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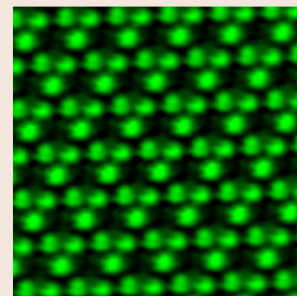
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## Temperature dependence of Raman-active optical phonons in $\text{Bi}_2\text{Se}_3$ and $\text{Sb}_2\text{Te}_3$

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Inelastic light scattering spectra of  $\text{Bi}_2\text{Se}_3$  and  $\text{Sb}_2\text{Te}_3$  single crystals have been measured over the temperature range from 5 K to 300 K. The temperature dependence of dominant  $A_{1g}^2$  phonons shows similar behavior in both materials. The temperature dependence of the peak position and linewidth is analyzed considering the anharmonic decay of optical phonons and the material thermal expansion. This work suggests that Raman spectroscopy can be used for thermometry in  $\text{Bi}_2\text{Se}_3$ - and  $\text{Sb}_2\text{Te}_3$ -based devices in a wide temperature range. © 2012 American Institute of Physics. [doi:10.1063/1.3685465]

Recently, much attention has been paid to the study of  $\text{Bi}_2\text{Se}_3$ ,  $\text{Sb}_2\text{Te}_3$ , and other layered stoichiometric compounds as a promising playground for the realization of a new class of quantum matter and topological insulators.<sup>1</sup> A topological insulator has a “conventional” energy gap in the bulk and surface gapless Dirac-like states, which are protected against any time-invariant perturbations such as crystal imperfections.<sup>2–4</sup> These topologically protected surface states hold great promise for a broad range of potential applications, including field effect transistors,<sup>5–7</sup> infrared-THz detectors,<sup>8,9</sup> and magnetic field sensors.<sup>10,11</sup> It is essential to understand the dynamics of phonons in these materials, particularly the phonon-phonon and electron-phonon interactions, in order to achieve the best device performance. While the room-temperature Raman characterizations of optical phonons in  $\text{Bi}_2\text{Se}_3$  and  $\text{Sb}_2\text{Te}_3$  have been well documented in the literature,<sup>12,13</sup> accurate measurements of the temperature dependence are still lacking. In this letter, we present a Raman spectroscopy study of  $\text{Bi}_2\text{Se}_3$  and  $\text{Sb}_2\text{Te}_3$  crystals in the temperature range between 5 K and 300 K. We uncover a characteristic temperature dependence of the phonon peak position and linewidth and interpret it in the context of thermal expansion and three-phonon anharmonic decay.

The  $\text{Bi}_2\text{Se}_3$  and  $\text{Sb}_2\text{Te}_3$  single crystals studied in this work were synthesized at the University of California – Riverside, Purdue University and the Sandia National Laboratories. Electronic transport characterization revealed that the as-grown crystals were naturally doped, with bulk carrier density in the range of  $10^{18}$ – $10^{19}\text{cm}^{-3}$ . The typical onset magnetic field for observing the Shubnikov-de Haas oscillations was found to be  $\sim 8\text{T}$ , corresponding to carrier mobility  $\sim 1200\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ . Raman scattering spectra were collected from fresh crystal surfaces prepared by mechanical exfoliation.

The Raman spectra were measured in a backscattering geometry using a 532 nm laser excitation. The laser light was injected into an optical fiber, guiding the excitation to the sample stage inserted into a helium-flow variable temperature cryostat. The excitation spot size was about  $20\ \mu\text{m}$  in diameter. The scattered light collected by a  $f/0.73$  lens was directed into a collection fiber, and then guided to a spectrometer equipped with a liquid-nitrogen-cooled CCD camera. The spectra were acquired in the spectral region from 110 to  $1000\text{cm}^{-1}$  with a spectral resolution of  $\sim 1\text{cm}^{-1}$ . The collected spectra were normalized to the background signal from a mirror to compensate for the effects of parasitic light scattering in the optical fibers. The Raman shift frequency was calibrated with reference to the spectra measured on an elemental sulfur reference sample. The peak widths were obtained after correcting for instrumental broadening following the procedure in Ref. 14. At a few selected temperatures, spectra were recorded during both cooling down and warming up and were found to be essentially identical within the experimental uncertainty.

