High pressure Raman study of layered semiconductor TlGaSe$_2$

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Raman spectroscopy measurements of a monoclinic layered semiconductor TlGaSe$_2$ were performed in a pressure range up to 10.24 GPa. The pressure-induced first-order phase transition accompanied by reconstruction of the layer structure was observed at the pressure P $\sim$ 0.9 GPa. The mode-Grüneisen parameters of intralayer bonds were calculated for TlGaSe$_2$. The contribution of thermal expansion to temperature changes of phonon frequencies was defined. The type of intralayer bonds and their pressure transformation were analyzed in layered TlGaSe$_2$. It was shown that the nature of intramolecular forces in molecular crystals and intralayer forces in layered GaS, GaSe and TlGaSe$_2$ is similar.

Keywords: *layered semiconductor; high pressure; Raman study*

1. Introduction

TlGaSe$_2$ compound belongs to the class of layered ternary chalcogenide semiconductors with the general formula A^{3}B^{3}C$^6_2$ (A-Tl; B-Ga, In, Fe; C-S, Se). This compound is a subject of intensive investigations connected with the prospects of practical application in optoelectronics [1] and phase transitions (PT) observed in TlGaSe$_2$ at hydrostatic pressure and low temperatures.

At ambient conditions, TlGaSe$_2$ adopts a monoclinic crystal structure with the space group C2/c [2–6]. The layers in TlGaSe$_2$ are formed by Ga$_4$Se$_{10}$ tetrahedrons, linked with each other by selenium atoms. Each of these tetrahedrons consists of four GaSe$_4$ tetrahedrons. Monovalent Tl ions are located in trigonal voids between Ga$_4$Se$_{10}$ complexes along [1 1 0] and [1 $\bar{1}$ 0] directions.

It is established, that at atmospheric pressure, with temperature decreasing, the monoclinic TlGaSe$_2$ undergoes phase transition (PT) to

an incommensurate (T$_i$ $\sim$ 120 K) and ferroelectric (T$_C$ $\sim$ 108 K) phases sequentially [7–11]. Recently, there has been no consensus about the presence of PT in TlGaSe$_2$ under pressure at T = 300 K until the publication [11]. The assumptions regarding the presence of a reversible PT in the TlGaSe$_2$ crystals at P $\sim$ 0.5 GPa were formulated in the literature [12, 13] on the basis of pressure dependences of some phonon modes in Raman and resonance Raman spectra. Thermodynamic investigations [14] also indicated the presence of reversible PT in this compound at a pressure up to 1.2 GPa. The influence of pressure up to 1.2 GPa and possible PT on the Raman and absorption spectra of TlGaSe$_2$ crystals were studied in the literature [15–19]. The changes of band gap pressure coefficient values in the pressure range of 0.76 to 0.91 GPa were noted [15, 19].

At the same time, the investigations of Raman and absorption spectra [20–22], carried out in considerably larger pressure range, did not reveal PT in TlGaSe$_2$ in the pressure range up to 1 GPa. The supposition on the possibility of PT existence in

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TlGaSe$_2$ only at P $\sim$ 1.85 GPa was reported as a result of investigations of absorption spectra in the pressure range up to 12 GPa [20]. The assumption of the existence of four phases of TlGaSe$_2$ in the pressure range up to 13 GPa on the base of non-monotonic shift of TlGaSe$_2$ optical transmission spectrum has been suggested in the literature [21]. In recent time, it has been revealed by neutron diffraction method that monoclinic TlGaSe$_2$ with parameter c $\sim$ 15.71 Å undergoes the PT without symmetry change in the pressure range of 0.2 GPa to 0.9 GPa [5]. It was shown that PT is characterized by reconstruction in the structure of the layer.

It is known that tendency to polytypism is the characteristic feature of layered crystals. This is caused by the fact that interaction between layers results from weak forces of Van der Waals type. As a result, the layer packages can easily move relative to each other which leads to formation of polytypic modifications. It is shown that polytypism essentially influences the physical properties, character and temperature of PT in TlGaSe$_2$ crystals [23–27]. It is clear that the identification stage of a sample to belong to a definite polytype should be preceded by investigations of physical properties of layered TlGaSe$_2$.

In this work, we present the results of the analysis of Raman spectrum of TlGaSe$_2$ at different pressures and T = 300 K in frequency region characteristic of intralayer vibrations.

