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Phase Transitions in Highly Anisotropic Ternary TlGaSe₂ Crystals Studied by High-Resolution Optical Spectroscopy

A.M. Pashayev, K.A. Asgarov, K.R. Allahverdiyev

Azerbaijan National Aviation Academy (Baku, Azerbaijan)

For correspondence:

Kerim Allahverdiyev / e-mail: kerim.allahverdi@gmail.com

Abstract

The infrared and terahertz spectroscopy of TlGaSe₂ crystals has been studied over a wide temperature range (3 ÷ 325 K). The appearance of new phonon modes in the TlGaSe₂ spectra below a temperature of T = 120K was detected, due to a structural phase transition; the phonon parameters of the crystal under study revealed features at temperatures of 30K, 60K, and 92.5K. The observed anomalies have been explained as related to the reaction of phonons to the formation of an antisegnetoelectric structure and a change in the latter with temperature. Splitting of some phonon modes at 60K may occur due to symmetry breaking due to increased interaction between two polar sublattices.

Keywords: two-dimensional materials, layered semiconductors, lattice dynamics, phase transitions, ternary chalcogenides, phonons, infrared.

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Yüksək çözünlüklü optik spektroskopiya ilə araşdırılan yüksək anizotrop üçlü TlGaSe₂ kristallarında faza keçidləri

A.M. Paşayev, K.A. Əsgərov, K.R. Allahverdiyev

Azərbaycan Milli Aviasiya Akademiyası (Bakı, Azərbaycan)

Xülasə

TlGaSe₂ kristallarının infraqırmızı və terahertz spektroskopiyası geniş temperatur aralığında (3 ÷ 325 K) tədqiq edilmişdir. TlGaSe₂ spektrlərində $T = 120$ K temperaturunun altındakı yeni fonon rejimlərinin meydana gəlməsi, struktur faza keçidinə görə aşkar edilmişdir; tədqiq olunan kristalın fonon parametrləri 30 K, 60 K və 92,5 K temperaturda xüsusiyyətləri aşkar etmişdir. 60 K-də bəzi fonon rejimlərinin parçalanması, iki qütb alt sandıq arasındakı qarşılıqlı əlaqənin artması ilə əlaqədar simmetriyanın pozulması səbəbindən baş verə bilər.

Açar sözlər: iki ölçülü materiallar, laylı yarımkəçiricilər, kristal qəfəs dinamikası, faza keçidləri, üçlü xalkogenidlər, fononlar, infraqırmızı radiasiya.

Фазовые переходы в сильно анизотропных тройных кристаллах TlGaSe₂, исследованные методом оптической спектроскопии высокого разрешения

A.M. Пашаев, К.А. Аскеров, К.Р. Аллахвердиев

Азербайджанская Национальная академия авиации (Баку, Азербайджан)

Аннотация

Исследована инфракрасная и терагерцовая (ТГц) спектроскопия кристаллов TlGaSe₂ в широком диапазоне температур (3 ÷ 325 K). Обнаружено появление новых фоновых мод в спектрах TlGaSe₂ ниже температуры $T = 120$ K, обусловленное структурным фазовым переходом; фоновые параметры исследуемого кристалла выявили особенности при температурах 30 K, 60 K и 92,5 K. Наблюдаемые аномалии были объяснены как связанные с реакцией фононов на формирование антисегнетоэлектрической структуры и изменением последней в зависимости от температуры. Расщепление некоторых фоновых мод при 60 K может происходить из-за нарушения симметрии из-за усиления взаимодействия между двумя полярными подрешетками.

Ключевые слова:

двумерные материалы, слоистые полупроводники, динамика кристаллической решетки, фазовые переходы, тройные халькогениды, фононы, инфракрасное излучение.

Introduction

Two-dimensional ferroelectric TlGaSe_2 crystals have semiconductor, photoconductor, and photoelectric properties, which determines the variety of possibilities for their application in modern technologies, including active laser elements. At the temperature of liquid nitrogen and the application of an external electric field (~ 15 V), the photoelectric signal in this crystal increases significantly. For example, in the ultraviolet (UV) range of the spectrum, the signal increases by ~ 40 times, which opens up the prospects of using these crystals as UV detectors [1]. High photosensitivity also favors the creation of phototransistors [2]. High sensitivity to an external electric field makes it possible to use TlGaSe_2 as elements in microelectronics capable of changing their resistance depending on the electric charge flowing through it (memristors) and rectifiers [1, 2].