$\text{Bi}_2\text{Se}_3$  and  $\text{Sb}_2\text{Te}_3$ , like other  $\text{V}_2\text{VI}_3$  materials, have 5 atoms in a rhombohedral unit cell, and crystallize in the  $R\bar{3}m$  ( $D_{3d}^5$ ) structure. Out of 12 optical phonons, four modes are Raman active,  $2E_g + 2A_{1g}$ , with the frequencies in the  $\sim 30$ – $200\text{cm}^{-1}$  range.<sup>12,13</sup> Figures 1(a) and 1(b) show 300 K spectra acquired at different excitation power levels. In  $\text{Bi}_2\text{Se}_3$ , high frequency  $E_g^2$  and  $A_{1g}^2$  modes are detected at  $131.5\text{cm}^{-1}$  and  $175.5\text{cm}^{-1}$ , respectively. In  $\text{Sb}_2\text{Te}_3$ , the  $E_g^2$  phonon frequency lies at the low-frequency onset of our apparatus, thus only the  $A_{1g}^2$  mode at  $168.8\text{cm}^{-1}$  is detected. Up to  $\sim 10^3\text{W/cm}^2$ , Raman peaks are insensitive to the power level. All the temperature dependent spectra presented below were obtained at power densities of  $670\text{W/cm}^2$  or less.

Typical Raman spectra measured at fixed temperatures between 300 K and 5 K are shown in Figs. 1(c) and 1(d). As the temperature decreases, the phonon peak exhibits blue

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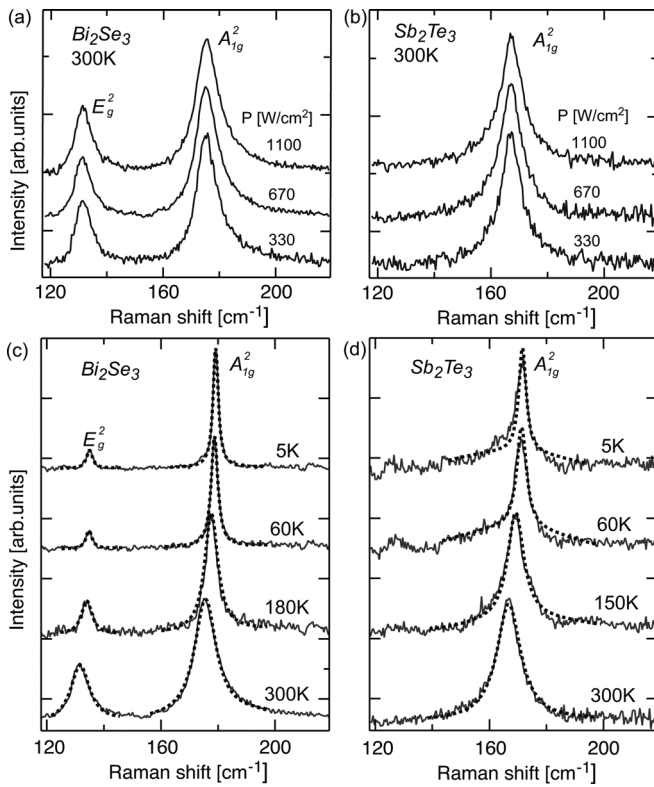


FIG. 1. Background corrected Raman spectra of  $\text{Bi}_2\text{Se}_3$  and  $\text{Sb}_2\text{Te}_3$ . (a) and (b) Spectra taken at 300 K at different excitation power levels. (c) and (d) Spectra measured at several temperatures between 5 K and 300 K. The spectra are shifted vertically for clarity.

shift and line narrowing. In the following, we focus on the temperature dependence of the dominant  $A_{1g}^2$  phonons. The extracted Lorentzian peak position and FWHM of the  $A_{1g}^2$  phonon peak are displayed as a function of temperature in Fig. 2.

