

Anharmonic line shift and linewidth of the Raman modes in TlInS₂ layered crystals

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Received 7 April 2003; Accepted 10 August 2003

The temperature dependence of the unpolarized Raman spectra from TlInS₂ layered crystal was measured between 10 and 300 K. The analysis of the experimental data showed that the temperature dependences of wavenumbers and linewidths are well described by considering the contributions from thermal expansion and lattice anharmonicity. The purely anharmonic contribution (phonon–phonon coupling) was found to be due to three-phonon processes. This work demonstrates that the two Raman modes at 280.9 and 292.3 cm⁻¹ exhibit changes toward high wavenumbers as the temperature is raised from 10 to 300 K. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: anharmonicity; layered crystals; TlInS₂; phonon–phonon coupling; phonon temperature dependence

INTRODUCTION

TlInS₂ is one of the highly anisotropic crystals whose properties have recently become the subject of extensive research.^{1–6} The high anisotropy arises from the fact that the bonding within the layers is considerably stronger than that perpendicular to them. In these compounds, van der Waals forces contribute predominantly to the interlayer interaction, while the bonding forces within the layers are ionic–covalent. High photosensitivity in the visible range of spectra, high birefringence in conjunction with a wide transparency range of 0.5–14 μm make this crystal useful for optoelectronic applications.⁷

Raman spectroscopy is a powerful technique for obtaining information on various vibrational modes in crystals. The wavenumber and linewidth of the phonon lines in the light scattering spectra depend on the crystal temperature. The shift and broadening of the phonon lines during heating are a manifestation of phonon–phonon interaction, and measurements of phonon wavenumber and linewidth as a function of temperature allow one to study the anharmonicity of the lattice vibrations. A large number of papers devoted to the study of the temperature dependence of the wavenumber and the

linewidth of the first-order Raman scattering in semiconductors may be found in the literature.^{8–18} They show that the Raman shift could be successfully modeled by including the effect of thermal expansion and phonon–phonon coupling.

The ternary layered crystal TlInS₂ is a chemical analog of TlSe (the thallium atom is univalent, whereas the indium atom is trivalent). The lattice consists of strictly periodic two-dimensional layers, each successive layer being turned by a 90° angle about the normal of the previous one. Interlayer bonding occurs between Tl and S atoms whereas the one intralayer bonding occurs between In and S atoms. A view of the crystal structure in the *ac* plane (*a* is the axis in the [110] direction) is given in Fig. 1, where the layers also shown. The fundamental structural unit of a layer is In₄S₆ adamantane-like units linked together by bridging S atoms. The combination of the In₄S₆ units into a layer results in trigonal prismatic voids where Tl atoms are located. Tl atoms form nearly planar chains along the [110] and [1 $\bar{1}$ 0] directions.

The unit cell of TlInS₂ contains four layers having the same space group as TlSe (*D*_{4h}¹⁸), the space group of the crystal being *C*_{2h}⁶. Group-theoretical analysis gives the following set of vibrations at the center of Brillouin zone:

$$\Gamma \equiv 10A_g + 14B_g + 10A_u + 14B_u$$

where *A*_u + 2*B*_u are acoustic modes. There should be 10 *A*_g + 14 *B*_g Raman-active modes.

The phonon spectra of TlInS₂ layered crystals have been reported previously from Raman measurements at different temperatures: 300 K,¹⁹ 22–205 K²⁰ and 6–300 K.²¹

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Contract/grant sponsor: Bilkent University Research Fund;

Contract/grant number: Phys-03-02.

