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Digital Object Identifier (DOI): 10.1063/1.4986512

Link: Link to publication record in Heriot-Watt Research Portal

Document Version: Publisher's PDF, also known as Version of record

Published In: Applied Physics Letters

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Evidence for hard and soft substructures in thermoelectric SnSe

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(Received 30 March 2017; accepted 2 June 2017; published online 21 June 2017)

SnSe is a topical thermoelectric material with a low thermal conductivity which is linked to its unique crystal structure. We use low-temperature heat capacity measurements to demonstrate the presence of two characteristic vibrational energy scales in SnSe with Debye temperatures $\theta_{D1} = 345(9)$ K and $\theta_{D2} = 154(2)$ K. These hard and soft substructures are quantitatively linked to the strong and weak Sn-Se bonds in the crystal structure. The heat capacity model predicts the temperature evolution of the unit cell volume, confirming that this two-substructure model captures the basic thermal properties. Comparison with phonon calculations reveals that the soft substructure is associated with the low energy phonon modes that are responsible for the thermal transport. This suggests that searching for materials containing highly divergent bond distances should be a fruitful route for discovering low thermal conductivity materials. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license [http://creativecommons.org/licenses/by/4.0/]. [http://dx.doi.org/10.1063/1.4986512]
shown in Fig. 1(b). The $U_{\text{iso}}$ values are large, in particular, for Sn, which is typical for lone-pair containing rocksalt-based thermoelectrics.\textsuperscript{26} The $U_{\text{iso}}$'s tend toward zero at low temperatures, demonstrating that the structure does not contain significant static disorder.

In order to obtain an estimate of the characteristic energy scales of the atomic motions the $U_{\text{iso}}$'s for Sn and Se were fitted below 800 K using\textsuperscript{29,30}

$$U_{\text{iso}} = \frac{3\hbar^2}{m k_B \theta_D} \left[ \frac{1}{4} + \left( \frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/T} \frac{x}{e^x - 1} \, dx \right] + \sigma^2. \quad (1)$$

Here, $\hbar$ is the reduced Planck constant, $k_B$ is Boltzmann’s constant, $\theta_D$ is the Debye temperature, and $\sigma^2$ is the displacement correlation function. In both cases, $\sigma^2 = 0$, confirming the absence of significant static structural disorder. The fitted $\theta_D$ values are 140(2) K for Sn and 195(3) K for Se, and the fits are shown as solid lines in Fig. 1. The 40% larger value for Se is in line with expected trends based on the atomic mass and bond strength. The $U_{\text{iso}}$(T) show considerable non-linearity in the Pnma phase. This is particularly evident for Sn and reflects the highly anharmonic bonding in this material.

The temperature dependence of the heat capacity ($C_p$) is given in Fig. 2(a) and is characterised by a linear increase beyond the Dulong-Petit value of $3R$/atom, consistent with the high-temperature data in the literature.\textsuperscript{7,9,19,23} A plot of $C_p/T$ versus $T^2$ reveals that there is no electronic contribution to the heat capacity at low-temperature, which is in keeping with the semiconducting nature of SnSe [Fig. 2(b)]. A plot of $C_p/T^3$ versus $T$ reveals an additional low-temperature contribution, which could arise from the contribution of either an Einstein mode or a Schottky anomaly to the specific heat [Fig. 2(c)].

Several models using combinations of Debye and Einstein (or Schottky) modes were tried. The most satisfactory fit was obtained using two Debye terms for the acoustic phonon bath, a low-temperature Schottky contribution to model the peak visible on the $C_p/T^3$ versus $T$ curve and a lattice dilation term\textsuperscript{31} to account for the linear increase at a high temperature

$$C_p = \sum_{i=1}^{2} \left[ \frac{9n_i R}{\theta_D} \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} \, dx \right]
+ \frac{g}{1 + ge^{-\Delta/T}} + 9Bv\xi^2T. \quad (2)$$

Here, $n_i$ is the number of oscillators for each Debye term, $R$ is the gas constant, $\theta_D$ are Debye temperatures, $\Delta$ is the energy gap for a two-level Schottky system, $g$ is the ratio of the degeneracies of the lower level to the upper level, $B = 31$ GPa is the isothermal bulk modulus,\textsuperscript{32} $v$ is the volume
per atom, and $\alpha$ is the thermal expansion coefficient. The thermal expansion coefficient was derived from the temperature evolution of the cell volume as

$$\alpha = (1/V)(dV/dT)\rho.$$  

The cell volume was fitted simultaneously (Fig. 3) using the following expression, which was adapted from Hayward et al.\textsuperscript{33} to include two Debye terms:

$$V = V_0 + a \sum_{i=1}^{2} \int_{0}^{T} 9n_iR\left(\frac{T}{\theta_i}\right)^3 T_{0i}e^{x}\frac{x^4e^{x}}{(e^{x} - 1)^2}dx. \quad (3)$$