In the harmonic approximation, the bare phonon frequency is obtained from the 2nd order expansion of the lattice potential in normal coordinates. The phonon-phonon

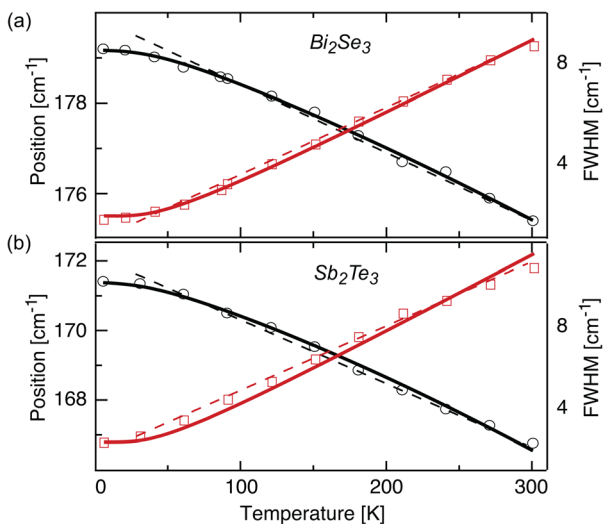


FIG. 2. (Color online) Temperature dependence of the  $A_{1g}^2$  phonon in  $\text{Bi}_2\text{Se}_3$ . Symbols are peak position (circles) and linewidth (squares) extracted from the experimental data. The solid lines are fits to the symmetrical three-phonon coupling model including thermal expansion contribution. Dashed lines are linear fits to the data in the 90-300 K range.

coupling leads to the renormalization of the phonon energy and lifetime, which can be described by higher order anharmonic terms assuming the decay of zone-center optical phonon into two or more acoustic phonons. The simplest anharmonic approximation, known as the symmetrical three-phonon coupling model,<sup>15</sup> takes into account the optical phonon decay into two phonons with equal energies and opposite momenta. While it provides a fairly accurate description of the phonon temperature dependence in diamond,<sup>16</sup> more general models have been suggested for other materials accounting for anharmonic contributions due to the thermal expansion and/or asymmetric decay into two or more different phonons.<sup>17-19</sup> The temperature dependence of the phonon frequency  $\omega(T)$  is commonly expressed as

$$\omega(T) = \omega_0 + \Delta\omega^{(1)}(T) + \Delta\omega^{(2)}(T), \quad (1)$$

where  $\omega_0$  is the bare harmonic frequency,  $\Delta\omega^{(1)}$  is the anharmonic, sometimes called quasi-harmonic, correction solely due to the lattice thermal expansion, and  $\Delta\omega^{(2)}$  is the anharmonic phonon-phonon coupling term. The thermal expansion contribution  $\Delta\omega^{(1)}(T)$  is given by

$$\Delta\omega^{(1)}(T) = \omega_0 \left[ \exp\left(-\gamma \int_0^T [\alpha_c(T') + 2\alpha_a(T')] dT'\right) - 1 \right], \quad (2)$$

where  $\gamma$  is the mode Grüneisen parameter, and  $\alpha_a(T)$  and  $\alpha_c(T)$  are the coefficients of linear thermal expansion along the  $a$  and  $c$  axes:  $\alpha_L = \frac{1}{L} \frac{dL}{dT}$ .