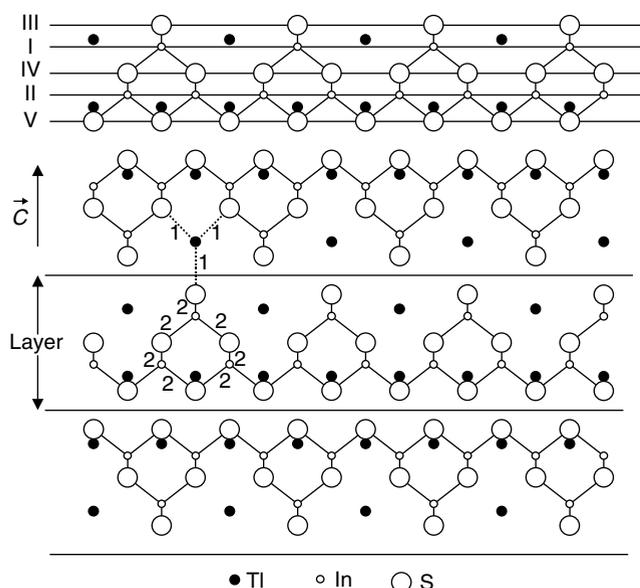


Figure 1. Projection of the structure in TlInS_2 crystal as seen from the ac plane: 1 shows the interlayer bonding between Tl and S atoms; 2 shows the intralayer bonding between In and S atoms.

Although much is known about the phonon spectra of TlInS_2 , the temperature dependences of the phonon wavenumber and linewidth have not yet been analyzed. The aim of the present study was to measure the wavenumber and linewidth [full width at half-maximum (FWHM)] of zone-center optical phonons in TlInS_2 layered crystals using Raman spectroscopy in the temperature range 10–300 K and to compare the experimental results with the existing theories of anharmonicity of lattice vibrations in crystals. We report softening and broadening of the optical phonon lines at the Brillouin zone center with increasing temperature, as observed in most other semiconductors. Our analysis and results indicate that the purely anharmonic contributions to the phonon wavenumber shift and line broadening are due to interaction with phonons of other branches.

EXPERIMENTAL

TlInS_2 single crystals were grown by the Bridgman method. The analysis of x-ray diffraction data shows that they crystallize in a monoclinic unit cell with parameters $a = 1.0942$, $b = 1.0484$, $c = 1.5606$ nm and $\beta = 100.70^\circ$. Crystals suitable for measurements were obtained by easy cleavage perpendicular to the optical c -axis. As-grown TlInS_2 is a p-type semiconductor having room temperature indirect and direct bandgaps with energies of 2.28 and 2.33 eV, respectively.^{1,2}

Raman scattering experiments in the TlInS_2 layered crystal were performed in back-scattering geometry in the wavenumber range 10–360 cm^{-1} . A 30 mW He–Ne laser (632.8 nm) was used as the light source for excitation.

The scattered light was analyzed using a double-grating spectrometer with a focal length of 1 m and a cooled GaAs photomultiplier supplied with the usual photon counting electronics. The Raman line positions were determined within an accuracy of $\pm 0.1 \text{ cm}^{-1}$. A closed-cycle helium cryostat was used to cool the crystals from room temperature to 10 K. The temperature was controlled within an accuracy of ± 0.5 K. In order to avoid sample-heating effects, we chose a cylindrical lens to focus the incident beam on the sample.

To achieve a signal-to-noise ratio of >100 , the slit width of the spectrometer was set to 150 μm . For slit widths $<150 \mu\text{m}$, the signal-to-noise ratio is small so that we could not measure the linewidth of some phonon modes with high enough accuracy. The measured low-wavenumber phonon lines of TlInS_2 crystal are so narrow that even with the indicated slit widths, one has to correct for the finite instrument resolution. The width of the response function of the spectrometer was determined by measuring the linewidth of the laser with the same slit openings as in the Raman experiment. An instrumental linewidth of 0.7 cm^{-1} was used in the analysis that follows. The observed peak is the convolution of the Lorentzian shape of the actual phonons with the response function of the spectrometer considered to be Gaussian. To make the deconvolution, we first fitted a Voigt profile to our experimental peaks, then we calculated the Lorentzian linewidth using the fitted width of the Voigt profile and the experimentally determined width of the spectrometer response function.

RESULTS AND DISCUSSION

Temperature dependence of mode wavenumbers

Figure 2 depicts the Raman scattering spectra of TlInS_2 at 10 and 300 K. Lowering of the temperature to 10 K brings about a variation in the spectra. A more distinct separation of bands closely spaced in wavenumber is observed for this temperature. Moreover, the shift and broadening of Raman-active modes with increasing temperature are seen.

The phonon spectra of the TlInS_2 layered crystal exhibit the typical features of vibrational spectra of molecular crystals, namely the presence of low-wavenumber translational modes of the system consisting of In_4S_6 units and Tl atoms (rigid-layer vibrations, vibrations of Tl atoms and vibrations of Tl atoms and In_4S_6 units) and high-wavenumber 'intramolecular' modes of the In_4S_6 units.

