high-temperature thermoelectric $\beta$-SnSe phase largely unexplored. Here, we examine phonons in SnSe at high temperatures by the inelastic neutron scattering (INS) experiments, discuss in detail behavior of the soft-phonon mode, and establish its role for the structural phase transition in this system using state-of-the-art density functional theory (DFT). This research provides atomic-scale insight into the mechanisms governing structural phase transformation in this thermoelectric material.

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## 2. Methodology

### 2.1. Experimental

Phonon dispersions in the HT-SnSe phase have been measured by INS on large single crystals ($40 \times 15 \times 15$ mm$^3$) grown from a gaseous phase by the Pizzarello method [17]. The crystalline quality of the specimens investigated was found to be adequate for the neutron scattering studies, with no detectable mosaic structure or twinning. Experiments were carried out with triple-axis spectrometer (1-T1) at the ORPHÉE reactor of the Laboratoire Léon-Brillouin (LLB) at CEA Saclay, France. Measurements were performed in the ($hk0$) scattering plane which has a mirror $m^z$ symmetry. Therefore, all phonon modes with the $z$-polarization belong to a different representation than those with $x$- and $y$-polarizations. The phonon modes with $z$-polarization could not be measured in our INS experiment due to the geometrical restriction imposed by the high-temperature furnace [18]. Hence, not more than eight out of twelve phonons per each $q$-point could be determined. Furthermore, the phonon frequencies in SnSe were found to lie close to one another, i.e. they were hardly separated with the finite resolution of the spectrometer. Phonon density of states in the LT-SnSe phase has been measured at 2 K for polycrystalline sample using the IN4C time-of-flight (TOF) spectrometer at the Institut Laue-Langevin (ILL) in Grenoble, France. The TOF experiments were carried out with two distinct incident neutron energies of 14.34 meV (2.4 Å) and 36.67 meV (1.5 Å). The neutron-weighted phonon density of states, i.e., the so-called generalized phonon density of states (GDOS) was evaluated from the INS spectrum as follows [19–21]: $G(\omega) = \sum_i c_i\,(\sigma_i/m_i)\,g_i(\omega)$, where $c_i$, $\sigma_i$, $m_i$, and $g_i(\omega)$ denote respectively concentration, total scattering cross section, mass, and the partial phonon density of states for the $i$-th atom. The neutron-weighting factors $\sigma_i/m_i$ for Sn ans Se atoms amount to 0.041 and 0.105 barn/a.m.u. [22], respectively. More details concerning extraction of the GDOS spectra from the measured scattering function can be found elsewhere [23].

### 2.2. Theoretical

Our theoretical studies have been performed within the DFT method implementing the projector-augmented wave (PAW) pseudopotentials [24–27] to describe the electron–ion interactions and the generalized gradient approximation with parametrization of Pedrew, Burke and Ernzerhof (GGA-PBE) [28,29] for the exchange-correlation functional. The Sn ($5s^25p^2$) and Se ($4s^24p^4$) electrons were explicitly treated as valence electrons. The semi-empirical corrections of Grimme et al. (DFT-D3) [30] have been incorporated to account for the van der Waals interactions which are important in the layered selenides [6,31]. The unit cells [12] of the *Cmcm* and *Pbnm* structures (both containing 8 atoms) were fully optimized using the $k$-point meshes of $12 \times 4 \times 12$ and $4 \times 12 \times 12$ generated according to the scheme of Monkhorst–Pack. A plane-wave expansion up to the energy cutoff of 280 eV was applied. To ensure a sufficient accuracy of calculations, the convergence criteria for the total energy and residual Hellman–Feynmann (HF) forces were set to $10^{-7}$ eV and $10^{-5}$ eV/Å, respectively.

Phonons in the LT- and HT-SnSe phases were determined within the direct method [32,33] and employing the $2 \times 2 \times 2$ supercells consisting of 64 atoms created from the respective optimized crystallographic unit cells. Such supercells were found to be large enough to avoid contributions from atoms belonging to the periodic images, as confirmed by the elements of the force constant matrices which decay almost four orders of magnitude at the distances smaller than the boundaries of the supercells. The non-vanishing Hellmann–Feynman forces were generated by displacing the symmetry inequivalent Sn and Se atoms from their equilibrium positions by the amplitude of ±0.01 Å. The total number of calculated displacements amounted to 12 due to symmetries of the $\alpha$- and $\beta$-SnSe structures. Frequencies and polarization vectors of phonons $\mathbf{e}(\mathbf{k}, j)$ were obtained by solving an eigenvalue problem for the respective dynamical matrices $D(\mathbf{k})$.

