

O.O. GOMONNAI,^{1,2} M. LUDEMANN,³ A.V. GOMONNAI,^{4,1} I.YU. ROMAN,⁴
A.G. SLIVKA,¹ D.R.T. ZAHN³

¹Uzhhorod National University

(46, Pidhirna Str., Uzhhorod 88000, Ukraine; e-mail: gomonnai.o@gmail.com)

²Vlokh Institute of Physical Optics

(23, Drahomanov Str., Lviv 79005, Ukraine)

³Semiconductor Physics, Chemnitz University of Technology

(D-09107 Chemnitz, Germany)

⁴Institute of Electron Physics, Ukr. Nat. Acad. Sci.

(21, Universytets'ka Str., Uzhhorod 88017, Ukraine)

TEMPERATURE DEPENDENCE OF RAMAN-ACTIVE MODES OF $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ SINGLE CRYSTALS

UDC 535

The unpolarized Raman spectra of $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystals in the frequency interval 16–340 cm^{-1} are studied in the temperature interval $30 \leq T \leq 293$ K. The Raman spectra are analyzed by a multipeak simulation using Lorentzian contours. The temperature behavior of the vibrational band parameters (half-width, intensity, and frequency) is studied with the emphasis on the temperature range, where changes related to phase transformations are revealed.

Keywords: Raman scattering, layered crystal, phase transition.

1. Introduction

The physical properties of layered ferroelectrics are determined by their quasi-two-dimensionality and a strong structural anisotropy, which make them interesting objects for investigation [1–4]. One of the materials of this class is TlInS_2 , which is characterized by a complex sequence of phase transitions (PTs) in the temperature interval 190–216 K [1, 2] and poly-critical phenomena in the (p, T) -phase diagram in the pressure interval $580 \leq p \leq 660$ MPa [5–8]. In the row of $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ crystalline solid solutions, the crystal structure changes from C_{2h}^6 to D_{4h}^{18} symmetry at a Se content x near 0.7–0.75 [9–12]. It was shown [12–14] that the isovalent S \rightarrow Se anionic substitution results in a downward shift of the structural phase transition temperatures with a simultaneous shrinking of the temperature interval of the incommensurate phase existence. It was concluded that, in the (x, T) phase diagram of $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ crystals, a Lifshitz type point can exist at $x = 0.05$ [12, 13]. Several works were devoted to Raman spectroscopic studies of $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ solid solutions ($0 < x < 1$), where the compositional transformation

of Raman spectra was investigated mostly at room temperature [15–19], as well as at lower temperatures [19]. With regard to the studies of vibrational spectra in a broad temperature range, including the phase transition range, such data were obtained for TlInS_2 crystals by several research teams [20–29]. A detailed analysis of the polarized Raman spectra of TlInS_2 was performed in a broad temperature range, including the temperature dependences of spectral positions and half-widths of low-frequency modes, and a conclusion was made on the existence of soft modes [24, 25]. Recently, several studies were published including the temperature-dependent analysis of the spectral positions and half-widths of other Raman modes in the TlInS_2 crystal spectra [26–29]. A detailed analysis of the spectral interval 120–400 cm^{-1} in the temperature interval 77–300 K is presented in Ref. [27], the spectral interval 35–150 cm^{-1} was analyzed in Ref. [28], polarized spectra in the 35–180 cm^{-1} interval at temperatures from 77 to 320 K are presented in Ref. [29]. With regard to infrared reflection spectroscopy of the $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ single crystal system, a detailed study of vibration band parameters (half-width, intensity, and frequency) down to the liquid nitrogen temperature was carried out only for crystals with $x = 0.2$ [30]. This motivates

the interest toward the investigation of sulfur-rich $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ mixed crystals by vibrational spectroscopy. Here, we present the results of Raman studies of $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystals in the temperature interval $30 \leq T \leq 293$ K.

2. Materials and Methods

$\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystals were grown by the Bridgman technique [16]. The crystal quality and chemical composition were checked by methods described in Ref. [16]. The results of X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy obtained for the samples under investigation agree well with the data for the C_{2h}^6 space group typical of TlInS_2 -type crystals at room temperature and atmospheric pressure [1, 2]. Raman measurements were performed using a Dilor XY 800 spectrometer equipped with a CCD camera. The instrumental resolution was in all cases better than 2 cm^{-1} . A Kr^+ laser operating at 647.1 nm was used for the excitation. Raman spectra were measured in the backscattering configuration from the (001) plane using the $Z(\text{XX}+\text{XY})\bar{Z}$ (unpolarized) geometry. The samples were placed in a cryostat coupled to a temperature control system that is capable of stabilizing the sample temperature with an accuracy of ± 0.01 K.