For various applications in ferroelectric memory elements, optoelectronics, and sensors, information about phase transitions in a crystal is important. The phase transition at a temperature of 100 K in TlGaSe_2 was first recorded by Raman, then information about the crystalline and ferroelectric states was refined by various methods, including measurements of dielectric properties, heat capacity, X-ray radiation, nuclear magnetic resonance (NMR), and others [3-5]. At temperatures $T = 120$ K and $T = 107$ K, two consecutive structural phase transitions occur. At $T_i = 107$ K, there is a transition of the first kind into the ferroelectric phase, accompanied by a fourfold increase in the unit cell. It is preceded by a transition of the second order at $T_i = 120$ K. In the temperature range of $107 \div 120$ K, an intermediate incommensurate state with a modulated wave vector $(\delta, \delta, 1/4)$, $\delta \approx$

0.02 is realized in units of the inverse lattice [6]. However, there is data on the modulation vector $(\delta, 0, 1/4)$, where $\delta = 0.04$ [7].

In addition to the well-known transitions at T_i and T_c , phase transitions at various temperatures have been discussed [8]. Several papers have suggested the coexistence of two competing polar sublattices in TlGaSe_2 [9, 10]. This is confirmed, in particular, by the study of the dielectric properties of a crystal in a static electric field. From this point of view, anomalies in the heat capacity curves could be interpreted both in the low-temperature phase ($T = 100$ K) and at high temperatures. In addition, based on dielectric measurements, the phase transition at $T^* = 65$ K was considered in the framework of a model of strongly interacting two polar sublattices. However, studies of the crystal structure and dynamics of the TlGaSe_2 crystal lattice at low temperatures are currently insufficient. The present work is aimed at eliminating this gap and contains a detailed study of the temperature dependence of TlGaSe_2 spectra, which can be used for analyses of the phase transitions.

In our work, crystals grown by the Bridgeman method in evacuated quartz ampoules were used [3, 5]. To record the transmission spectra, thin plates on magnetic tape, oriented in the cleavage plane, with a thickness of up to $10 \mu\text{m}$, were used. Thus, all the presented spectra were recorded with the polarization of the incident radiation $E \perp c$ (previously, new lines at phase transition temperatures were recorded only in spectra with such polarization). The spectra were recorded on a Bruker IFS 125HR spectrometer (Bruker Optik GmbH, Ettlingen, Germany) with a spectral resolution of 0.5 cm^{-1} in the spectral range of $10 \div 100 \text{ cm}^{-1}$ and 0.8 cm^{-1} in the range of $100 \div 400 \text{ cm}^{-1}$. The crystal was

cooled in a Sumitomo SRP096 closed-loop helium cryostat; the temperature range was $3 \div 325$ K. A helium-cooled bolometer was used as the signal sensor.

TlGaSe₂ crystals at room temperature have the space group C_{2h}^6 . The crystal structure is shown in Figure 1. GaSe₄ tetrahedra are combined into Ga₄Se₁₀ polyhedra, each polyhedron is connected to four neighboring ones through a common Se atom, forming a layer lying in the (001) plane. Each neighboring layer is rotated relative to the previous one by an angle of 90° (L1 and L2 in the Figure. 1).

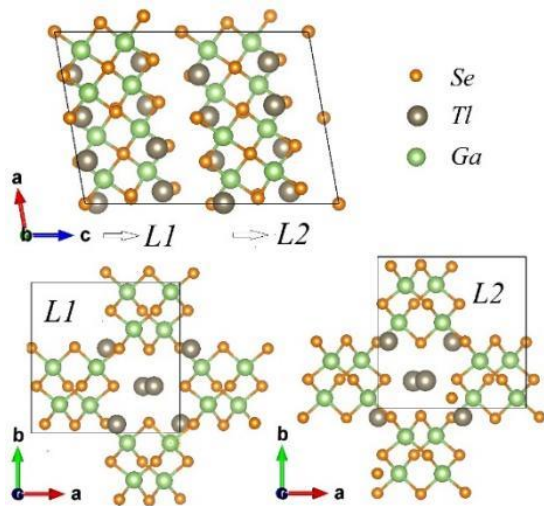


Figure 1 – The unit cell of the TlGaSe₂ crystal in the paraelectric state: a projection along the b- axis and two projections along the c- axis corresponding to two layers of combined Ga₄Se₁₀ polyhedra rotated relative to each other by an angle of 90°.

