Supplementary materials for:
Nesting-like band gap in bismuth sulfide Bi_2S_3

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Photoacoustic spectroscopy on Bi_2S_3

Photoacoustic (PA) spectroscopy is known to be sensitive to both indirect and direct transitions and in addition it is insensitive to scattered light, with the generated signal being (up to the saturation regime) proportional to the optical absorption coefficient of the studied material[1–3]. The Bi_2S_3 crystal was mounted inside a cylindrical cell equipped with a quartz window for optical access. It was then excited by amplitude modulated (20 Hz) monochromatic light beam (Horiba iHR 320 grating monochromator), with the wavelength scanned to obtain a broadband photoacoustic spectrum (light spot size 1 mm×2 mm). Nonradiative recombination processes cause periodic sample surface temperature changes, further detected as pressure oscillations with an electret condenser microphone sealing the measurement cell. Photoacoustic signal amplitude was obtained by means of phase-sensitive lock-in system (Stanford Research Systems SR830), further corrected using a reference signal response of carbon powder. The measurement was performed at room temperature. The PA spectrum is presented in Fig. S1 and compared with a standard absorption spectrum.
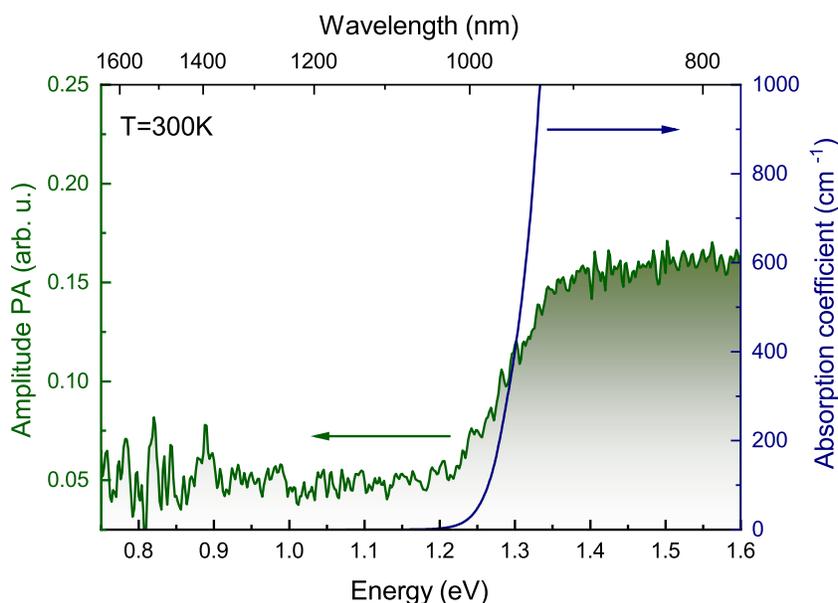

Fig. S1 (Color online) Photoacoustic (green line) and absorption (blue line) spectra of Bi_2S_3 measured at room temperature. No evidence of indirect transition is seen.

Raman spectroscopy on Bi_2S_3

Raman measurements were performed using a 532-nm line of a diode-pumped solid state laser (DPSS) laser which was focused on the sample by a long working distance objective (50× magnification, NA = 0.55); the diameter of the laser spot was estimated to be

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below 2 μm. Raman spectra were measured using a single-grating 0.55-m focal length monochromator with a multichannel liquid nitrogen cooled Si CCD array detector. Figure S2 displays the Raman spectrum of bulk Bi_2S_3, excited at 532 nm. This spectrum shows well-defined peaks at 168.37, 190.18, 239.86, and 266.89 cm^{-1}. These signals match well with the values reported by Zumeta-Dubé *et al.*[4]. The Raman spectrum of Bi_2S_3 was fitted by Lorentzian curves.
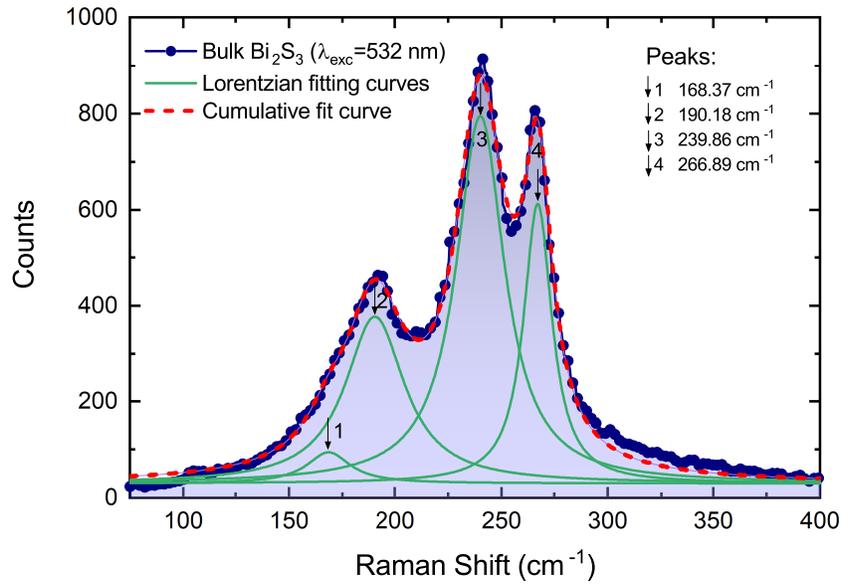

