

PRESSURE AND TEMPERATURE EFFECTS ON ELECTRONIC SPECTRA OF TlGaSe₂ TYPE CRYSTALS

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The deformation effects in electronic spectra of ternary layered TlGaS₂, TlGaSe₂ and TlInS₂ semiconductors are considered. It is shown that the influence of hydrostatic pressure, thermal expansion, variation of composition in solid solutions on the band gap of investigated crystals can be described in the framework of one common model of deformation potentials.

This model is close to that in layered semiconductors of A₃B₆ group and testifies the fact that the main principles of formation of band structure in these two groups of layered crystals are the same.

1. Introduction

The ternary TlGaS₂, TlGaSe₂ and TlInS₂ semiconductors have layered crystalline structure and according to existing data [1-5] all three compounds crystallize to the same monoclinic structure. It's shown that monoclinic structure of these crystals is very close to tetragonal, and due to absence of anisotropy in the layers plane elastic and thermal properties can be treated even in the framework of hexagonal structure [6, 7].

The great number of investigations of ternary compounds concentrates on the phase transitions, which are observed obviously at least in TlGaSe₂ and TlInS₂ [5, 8]. It's known, that both of these crystals undergo a phase transitions with lowering the temperature from paraelectric phase to incommensurate phase ($T_i=216\text{K}$ in TlInS₂ and $T_i=120\text{K}$ in TlGaSe₂) and then to ferroelectric phase ($T_c=202\text{K}$ in TlInS₂ and $T_c=107\text{K}$ in TlGaSe₂) with quadrupling of unit cell along the "C" axes.

The influence of phase transitions on different physical properties in particular on the electronic spectra near the absorption edge is studied in various works [8-10]. However, it's difficult to interpret the obtained results because of lack of the model explaining the deformation effects in ternary layered semiconductors (TLS). The construction of such a model is a main goal of present work.

2. The model of deformation potential in ternary layered TlGaS₂, TlGaSe₂ and TlInS₂ semiconductors.

First of all the results of investigations of deformation effects in TLS are summarized below.

1. In [11] the unusual behavior of exciton absorption peak with temperature was observed in TlGaS₂: the energy position of exciton peak (E_{exc}) was shifted to the higher energies with increasing temperature in 4,2÷200K range in which exciton absorption peak was observed (fig.1).

Because of lack of appropriate deformation potentials it was not possible to evaluate the contribution of lattice deformation to the temperature dependence of energy gap (E_g) in TlGaS₂. In figs. 1 and 2 the temperature dependences of exciton positions in TlGaSe₂, TlGaS₂ [11], TlInS₂ [10], which reflect the $E_g(T)$ dependences, and linear expansion coefficients parallel ($\alpha_{||}$) and perpendicular (α_{\perp}) to the layers plane for all three crystals [7, 12, 13] are shown. As it is seen from fig.1 the $E_{exc}(T)$ dependences in TlGaSe₂ and TlInS₂ are quite different from that in TlGaS₂. At the same time the $\alpha_{||}(T)$ and $\alpha_{\perp}(T)$ dependences are very close, for example, in

TlGaS₂ and TlInS₂ in the temperature region far from phase transition point in TlInS₂ (fig.2).

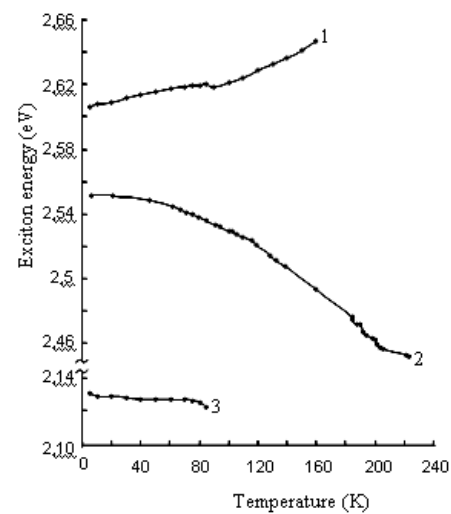


Fig.1. Temperature dependences of exciton energies in TlGaS₂ (1) [11], TlInS₂ (2) [10] and TlGaSe₂ (3) [11].

2. In [8] the influence of hydrostatic pressure on the absorption edge of all three TLS was investigated at room temperature – the results are presented in fig.3. At small pressures ($P \leq 0,5\text{GPa}$) the behavior of band gap with pressure is the same in all crystals: baric coefficient, dE_g/dP , is negative, which is typical for almost all semiconductors with layered structure [14]. With increasing of pressure, however, the behavior of baric coefficients in TLS becomes different.

In TlInS₂ dE_g/dP changes the sign at pressures $P \geq 0,59\text{GPa}$ and remains positive up to $P \sim 0,9\text{GPa}$. At higher pressures dE_g/dP in TlInS₂ again changes the sign and becomes negative but the absolute value of dE_g/dP increases: $dE_g/dP \approx -22 \times 10^{-11} \text{eV} \times \text{Pa}^{-1}$ ($dE_g/dP = -8,5 \times 10^{-11} \text{eV} \times \text{Pa}^{-1}$ at $P < 0,59\text{GPa}$). It's shown in [13, 14], that phase transitions take place in TlInS₂ at pressures $P \sim 0,59\text{GPa}$ and $P \sim 1,0\text{GPa}$.

