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Research Article

Resonance Raman Scattering in $TlGaSe_2$ Crystals

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The resonance Raman scattering for geometries $Y(YX)Z$ and $Y(ZX)Z$ at temperature 10 K and infrared reflection spectra in $E \parallel a$ and $E \parallel b$ polarizations at 300 K were investigated. The number of A_a (B_a) and A_u (B_u) symmetry vibrational modes observed experimentally and calculated theoretically agree better in this case than when $TlGa_2Se_4$ crystals belong to D_{2h} symmetry group. The emission of resonance Raman scattering and excitonic levels luminescence spectra overlap. The lines in resonance Raman spectra were identified as a combination of optical phonons in Brillouin zone center.

1. Introduction

$TlGaSe_2$ crystals are triple thallium chalcogenides with a layered structure [1, 2]. One of these crystals features is the strong anisotropy of physical characteristics due to the specificity of the crystals lattice [1–3]. Optical spectra in the absorption edge region [4–11] and resonance Raman scattering for different geometries and temperatures (77–400 K) [12] were investigated in $TlGaSe_2$ crystals. Reflection spectra for the 50–4000 cm^{-1} region were studied and polar vibrational modes LO and TO and their parameters were determined. Such crystals had an effect of switching of current-voltage and acoustooptic characteristics [13–15]. There are a lot of materials dedicated to the investigations of these materials (see [4–16] and the references therein). But resonance Raman scattering in $TlGaSe_2$ crystals has not been investigated.

2. Experimental Methods

Raman scattering spectra of $TlGaSe_2$ crystals were measured on double high-aperture spectrometers DFS-32 with linear dispersion of 5 Å/mm and relative aperture of 1 : 5 and resonance Raman scattering spectra on spectrometer SDL-1 with dispersion of 7 Å/mm and relative aperture of 1 : 2. The photomultiplier working in the photon counting regime was used as a detector. Resonance Raman spectra had an accuracy of ±0.5 meV. Reflection spectra in $E \parallel a$ and $E \parallel b$ polarizations in the range 50–400 cm^{-1} were measured on a vacuum spectrometer KSDI-82 using an acoustooptical receiver with an accuracy of ±1 cm^{-1}. Cleft crystals of $TlGaSe_2$ with different thicknesses mounted on a cold finger of a closed-circuit helium cryostat LTS-22 C 330 optical cryogenic system were used in the measurements. The Raman scattering was excited by 6328 Å line of a He-Ne laser. The resonance Raman scattering was excited by lines 4579 Å and 5145 Å of an Ar^+ laser.

3. Experimental Results and Discussions

According to the crystallographic data, the $TlGaSe_2$ structure is described by the space group $C2/c$ (C_{2h}^6). The unit cell contains 8 formula units of $TlGaSe_2$. The main motive of the structure is formed by tetrahedral polyhedrons of Ga_4Se_{10}, consisting of 4 tetrahedrons of $GaSe_4$. These tetrahedrons have common atoms of selenium on the tops of the octahedron [1–3]. These tetrahedral polyhedrons have common vertices of 4 selenium atoms and take up layered positions perpendicular to the c axis. The layers are rotated to each other at 90°. The edges of polyhedrons lie in the xy plain and are situated along the diagonal of the base square. Thus, the $TlGaSe_2$ compound has a monoclinic pseudotetragonal