The 'intramolecular' (internal) modes in the wavenumber range 260–360 cm^{-1} correspond to the vibrations of In and S atoms forming the In_4S_6 units. The modes in the range 260–310 cm^{-1} are associated with the mutual displacements of In and S atoms, whereas the modes in the range 310–360 cm^{-1} are due only to the vibrations of S atoms.¹⁹

The majority of modes of the TlInS_2 crystal show, as expected, a wavenumber decrease with increasing temperature. However, the modes at wavenumbers 280.9 and 292.3 cm^{-1} , in which the indium and sulfur atoms are

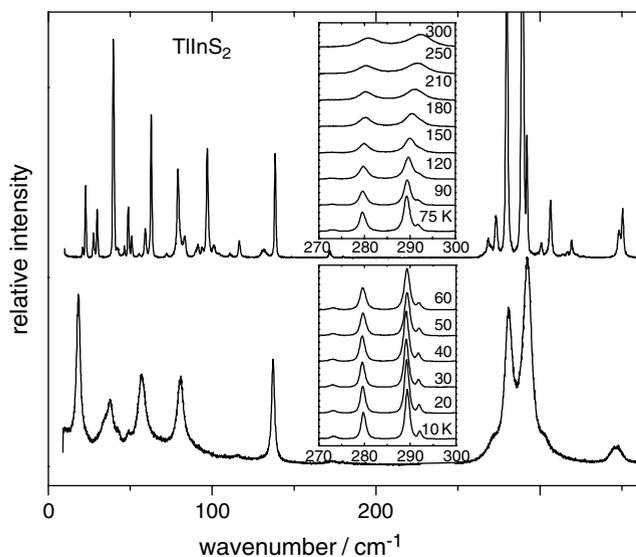


Figure 2. Raman spectra of TlInS₂ crystal at $T = 10$ K (top) and 300 K (bottom). The insets show the extended parts of Raman spectra in the range 270–300 cm⁻¹ at different temperatures.

involved in the atomic vibrations, show hardening with increasing temperature (see Fig. 2, insets). These wavenumber shifts in the temperature range 10–300 K are equal to 1 and 3 cm⁻¹ for the 280.9 and 292.3 cm⁻¹ modes, respectively, and may be attributed to the anomalous character of the vibrational properties of these layered crystals.

Similar anomalous behavior with a slight increase in wavenumbers has been observed for the Raman-active modes at 146.3 and 1060 cm⁻¹ in GaPO₄ and 1112 cm⁻¹ in AlPO₄ chain crystals.²² Such dependences have been reported also for two infrared-active TO lines (364 and 495 cm⁻¹) in α -quartz and connected with a weak hardening of these phonons with volume expansion.²³ The anisotropic elastic properties of the solids may be the cause of such effects, as suggested by Sherman considering the case of anisotropic Se and Te crystals.²⁴ According to Sherman, the increasing temperature forces the layers further from each other. This process weakens and lengthens the interlayer bonds, whilst strengthening and shortening the intralayer bonds.

Elastic constants C_{33} and C_{11} , which characterize the interlayer and intralayer interactions in TlInS₂ crystals, were found to be 51.9 and 73.3 GPa, respectively.²⁵ Owing to the anisotropic elastic constants C_{33} and C_{11} of the TlInS₂ crystal, increasing temperature leads to shortening of the intralayer bonds, resulting in the observed wavenumber increase with increasing temperature for intralayer modes in which the indium and sulfur atoms take part in the vibrations (see Fig. 2, insets). No unusual behavior was observed for the changes in the linewidth of the Raman peaks observed in the high-wavenumber region.

We will analyze in detail the temperature dependences of 10 Raman-active modes observed at room temperature with wavenumbers 18.4, 37.9, 57.1, 80.7, 137.5, 280.9, 292.3, 302.0, 344.5, 348.0 cm⁻¹. These wavenumbers are in agreement with those reported by different workers.^{5,19,21} There is large difference between the mode Grüneisen parameters (γ) of low-wavenumber translational (16.2–21.9) and high-wavenumber ‘intramolecular’ (0.4–3.1) modes of TlInS₂ layered crystals.⁵ The difference in the mode Grüneisen parameters represents the difference in the translational and ‘intramolecular’ restoring forces. The wavenumber shifts of TlInS₂ Raman modes in the temperature range 10–300 K were found to be from 1.0 to 5.7 cm⁻¹ for different modes.