2.   Experimental

Powder samples under investigation have been obtained from a single crystal block grown by the Bridgman method. The polycrystalline product synthesized beforehand was prepared by fusing the corresponding components taken in the stoichiometric ratio in evacuated (1.33×10^{-2} Pa) quartz cells. The initial components were selenium of the purity 99.9999 %, thallium 99.9999 % and gallium 99.9999 %.

X-ray diffraction (XRD) studies were conducted at ambient temperature and pressure using high-brilliance FRD rotating anode generator (MoKα radiation, λ = 0.7115 Å), FluxMax focusing optics, and Bruker APEX CCD area detector. The two-dimensional XRD images were converted to one-dimensional diffraction patterns using the FIT2D program [28]. Experimental data of the X-ray diffraction experiments were analyzed by the Rietveld method using the Fullprof program [29].

Non-polarized Raman spectra at ambient temperature and pressure up to 10.3 GPa were collected using a LabRam spectrometer (He–Ne excitation laser with wavelength of 632.8 nm, Raman frequency range of 150 cm^{-1} to 300 cm^{-1}), 1800 grating, confocal hole of 1100 μm, and a 50× objective. The BX90 type diamond anvil cell was used for Raman experiments [30]. The sample was loaded into a hole of the 125 μm diameter made in the Re gasket intended to about 200 μm thickness. The diamonds with culets of 250 μm were used. A methanol-ethanol mixture with the ratio of 4:1 was used as a pressure transmitting medium. The pressure was determined by the ruby fluorescence technique with an accuracy of 0.05 GPa.

3.   Results and discussion

Raman spectra of TlGaSe$_2$ at different pressures are shown in Fig. 1. The frequencies of the vibrational modes were determined by the decomposition of obtained Raman spectra using the Gaussian function. The values of phonon frequencies (v$_i$) at P = 0 GPa along with results of other works [4, 12, 31] are given in Table 1. The recorded mode frequencies are in good agreement with the ones found in previous studies [4, 12, 31, 32]. The lattice vibrational modes can be divided into two groups: intralayer modes, related to vibrations of Ga$_4$Se$_{10}$ complexes, and low-frequency interlayer (Ag + 2Bg) modes, related to vibrations of thallium ions and Ga$_4$Se$_{10}$ complexes. For the monoclinic C2/c symmetry, the group theory predicts 48 Raman active modes, Γ_{Ram} = 23Ag + 25Bg vibrations [4].

Pressure dependences of the intralayer modes of TlGaSe$_2$ are shown in Fig. 2. As can be seen from Fig. 2, the frequencies of these modes almost

linearly increase upon compression up to 0.63 GPa. In the pressure range of 0.85 GPa to 1.21 GPa, the phonon frequencies of the mode 5 and mode 7 abruptly decrease at ~ 10 cm^{-1}, and the pressure coefficient of the mode frequency decreases with increasing pressure for all modes (Fig. 2).
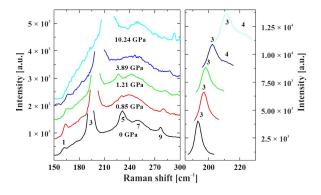

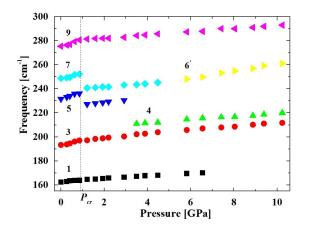Fig. 1. Raman spectra of TlGaSe₂ at different pressures.

Fig. 2. Pressure dependences of TlGaSe₂ phonon frequencies. The Raman modes are assigned by numbers from 1 to 9. The vertical dashed line shows the PT pressure.

The anomalous pressure dependences of phonon modes described above (Fig. 2) are a sign of existence of first-order PT in the crystal, which was also observed in previous studies on TlGaSe₂ using differential thermal analysis method [14] and optical transmission spectra [21]. It is worth to note that in the isostructural compound TlGaS₂, the first-order PT caused by layer structure reconstruction was observed at essentially high

pressure [33]. The manifestation of PT near $P_{cr} \sim 0.5$ GPa in the frequency range characteristic of intralayer vibrations [12, 13], was not revealed in the present work. It could be due to the small number of experimental points in the pressure interval up to 0.5 GPa.

