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TERAHERTZ SPECTRA OF LAYERED TlInS₂ CRYSTALS

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Abstract: Vibrational spectra of TlInS₂ crystals in the terahertz frequency range (0.1–3 THz) were acquired and analyzed. An observed low-frequency band is attributed to the libration oscillations of nanolayers (so-called boson peak). A correlation between the coherent low-frequency oscillation and a disordered character of the crystal structure is shown. A conclusion is made on the presence of a topological disorder that manifests itself on the layered subsystem level.

Keywords: nanolayers, terahertz frequency, crystal structure

1. Introduction

Advances in modern solid state physics and solid state electronics tend to rely upon the use of new physical phenomena, which are based on the disordered character of the structure of solid matter. With the crystallographic symmetry of arrangement of centers of the structural matrix remaining perfect, a disorder may arise due to the infringement of periodical occupation of these centers (solid solutions), of electron spin orientations (spin disorder), etc. Disordered materials comprise a wide class of objects that have specific features in low-energy vibrational spectra.

The relaxation mechanism of dielectric properties is changed and certain peculiarities in the charge transfer process are observed in these materials. Recently, conducting materials of limited dimensionality, topological disordered systems, and nanocomposites (low-dimensional systems) have been intensively studied, in which the quantum Hall effect, giant magnetoresistance, giant dielectric relaxation, relaxor behavior, and other phenomena are observed. Terahertz spectroscopy methods play an essential role among modern methods of investigation of these materials.

In this paper, results of studies of the transmission spectra of a TlInS₂ crystal in the terahertz range (0.1–3 THz) are presented; the nature of the observed lines and their relation to the structural peculiarities are analyzed.

2. Experimental

Single crystals of TlInS₂ were grown from melt bidirectional crystallization (Bridgman–Stockbarger method) from high-purity chemicals: Tl (99.999%), In (99.9999%), and S (99.99%; sulfur was additionally rectified by sublimation in vacuum). The synthesis was conducted in evacuated quartz ampoules by melting initial components (Tl, In, and S) taken in the stoichiometric amounts corresponding to the composition TlInS₂. Homogeneity of obtained samples was controlled by differential thermal analysis and X-ray phase analysis [1–3].

Transmission spectra were measured using a standard scheme for time-domain terahertz spectroscopy (THz-TDS) [4–9]. Femtosecond titanium sapphire laser (60 fs FWHM) with a modulated delay line and pulse repetition rate of 75 MHz was used in the experiments.

The emitter and receiver were made from GaAs. Four gilded parabolic mirrors were used in the measurements. The terahertz beam was split into two beams; the mechanical delay line allowed achieving the maximal frequency resolution of 3 GHz. Duration of a THz-pulse was less than 1 ps in the measurements of transmission spectra. Spectra after Fourier transform were expanded to 5 THz so that the signal became less than the noise. The maximal dynamic range was about 60 dB in the 500 GHz range.

In a classical variant of THz-TDS, the wave shapes in the time domain of the incident and passed through the sample signals are acquired. Then numerical Fourier transform of both signals is made. A combined technique was employed in the measurements of transmission and reflection THz-TDS spectra [4]. In the transparency spectral range, the refraction index n was obtained with a sufficient accuracy based on the transmission data. Errors were then corrected using the data of reflection and transmission spectra; analogous procedure was performed in other transparency ranges of the measured spectrum. Thus, the n value was defined accurately from transmission spectra in the transparency range, while in the ranges of intensive absorption the data on the refraction index was taken from the reflection spectra. In a similar manner, the absorption coefficient was found based on the transmission spectra in the transparency range. The refraction index was also estimated in the whole spectral range using the Kramers–Kronig relations.

3. Results and discussion

Structural data [1–3] show that TlInS₂ at the room temperature has a monoclinic lattice described by the $C2c \equiv C_{2h}^6$ spatial group and unit cell parameters of $a \approx b = 10.77 \text{ \AA}$, $c = 15.64 \text{ \AA}$, and $\beta = 100^\circ$. The unit cell consists of $Z = 16$ formula units of TlInS₂ (two layers); since the unit cell is base-centered, a primitive cell contains $Z = 8$ formula units.

