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LOW-TEMPERATURE PHASE TRANSITIONS IN $TlGaS_2$ LAYER CRYSTALS

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Polarized Raman scattering spectra of $TlGaS_2$ layer crystals have been studied for the first time as a function of temperature between 8.5 and 295 K. No evidence for a soft mode behaviour has been found. The anomalies observed in the temperature dependence of low- and high-frequency phonon modes at ~ 250 and ~ 180 K, respectively, are explained as due to the phase transitions. It is supposed that the phase transitions are caused by the deformation of structural complexes GaS_4, rather than by slippage of Tl atom channels in [1 1 0] and [1 $\bar{1}$ 0] directions, which is mainly responsible for the appearance of the low-temperature ferroelectric phase transitions in other representatives of $TlBX_2$ layer compounds.

FOR THE last few years there has been considerable interest in the investigation of the physical properties of layer ternary semiconductors with chemical formula $TlBX_2$, where B = Ga or In and X = S or Se [1]. The lattice of $TlBX_2$-type crystals consists of strictly periodic two-dimensional layers arranged parallel to the (0 0 1) plane [2]. Each successive layer is turned by a right angle with respect to the previous one. The fundamental structural unit of a layer is the B_4X_{10} polyhedron representing a combination of four elementary BX_4 tetrahedra linked together by bridging X atoms. The Tl atoms are in trigonal prismatic voids resulting from the combination of the B_4X_{10} polyhedra into a layer. The Tl atoms form nearly planar chains along the [1 1 0] and [1 $\bar{1}$ 0] directions.

$TlInS_2$ and $TlGaSe_2$ crystals, which have the symmetry $C2/c$ at room temperature, sequentially undergo low-temperature phase transitions to an incommensurate phase and a ferroelectric phase at $T_i = 213$ K, $T_c = 189$ K and $T_i = 120$ K, $T_c = 107$ K, respectively. Occurrence of a soft mode in $TlInS_2$ [3, 4] and $TlGaSe_2$ [5, 6] were reported. The interaction of two, hard, optical modes at 38 and 42 cm^{-1} has been observed in Raman spectra of $TlInS_2$ in the temperature range from 55 to 65 K [7].

Two structural deformation mechanisms have been proposed for the ferroelectricity in $TlGaSe_2$. Hochheimer and co-workers [8] suggested that the ferroelectricity originates from small positional shift of the Tl atoms in the *ab* plane (displacive transition). Shift of the thallium atoms in the trigonal prisms changes their coordination from CN = 6 into CN = 3 + 3 and it is accompanied by a discontinuity in the axial ratios. As a result, of this an inversion center is lost and the space group changes from $C2/c$ to Cc. This suggestion have been confirmed by Yee and Albright in their calculation of bonding and structure of $TlGaSe_2$ by tight-binding model [1]. According to Burlakov *et al.* [9] the ferroelectric phase transition in $TlGaSe_2$ is created by angular deformations in $GaSe_4$ tetrahedra.

The Raman spectra of $TlGaS_2$ crystals show no sharp anomalies when temperature is lowered down to 90 K although a slow evolution of the spectra in the temperature range 90–300 K is mentioned in [10,11]. Relatively insignificant anomalies, indicating the existence of a sequence of phase transitions, were observed in the temperature dependence of specific heat of $TlGaS_2$ at temperatures: 73.5; 91; 101; 114; 133.5; 187 K [12].

In the present work the results of the polarized Raman scattering measurements of $TlGaS_2$ in the temperature region 8.5–295 K are reported. The experimental results below 90 K were described for the first time. The purpose of these measurements was to search for a possible existence of a soft mode in Raman scattering spectra and

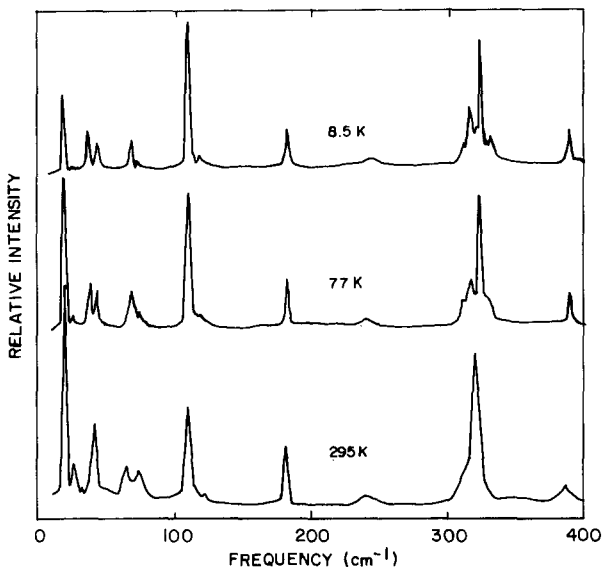

Fig. 1. Raman spectra of $TlGaS_2$ at various temperatures in the $z(yx)y$ geometry.