The changes, observed on $v_i(P)$ dependences close to frequency of 210 cm^{-1} (Fig. 1 and Fig. 2) at a pressure $P \sim 3.5$ GPa, took our attention. The investigations on the crystal structure of TlGaSe₂ using neutron diffraction method [5] did not reveal the presence of any PT at a pressure near 3.5 GPa. The comparison of our results obtained at ambient pressure with the results of other authors at $P = 0$ (Table 1) allows us to elucidate the changes observed in Raman spectra and $v_i(P)$ dependences (Fig. 2) near 3.5 GPa. The mode, recorded on a high-frequency wing of mode 3 at $P > 3.5$ GPa, is probably the mode 4, recorded at atmospheric pressure in the literature [31] (Table 1).

The anomalous behavior of the vibrational modes 7 and 6′, close to the frequency of 245 cm^{-1} in the pressure range of 4.48 to 5.82 GPa can be an evidence of another PT in TlGaSe₂ [21], but previous and present experimental data are insufficient for making a confident assertion. This feature can be caused also by the difference in pressure dependences of mode 7 and mode 6 ($v_i = 240$ cm^{-1} at $P = 0$ GPa) [31], their crossing and the fact that above 5.8 GPa only the mode 6 (6′) is recorded. We did not reveal any feature in pressure behavior of TlGaSe₂ intralayer modes in the pressure range from 8.5 GPa to 9.7 GPa, in which, according to authors [21], the crystal undergoes the PT.

It is known that pressure induced changes of optical phonon frequencies v_i are connected with the value of mode Grüneisen parameter (Γ_i) by following expression:

$$\Gamma_i = \frac{1}{\beta} \cdot \gamma_i = \frac{1}{\beta} \cdot \frac{1}{v_i} \cdot \frac{dv_i}{dP} \qquad (1)$$

In crystals of AIV type with covalent bonds $\Gamma_i \approx 1$ and in crystals of AIII-BV and AII-BVI types with ion-covalent bonds $\Gamma_i \approx 2$ [34]. In layered crystals of As₂S₃, ε-GaSe and ZnInS₂ types,

Table 1. TlGaSe$_2$ Raman frequencies v_i at P = 0 and mode-Grüneisen parameters γ_i obtained in the present work and in the literature [4, 12, 31] (Raman shift 150 cm⁻¹ to 300 cm⁻¹).

No. modes	[30] v_i [cm⁻¹]	0 – 0.5 [GPa] [12]		0.5 – 0.93 [GPa] [12]	0 – 2.5 [GPa] [4]		0 – 0.63 [GPa]		P > 1.21 [GPa]
		v_i [cm⁻¹]	γ_i [10⁻² GPa⁻¹]	γ_i [10⁻² GPa⁻¹]	v_i [cm⁻¹]	γ_i [10⁻² GPa⁻¹]	v_i [cm⁻¹]	γ_i [10⁻² GPa⁻¹]	γ_i [10⁻² GPa⁻¹]
1	163	–			–		162.6	1.4	0.6 (1.21 – 6.55 [GPa])
2	–	–			177.2	1.7	–		
3	194	194	2.6	1.2	193.6	1.3	193.4	2.3	0.9 (1.21 – 10.24 [GPa])
4	198	–			–		–		0.7 (3.50 – 10.24 [GPa])
5	230	231	4.4	2.2	229.0	4.0	231.6	3.0	0.9 (1.21 – 2.92 [GPa])
6	240	–			–		–		
6′		–			–		–		1.3 (5.82 – 10.24 [GPa])
7	250	–			249		248.8	1.9	0.6 (1.21 – 4.48 [GPa])
8	268	–			–		–		
9	278	278	2.5	1.3	277.7	1.2	275.4	2.2	0.6 (1.21 – 0.24 [GPa])

Γ_i values for interlayer vibrations are of one or two order higher than for intralayer ones [12, 35].

The values of shift parameters v_i for observed phonon modes in different pressure ranges are given in Table 1. The data from the literature [4, 12, 30] are given in Table 1 for comparison.

The value of isothermal compressibility of TlGaSe$_2$, obtained by investigation of pressure behavior of unit-cell parameters [5] and estimated on the base of experimentally determined values of elastic constants at T = 300 K and low pressures [36] is 0.04 GPa⁻¹ and 0.034 GPa⁻¹, correspondingly.