We are not aware of temperature-dependent data on the thermal expansion coefficients in  $\text{Bi}_2\text{Se}_3$  and  $\text{Sb}_2\text{Te}_3$ . We employed x-ray powder diffraction (XRD) to measure lattice constants of  $\text{Bi}_2\text{Se}_3$  and  $\text{Sb}_2\text{Te}_3$  at temperatures between 10 K and 270 K. Details about the XRD results are described elsewhere.<sup>20</sup> Using the XRD data, we find that the temperature dependence of lattice parameters in  $\text{Bi}_2\text{Se}_3$  can be approximated between 10 K and 270 K with better than 0.8% accuracy by the following polynomials:  $a(T) = 4.13 + 1.59 \times 10^{-5}T + 8.87 \times 10^{-8}T^2$  and  $c(T) = 28.48 + 2.26 \times 10^{-4}T + 6.86 \times 10^{-7}T^2$ . For  $\text{Sb}_2\text{Te}_3$ , the polynomial approximation with better than 1.5% accuracy in the same temperature range is given by  $a(T) = 4.24 + 9.3 \times 10^{-6}T + 1.25 \times 10^{-7}T^2$  and  $c(T) = 30.18 + 3.5 \times 10^{-4}T + 7.4 \times 10^{-7}T^2$ . Estimated Grüneisen parameters at 270 K are 1.4 for  $\text{Bi}_2\text{Se}_3$ , and 2.3 for  $\text{Sb}_2\text{Te}_3$ .<sup>20</sup>

We find that the thermal expansion contribution term  $\Delta\omega^{(1)}(T)$  accounts for  $\sim 40\%$  of the total phonon frequency change with temperature. Detailed analysis further reveals that the observed temperature dependence can be well described within a symmetrical three-phonon coupling approximation, where the optical phonon frequency  $\omega(T)$  and linewidth  $\Gamma(T)$  are modeled as

$$\omega(T) = \omega_0 + \Delta\omega^{(1)}(T) + A[1 + n(\omega_1) + n(\omega_2)], \quad (3)$$

$$\Gamma(T) = B[1 + n(\omega_1) + n(\omega_2)], \quad (4)$$

$\omega_1 = \omega_2 = \omega_0/2$ ,  $n(\omega) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ ,  $A$  and  $B$  are fitting parameters. Note that the linewidth is expressed in terms of anharmonic coupling only and does not depend on

TABLE I. Temperature dependence of the  $A_{1g}^2$  phonon: fitting parameters using the linear model (left) and the symmetrical three-phonon coupling model (right, Eqs. (3) and (4)).

	Linear fit (90-300 K)				3-phonon decay model		
	$\omega_0^*$ ( $\text{cm}^{-1}$ )	$d\omega/dT$ ( $\text{cm}^{-1}/\text{K}$ )	$\gamma_0^*$ ( $\text{cm}^{-1}$ )	$d\gamma/dT$ ( $\text{cm}^{-1}/\text{K}$ )	$\omega_0$ ( $\text{cm}^{-1}$ )	A ( $\text{cm}^{-1}$ )	B ( $\text{cm}^{-1}$ )
$\text{Bi}_2\text{Se}_3$	179.9(6)	-0.015	0.8	0.026	179.8(8)	-0.7	1.89
$\text{Sb}_2\text{Te}_3$	172.2(1)	-0.018	1.62	0.031	172.1	-0.7	2.33

the thermal expansion contribution. The comparison between the calculated and the experimental position and linewidth is shown in Fig. 2.

Finally, we observe that at temperatures above 90 K, the frequency and linewidth of the  $A_{1g}^2$  phonon change linearly with temperature,  $\omega(T) = \omega_0^* + \frac{d\omega}{dT}T$ ,  $\gamma(T) = \gamma_0^* + \frac{d\gamma}{dT}T$ . The overall peak frequency change is about  $4 \text{ cm}^{-1}$  in the temperature range between 90 K and 300 K and thus offers an effective way to measure the local temperature. The metrology based on the linewidth measurements could be more accurate because of the larger relative variation, though it would require the use of a high-resolution spectrometer. The extracted values of the linear fit and the symmetrical three-phonon coupling model are summarized in Table I.

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