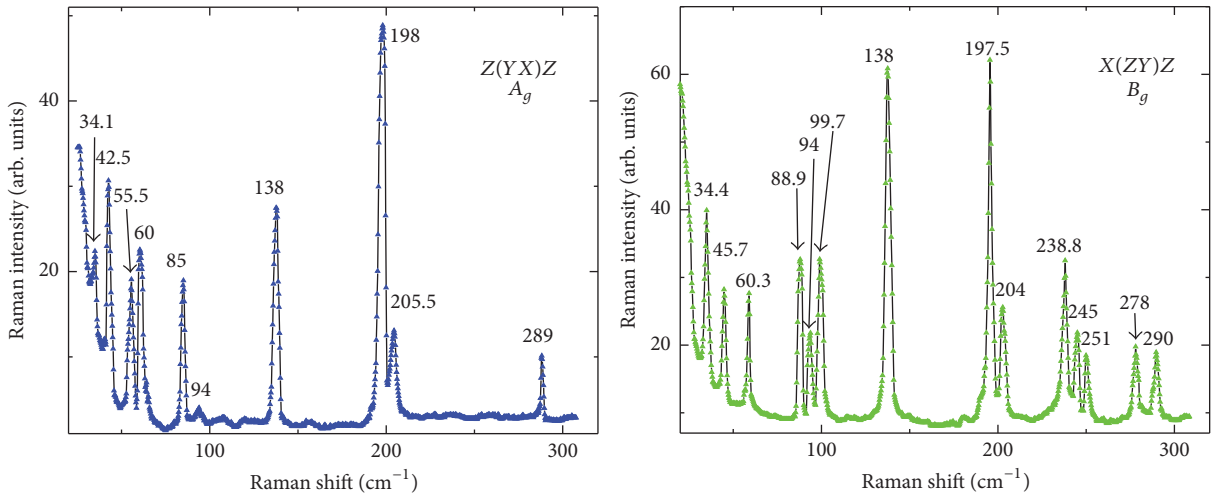

FIGURE 1: Raman scattering of $TlGaSe_2$ crystals.

structure with the following parameters: $a = b = 10.75$ Å, $c = 15.56$ Å, and $\beta = 100.0^\circ$. The distances between Tl-Se, Se-Se, and Tl-Tl are equal to 3.45 Å, 3.92 Å, and 3.42 Å, respectively. This distance corresponds to the sum of ionic radiuses Tl^1-Se (3.38 Å) [1–3].

The next vibrational modes should be observed in Brillouin zone center of the above-mentioned crystals:

$$\Gamma = (A_u + 2B_u)_{ac} + 23A_g + 25B_g + 22A_u + 23B_u. \quad (1)$$

The phonons of A_g and B_g symmetry should be observed in Raman spectra and A_u and B_u in IR reflection spectra in $E \parallel a$ and $E \parallel b$ polarizations, respectively. The scattering tensors are next:

$$A_g = \begin{vmatrix} a & d & 0 \\ d & b & 0 \\ 0 & 0 & c \end{vmatrix}, \qquad B_g = \begin{vmatrix} 0 & 0 & e \\ 0 & 0 & f \\ e & f & 0 \end{vmatrix}. \quad (2)$$

Figure 1 shows the Raman scattering of $TlGaSe_2$ crystals measured at a temperature of 10 K and in $X(ZY)Z$ and $Z(YX)Z$ geometries. The structure of vibrational modes depends on polarization. It was reported in [12] that 8 and 6 modes of A_g symmetry were recognized at temperatures of 77 K and 300 K, respectively. One can see from the analysis of the above-mentioned spectra that, even at 10 K, the number of experimentally observed modes is smaller than the number of modes theoretically predicted by group-theoretic calculations. 14 modes of B_g symmetry and 10 modes of A_g symmetry were observed. Hence, the amount of the observed vibrational modes as in IR reflection spectra as in Raman spectra is lower than expected according to the theory.

The most intensive modes in reflection spectra for both polarizations are high-frequency modes (see Figure 2). Thus, in reflection spectra of $TlGaSe_2$ crystals, 23 and 22 modes are expected in the region of single-phonons vibrational modes, but only 5 modes and 8 modes have been observed in $E \parallel a$ and $E \parallel b$ polarizations, respectively (Figure 2).

Compounds $TlGaS_2$ and $TlGaSe_2$ belong to thallium based crystals. This group of crystals ($TlMX_2$, where M = Ga, In and X = S, Se, Te) has a family likeness of optical spectra and energy band structures. The analogs are observed in all well-studied compounds (Si, Ge, $A^{III}B^{V}$ and $A^{II}B^{VI}$). The results of band structure calculations for $TlMX_2$ crystals have a common character and reflect only its main features. This leads to proximity of the above-mentioned compounds lattices. Crystal structures of $TlGaS_2$ and $TlGaSe_2$ compounds are different only in the replacement of S atoms by Se atoms in the crystal lattice. The structure of the layer $TlGaS_2$ in [12] is symmetrized by an insignificant shift of atoms inside the layer to achieve a tetragonal structure with $D_{2d}{}^5$ space group. The hypothetic structure with space group $D_{2h}{}^{15}$ with unit cell comprising two layers was achieved by the authors of [12], introducing the interlayer inversion operation with preserving the elements of layer symmetry. Similarly, we analyze and investigate $TlGaSe_2$ crystals. Using the same assumption, one can obtain a better agreement in the number of theoretically predicted and experimentally measured vibration modes in the case of $TlGaSe_2$ crystals. Based on the analysis of polarization dependences of Raman and IR reflection spectra, the $TlGaS_2$ and $TlGaSe_2$ crystals can be attributed to symmetry group D_{2h} or D_{4h}.

The emission lines (1–20) of resonance Raman scattering in the region of excitonic resonances at excitation of 514.5 nm laser line of $TlGaSe_2$ crystals at a temperature of 10 K and $Z(YY)Z$ geometry were observed (see Figure 3 and Table 1). These lines (1–20) skirt the broad emission lines at 2.17–2.19 eV, 2.30 eV, and 2.39 eV in resonance Raman scattering spectra of $TlGaSe_2$ crystals. These broad lines are caused by emission of ground states A, B, and C excitons.