3. Results and Discussion

It is worth noting that the analysis of compositional dependences of frequencies, half-widths, and integrated intensities of Raman bands in $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ ($0 \leq x \leq 0.25$) single crystal spectra measured at 30 K in the $Z(\text{XX} + \text{XY})\bar{Z}$ configuration was performed in our earlier paper [19]. Below, we present the experimental data and analysis of the temperature behavior of frequencies, half-widths, and intensities of first-order Raman-active optical phonons of $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ crystals. This can be helpful for acquiring the additional information about the character of forces and bonds in the crystal lattice and their transformation under structural phase transitions in the $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ mixed crystal system.

The Raman spectra of $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystals were studied in the interval $16\text{--}350 \text{ cm}^{-1}$ at temperatures $30 \leq T \leq 293$ K (Figs. 1 and 2). The number of Raman bands and their spectral positions at $T = 30$ K and $T = 293$ K agree with the data available from the literature for TlInS_2 crystals [20–29] in

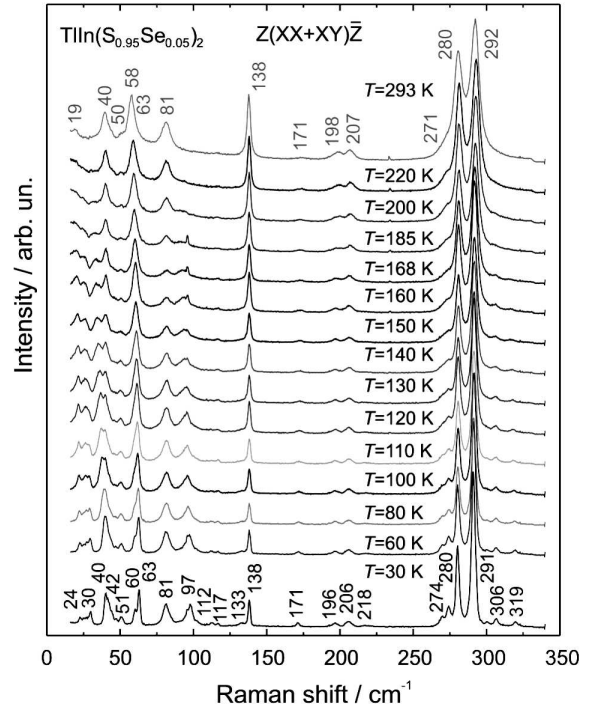


Fig. 1. Raman spectra of a $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystal in the $Z(\text{XX}+\text{XY})\bar{Z}$ configuration at different temperatures

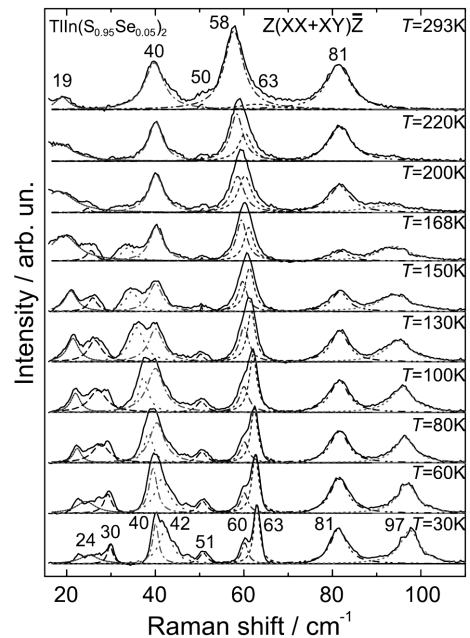


Fig. 2. Raman spectra of a $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystal in the $Z(\text{XX}+\text{XY})\bar{Z}$ configuration in the interval $16\text{--}110 \text{ cm}^{-1}$ at $30\text{--}293$ K and their multipeak Lorentzian simulation

view of the known features of a compositional transformation of the Raman spectra for $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ single crystals [19]. The experimental Raman spectra of $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystals were analyzed by multiplex simulation using Lorentzian contours, and the band parameters (frequencies, half-widths, and integrated intensities) were determined. An example of such simulation is shown in Fig. 2.

