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Anharmonic phonon effects on linear thermal expansion of trigonal bismuth selenide and antimony telluride crystals

Chee Kwan Gan*, Ching Hua Lee

Institute of High Performance Computing, 1 Fusionopolis Way, #16-16 Connexis, Singapore 138632, Singapore

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ABSTRACT

We adopted and extended an efficient Grüneisen formalism to study the phonon anharmonicity and linear thermal expansion coefficients (TECs) of trigonal bismuth selenide (Bi_2Se_3) and antimony telluride (Sb_2Te_3). Anharmonicity of the systems is studied via extensive calculation of Grüneisen parameters that exploit symmetry-preserving deformations. Consistent with experimental findings, a large anisotropy between the TECs in the *a* and *c* directions is found. The larger anharmonicity inherent in Sb_2Te_3, as compared to Bi_2Se_3 is offset by the volumetric effect, resulting in comparable temperature dependence of their linear TECs. The Debye temperatures deduced from our first-principles data also agree very well with the existing tabulated values. The highly efficient methodology developed in this work, applied for the first time to study the linear TECs of two trigonal thermoelectric systems, opens up exciting opportunities to address the anharmonic effects in other thermoelectrics and other low-symmetry materials.

1. Introduction

Bismuth selenide (Bi_2Se_3) and antimony telluride (Sb_2Te_3) belong to a large family of metal dichalcogenides that hosts excellent thermoelectric materials [1] and topological insulators [2–4]. As paradigmatic examples of materials that simultaneously host enigmatic 3D Z_2 topological states, these two materials have been extensively studied experimentally [5–8] and theoretically [9,10] due to their technological importance and fundamental interest. The linear and volumetric thermal expansion coefficients (TECs) of Bi_2Se_3 and Sb_2Te_3 have been determined experimentally [5] where a high anisotropy is found between linear TECs in the *a* and *c* directions for these two systems.

For engineering applications of these materials, good device performance hinges on a solid understanding of thermal expansion behavior because phonon dynamics is intimately affected by temperature-induced crystal deformations. In fact, TEC has been identified as a key design parameter for thermoelectric materials [11]. Thermal expansion and electron-phonon coupling have been shown to drive the temperature dependence of the band structure of topological insulators [12]. The strain caused by thermal expansion could induced a topological phase transition in topological insulators [13]. As found in [14,15], knowledge of the linear thermal expansion and phonon anharmonicity can be captured through phonon frequency lineshifts through the Grüneisen parameters. Such calculations of the thermal expansion properties are commonly performed using a quasi-harmonic approximation (QHA), which involves many phonon calculations on many possible combinations of lattice parameters. But due to its complexity, the QHA is efficient only when dealing with highly symmetric systems such as cubic lattice structures. However, many technologically important crystals are not cubic, and other more efficient approaches are necessary, such as the efficient self-consistent quasiharmonic approximation [16]. In this paper, we adopted and extended an efficient Grüneisen approach by Refs. [17–20] to study Bi_2Se_3 and Sb_2Te_3 with a minimal set of relatively expensive (compared to standard density-functional total-energy calculations) phonon calculations. Through it, we are able to perform a systematic investigation on the anharmonicity of these two materials with relatively low symmetry, and make consistent comparisons between some of their important thermal properties such as linear TECs.

2. Methodology

The trigonal Bi_2Se_3 and Sb_2Te_3 belong to the symmorphic space group $R\bar{3}m$ (No. 166). There are three inequivalent atoms: an Sb atom occupies $6c(0,0,\mu)$ site, a Te atom occupies $3a(0,0,0)$ site, and a second Te atom occupies $6c(0,0,\nu)$ site. This gives a total of 15 atoms in the conventional hexagonal unit cell. However, in order to reduce the amount of computing time, we use a primitive rhombohedral cell of five atoms that is three times smaller than the conventional hexagonal cell. The rhombohedral cell length a_r and angle α_r can be deduced from the

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* Corresponding author.
E-mail address: ganck@ihpc.a-star.edu.sg (C.K. Gan).

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hexagonal lattice parameters a_h and c_h, and vice versa. The relations are: $a_h = 2a_r\sin(\alpha_r/2), c_h = a_r\sqrt{3 + 6\cos\alpha_r}$. On the other hand, $a_r = (a_h/3)\sqrt{\eta^2 + 3}, \cos\alpha_r = (2\eta^2 - 3)/(2\eta^2 + 6)$ where $\eta = c_h/a_h$.

