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EFFECT OF PRESSURE AND THERMAL EXPANSION ON THE OPTICAL ABSORPTION EDGE AND DEFORMATION POTENTIAL MODEL IN A LAYERED TLGAS2 CRYSTAL

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Annotation: The influence of pressure and thermal expansion on the optical absorption edge and the model of the deformation potential in a layered TlGaS2 crystal are investigated. It was found that compression along the C axis leads to an increase in Eg (as in AIIIBVI crystals) by ~10 meV at P = 1kbar. At the same time, the layer stretching leads to a decrease in Eg by ~13 meV – as a result, Eg decreases by ~3 meV.

Key words: thermal expansion, optical absorption edge, model of deformation potential, compression, stretching, deformation, phenomena.

Introduction: The optical properties of $TlGaS_2$ single crystals in the region of the fundamental absorption edge were studied in [1-5], but the question of the presence of indirect transitions in these crystals remains controversial. Although the analysis of the spectral dependence of the absorption coefficient [2] indicates the possibility of the existence of such transitions, it was not possible to obtain proof of this at low temperatures.

At 77K, an exciton absorption band with λ = 476.8nm and a half-width of 5nm was found, which has a positive temperature coefficient of $1 \cdot 10^{-4}$ eV/K. This band was polarized mainly in $\mathbf{E} \perp \mathbf{C}$. The dispersion of the refractive index near the edge of the fundamental absorption band was also studied [5], taking into account multiple reflection and intrinsic interference.

The authors of [6] studied the absorption, exciton luminescence, and Raman spectra in $TlGaS_2$ single crystals at a temperature of 1.8 K. Multiband photoluminescence in the region of 2.48 - 2.54 eV, due to radiative recombination of an indirect exciton with phonon emission, was found. The energy positions of direct (2.606 eV) and indirect (2.540 eV) excitons are found, their binding energies are 23 and 1 meV, respectively.

It was shown in [7] that when a $TlGaS_2$ single crystal is compressed perpendicular to the layers, the exciton band shifts towards lower energies, but its temperature behavior in the range 4.2 – 120 K does not change.

In [8], as a result of a series of experiments on optical absorption using unpolarized and linearly polarized light, it was found that the shape of the absorption spectra of thin $TlGaS_2$ samples is practically independent of the orientation of the electric vector of light incident on the sample. In the same work, the sign of the deformation potential (positive) for the band gap of $TlGaS_2$ single crystals was experimentally determined.

Detailed studies [9] of the Raman spectra in $TlGaS_2$ revealed low - frequency phonons with energies of 4; 6 and 9cm^{-1} which apparently correspond to weak interlayer bonds of this crystal. It is assumed that these low - frequency phonons correspond to the excitation of bending vibrations of the $TlGaS_2$ crystalline layers.

The anomalous temperature dependence of the energy position of the exciton peak in $TlGaS_2$ was studied in [8, 9]. Taking into account that the exciton binding energy changes slightly with temperature, it can be argued that the band gap of $TlGaS_2$ also has a positive temperature coefficient.

The electron-phonon interaction cannot explain this behavior of E_g with temperature; therefore, this is the contribution of thermal expansion, i.e. lattice parameter changes. Comparing the temperature dependences of the coefficients of linear thermal expansion in $TlGaS_2$ crystals with the behavior of $E_{exp}(T)$, the authors of [8] came to the conclusion that the thermal expansion of $TlGaS_2$ crystals not only makes a significant contribution to the dependence $E_{exp}(T)$ at sufficiently high temperatures $T > 150$ K, but also determines its form at low $T < 100$ K temperatures.