One should note that the temperature variation of the $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystal Raman spectra includes the typical temperature dependence of phonon band characteristics in crystals (a slight frequency decrease, increasing half-widths and integrated intensities with temperature), as well as a phase transition-related transformation of phonon spectra. The latter can be revealed in different frequency ranges as an essential frequency decrease, a considerable increase of half-widths, and a redistribution of intensities of several modes, as well as a possible drastic spectral transformation with temperature manifested as a change of the number of first-order Raman active optical phonon modes. As can be seen from Fig. 1, the transformation of the Raman spectra is observed in the low-frequency interval 16–100 cm^{-1} and in higher-frequency intervals 190–220 cm^{-1} and 270–320 cm^{-1} .

In the low-frequency interval 16–50 cm^{-1} , a complicated transformation of the spectra with temperature is observed (Figs. 1 and 2). The band centered at 24 cm^{-1} ($T = 30$ K) shifts down to 19 cm^{-1} ($T = 293$ K), while the band centered at 30 cm^{-1} ($T = 30$ K) vanishes with increasing temperature at 293 K. Note that a detailed analysis of the band half-widths and intensities in this lowest-frequency spectral range in the temperature interval 180–220 K is encumbered by the Rayleigh wing, the intensity of which increases, while approaching this temperature interval. The transformation of the 40 cm^{-1} and 42 cm^{-1} bands is of complicated character. As can be seen from Figs. 1 and 2, at $T = 30$ K, two bands at 40 cm^{-1} and 42 cm^{-1} are registered. Their intensities increase with the temperature and are nearly equal at $T = 100$ K.

One should note the importance of a comparison of spectra measured at $T = 60$ K and $T = 80$ K. The comparison of the intensities shows that, apparently, the spectral position of the band at 40 cm^{-1} ($T = 30$ K) remains practically unchanged, while the other band centered at 42 cm^{-1} at 30 K de-

creases. With a further increase in the temperature, the intensity of the latter band decreases, and its half-width increases (Fig. 3). At $T = 220$ K, this band is no longer observed in the spectrum. Considering the other band (40 cm^{-1} at $T = 30$ K), its spectral position remains stable up to room temperature. Such “crossing” of the temperature dependences of Raman modes near 40–42 cm^{-1} in the temperature interval 60–80 K is a clear evidence of their different symmetry, similarly to the case of a PbTiO_3 single crystal [31]. With regard to the temperature behavior of TlInS_2 single crystals, there are two points of view concerning the Raman bands in the 38–50 cm^{-1} interval [24, 25, 29]. According to Ref. [29], the higher-frequency band position (48.7 cm^{-1} at 77 K) does not vary with temperature and is no longer registered at 218 K, while the lower-frequency band position (38.8 cm^{-1} at 77 K) increases at a rate $\partial\nu/\partial T = 6.4 \times 10^{-3}$ cm^{-1}/K , and the intermediate band frequency (45.2 cm^{-1} at 77 K) decreases to 41.5 cm^{-1} . In earlier publications [24, 25], a somewhat different behavior of a transformation of the vibrational bands was reported. The authors of Ref. [25] claim that the behavior of the band at 42 cm^{-1} ($T = 12$ K) is characteristic of a soft mode. This conclusion was made from the temperature behavior of the band frequency and half-width. At least, its frequency is the most strongly temperature-dependent in comparison with other low-frequency modes. A detailed analysis of the temperature dependences of TlInS_2 crystal vibrational modes [24] revealed, in particular, two bands at 24 cm^{-1} and 42 cm^{-1} ($T = 22$ K) in the Z(YX)Y scattering configuration, which are claimed to possess a soft mode character, interacting with rigid modes [24]. One should note that, according to these authors, the modes at 39 cm^{-1} and 42 cm^{-1} ($T = 10$ K) interact at temperatures below $T = 100$ K [24]. Temperature changes can also be observed for other spectral intervals of the $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystal Raman spectra (Figs. 1 and 4). In particular, the band at 97 cm^{-1} vanishes at 200 K. The band at 218 cm^{-1} is no longer observed above 160 K, while the bands at 133 cm^{-1} , 306 cm^{-1} , and 319 cm^{-1} vanish above 168 K, which can be also related to their weak intensities. For other (not discussed above) translational and “intermolecular” modes of $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystals, the temperature-related broadening and integrated intensity increase (see, e.g., Fig. 3) and