Analysis of the temperature dependence of the wavenumber shift for the low-wavenumber mode (18.4 cm⁻¹) does not yield a physically meaningful decay channel. This is consistent with the narrow linewidth of this mode, which indicates a long lifetime. Figures 3 and 4 show the experimental results (open circles) for the line positions $\nu(T)$ of one of the translational modes and one of the ‘intramolecular’ modes, respectively. The phonon wavenumber shift with temperature can be described by the expression^{8–12}

$$\nu(T) = \nu_0 + \Delta_1(T) + \Delta_2(T) \quad (1)$$

where $\nu_0 + \Delta_2(0)$ is the Raman wavenumber as T approaches 0 K, $\Delta_1(T)$ represents the volume dependence of the phonon wavenumber due to the thermal expansion of the crystals and $\Delta_2(T)$ specifies the contribution of anharmonic coupling to phonons of other branches.

$\Delta_1(T)$ can be written as

$$\Delta_1(T) = \nu_0 \left[\exp\left(-3\gamma \int_0^T \alpha(T')dT'\right) - 1 \right] \quad (2)$$

where $\alpha(T)$ is the coefficient of linear thermal expansion.

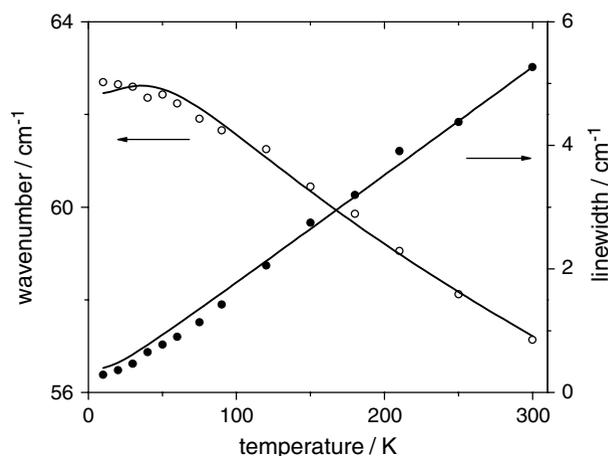


Figure 3. Temperature dependences of the translational mode wavenumber 57.1 cm⁻¹ (open circles) and linewidth (solid circles) in TlInS₂ crystal. The solid curves, wavenumber and linewidth, give the theoretical fits using Eqns (1)–(3) for wavenumber and Eqn (4) for linewidth.

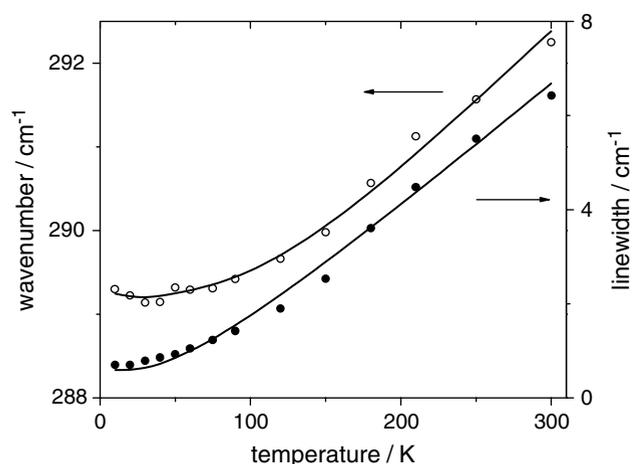


Figure 4. Temperature dependences of the ‘intramolecular’ mode wavenumber 292.3 cm^{-1} (open circles) and linewidth (solid circles) in TlInS_2 crystal. The solid curves, wavenumber and linewidth, give the theoretical fits using Eqns (1)–(3) for wavenumber and Eqn (4) for linewidth.