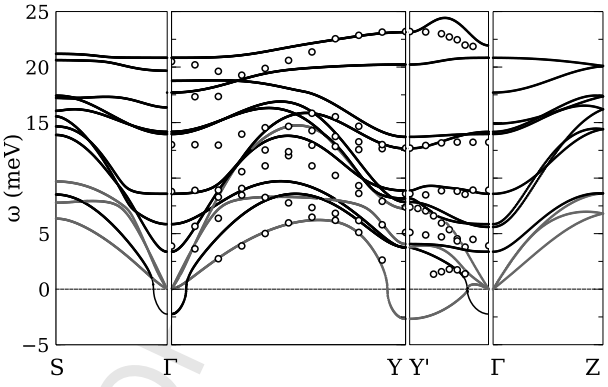


**Fig. 1.** (left) Phonon dispersions in the high-temperature $\beta$-SnSe phase measured by INS at 853 K (symbols) and calculated by the DFT method at the ground state (curves). Acoustic and optic branches are marked by gray and black lines, respectively. The high symmetry points are labeled as: $\Gamma(0,0,0)$, $S(\frac{1}{2},0,0)$, $Y(\frac{1}{2},\frac{1}{2},0)$, $Y'(-\frac{1}{2},\frac{1}{2},0)$, $Z(0,0,\frac{1}{2})$. Negative values $\omega^2(\mathbf{k}, j) < 0$ denote imaginary frequencies.

SnSe is a narrow band gap semiconductor [34,35] and hence the long-range macroscopic electrostatic field which accompanies atomic displacements results in the splitting of infrared-active optic phonon modes into the transverse (TO) and longitudinal (LO) components. The LO-TO splitting was determined by incorporating the effects of long-range Coulomb interactions via the formalism [36] based on the Born effective charge tensor $Z^*$ and electronic part of the dielectric constant ($\epsilon_\infty$). $Z^*$ and $\epsilon_\infty$ were calculated using the linear-response method [37].

## 3. Results and discussion

According to earlier neutron diffraction studies [12], suggesting a zone-boundary soft-phonon mode of the $\beta$-phase to be the driving mechanism of the phase transition in SnSe, we have measured dispersion relations of phonons in the SnSe single crystal above $T_c$. The resulted phonon dispersions from the ($hk0$) scattering plane are depicted in Fig. 1. A comparison is made to the theoretical dispersion curves determined for the fully optimized SnSe structure under the symmetry constraints of the *Cmcm* space group. The primitive unit cell of the HT $\beta$-SnSe consists of 4 atoms (2 formula units), whereas its crystallographic unit cell is twice larger. The DFT optimized lattice constants of the $\beta$-SnSe unit cell amount to $a = 4.2625$ Å, $b = 11.7985$ Å, and $c = 4.2406$ Å. Both Sn and Se atoms occupy ($4c$) Wyckoff positions with coordinates $\pm(0, y, \frac{1}{4})$, where $y_{\mathrm{Sn}} = 0.1246$ and $y_{\mathrm{Se}} = 0.8568$. The calculated structural parameters of $\beta$-SnSe remain consistent with those determined by the previous x-ray and neutron diffraction experiments [11,12] as well as the recent theoretical studies [2,5,9,10]. The dipole–dipole interactions yielding the LO-TO splitting are considered by employing $Z^*$ and $\epsilon_\infty$ tensors with components along the $(x, y, z)$ crystallographic axes of $(5.756, 3.209, 5.768)$ and $(29.894, 17.705, 42.451)$, respectively.

The experimental transverse acoustic (TA) phonon branch along the $\Gamma - Y$ direction undergoes pronounced softening while approaching the zone-boundary at $Y(\frac{1}{2},\frac{1}{2},0)$ likewise the TA branch along the $\Gamma - Y'(-\frac{1}{2},\frac{1}{2},0)$ path. Such a behavior is also reflected by the respective theoretical TA branches, which indicates instability of the *Cmcm* structure at the ground state due to soft-phonon with energy of $i2.67$ meV at the $Y \equiv Y'$ reciprocal lattice point. Additionally, the second soft-mode with the energy of $i2.24$ meV



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