The main structure block is a tetrahedral In₄S₁₀ complex made of four elementary InS₄ tetrahedra (Fig. 1). The In₄S₁₀ complexes are bound through common selenium atoms into a quasi-two-dimensional net in the ab plane. Thallium ions occupy trigonal-prismatic vacancies between the InS₄ complexes. The two layers of the unit cell are rotated by 90° with respect to each other and are transformed into each other by an operation of inversion.

The lowest frequency in layered crystals is usually determined by rigid-layer oscillation modes. In the presence of heavy atoms (such as thallium) or complexes (InS₄, In₄S₁₀), however, optical branches of corresponding outer modes may also have a sufficiently low frequency. Due to crossing and anticrossing of these branches in the low-symmetry zone, the resulting dispersion pattern is quite complicated.

Layered crystals of the TlInS₂ family are known to exist as several polytypic modifications differing by the number of layers in the unit cell [1–3, 10]. A unit cell of TlInS₂ contains eight formula units, which means that there should be 93 optical modes in its phonon spectrum; however, no more than 25 optical modes are observed in practice in infrared and Raman spectra [10–13]. It is also worth noting that in various measurements (optical, dielectric, electrical) anisotropy in the ab plane is never observed, though it must exist in the case of monoclinic crystal symmetry.

Discrepancy between the results of X-ray analysis and the data of spectroscopic, dielectric, and electrical measurements allow suggesting the presence of one dimensional disorder along the pseudo tetragonal axis c , which is connected with violations in joining of the layers [10].

For layered crystals containing n layers in a unit cell, the Brillouin zone is $1/n$ times as large as the Brillouin zone of a monolayered crystal along the [001] direction (perpendicular to the layers). If interaction between the layers is weak, the dispersion curves of an n -layered crystal can be obtained by a simple representation of the dispersion curves of the single-layered polytype. As a consequence of representation of the acoustic branches, rigid-layer modes appear in the low-

frequency spectrum. This mechanism is probably responsible for the presence of multiple lines in the reflection spectra of the TlInS₂ crystal [10].

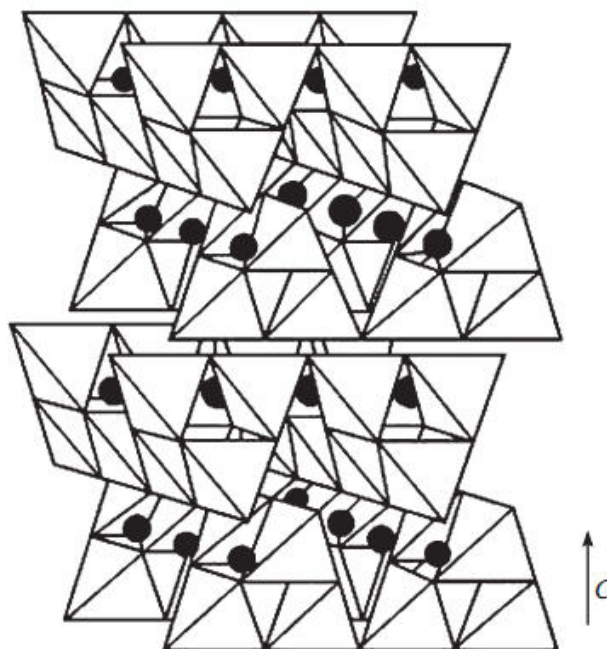


Fig. 1. Crystalline structure of TlInS₂. Circles represent the Tl ions; tetrahedra InS₄ and In₄S₁₀ complexes

The rigid-layer modes usually possess the maximal value of the Gruneisen parameters. Authors of [11] used a linear chain model for identification of experimental lines with respect to the motion types. It was shown that lines with frequencies below 70 cm⁻¹ (2.1THz) correspond to the translation-type modes.