We perform density-functional theory (DFT) calculations within the local density approximation (LDA) as implemented in the plane-wave basis suite QUANTUM ESPRESSO [21] (QE), with wavefunction and density cutoffs of 60 and 480 Rydberg, respectively. A 10 × 10 × 10 Monkhorst-Pack mesh is used for the k-point sampling. LDA has been shown [22] to reasonably reproduce the experimental results for the mean-square displacements (MSD) for Sb_2Te_3. However, we note that future studies should include the van der Waals bonding in the interplanar (i.e., c) direction and spin-orbit interactions. The pseudopotentials for Bi, Se, Sb, and Te are generated using the pslibrary.1.0.0 that is based on the Rappe-Rabe-Kaxiras-Joannopoulos [23] scheme. We relax the structures fully before carrying out the phonon calculations. For Bi_2Se_3, we obtain $(a,c) = (4.110, 27.900)$ Å. This is in good agreement with the experimental [24] result of (4.143,28.636) Å. For Sb_2Te_3, we obtain $(a,c) = (4.244, 29.399)$ Å, which is in good agreement with the experimental [5] result of (4.242,30.191) Å.

According to the Grüneisen approach [17–20,25,26], the linear TECs in the a and c directions, denoted as $\alpha_a(T)$ and $\alpha_c(T)$, respectively, are given by

$$\begin{pmatrix}\alpha_a\\ \alpha_c\end{pmatrix} = \frac{1}{\Omega D}\begin{pmatrix}C_{33} & -C_{13}\\ -2C_{13} & [C_{11}+C_{12}]\end{pmatrix}\begin{pmatrix}I_1\\ I_3\end{pmatrix} \tag{1}$$

where $D = (C_{11} + C_{12})C_{33} - 2C_{13}^2$. We note that Eq. (1) is a special case of a general treatment presented in Ref. [17]. For clarity, the explicit dependence of α's and I_i's on temperature T is suppressed in Eq. (1). We will discuss more about I_i later. The C_{ij} are the elastic constants. The linear TECs are inversely proportional to the volume Ω of primitive cell at equilibrium. We note that Bi_2Se_3 has a smaller Ω than Sb_2Te_3 (i.e., 136.05 Å^3 vs 152.87 Å^3). From a series of symmetry-preserving deformations with strain parameters ranging from −0.01 to 0.01, the elastic constants are deduced from parabolic fits to the energy-strain [27] curves. For Bi_2Se_3, $C_{11} + C_{12} = 121.74, C_{13} = 30.18$, and $C_{33} = 54.45$ GPa. For Sb_2Te_3, $C_{11} + C_{12} = 110.73, C_{13} = 32.16$, and $C_{33} = 60.97$ GPa. We note that the expression for TECs in Eq. (1) is identical to the hexagonal case [20] since a trigonal cell can be perfectly embedded in a hexagonal cell.

Central to our Grüneisen formalism is the temperature dependent heat capacity weighted by the Grüneisen parameter,

$$I_i(T) = \frac{\Omega}{(2\pi)^3}\sum_\lambda \int_{\mathrm{BZ}} d\boldsymbol{q}\; \gamma_{i,\lambda\boldsymbol{q}}\, c(\nu_{\lambda\boldsymbol{q}}, T) \tag{2}$$

where the integral is over the first Brillouin zone (BZ). Here $\gamma_{i,\lambda\boldsymbol{q}} = -n^{-1}\nu_{\lambda\boldsymbol{q}}^{-1}\partial\nu_{\lambda\boldsymbol{q}}/\partial\epsilon_i$ are the mode-dependent and deformation-dependent Grüneisen parameters, which measures the rate of change of the phonon frequency $\nu_{\lambda\boldsymbol{q}}$ (of mode index λ and wavevector $\boldsymbol{q}$) with respect to the strain parameter ε_i. n equals to 1 (2) for a uniaxial (biaxial) strain. The specific heat contributed by a phonon mode of frequency ν is $c(\nu, T) = k_B(r/\sinh r)^2, r = h\nu/2k_BT$. k_B and h are the Boltzmann and Planck constants, respectively. To keep track of the origin of anharmonicity more precisely, we further define the density of phonon states weighted by Grüneisen parameter, $\Gamma_i(\nu)$, given by

$$\Gamma_i(\nu) = \frac{\Omega}{(2\pi)^3}\sum_\lambda \int_{\mathrm{BZ}} d\boldsymbol{q}\; \delta(\nu - \nu_{\lambda\boldsymbol{q}})\gamma_{i,\lambda\boldsymbol{q}} \tag{3}$$