Tl atoms occupy the voids formed between the combined Ga₄Se₁₀ polyhedra. The unit cell contains two layers. The layer has tetragonal symmetry, but due to the displacement of each layer relative to the other by 0.25 (a + b) during the transition from one layer to another, tetragonal symmetry is broken, thus, the structure of the entire crystal is reduced to monoclinic. In real crystals,

displacement of Ga₄Se₁₀ polyhedra of neighboring layers is observed. At the same time, there is also a good cleavage parallel to the plane of the layer (001), and the Ga₄Se₁₀ polyhedra are not susceptible to splitting. The symmetry analysis of the C_{2h}^6 monoclinic cell leads us to the following mode distribution: $G = 23A_g + 25B_g + 23A_u + 25B_u$, of which 45 modes: $22A_u(z)$ and $23B_u(x,y)$ are IR-active.

It is difficult to analyze the symmetry of the real structure. In [11], instead of a real disordered crystal, a model crystal was considered in which neighboring layers were connected to each other using an inversion operation, which led to a D4h group for the entire cell. The mode distribution in this case has the form: $G = 7A_{1g} + 3A_{2g} + 8B_{1g} + 2B_{2g} + 14E_g + 2A_{1u} + 8A_{2u} + 3B_{1u} + 7B_{2u} + 14E_u$, of which $7A_{2u}(z) + 13E_u(x, y)$ oscillations are IR-active. Figure 2 shows the transmission spectra of a TlGaSe₂ crystal in the $10 \div 300$ cm⁻¹ spectral region.

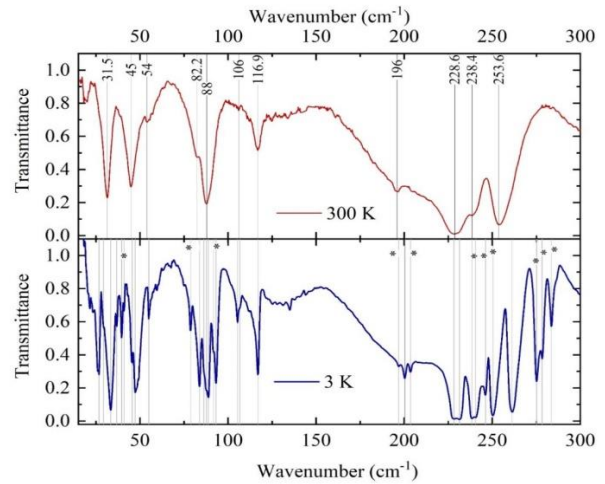


Figure 2 – Transmission spectra of TlGaSe₂ crystal at temperatures of 3 and 300 K. Asterisks mark new lines that appear at $T_i = 120$ K. The vertical lines indicate the frequencies of all recorded phonons (in particular, the components observed during phonon splitting at temperatures below 60 K). The labels above the vertical lines indicate the frequencies of the corresponding phonons at room temperature.

The spectrum recorded at room temperature is in agreement with the spectra given in the work [12]. At room temperature, 13 lines are observed in the spectrum, which corresponds to the results given in [11]. At a temperature of $T_i = 120$ K, new weak modes appear in the spectrum, the intensity of which gradually increases with a further decrease in temperature. A similar phenomenon occurs during phase transitions of the second kind. With a further decrease in temperature, some lines split. The detailed temperature dependence of the phonon spectra will be discussed below. The frequencies of all modes observed at temperatures $T = 300$ K, $T = 107$ K, and $T = 3$ K are shown in Table 1.

Phonons associated with translational oscillations of Tl ions and Ga₄Se₁₀ complexes are active in this range. The intense mode is observed at 31.5 cm⁻¹ at room temperature. Two new modes can be observed at temperatures $T < T_i = 120$ K: the weak mode 38.8 cm⁻¹ and the wide mode 23 cm⁻¹ (data are given for $T = 107$ K, as indicated in Table 1).

The weak mode splits at temperatures around 60 K (as can be seen from the inset of Figure 3 (a)), while the wide mode abnormally hardens as the temperature decreases. The intense mode of 31.5 cm⁻¹ also exhibits a temperature dependence: upon cooling, it narrows down to the temperatures of phase transitions, then begins to widen and acquires a complex contour (as seen in the left inset of Figure 3 (a)). The peculiarities of these two modes will be considered below.

The lowest frequency mode most likely refers to the so-called rigid layer modes or interlayer modes resulting from the addition of acoustic branches of the Brillouin zone in layered compounds.

Table 1 – Phonon mode frequencies (cm⁻¹) determined from reflection spectra at temperatures $T = 300$ K, $T = 107$ K, and $T = 3$ K. Index (a) indicates weak modes. New modes that appear in the spectra below the temperature $T_i = 120$ K are highlighted in bold. Index (b) indicates the components that are observed during splitting of respective phonons at temperatures below 60 K.