Transverse acoustic branch in the [001] direction was measured in TlGaS₂ (a structural analogue of TlInS₂) by inelastic neutron scattering [12]. Corresponding frequency of the rigid-layer mode can be estimated based on these measurements. It is known that the dispersion relation for an acoustic phonon is described by the equation

$$\omega^2 = 2/M \sum_n f_n [1 - \cos(nkd)] \quad (1)$$

Where f_n is the force constant for the layers placed at the distance of nd from each other (d is the distance between neighbor layers), and M is the mass of the unit cell. If the contribution from the interaction between the closest neighbors dominates over the other interlayer forces, then the first term in (1) is the biggest one, and the acoustic branch has a sine shape

$$\omega = 2(f_1/M)^{1/2} \sin(kd/2) \quad (2)$$

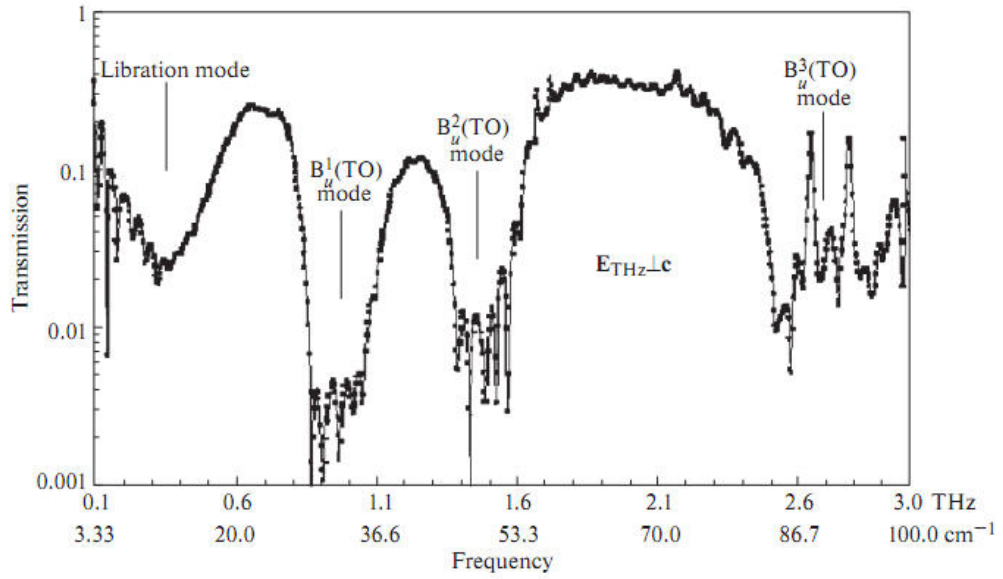


Fig. 2. Transmission spectrum of with the polarization $E_{\perp c}$

This expression can help to calculate the frequency of the shift rigid-layer mode, assuming that the rules of representation of the branches are fulfilled. The best results of approximating the data from [13] by Eq. (2) show that the frequencies of the mentioned modes are close to 14–15 cm^{-1} (~ 0.5 THz).

According to the factor group analysis, the mechanical representation for TlInS_2 in the C_{2h}^6 phase has the following form:

$$\Gamma_{vib} = 24A_u + 24B_u + 24A_g + 24B_g \quad (3)$$

The mode frequencies which are observed in the submillimeter range (0.2–0.6 THz) [13] are close to the estimated frequencies of the shift modes at room temperature. On the other hand, the rigid-layer modes are transformed by even representations of C_{2h} factor group (3) due to the presence of the inversion center, and hence they should not be observed in IR spectra. Therefore, the authors of [13] suppose that the soft mode in the submillimeter spectral range corresponds to another optical oscillation with the A_u symmetry, probably of a libration type.

The spectrum of lattice vibrations of the TlInS_2 crystal was studied in detail by Raman scattering, far-infrared spectroscopy, and inelastic neutron scattering [10]. In this paper, a transmission spectrum of a TlInS_2 crystal measured in the terahertz range by means of time-domain spectroscopy is presented. The absorption lines observed until 20 cm^{-1} (~ 0.6 THz) are transverse (TO) modes with the B_u symmetry, which coincide with the frequencies measured in infrared reflection spectra [10]. These are the frequencies $B_u^1(\text{TO}) = 1$ THz (33.3 cm^{-1}), $B_u^2(\text{TO}) = 1.5$ THz (50.0 cm^{-1}), and $B_u^3(\text{TO}) = 2.7$ THz (90.0 cm^{-1}) of the translational modes of the TlInS_2 crystal.