In general, the purely anharmonic contribution to the wavenumber shift can be modeled as

$$\Delta_2(T) = A \left(1 + \frac{1}{e^{x_1} - 1} + \frac{1}{e^{x_2} - 1} \right) \quad (3)$$

which represents the optical phonon coupling to two different phonons (three-phonon processes). Here, $x_1 = hc\nu_1/k_B T$ and $x_2 = hc\nu_2/k_B T$. In the present study, the experiments were carried out at temperatures below the Debye temperature of TlInS_2 crystals ($\theta_D = 557\text{ K}$).³ Hence the three-phonon process is dominant and the higher order processes can be neglected.

The wavenumber shifts for Raman modes of TlInS_2 crystal were fitted by means of Eqns (1)–(3) using the experimental values of γ and $\alpha(T)$ ^{5,26} for TlInS_2 with A , ν_0 , ν_1 and ν_2 as adjustable parameters, keeping the sum $\nu_1 + \nu_2 = \nu_0$ constant (energy conservation). For all modes, the agreement between the theoretical and experimental dependences was found to be good. Figures 3 and 4 show this agreement for two representatives of translational and ‘intramolecular’ modes with wavenumbers 57.1 and 292.3 cm^{-1} , respectively. The resulting parameters for all modes are given in Table 1. Generally, to identify the decay channels of phonon modes, all possible interactions should be considered for the decay processes taking into account the phonon dispersion curves. Unfortunately, the lack of phonon dispersion curves for TlInS_2 does not allow confirmation of decay channels determined by fitting Eqns (1)–(3) to the experimental data.

We also calculated separately the thermal-expansion contribution [$\Delta_1(T)$] from Eqn (2) and the purely anharmonic contribution [$\Delta_2(T)$] from Eqn (3) to the line shift for Raman modes of the TlInS_2 crystal by using the values of adjusted parameters A , ν_0 , ν_1 and ν_2 obtained above. For all modes,

Table 1. Parameters for fitting the temperature dependences of Raman wavenumber and linewidth of the TlInS_2 crystal

ν_0/cm^{-1}	ν_1/cm^{-1}	ν_2/cm^{-1}	A/cm^{-1}	C/cm^{-1}
37.6	18.8	18.8	0.40	0.32
61.8	30.9	30.9	0.67	0.29
83.8	41.9	41.9	−0.57	1.06
139.1	69.5	69.6	−0.79	0.44
278.3	104.6	173.7	1.34	0.79
284.4	78.9	205.5	4.86	0.70
303.8	48.2	255.6	2.46	0.98
347.5	48.9	298.6	0.59	1.54
348.3	139.3	209.0	2.11	0.93

the $\Delta_1(T)$ and $\Delta_2(T)$ contributions have opposite signs. For the modes with wavenumbers 80.7 and 137.5 cm^{-1} , having negative Grüneisen parameters, $\Delta_1(T)$ positive. However, for the modes with positive Grüneisen parameters, $\Delta_1(T)$ is negative. The variations of $\Delta_1(T)$ and $\Delta_2(T)$ are shown in Fig. 5 for two representatives of translational and ‘intramolecular’ modes with wavenumbers 57.1 and 292.3 cm^{-1} , respectively, together with the experimental wavenumber shifts. An interesting feature of these plots is that for the translational mode with a high value of the Grüneisen parameter ($\gamma = 16.2$), the $\Delta_1(T)$ contribution prevails over $\Delta_2(T)$, having opposite signs. However, for the ‘intramolecular’ mode with a low value of the Grüneisen parameter ($\gamma = 2.4$), $\Delta_2(T)$ prevails over $\Delta_1(T)$, also having opposite signs. This may be associated with the difference in sets of atomic displacements for these modes. In the ‘intramolecular’ mode the restoring forces are due to the strong intralayer indium–sulfur bonds (see Fig. 1). On the other hand, in the translational mode weak bonds are involved in the restoring forces.