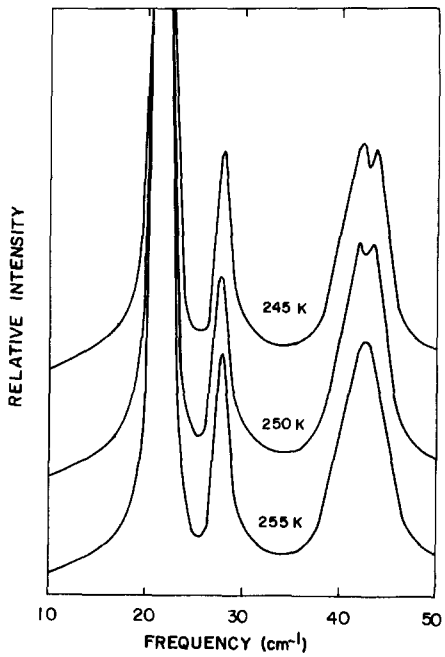

Fig. 2. Low-frequency part of the Raman spectra of $TlGaS_2$ at various temperatures in the $z(yx)y$ geometry.

to find other possible anomalies caused by the phase transitions.

$TlGaS_2$ polycrystals were synthesized from particular high-purity elements (at least 99.999%) taken in stoichometric proportions. Single crystals studied were grown by a modified Bridgman method. The crystals obtained were easily spalled along the cleavage plane (0 0 1) perpendicular to the optical c-axis. In order to obtain Raman spectra in $z(yx)y$ and $z(xx)y$ geometries, the crystals were cut perpendicular to the cleavage plane and the surfaces produced were "gently" grounded and polished. Here, we used the standard notation where the first and the second letters of designation, for example in $z(yx)y$, designate the direction and polarization of the incident light, whereas the third and the fourth letters designate the polarization and direction, respectively, of the scattered light.

The Raman spectra of $TlGaS_2$ crystals were excited with the 514.5 nm radiation from a Spectra-Physics argon-ion laser. The laser beam power incident on the samples was kept between 70 to 80 mW. Polarized measurements in the frequency range from 10 to 400 cm^{-1} were carried out in right-angle scattering geometry with scattered light being dispersed by a U-1000 "Jobin Yvon" spectrometer. The optical phonon frequencies were determined within an accuracy not worse than 1 cm^{-1}. A Cryogenics M-22 closed-cycle helium cryostat was used to cool the crystals. The temperature was controlled to within 1 K.

The Raman spectra of $TlGaS_2$ crystal in $z(yx)y$ geometry at 295, 77, and 8.5 K are shown in Fig. 1. In general, when cooling the crystal, all the bands are narrowed and slightly shifted to higher frequencies. No noticeable changes were observed in the frequency range from 50 to 300 cm^{-1} at all the measured temperatures, that is why this part of the spectrum will not be discussed at the present work. However, noticeable changes with temperature were observed in the frequency ranges from 10 to 50 cm^{-1} and from 300 to 350 cm^{-1}.

The low-frequency part of recorded spectra in $z(yx)y$ scattering geometry at 255, 250 and 245 K is shown in Fig. 2. The most prominent feature one observes when lowering the temperature is the splitting of the band centered at 42.5 cm^{-1} into two bands at 42 and 43 cm^{-1}. The splitting starts at $\sim$ 250 K and is well resolved at $\sim$ 245 K. Further cooling the crystal down to 8.5 K only slightly increases the splitting (38 and 44 cm^{-1}). At all temperatures, the bands at 42 and 43 cm^{-1} had different symmetry properties. The first one is stronger at $z(xx)y$ geometry (A_g mode), whereas the line 43 cm^{-1} is stronger at $z(yx)y$ scattering geometry (B_g mode). For this reason this pair cannot be considered as a Davydov doublet, that one can expect in layer crystals as a result of splitting of the intralayer vibrational modes due to weak interlayer interaction. The splitting of the band in the narrow temperature range (250–245 K) can be explained if