300 K	107 K	3 K
-	-	26.7
-	29.4 ^a	29.4 ^a
31.5	32.4	33.4 ^a 36.8 ^{a,b}
-	38.8	39.6 ^{a,b} 41 ^{a,b}
-	42 ^a	42 ^{a,b} 43 ^{a,b}
45	46.5 49 ^a	45.5 ^b 47.3 ^b 48.4 ^{a,b} 49.1 ^{a,b}
54 ^a	54.9	55
-	78.6	78.7
82.2	82.9	83.8
88	87.4	86.3 ^b 87.6 ^b 88.8 ^b
90.8 ^a	92.5	91.8 ^b 93.2 ^b
106	106 ^a	105.4 ^b 106.7 ^a
116.9	116.9	117
-	-	196.9 ^a
196	198.7	200.3
-	-	203.6 ^a
228.6	231.5	228.3 ^b 231.3 ^b
-	239	238.4 ^b 240.5 ^b
238.4	-	-
-	245	246.1
-	250.7	250.5
253.6	258.5	261.2
-	274.3	275.1 ^b 278.3 ^b
-	282.1	283.6 ^b 286.6 ^b

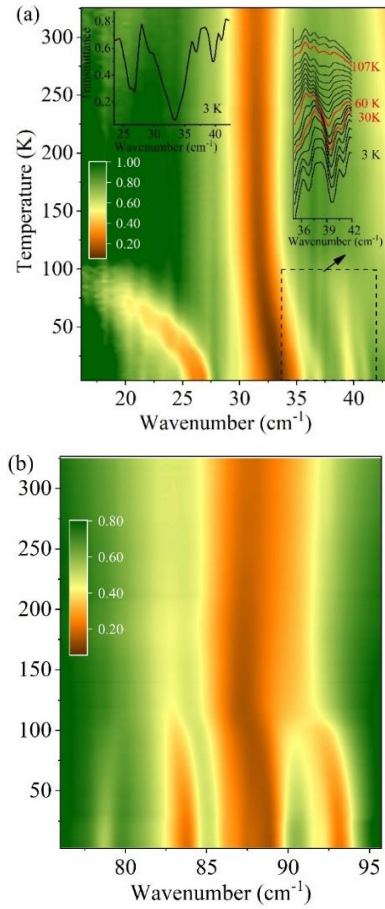


Figure 3 – Intensity maps of the TlGaSe₂ crystal transmission spectra in the ranges 15 ÷ 45 cm⁻¹ (a), 75 ÷ 95 cm⁻¹ (b) at temperatures of 3 ÷ 300 K. The left inset of Figure (a) shows the transmission spectrum at a temperature of 3 K. The right-hand inset of Figure (a) shows the transmission spectra in the dotted area of the intensity map.

Such modes are characterized by a strong and anomalous nonmonotonic temperature dependence of the parameters, which is sensitive to ferroelectric and magnetic states.

In the process of studying the temperature dependence of the ferroelectric soft mode by submillimeter dielectric spectroscopy, the splitting of the soft mode into two components have been considered [13]. The first, longer-wavelength component exhibits the behavior of the classical ferroelectric soft mode. The square of its frequency decreases linearly with decreasing

temperature, approaching zero as it approaches the phase transition point. The shorter wavelength component behaves nonmonotonously: as the temperature decreases, its frequency first decreases, then increases and continues to increase as it approaches T_i . In the present experiment, the choice of spectral region was limited by the capabilities of the beam splitter: at frequencies nearly about 15 cm⁻¹, the spectra were noisy, and the region < 15 cm⁻¹ was inaccessible.

No measurements of the split component in the ferroelectric phase were carried out. Thus, we do not have a complete picture, however, it is likely that we observed the same mode, but in a different temperature range. The simulation of the dispersion of the acoustic branch, measured by the method of inelastic neutron scattering in the [001] direction in the paraelectric phase, allowed us to estimate the frequency of the rigid layer mode at 15 cm⁻¹ (observed also in combinational light scattering spectra) for the case of two layers in a unit cell. This corresponds to the high-frequency component. Figure 3 (b) shows a map of transmission spectrum intensities in the range of 75 ÷ 95 cm⁻¹ at the temperature 320 K.

The corresponding spectra in a narrower temperature range of 3 ÷ 165 K are shown in Figure 4 (a). At room temperature, there is an intense mode of about 90 cm⁻¹ and an overdamping mode of 82 cm⁻¹, which narrows strongly and increases in intensity below T_i . The new mode appears at 78 cm⁻¹ at temperatures below T_i , and when cooled, its intensity increases smoothly, but the frequency does not change.