such that $I_i(T) = \int_{\nu_{\min}}^{\nu_{\max}} d\nu\, \Gamma_i(\nu)c(\nu, T)$. ν_{min} (ν_{max}) is the minimum (maximum) frequency in the phonon spectrum. The functions $\Gamma_i(\nu)$ provide a deeper understanding about $I_i(T)$ since it isolates the anharmonicity-dependent contributions from the harmonic specific heat capacity $c(\nu, T)$, which has a well-known universal form [19]. Finally we note that $I_i(T)$is related to the macroscopic [29] Grüneisen parameters, $\gamma_{m,i}(T)$ by the relation $\gamma_{m,i}(T) = I_i(T)/C_v(T)$ where $C_v(T) = \frac{\Omega}{(2\pi)^3}\sum_\lambda \int_{\mathrm{BZ}} d\boldsymbol{q}\; c(\nu_{\lambda\boldsymbol{q}}, T)$ is the specific heat at constant volume. Therefore $\gamma_{m,i}(T)$ can be interpreted as an average over Grüneisen parameters weighted by the mode dependent heat capacity. Its physical meaning is clearest in the large-T limit, where $\gamma_{m,i}$ reduces to a simple arithmetic average of all Grüneisen parameters in the BZ since the heat capacities for each mode approaches unity (in units of k_B) in this limit.

To calculate the Grüneisen parameters resulted from a deformation of the crystal [26] due to an xy biaxial strain, a strain-parameter set of $(\epsilon_1, \epsilon_1, 0,0,0,0)$ (in Voigt's notation) is used, where the rhombohedral cell has a new lattice parameters $a_r' = a_r\sqrt{[\eta^2 + 3(1 + \epsilon_1)^2]/(\eta^2 + 3)}$ and $\cos\alpha_r' = [2\eta^2 - 3(1 + \epsilon_1)^2]/[2\eta^2 + 6(1 + \epsilon_1)^2]$. For a z uniaxial strain, we use the strain-parameter set of $(0,0, \epsilon_3, 0,0,0)$, where the rhombohedral cell has $a_r' = a_r\sqrt{[\eta^2(1 + \epsilon_3)^2 + 3]/(\eta^2 + 3)}$ and $\cos\alpha_r' = [2\eta^2(1 + \epsilon_3)^2 - 3]/[2\eta^2(1 + \epsilon_3)^2 + 6]$. Importantly, these two deformations preserve the space group of the crystal so that we can use the QE symmetry switch of IBRAV = 5. We use small strains of $e_1 = \pm 0.25\%$ and $e_3 = \pm 0.5\%$ for the calculation Grüneisen parameters using finite-differences. For phonon calculations under the QE implementation, we use a q mesh of 5 × 5 × 5, which is equivalent to a 5 × 5 × 5 supercell [30] for the determination of interatomic force constants. A recent work shows that for commensurate wavevectors one may use smaller supercells [31].

3. Results

The Grüneisen parameters along the representative high-symmetry directions for Bi_2Se_3 and Sb_2Te_3 due to an xy biaxial strain are shown in Fig. 1(a) and (c), respectively. Similarly, the results due to a z uniaxial

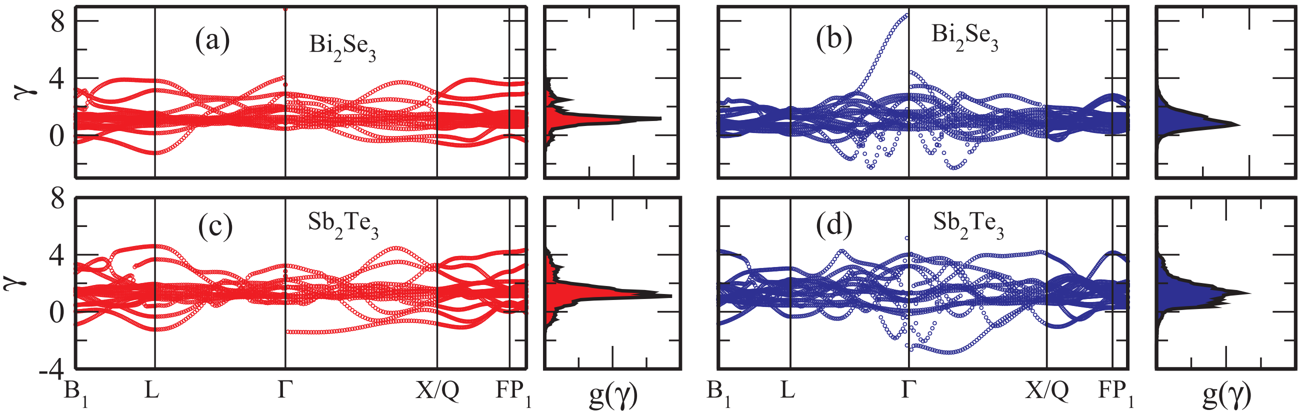

Fig. 1. The Grüneisen parameters for Bi_2Se_3 due to (a) an xy biaxial strain and (b) a z uniaxial strain. The corresponding results for Sb_2Te_3 are shown in (c) and (d), respectively. The label and coordinates of the k points are taken from Ref. [28]. The densities of Grüneisen parameters, $g(\gamma)$, shown on the right side of each figure are obtained with a sampling of 30 × 30 × 30 k points.

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