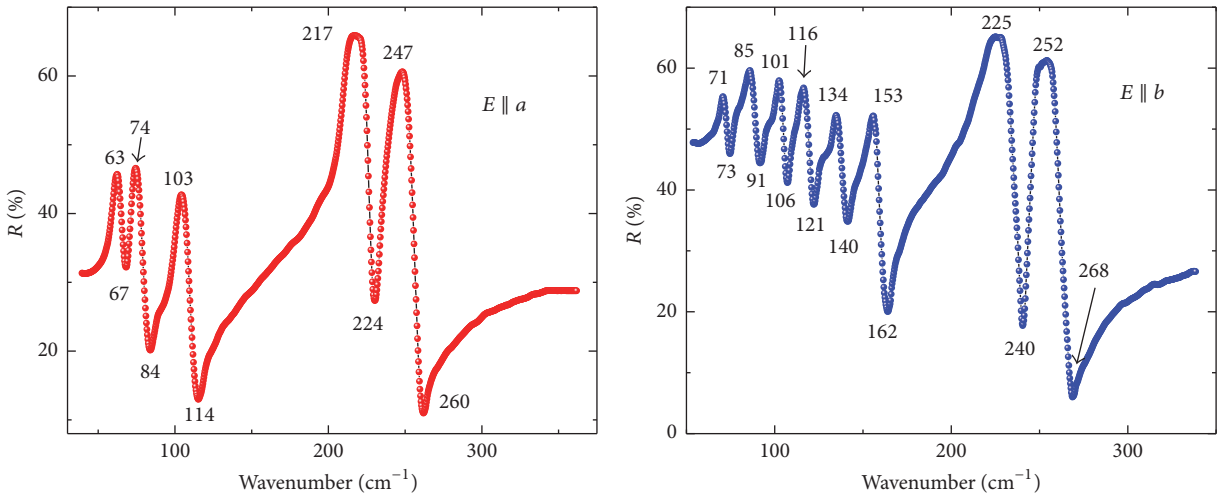

Figure 2: Reflection spectra of $TlGaSe_2$ crystals in $E \parallel a$ (a) and $E \parallel b$ (b) polarizations.

Table 1: Emission lines of resonance Raman scattering in $TlGaSe_2$ crystals measured at 10 K and excited by 514.5 nm Ar^+ laser line in $Z(YY)Z$ geometry and possible phonons combinations (symmetry, modes, and frequencies) responsible for resonance scattering.

Line, n	Wavenumber shift, cm^{-1}	Assignment
1	120	A_u(LO), 121;
2	134	B_u(LO), 67 + B_u(LO), 67;
3	140	A_u(LO), 140;
4	151	B_u(LO), 67 + B_u(LO), 84;
5	163	A_u(LO), 73 + A_u(LO), 91;
6	187	A_u(LO), 106 + B_u(LO), 84; B_u(LO), 114 + A_u(LO), 73;
7	238	B_u(LO), 114 + A_u(LO), 121;
8	313	A_u (LO), 240 + A_u(LO), 73;
9	436	2A_u(LO), 106 + B_u(LO), 224;
10	480	A_u(LO), 240 + A_u(LO), 240;
12	590	B_u(LO), 260 + A_u(LO), 91 + A_u(LO), 240;
13	634	B_u(LO), 260 + B_u(LO), 260 + B_u(LO), 114;
14	732	A_u(LO), 240 + B_u(LO), 224 + A_u(LO), 268;
15	960	A_u(LO), 240 + A_u(LO), 240 + A_u(LO), 240 + A_u(LO), 240;
16	999	A_u(LO), 240 + A_u(LO), 240 + B_u(LO), 260 + B_u(LO), 260;
17	1075	A_u(L), 73 + A_u(LO), 240 + A_u(LO), 240 + B_u(LO), 260 + B_u(LO), 260;

Figure 3 shows resonance Raman scattering spectra in $TlGaSe_2$ crystals measured at a temperature of 10 K in $Z(YY)Z$ geometry and excited by 496.5 nm Ar^+ laser line. The narrow lines (1–17) that skirted the line at 2.4 eV were observed in these spectra. The observed lines of resonance Raman scattering and possible combination of phonons responsible for these emission lines are presented in Tables 1 and 2. At high frequencies, these data do not include all possible combinations of phonons responsible for lines of resonance Raman scattering.