The effect of hydrostatic pressure up to 1.2 GPa on the absorption coefficient spectrum of $TlGaS_2$ near the fundamental edge at room temperature was studied in [10]. It is shown that in this pressure range the shape of the optical absorption edge, determined by direct allowed transitions, does not change, the isoabsorption curves have a linear dependence on pressure, and in the pressure range from 0 to 0.3 GPa, $dE_g/dP = -(7.25 \pm 0.25)\ 10^{-11}$ eV/Pa, and for pressures from 0.4 to 1.2 GPa, $dE_g/dP = -(8.5 \pm 0.25)\ 10^{-11}$ eV/Pa.

Thus, the hydrostatic pressure leads to a shift of the optical absorption edge of $TlGaS_2$ single crystals to longer wavelengths. It is known from the above review results that there are a fairly large number of works in the literature devoted to the study of the optical properties of $TlGaS_2$ single crystals. Despite the large number of studies on the optical properties of $TlGaS_2$ single crystals there are almost no data in the literature on deformation effects in $TlGaS_2$ single crystals. The solution of these problems is an urgent problem of solid state physics, and it requires the results of the latest research in the field of optoelectronics, which is directly related to the development of the technical capabilities of nanotechnology.

Therefore, the purpose of this study was to study the influence of pressure and thermal expansion on the optical absorption edge and the deformation potential model in a layered TlGaS2 crystal.

Experimental technique: Investigations of the optical properties of semiconductors were carried out using a facility developed by us based on KSVU -6M and a helium cryostat "UTREX" (Fig. 1) with automatic temperature stabilization in the range of 4 - 300K (stabilization accuracy was ± 0.01K). The cryostat had a specially made holder for carrying out optical studies of crystalline samples with the application of uniaxial controlled pressure (Fig. 2).

Samples for measurements were obtained by cleaving single - crystal blocks onto plane - parallel plates, for which the optical axis is normal to the surface and had the form of thin plates with a thickness of 10 to 100 μk [11, 12].

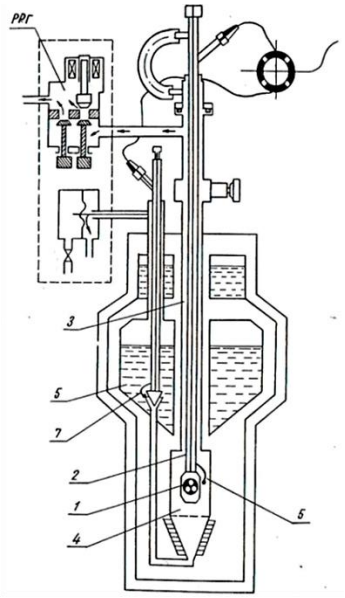

Fig.1. Schematic diagram of the optical cryostat "UTREX": 1- sample, 2 - holder for adjusting the sample, 3 - channel for the release of helium vapor, 4 - working chamber for the sample, 5 - liquid helium, 6 - thermocouple for maintaining the set temperature 7 - automatic valve for launching liquid helium

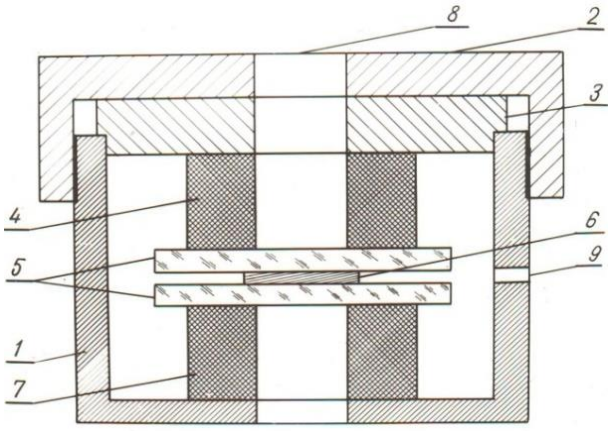

Fig.2. Schematic view of a special holder for carrying out optical studies of crystalline samples with the application of uniaxial controlled pressure: 1 - a cylindrical body made of metal, 2 - a cover screwed onto it, 3 - a metal washer for transferring deformation to the master piezoceramic, 4 - a master piezoceramic of a cylindrical shape, 5 - conductive glasses, 6 - a sample, 7 - a receiving piezoceramic, 8 - a hole for light supply, 9 - a small hole for the output of contacts from conductive glasses.