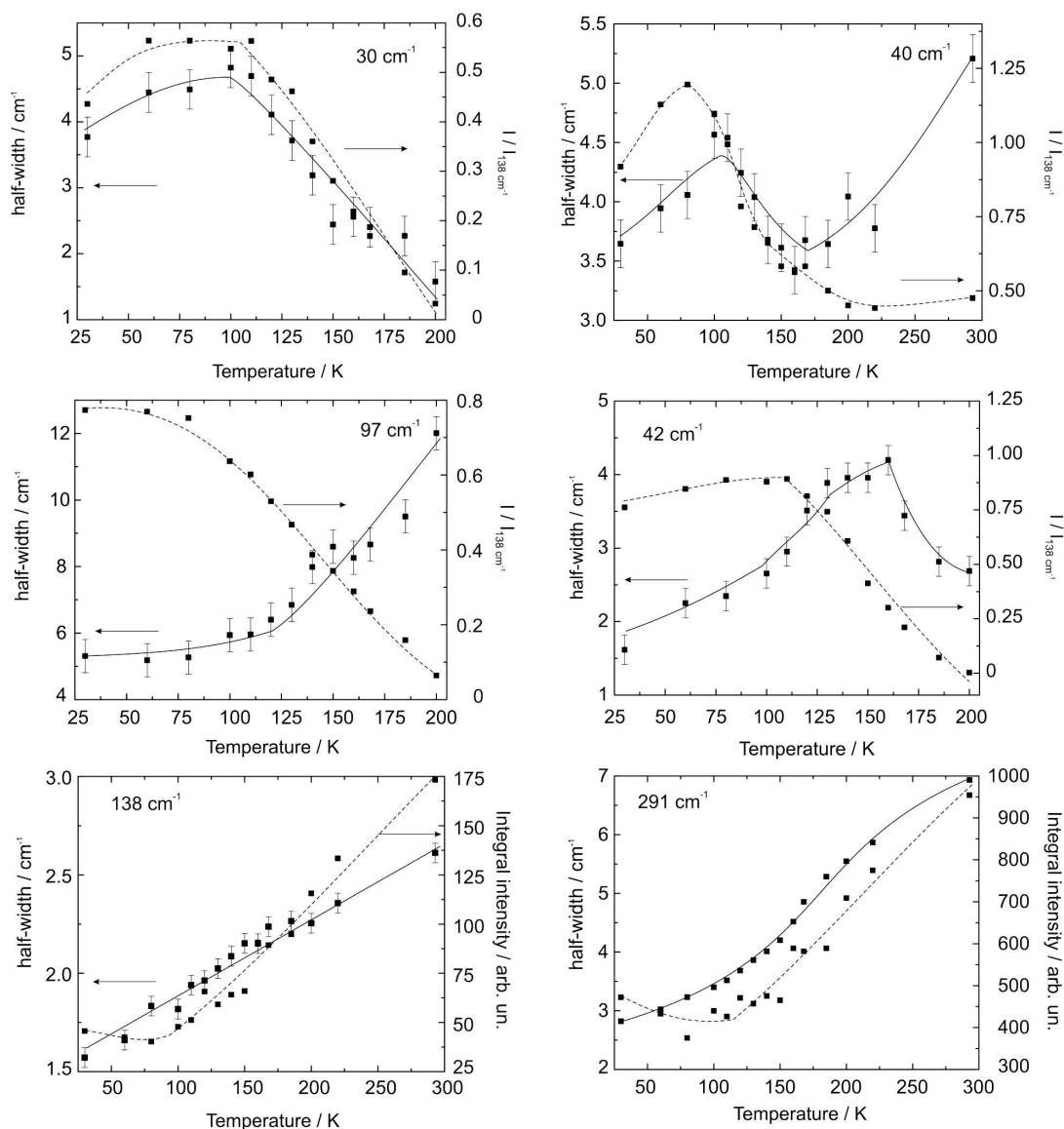


Fig. 3. Temperature dependences of half-widths, normalized intensities of Raman peaks centered at 30 cm^{-1} , 40 cm^{-1} , 42 cm^{-1} , and 97 cm^{-1} ($T = 30\text{ K}$), and integral intensities at 138 cm^{-1} , 291 cm^{-1} ($T = 30\text{ K}$) for a $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystal

the slight frequency decrease (Figs. 1 and 4) are due to the anharmonicity of lattice vibrations and the thermal expansion, similarly to InS [32] and TlInS_2 [26] layered crystals. Unpolarized Raman studies of TlInS_2 crystals in the temperature range 10–300 K showed that, for all modes except for those at 280.9 and 292.3 cm^{-1} , the frequencies decrease with temperature [26]. Note that our earlier spectroscopic ellipsometry studies and dielectric constant measure-

ments by an ac bridge of $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ single crystals [33] enabled us to conclude on the existence of phase transitions in a $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ crystal in the interval 170–220 K. As can be seen from Figs. 1 and 3 and the above analysis, it is this temperature interval where the transformations of the $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ Raman spectra occur. Thus, the temperature studies of the $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ Raman line frequencies, half-widths, and integrated intensities show that the