4. Conclusions

The resonance Raman scattering in $Y(YX)Z$ and $Y(ZX)Z$ geometries excited by He-Ne laser was investigated at a temperature of 10 K. The energies of phonons with A_g and B_g symmetries were determined. It was shown that the amount of modes in Raman scattering and IR reflection spectra measured at 10 K is half the expected according to group theory calculations. The experimental and theoretical results coincide if the crystal is described by symmetry

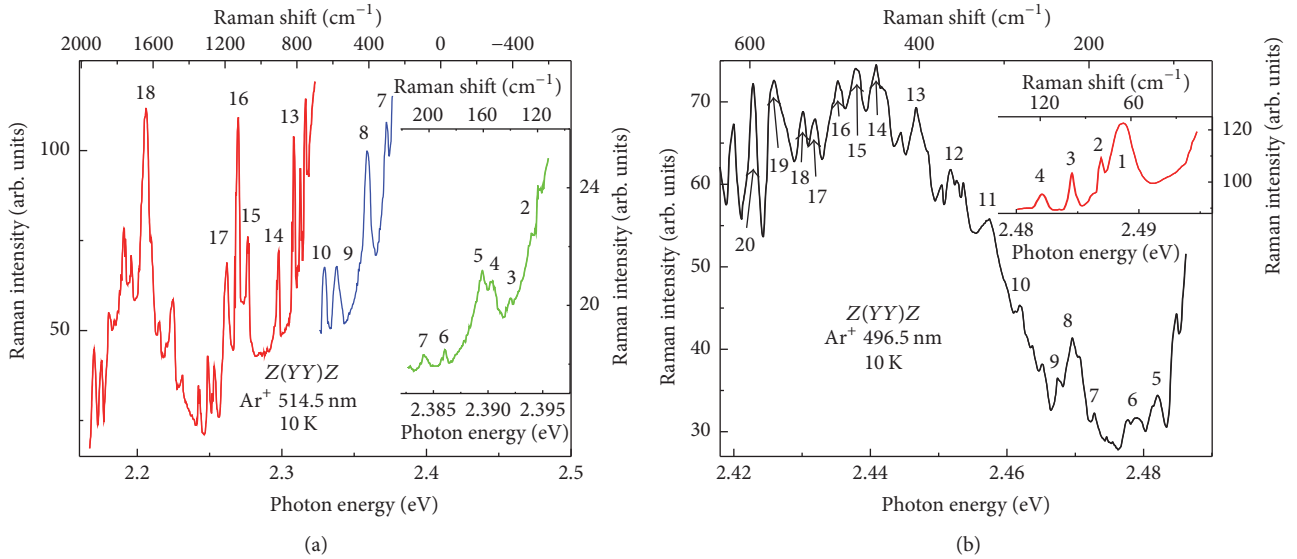

FIGURE 3: Resonance Raman scattering in $TlGaSe_2$ crystals measured at a temperature of 10 K and excited by lines 514.5 nm (a) and 496.5 nm (b) of an Ar^+ laser in $Z(YY)Z$ geometry.

TABLE 2: Emission lines of resonance Raman scattering in $TlGaSe_2$ crystals measured at 10 K and excited by 496.5 nm Ar^+ laser line in $Z(YY)Z$ geometry and possible phonons combinations (symmetry, modes, and frequencies) responsible for resonance scattering.

Line, n	Wavenumber shift, cm^{-1}	Assignment
1	66	B_u(LO), 67;
2	75	A_u(LO), 73;
3	85	B_u(LO), 84;
4	96	A_u(LO), 91;
5	117	A_u(LO), 121; A_u(TO), 116; B_u(LO), 114;
6	142	A_u(LO), 140; B_u(LO), 67 + A_u(LO), 73;
7	194	B_u(LO), 114 + B_u(LO), 84; A_u(LO), 121 + A_u(LO), 73;
8	217	A_u(LO), 106 + B_u(LO), 106;
9	236	A_u(LO), 121 + B_u(LO), 114; A_u(LO), 162 + A_u(LO), 73;
10	279	B_u(LO), 114 + A_u(LO), 162;
11	322	A_u(LO), 240 + B_u(LO), 84; A_u(LO), 162 + A_u(LO), 162;
12	355	A_u(LO), 268 + B_u(L), 84;
13	401	A_u(LO), 240 + B_u(LO), 260;
14	446	B_u(LO), 224 + B_u(LO), 224;
15	482	B_u(LO), 260 + B_u(LO), 224;
16	493	A_u(LO), 268 + B_u(LO), 224;
17	525	B_u(LO), 260 + A_u(LO), 268;

group D_{2h}. The superposition of excitonic luminescence with resonance Raman scattering emission was observed. The lines of resonance Raman emission were identified and attributed to optical phonons in Brillouin zone center.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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