The fitted values are $n_1 = 0.96(4)$, $n_2 = 1.04(4)$, $\theta_{D1} = 345(9)$ K, $\theta_{D2} = 154(2)$ K, $g = 0.38(2)$, $\Delta = 64(1)$ K, and $V_0 = 210.32$ Å$^3$, $a = 1.8 \times 10^{-4}$. The model for $C_p$ takes into account all important features of the data including the low temperature peak and the linear increase at a higher temperature (Fig. 2). The $V(T)$ data are fitted well below 600 K, while the experimental volume expands more rapidly at elevated temperatures. The fitted values are $D_2 = 154(2)$ K do not directly map onto the values obtained for Sn and Se from $U_{iso}(T)$. This suggests that different structural fragments are responsible for the different vibrational energy scales observed here. The Pbnm low-temperature structure has three strong and three weak bonds with bond distances of $\sim 2.8$ Å and $\sim 3.4$ Å at 300 K. The Debye temperature (highest phonon frequency) $\theta_D \propto \sqrt{nk/m}$, where $n$ is the number density, $k$ is the bond strength, and $m$ is the reduced mass of the oscillator. From the $C_p$ fitting, the number densities of both oscillators are equal and assuming a similar reduced mass, the ratio of the fitted $\theta_D$ values is proportional to the square root of the bond strengths. We can approximate the bond strength using bond valence sums (BVS), which are directly calculated from the Sn-Se bond distances. The BVS ratio of $3.5$ at 300 K, which is in good agreement with calculated values between 2 and 4 depending on the crystal direction.\textsuperscript{3}

Modelling of low-temperature heat capacity data provides important insight into the link between structure and lattice dynamics. A model using two Debye oscillators of equal abundance was found to give the best fit to the data. This demonstrates that there are two important vibrational energy scales, corresponding to conceptual hard and soft substructures with an equal weighting. As discussed above, $\theta_{D1} = 345(9)$ K and $\theta_{D2} = 154(2)$ K do not directly map onto the values obtained for Sn and Se from $U_{iso}(T)$. This suggests that different structural fragments are responsible for the different vibrational energy scales observed here. The Pbnm low-temperature structure has three strong and three weak bonds with bond distances of $\sim 2.8$ Å and $\sim 3.4$ Å at 300 K. The Debye temperature (highest phonon frequency) $\theta_D \propto \sqrt{nk/m}$, where $n$ is the number density, $k$ is the bond strength, and $m$ is the reduced mass of the oscillator. From the $C_p$ fitting, the number densities of both oscillators are equal and assuming a similar reduced mass, the ratio of the fitted $\theta_D$ values is proportional to the square root of the bond strengths. We can approximate the bond strength using bond valence sums (BVS), which are directly calculated from the Sn-Se bond distances. The BVS ratio of $3.5$, while the ratio of $\theta_{D1}/\theta_{D2} \approx 5$, signalling an almost perfect agreement between bond strength and the $\theta_D$ values. The data therefore suggest that the harder substructure ($\theta_{D1} = 345(9)$ K) is linked to the short bonds, while the softer substructure ($\theta_{D2} = 154(2)$ K) is linked to the weaker bonds within and between the rocksalt layers (Fig 1(a)).

Computational and inelastic neutron scattering phonon studies show two discrete regions in the phonon density of states (PDOS).\textsuperscript{8–10} A lower band spanning 0–13 meV containing 3 acoustic and 9 optic modes and a higher energy band from 13 to 25 meV with the remaining 12 optic modes. The upper energies for these two bands correspond very closely to highest phonon frequency for the fitted Debye modes ($k_B\theta_{D1} = 29.7(8)$ meV and $k_B\theta_{D2} = 13.2(2)$ meV). The equal number of phonon modes in the two bands in the PDOS is in agreement with the equal weighting of the Debye oscillators. It is therefore reasonable to conclude that two Debye modes correspond to the two bands in the PDOS. The phonon calculations reveal that the modes in the lower band are more strongly associated with Sn displacements, with a pronounced peak associated with motions perpendicular to the rocksalt layers.\textsuperscript{6} The higher energy band in the PDOS is more strongly associated with Se displacements. This is consistent with our link to the weak and strong bonds in the crystal structure, where the weaker bonds allow for low-energy anharmonic Sn displacements, while Se is less strongly displaced.

Finally, we note that the presence of two lattice energy scales is similar to the skutterudite and clathrate Phonon Glass Electron Crystal (PGEC)\textsuperscript{38} materials.\textsuperscript{29,39–42} These rattling systems show several characteristic lattice energy scales, typically one high corresponding to the framework and one or several low ones corresponding to weakly bound rattling cations, which are usually described using Einstein modes with $\theta_E < 100$ K (i.e., $\theta_E = 125$ K using $\theta_E/\theta_D$ ratio of $2.5$ at 300 K, which is in good agreement with calculated values between 2 and 4 depending on the crystal direction.\textsuperscript{7}
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