In the vibration spectrum of the TlInS_2 crystals shown in Fig. 2, a low-frequency line appears ($0.2 \text{ THz} \approx 7 \text{ cm}^{-1}$), which was not observed earlier in far-infrared reflection spectra of crystalline TlInS_2 [10]. As was noted above, this mode is probably connected with libration-type oscillations of heavy layers formed by InS_4 and In_4S_{10} complexes. Frequency dependences of the refraction index (solid lines) and absorption coefficient (dotted line) of the TlInS_2 crystal are plotted in Fig. 3.

It is evident from Fig. 3 that TlInS_2 crystals show a prominent absorption in the terahertz band due to the single phonon resonance lines (frequencies of the single phonon bands are shown in Fig. 2) and an intensive absorption peak which is usually connected with the boson peak.

Low-frequency dynamics of disordered solids differs from that of ordered crystals and possesses a number of peculiarities due to an excessive density of vibrational states (as compared to the density in the Debye model) [14–19]. This behavior of the density of vibrational states is typical of strongly disordered systems: amorphous, vitreous solids, and polymers. A similar feature is observed in ternary thallium chalcogenides, which points to the disordered character of their crystal structure. Excessive density of vibrational states is associated with the appearance of a low-frequency mode (boson peak) in infrared and Raman spectra [16, 17].

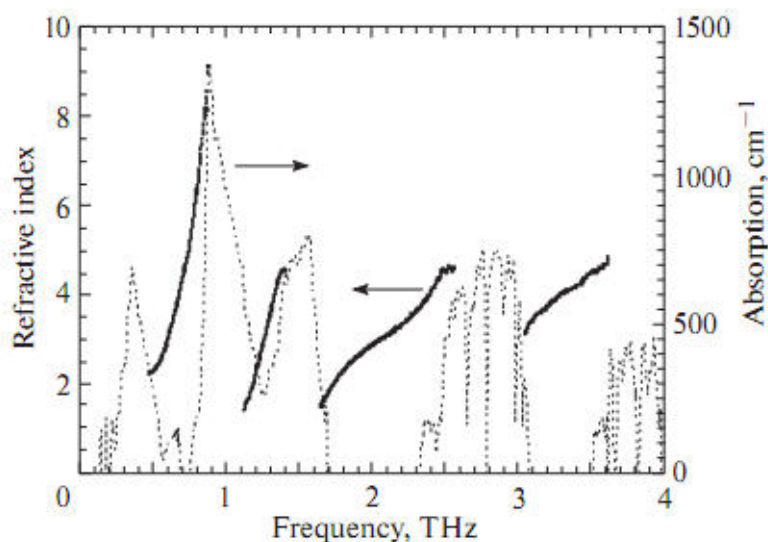


Fig. 3. Frequency dependence of the refraction index (solid lines) and the absorption coefficient (dotted lines) of the $TlInS_2$ crystal with the polarization $\mathbf{E} \perp \mathbf{c}$.

These modes, which appear at frequencies lower than the phonon frequency, are generally accepted to arise due to quasilocal vibrational modes [13]. The nature of these modes is being widely discussed. Some authors suggest that they are local oscillations of structural formations: fractals, domains, and nanosized inhomogeneities of topological disorder [15–19].

Others ascribe these modes to correlated oscillations of molecular clusters. A correlation between the boson peak and relaxation properties of vitreous solids is also considered [17].

Investigations of physical properties of crystals of layered ternary thallium chalcogenides with a general composition $A^3B^3C_2^6$ reveal some peculiarities typical of strongly disordered systems. These are:

- 1) Hopping character of conductivity described in terms of the Mott approximation, which was developed for amorphous systems.
- 2) Presence of superionic conductivity and S-shaped volt-ampere characteristics, which are observed in semiconductors with a large amount of defects or dopants.
- 3) Wide temperature ranges of the relaxor behavior of dielectric spectra, described with the Vogel–Fulcher laws (this behavior is typical of strongly disordered systems).
- 4) Existence of multiple polytypic modification and a mix of polytypes, which results in pseudo tetragonal behavior of monoclinic crystals (in particular, isotropic optical spectra in the cleavage plane).
- 5) Wide temperature ranges with incommensurate super-structural translations, which are revealed in neutron diffraction and X-ray studies.
- 6) Experimental studies of the phonon state density in $TlSe$ crystals in the range of elastic oscillations (made by incoherent inelastic neutron scattering) yield over estimated values as

compared to the calculated ones (obtained in the approximation of rigid ions or in the first principles calculations).