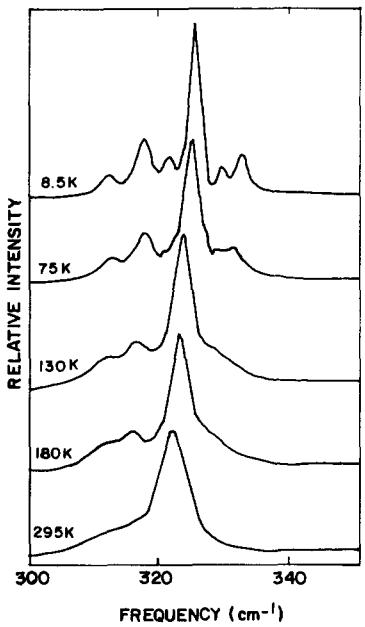

Fig. 3. High-frequency part of the Raman spectra of $TlGaS_2$ at various temperatures in the $z(yx)y$ geometry.

one suppose that the $TlGaS_2$ crystal undergoes a phase transition at this temperature interval.

Figure 3 represents the high-frequency part of the Raman spectra of $TlGaS_2$ crystal recorded in $z(yx)y$ geometry at 295, 170, 130, 75, and 8.5 K. The most prominent changes with temperature in this part of the spectra take place around the band centered at $322\,cm^{-1}$ ($T = 295$ K). Cooling the crystal to ~ 180 K leads to the appearance of a new line at $316\,cm^{-1}$. This temperature is in satisfactory agreement with the more pronounced anomaly of specific heat of $TlGaS_2$ at 187 K observed by the authors of [12]. When lowering the temperature from ~ 180 K new lines appear around the band centered at $328\,cm^{-1}$. The intensity of these lines increases in the temperature range 180–8.5 K gradually and they are well resolved at 8.5 K having frequencies 312, 317, 321, 325, 329, and $333\,cm^{-1}$. We attribute these changes in the Raman spectra to a phase transition in $TlGaS_2$ at ~ 180 K. Polarized Raman measurements permitted to establish that the lines at 312 and $317\,cm^{-1}$, 325 and $329\,cm^{-1}$ have A_g symmetry (stronger in $z(xx)y$ geometry), whereas a pair 321 and $333\,cm^{-1}$ can be assigned by B_g symmetry. It is not excluded that the pairs 312–$317\,cm^{-1}$ and 325–$329\,cm^{-1}$ form Davydov doublets. For a large value of separation between 321–$333\,cm^{-1}$ pair they can not be considered as a Davydov doublet.

No soft mode or interaction of hard modes have been observed in our measurements. This result is in agreement with IR measurements published in [13].

In conclusion one can see that at low temperatures $TlGaS_2$ crystals undergo phase transitions. But these transitions, at least when studied by Raman scattering spectroscopy, are not well pronounced in a narrow temperature range, as it has been seen for other representatives of ternary layer chalcogenides. The reason for this, as we think, is that in $TlGaS_2$ crystals the origin of the phase transitions is caused not by the slippage of the two Tl atom channels parallel to the [1 1 0] and [1 $\bar{1}$ 0] directions (as it takes place in the case of $TlGaSe_2$ and $TlInS_2$) but it is caused by angular deformations in GaS_4 tetrahedra. This assumption is in agreement with [14] where the authors showed that the unit cell volume of $TlGaS_2$ crystal ($1.59\,nm^3$) is less than those of $TlGaSe_2$ ($1.78\,nm^3$) and $TlInS_2$ ($1.76\,nm^3$) crystals. Therefore, the average distances between the Tl atom channels in $TlGaS_2$ crystals also get shorter as compared with those of $TlGaSe_2$ and $TlInS_2$ crystals. Thus, the Tl atom channel slippages in the smaller unit cell do not easily take place so that they may not be sufficient to destroy the inversion center in $TlGaS_2$ crystal which is necessary for the occurrence of ferroelectricity.

We have explained the temperature dependence of the Raman scattering spectra of $TlGaS_2$ crystals by the phase transitions at ~ 250 K and ~ 180 K. In our opinion, $TlGaS_2$ at low temperatures undergoes the transitions to a phase which has much weaker ferroelectricity in comparison with $TlGaSe_2$ and $TlInS_2$. And these transitions can be considered as isomorphic ones. However, there is no reliable information on the structural change at low temperatures determined by other experimental methods. One still needs to look for other experimental evidences to support the above interpretation.

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