Fig. S2 (Color online) Raman spectrum for bulk Bi_2S_3, excited at 532 nm. The arrows indicate maxima of components, obtained from Lorentzian fitting.

Theoretical calculation DFT of the Bi_2S_3 band structure

The band nesting

Here we show the energy difference dispersion of the bands between the optical transition occurs (Fig. S3). The nesting region is flat.
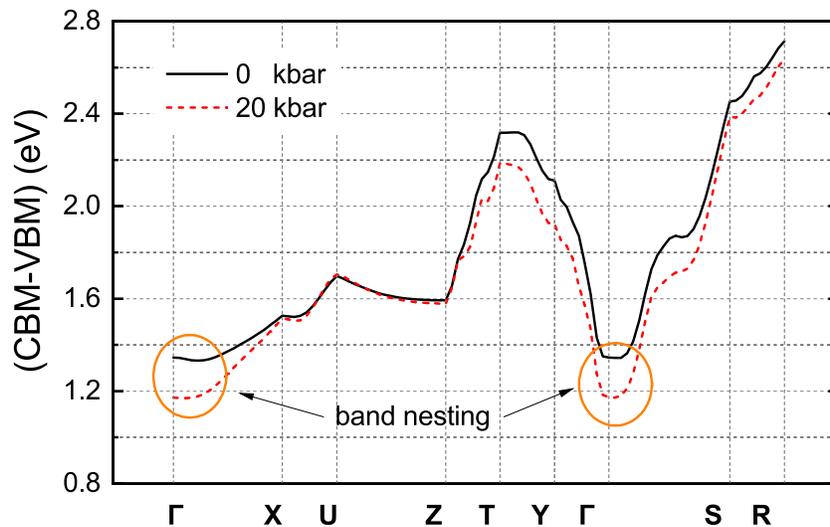

Fig. S3 (Color online) The energy difference dispersion of the conduction band minimum and valence band maximum for 0 kbar and 20 kbar of hydrostatic pressure.

Matrix elements

Band structure of Bi_2S_3 near the Γ-point in the direction of X-point of the Brillouin zone with calculated matrix elements is shown in Fig. S4. "Zeros" in the band transitions indicate forbidden transitions. The strongest matrix element occurs between the third valence band below 0 eV and the first conduction band (v3->c1), which energetically corresponds to transition E_2 in PR spectra.
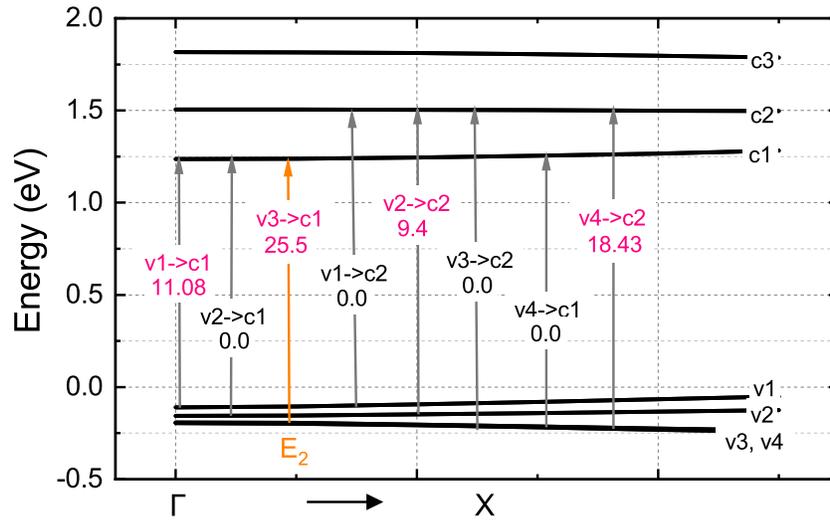

Fig. S4 (Color online) Band structure of Bi_2S_3 near the Γ-point in the direction of X-point of the Brillouin zone with calculated matrix elements. "Zeros" in the band transitions indicate forbidden transitions. The strongest matrix element is between the third valence band and the first conduction band (v3->c1), which energetically correspond to transition E_2 in PR spectra.

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