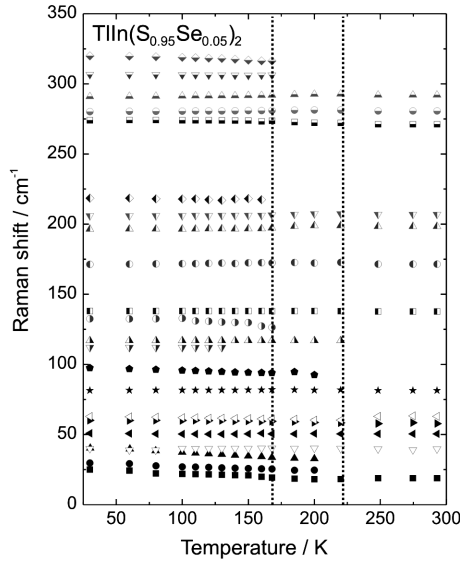


Fig. 4. Dependence of the Raman line frequencies for a $\text{TIIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystal on the temperature

changes in the phase transition range are similar to those observed by different research groups for TIInS_2 crystals [24–26, 29]. Hence, in our opinion, $\text{TIIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystals can be characterized by a phase transition sequence similar to TIInS_2 rather than by a Lifshitz-type point in the (x, T) phase diagram of $\text{TIIn}(\text{S}_{1-x}\text{Se}_x)_2$ crystals at $x = 0.05$, as claimed in Ref. [12]. Note that, in order to build the (x, T) phase diagram and to judge on a possibility of the existence of the Lifshitz point at $x = 0.05$, one should perform all-round detailed studies of sulfur-rich $\text{TIIn}(\text{S}_{1-x}\text{Se}_x)_2$ crystals using various techniques.

4. Conclusions

The Raman spectra of $\text{TIIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystals in the frequency range of 16–340 cm^{-1} are studied experimentally in the temperature interval $30 \text{ K} \leq T \leq 293 \text{ K}$ in the $Z(\text{XX}+\text{XY})\bar{Z}$ configuration. The Raman spectra are analyzed by a multipeak simulation using Lorentzian contours. The temperature behavior of the vibration band parameters (half-width, intensity, and frequency) was studied. A complicated transformation of the low-frequency spectral interval 16–50 cm^{-1} with temperature is observed. Two modes at 24 cm^{-1} and 42 cm^{-1} (at $T = 30 \text{ K}$) exhibit the most pronounced temperature dependence in the temperature range $30 \leq T \leq 200 \text{ K}$ in comparison with other low-frequency bands. Note that a

“crossing” behavior of the temperature dependences of two Raman modes near 40–42 cm^{-1} in the temperature interval 60–80 K is a clear evidence of the different symmetries of the relevant vibrations. At temperatures above 168 K, the number of modes in the spectra is reduced. This is related to the existence of phase transitions: the bands at 30 cm^{-1} , 42 cm^{-1} , and 97 cm^{-1} vanish at $T > 200 \text{ K}$, while the bands at 132 cm^{-1} , 218 cm^{-1} , 306 cm^{-1} , and 319 cm^{-1} are no longer observed above 160 K, which may, however, be related to their low intensities.

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O.O. Гомоннай, М. Людемани,
O.B. Гомоннай, I.Yu. Роман, O.G. Сливка, Д.Р.Т. Цан

ТЕМПЕРАТУРНА ЗАЛЕЖНІСТЬ
РАМАНІВСЬКИХ АКТИВНИХ МОД
КРИСТАЛІВ $\text{TlIn}(\text{S}_{0,95}\text{Se}_{0,05})_2$

Резюме

Досліджено неполяризовані спектри раманівського розсіювання світла монокристалів $\text{TlIn}(\text{S}_{0,95}\text{Se}_{0,05})_2$ в діапазоні частот $16\text{--}340\text{ см}^{-1}$ в температурному інтервалі $30\text{ К} \leq T \leq 293\text{ К}$. Проведено апроксимацію експериментальних спектрів суперпозицією лоренцових контурів і визначено температурні залежності напівширин, інтенсивностей та частот оптичних мод. Показано, що деякі особливості температурних залежностей пов'язані з існуванням фазових переходів у досліджуваних об'єктах.