The intense mode around 90 cm⁻¹ consists of two components with peaks at 88 cm⁻¹ and 90.8 cm⁻¹.

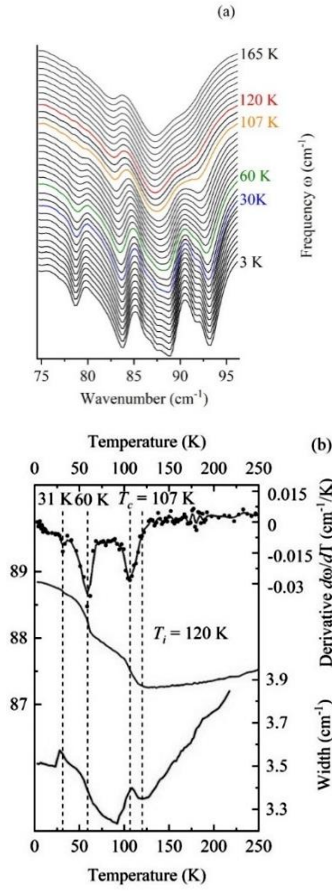


Figure 4 – The transmission spectra of the TlGaSe₂ crystal in the range 75 ÷ 95 cm⁻¹ (a). The spectra at T_i = 120 K, T_c = 107 K, as well as the spectra at T* = 60 K and T = 30 K, at which features in the dependences of the parameters of the most intense mode in this range are observed, are shown in different colors.

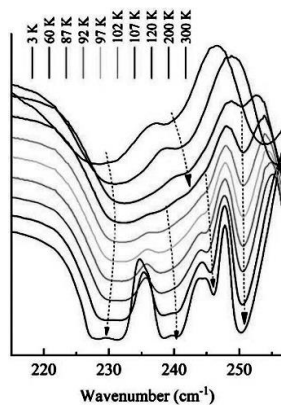


Figure 5 – TlGaSe₂ transmission spectra in the temperature range of 3 ÷ 300 K, in the frequency range of 215 ÷ 255 cm⁻¹. The arrows are shown for clarity

The highest frequency component of overdamping at room temperature narrows strongly at T < T_i = 120 K and abruptly shifts to a higher frequency region. This is most likely directly related to the interlayer ordering and the increase in the corresponding force constants. Upon further cooling, the mode shows practically no temperature dependence (Figure 4b).

Figure 5 shows the transmission spectra of a TlGaSe₂ crystal in the temperature range of 3 ÷ 300 K in the frequency range of 215 ÷ 255 cm⁻¹. The main contribution to the spectrum in this range is made by internal vibration of Ga₄Se₁₀ complexes.

At room temperature, two modes with frequencies of about 230 and 240 cm⁻¹ are observed. As the temperature decreases, as it approaches T_i = 120 K, the modes expand and spread out, and at T_c = 107 K they merge into one wide band, on which about four weaker peaks can be distinguished. In addition, at T_i = 120 K, a line of about 250 cm⁻¹ appears. Below T_c = 107 K, the wide band smoothly splits into three peaks with frequencies around 230, 240, and 245 cm⁻¹. Below T* = 60 K, each of the peaks at 230 and 240 cm⁻¹ is partially splits into two components. The most noticeable difference between the temperature behavior of these modes and the temperature regime of the band at 88 cm⁻¹ is the broadening of the bands at T > T_i = 120 K (the 88 cm⁻¹ line begins to widen only below the transition point to i).

Conclusion

Detailed temperature studies of the IR transmission spectra of a TlGaSe₂ crystal with incident light polarization E ⊥ c was carried out. Data processing, which included the construction of temperature dependences of

phonon mode parameters, made it possible to identify a number of phase transitions. In addition to the well-known phase transitions at $T_i = 120$ K and $T_c = 107$ K, we recorded a number of anomalies at $T = 93$ K, $T^* = 60$ K and $T = 30$ K. The first feature is probably related to the transition of the crystal to a peculiar antiferroelectric state, which was discussed earlier in [9,10]. Below $T^* = 60$ K, we detected splitting of some lines in the spectrum, which is most likely a sign of a

decrease in symmetry due to a change in the interaction of two polar sublattices in TiGaSe_2 . Further calorimetric, dielectric, and X-ray studies of the crystal are needed to determine the nature of the anomaly at a temperature of 30 K.

Conflict of Interests

The authors declare there is no conflicts of interests related to the publication of this article.

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