Results of the study and their discussion: It is no coincidence that we begin our analysis of deformation phenomena in ternary layered semiconductors with $TlGaS_2$. The point is that in these crystals, apparently, no phase transitions are observed; in any case, no serious anomalies of the main physical parameters have been found in the temperature range of 0 – 300 K. The optical absorption edge of $TlGaS_2$ single crystals is formed by direct allowed transitions, and here there is a clear exciton peak traceable to fairly high temperatures (160 - 180 K), and, therefore, there are reliable data on the temperature dependence of the band gap, which, moreover, exhibits anomalous temperature dependence, which is very rare in semiconductors [8].

It is known [10] that, under the action of hydrostatic pressure, the band gap of this crystal decreases with a baric coefficient of $-7.25 \cdot 10^{-6}$ eV/bar, and this dependence is monotonic, without any peculiarities. Using this result and assuming that the crystal has uniaxial symmetry, which is acceptable, since **a≈b**, we can write a simple equation for changing the band gap under hydrostatic compression:

$U_{zz} \cdot D_{||} + 2U_{xx} \cdot D_{\perp} = P \cdot dE_g/dP$ (1) $D_{||}$ и $D_{\perp}$

Here $D_{||}$ and $D_{\perp}$ are the deformation potentials along and perpendicular to the **c** axis, respectively, U_{zz} and U_{xx} are the diagonal components of the strain tensor, which can be determined using the values of the elastic constants from [13] (due to the fact that the elastic constants for $TlGaS_2$ crystals experimentally not determined, we are forced to use constants close to them in terms of elastic properties of $TlGaSe_2$ crystals). From the known relations of the theory of elasticity [14]:

$U_{zz} = - P(C_{11} + C_{12} - 2C_{13})/[(C_{11} + C_{12})C_{33} - 2C_{13}^2]$ (2)

$U_{xx} = U_{yy} = - P(C_{33} - C_{13})/[(C_{11} + C_{12})C_{33} - 2C_{13}^2]$

Substituting the necessary values and performing calculations, we obtain the following equation for unknown deformation potentials:

$-1{,}8D_{||} \cdot 10^{-11}Pa^{-1} - 1{,}47D_{\perp} \cdot 10^{-11}Pa^{-1} = -7{,}25 \cdot 10^{-11}eV \cdot Pa^{-1}$ или, после сокращения, $-1{,}8D_{||} - 1{,}47D_{\perp} = -7{,}25eV$ (3)

As already noted, the band gap (E_g) in $TlGaS_2$ exhibits a rather rare feature: it increases with increasing temperature in a wide temperature range from 0 to (at least) 200 K. Since the increase in Eg with temperature can be due only to the contribution of thermal expansion to the change in Eg, it can be assumed that the observed increase in $E_g(T)$ in $TlGaS_2$ is completely due to the contribution of thermal expansion. Thus, the available data on the temperature dependence of $E_g(T)$ and the coefficients of linear expansion of $TlGaS_2$ single crystals [7] make it possible, after substitutions and reductions, to compose the second equation for the desired deformation potentials (in the temperature range 0 –100 K):

$3{,}5 \cdot 10^{-3}D_{||} + 2{,}6 \cdot 10^{-3}D_{\perp} = 20 \cdot 10^{-3}eV$ (4)

Solving the system of equations (3) and (4), we find $D_{||}$ = 21.6 eV and $D_{\perp}$ = -21.5 eV. Now we can see due to what deformations the band gap decreases under hydrostatic pressure, and increases with temperature . It can be seen that the change in E_g under the action of hydrostatic pressure consists of two parts:

$-38.9 \cdot 10^{-11}$ eV/Pa - due to compression along the **z** axis and $31.6 \cdot 10^{-11}$ eV/Pa due to compression of the layer itself. These parts have different signs and close values, therefore, in the aggregate, the pressure coefficient turns out to be small:

$-7.25 \cdot 10^{-11}$ eV/Pa.