Using the v_i values (Table 1) and averaged value β = 0.037 GPa⁻¹ for pressure range of 0 GPa to 0.63 GPa with the help of expression 1 for mode 1, mode 3, mode 5, mode 7 and mode 9, we found the values of mode Grüneisen parameter Γ_i. The obtained values of Γ_i of 0.35 to 0.78 for high-frequency modes allow us to conclude that the intralayer bonds in TlGaSe$_2$ in low pressure range (0.63 GPa > P > 0 GPa) are mainly covalent ones [34].

The important information on the character of bond forces in crystal can be obtained by allocating the thermal expansion contribution into temperature change of phonon frequencies. It is known [37] that phonon frequencies change in dependence on temperature by two reasons: phonon-phonon interaction and lattice deformation with temperature change as follows:

$$\frac{\partial v_i}{\partial T} = \left(\frac{\partial v_i}{\partial T}\right)_v - \left(\frac{\partial v_i}{\partial P}\right)_T \cdot \frac{\partial P}{\partial V} \cdot \frac{\partial V}{\partial T} \quad (2)$$

where V is the crystal volume. The contribution of phonon-phonon interaction in $\frac{\delta v_i}{\delta T}$ is considered as anharmonic one [37] and it presents the phonon frequency change with temperature changing at a constant volume $\left(\frac{\delta v_i}{\delta T}\right)_V$. The contribution of thermal expansion is described by the second member on the right part of expression 2, and it is considered as harmonic.

In the literature [37] it has been shown that the contributions of thermal expansion and phonon-phonon interaction have the defined values in dependence on the nature of chemical bonds in crystal. The confirmation of covalent character of a chemical bond inside the molecules in molecular crystals is the prevailing contribution of phonon-phonon interaction upon the change

of intramolecular oscillations frequency with temperature changing. The shift of intermolecular oscillation frequencies with temperature changing is caused mainly by thermal expansion [37]. The contribution of thermal expansion to temperature changes of phonon frequencies can be estimated numerically by the parameter η_i [37]:

$$\eta_i = -\frac{\partial v_i}{\partial P} \cdot \frac{\alpha}{\beta} / \frac{\partial v_i}{\partial T} \qquad (3)$$

where α is the thermal expansion coefficient. Taking into consideration the weak anisotropy of TlGaSe$_2$ crystals in plane of layers, the value of volume thermal expansion coefficient can be calculated on the base of known values of linear thermal expansion coefficient in directions parallel ($\alpha_{||} = 12.5 \times 10^{-6}$ K^{-1}) and perpendicular ($\alpha_{\perp} = 17.5 \times 10^{-6}$ K^{-1}) to crystal layers [16, 17, 28]:

$$\alpha = \alpha_{\perp} + 2\alpha_{||} = 42.5 \times 10^{-6} \text{ K}^{-1} \qquad (4)$$

Using the above mentioned values v_i (Table 1), α, β and $\frac{\delta v_i}{\delta T}$, estimated from high-temperature linear sections of $v_i(T)$ dependences (200 K < T < 320 K) [34] as well as the values of parameter η for phonons with frequencies 275.4 cm^{-1} ($\eta = 0.27$), 231.3 cm^{-1} ($\eta = 0.27$) and 193.4 cm^{-1} ($\eta = 0.46$) have been determined. The obtained η_i values are typical of phonons, which are responsible for intramolecular vibrations in inorganic molecular crystals [37] and intralayer vibrations in layered crystals GaS and GaSe [39]. Also, the values of Γ_i, determined by us for TlGaSe$_2$, indicate the dominating covalent character of forces of these bonds [37].

Thus, it is clear that the nature of intramolecular forces in molecular crystals and intralayer forces in layered GaS, GaSe and TlGaSe$_2$ is similar.

4. Conclusions

The vibration spectra of monoclinic TlGaSe$_2$ at a pressure up to 10.24 GPa have been studied by Raman spectroscopy methods. The pressure dependences of phonon modes frequencies indicate the presence of first-order PT at P $\sim$ 0.9 GPa,

which is accompanied by the reconstruction of intralayer bonds. The values of mode Grüneisen parameter and contribution of thermal expansion to temperature changes of phonon frequencies confirm the dominating covalent character of the forces of intralayer bonds.

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