Temperature dependence of mode linewidths

The linewidth of the TlInS_2 phonons was studied systematically as a function of temperature in the range 10 – 300 K . At low temperatures, the measured linewidth (0.8 cm^{-1}) of the low-wavenumber mode (18.4 cm^{-1}) became comparable to the instrumental linewidth (0.7 cm^{-1}). Therefore, we did not analyze the temperature dependence of the linewidth of this mode. The corrected linewidths of nine Raman modes observed at room temperature were found to be 3.8 , 5.3 , 3.8 , 1.9 , 5.7 , 6.1 , 7.2 , 5.1 and 5.3 cm^{-1} . The linewidth of all optical modes are found to increase with temperature. The broadening of the phonon lines is due to anharmonicity of the lattice vibrations. The presence of anharmonic forces in a crystal leads to interactions between the harmonic normal modes. These interactions produce a temperature-dependent lifetime of the normal modes.

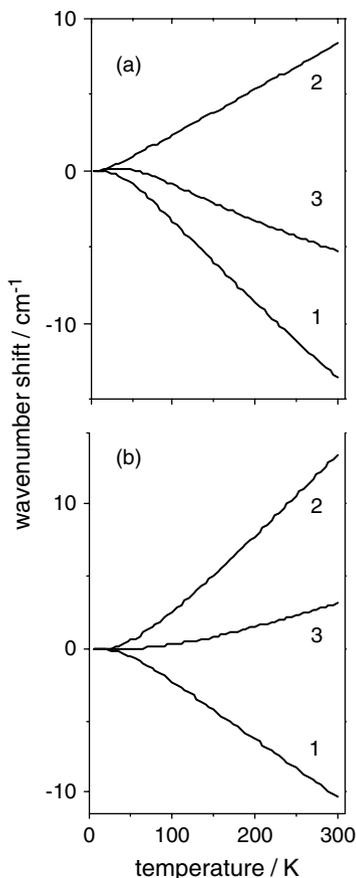


Figure 5. Experimental Raman wavenumber shifts of translational 57.1 cm⁻¹ (a) and 'intramolecular' 292.3 cm⁻¹ (b) modes as a function of temperature (curves 1). Curves 2 and 3 are the thermal-expansion [$\Delta_1(T)$] and the purely anharmonic [$\Delta_2(T)$] contributions to the wavenumber shifts, respectively.

The temperature dependence of the phonon linewidth can be described as follows:^{9,10,12,13}

$$\Gamma = C \left(1 + \frac{1}{e^{\nu_1} - 1} + \frac{1}{e^{\nu_2} - 1} \right) \quad (4)$$

where C is the broadening of the phonon line due to the cubic anharmonicity at absolute zero (the decrease in phonon lifetime, τ , due to the decay of the optical phonon into two different phonons).

Figures 3 and 4 represent the linewidth broadening with increasing temperature for two representatives of translational and 'intramolecular' modes with wavenumbers 57.1 and 292.3 cm⁻¹, respectively. The experimental data of the phonon linewidth for Raman modes of TlInS₂ crystal were fitted by means of Eqn (4) with C, ν_1 and ν_2 as fitting parameters, keeping the sum $\nu_1 + \nu_2 = \nu_0$ constant. We obtained quantitative agreement between calculated curve and experimental points (Figs 3 and 4). The fitting parameters for all Raman modes are listed in Table 1.

We obtained a good fit to the experimental data for low-wavenumber modes with $\nu_1 = \nu_2$ (see Table 1). For

many semiconductors a reasonable fit to the temperature dependence of linewidth broadening is obtained using $\nu_1 = \nu_2$.^{10,12,14,15,27} The existence of a dominant contribution to the linewidth broadening for $\nu_1 = \nu_2$ has been confirmed by *ab initio* calculations for diamond,²⁸ InP and AlAs,¹⁶ although for Ge and Si,²⁸ GaAs and GaP¹⁶ $\nu_1 = 2\nu_2$ seems to give a better approximation to the linewidth versus temperature data.

CONCLUSIONS

The temperature evolution of Raman wavenumbers and linewidths in the TlInS₂ crystal is well described by purely anharmonic (phonon-phonon coupling) and purely volume (thermal expansion) contributions. The cubic (three-phonon) process with energy conservation is responsible for the purely anharmonic contributions to the wavenumber shift and broadening of phonon lines. It was found that the two Raman modes at 280.9 and 292.3 cm⁻¹ exhibit changes toward high wavenumbers as the temperature is raised from 10 to 300 K.

Acknowledgement

This work was supported by Bilkent University Research Fund (Project Code: Phys-03-02).

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