This result is interesting because there is an analogy with the picture of the influence of deformation on the band structure in crystals of the $A^{III}B^{VI}$ group. They also have small baric coefficients, since compression of the layer increases the band gap, and compression of the interlayer gap (deformation along the **z** axis) reduces it, i.e. these contributions partially offset each other. Another interesting result follows from consideration of thermal expansion: the short - wavelength temperature shift of the absorption edge (exciton) is determined mainly by the deformation of the crystal along the **z** axis.

Having determined the deformation potentials, one can try to explain other deformation effects in this crystal. We have carried out experiments to study the effect of uniaxial compression on the band gap of

$TlGaS_2$ single crystals at low temperatures (in the region where an exciton peak can be observed). The pressure was applied perpendicular to the layers of the crystal.

The results of experiments for a temperature of 10 K are shown in Fig.3. With increasing pressure, the exciton peak shifts to longer wavelengths according to a linear law with the baric coefficient $dE_{ex}/dP = -3 \cdot 10^{-11}$ eV/Pa.

These measurements were carried out for the region of elastic deformation of the studied $TlGaS_2$ samples, which was controlled as follows: the spectrum of the unloaded sample was recorded, then the load increased to a maximum and was removed, after which the spectrum of the unloaded sample was recorded again. The identity of the spectra indicated the absence of plastic deformation.

Let us write the equation for the energy shift under uniaxial deformation along the **z** axis: Let us write the equation for the energy shift under uniaxial deformation along the z axis:

$$U_{zz} \cdot D_{||} + 2U_{xx} \cdot D_{\perp} = P \cdot dE_g/dP \qquad (5)$$

Here U_{zz} and U_{xx} will be determined from the following relations [12]:

$$U_{zz} = - P(C_{11} + C_{12})/[(C_{11} + C_{12})C_{33} - 2C_{13}^2] \qquad (6)$$

$$U_{xx} = U_{yy} = PC_{13}/[(C_{11} + C_{12})C_{33} - 2C_{13}^2]$$

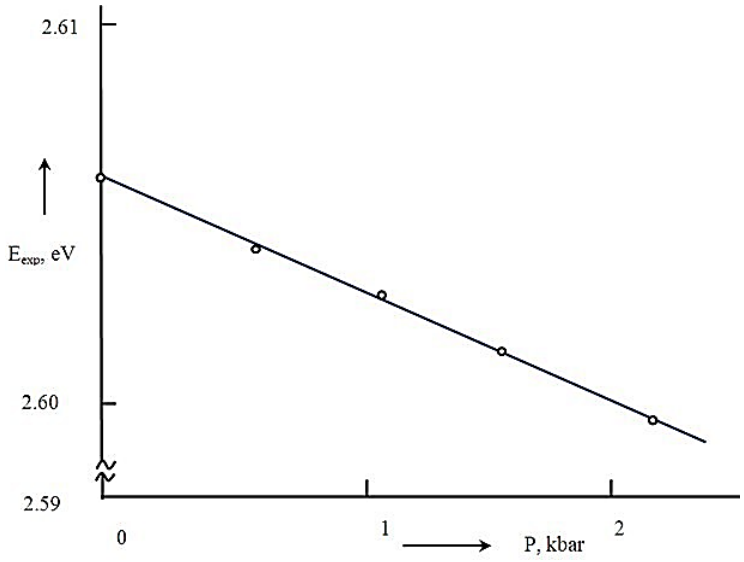

Fig. 3. Dependence of the position of the exciton peak of a $TlGaS_2$ single crystal on uniaxial compression along the c axis at T = 10 K

Substituting into (5) the deformation potentials obtained by us and the values of the diagonal components of the strain tensor calculated from relations (6), we obtain that ΔE_g should be – 66 meV in the case of pressure application P = 1kbar, i.e. we should have observed large long-wavelength shifts of the exciton peak under uniaxial compression of the $TlGaS_2$ crystal. Our experiments (see Fig. 3) give a long-wavelength shift of the exciton peak of 3 meV per 1 kbar, i.e. more than 20 times less than the expected value.