Note also that the crystals of the $A^3B^3C_2^6$ family have a wide range of homogeneity [2]. According to the phase diagram, the segregation coefficient in the homogeneity range is less than a unit. Therefore, deviation from the stoichiometry is quite probable in the growing of single crystals; that is, a certain temperature range exists between the liquidus and solidus points in compositions based on $TlInS_2$. This is, apparently, the reason for the one-dimensional disordered character of the structure of these materials: appearing of polytypes, mix of polytypes, incommensurate structures, and superstructures. Thus, the structure within the layers of these crystals corresponds to the stoichiometric relation, but there are different variants of joining the layers. This suggestion may be proved by incommensurate superstructures observed in neutron diffraction spectra, which can be described as alternating commensurate and disordered (discommensurate) regions.

Thus, the crystals of the $TlInS_2$ family possess a mesoscopic structure with periodically alternating commensurate and discommensurate layers. These crystals comprise a vast class of ternary layered semiconductors. A typical feature of these layered crystals is a rich low-energy spectrum (with respect to the phonon frequencies) caused by oscillations of heavy translational-nonequivalent layers, transforming into each other by the operation of inversion. The presence of such a big number of universal correlations typical of disordered systems and observed in the $TlInS_2$ crystals allows suggestion that they result from the common structural features of these materials. Compounds of the $TlInS_2$ family are not just "bad" crystals or amorphous systems; most probably, in this case we have topologically disordered mesoscopic structures with a characteristic spatial scale. "Chaos" in these systems does not possess an absolute character: experiments on neutron and X-ray diffraction, and vibrational spectra (Raman scattering, infrared absorption, inelastic coherent neutron scattering) show that the periodical arrangement of atoms (translational order) is present on the scale of several coordination spheres and is violated on larger distances.

4. Conclusions

The investigated class of compounds should be referred to as topologically disordered solids. The disorder arises in the topology of their layer (or chain) subsystem; in other words, in spatial (geometric) arrangement of the structural complexes (layers and chains), which are responsible for the low-frequency dynamics of the studied materials.

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ОСОБЕННОСТИ ТЕРАГЕРЦОВЫХ СПЕКТРОВ СЛОИСТЫХ КРИСТАЛЛОВ TlInS_2

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Резюме: Получены и проанализированы колебательные спектры кристаллов TlInS_2 в терагерцовой (0,1-3 ТГц) области. Наблюдаемая низкочастотная полоса связывается с либрационными колебаниями нанослоев (“бозонный пик”). Показана связь когерентного низкочастотного колебания с неупорядоченным характером структуры кристалла. Делается вывод о наличии топологической неупорядоченности, которая проявляется на уровне слоистой подсистемы.

Ключевые слова: нанослои, терагерцовые спектры, структуры кристалла

LAYLI TlInS_2 KRİSTALININ TERAHERS SPEKTRİNİN XÜSUSİYYƏTLƏRİ

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Xülasə: Terahers (0,1-3 THs) tezlik oblastında TlInS_2 kristalının rəqsi spektri alınmış və tədqiq edilmişdir. Nanolayların (bozon pikləri) «librasion» rəqslərinin aşağı tezlikli zolağın rəqsləri ilə bağlılığı müşahidə olunmuş. Göstərilmişdir ki, koherent aşağı tezlikli rəqslər kristalın nizamsız quruluşlu xarakteri ilə bağlıdır. Bu da laylı alt sistemlər səviyyəsində özünü göstərən topoloji nizamsızlığın olması nəticəsinə gəlməyə imkan verir.

Açar sözlər: nanolay, terahers spektri, kristal quruluş