Note that a similar situation was observed in the study of deformation effects in layered crystals of the $A^{III}B^{VI}$ group [15]. It was found that in $A^{III}B^{VI}$ crystals the contribution of the crystal deformation along the **z** axis to the change in E_g with temperature depended substantially on temperature. In other words, the deformation potential $D_{||}$ changed its sign from positive to negative near 80K as the temperature dropped. The physical reasons for this effect are as follows.

In $A^{III}B^{VI}$ type crystals, the hydrostatic pressure led to a decrease in the band gap, since According to band structure calculations, a decrease in the distance between layers should lead to a decrease in E_g due to the splitting of the top of the valence band and the bottom of the conduction band. Under uniaxial compression of GaSe crystals at liquid helium temperature, instead of large long - wavelength shifts of the GaSe straight edge, clear short - wavelength shifts were found. Hence, it was concluded that at low temperatures, the main contribution to the change in E_g is made not so much by the change in the distance between the layers, but by the compression of the layer itself, since, according to the calculations of the band structure, only compression of the layers can lead to an increase in E_g.

In $TlGaS_2$ single crystals at $P \parallel \mathbf{c}$, short-wavelength shifts are not observed, but long-wavelength shifts are much less than expected. Thus, at low temperatures, the deformation potential $D_{||}^{H}$ is not equal to $D_{||}$ determined at room temperature. By analogy with $A^{III}B^{VI}$, we assume that $D_{\perp}$ does not change with temperature, and $D_{||}^{H}$ can be calculated by substituting into equation (5) the shift of the exciton line determined by direct experiment during compression of the $TlGaS_2$ crystal along the c axis. As a result, we obtain the value $D_{||}^{H}$ = - 4.2 eV, i.e. the deformation potential has changed sign.

Estimating the contributions of deformations along and perpendicular to the layers when pressure $P \parallel \mathbf{c}$ is applied at low temperatures, we can conclude: compression along the c axis leads to an increase in E_g (as in $A^{III}B^{V}$ crystals) by ~10 meV at P = 1 kbar. At the same time, stretching of the layer leads to a decrease in E_g by ~13 meV; as a result, E_g decreases by ~3 meV. The situation is reminiscent of the case with the behavior of E_g^{indir} in GaS: the resulting change in E_g at $P \parallel \mathbf{c}$ was determined by the stretching of the layer.

When determining the deformation potentials at low temperatures, we used the values of the elastic constants at room temperature. If the temperature dependence of the elastic constants is taken into account, then the values of the deformation potentials will change somewhat, but this will not affect our conclusion about the sign change of $D_{||}$.

Conclusion. From the above analysis, the following conclusions can be drawn:

1. The values of the deformation potentials of $TlGaS_2$ single crystals are found and the similarity of the deformation effects with those in crystals of the $A^{III}B^{VI}$ type is found.
2. The uniaxial pressure perpendicular to the layers in $TlGaS_2$, just as in $A^{III}B^{VI}$, cannot be described at low temperatures by the same deformation potentials as at room temperature. The temperature dependence of the deformation potentials is a common feature of the band structure of layered crystals.
3. The pattern of deformation phenomena for the straight edge of a $TlGaS_2$ single crystal is very similar to the pattern of deformation phenomena for the indirect edge in GaS and GaSe. This may indicate that the same orbitals are involved in the formation of the absorption edge of $TlGaS_2$ as in the formation of the indirect edge of GaS and GaSe. Unfortunately, it is impossible to draw more accurate conclusions, because to date, there are no necessary calculations of the band structure of these crystals.

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