In TlGaSe₂ baric coefficient remains negative up to $P \sim 0,92\text{GPa}$, $dE_g/dP = -12,5 \times 10^{-11} \text{eV} \times \text{Pa}^{-1}$. At $P > 0,92\text{GPa}$ dE_g/dP stays negative, but $|dE_g/dP|$ increases drastically, $dE_g/dP = -20 \times 10^{-11} \text{eV} \times \text{Pa}^{-1}$.

In TlGaS₂ $dE_g/dP \approx -7,2 \times 10^{-11} \text{eV} \times \text{Pa}^{-1}$ and remains practically unchanged in all investigated range of pressures.

Again, because of lack of deformation potentials it was not possible to interpret the common and different features of baric coefficients behavior in TLS.

3. In [17] the influence of uniaxial, perpendicular to the layers plane, pressure on the exciton absorption peak position in TlGaS₂ and TlGaSe₂ were investigated at low temperatures, 4,2K<T<100K. Baric coefficients were appeared to be approximately the same in both crystals: $dE_g/dP \approx -3 \times 10^{-11} \text{ eV} \times \text{Pa}^{-1}$ in the investigated range of temperatures.

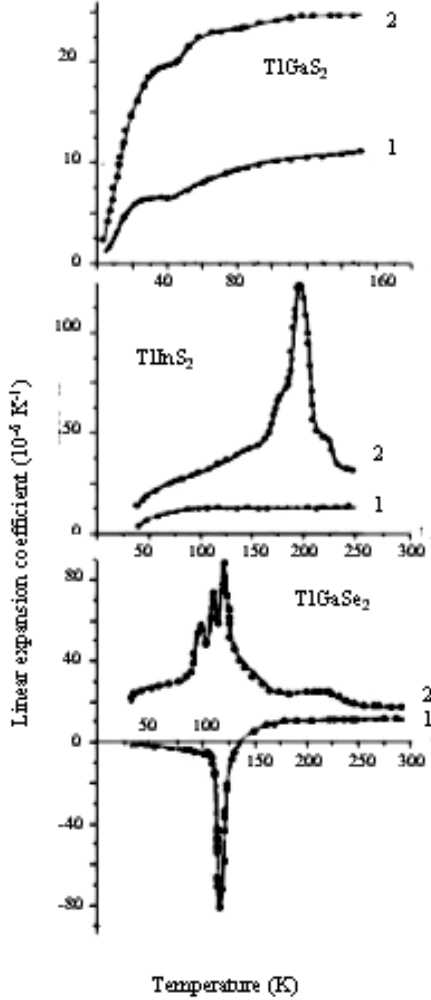


Fig.2. Linear expansion coefficients for TlGaS₂, TlGaSe₂ and, TlInS₂ parallel (1) and perpendicular (2) to the layers plane [7, 12, 13].

We tried to explain all results described above on the basis of a simple model, introducing two deformation potentials D_{\perp} and D_{\parallel} . In this model the dependence of E_g on deformation is: $\Delta E_g = D_{\perp} U_{\perp} + 2D_{\parallel} U_{\parallel}$, where U_{\parallel} and U_{\perp} deformations in the layers plane and in the perpendicular direction, respectively. Such a model allowed explanation of all types of deformation phenomena in layered semiconductors of A₃B₆ group [14].

For determining the deformation potentials D_{\perp} and D_{\parallel} the results of at least two independent deformation experiments are needed. We have chosen the results of influence of hydrostatic pressure on the optical absorption spectra (fig.3). The results of uniaxial deformation experiments which are known for TlGaS₂ and TlGaSe₂ at low temperatures can not be used because, as it was shown in A₃B₆ group layered crystals, the deformation potential D_{\perp} , may depend strongly on temperature and pressure.

Supposing that TlInS₂, TlGaSe₂ and TlGaS₂ have close deformation potentials and using the results of hydrostatic pressure influence on E_g at low pressures ($P \leq 0,5 \text{ GPa}$) the deformation potentials, D_{\parallel} and D_{\perp} were obtained. The data for TlInS₂ and TlGaSe₂ were used because only for these crystals the values of elastic constants are known [6] (table 1). By calculating D_{\parallel} and D_{\perp} in TlInS₂ and TlGaSe₂ we used the value of elastic constant $C_{13} = 1,5 \times 10^{10} \text{ Pa}$ which is almost the same in the majority of layered crystals [14]. This elastic constant was not measured in TlInS₂ and TlGaSe₂ because of significant experimental difficulties that always appear measuring this elastic constant in layered crystals. Simple calculations [14] give the values: $D_{\parallel} = -7,3 \text{ eV}$ and $D_{\perp} = 11,9 \text{ eV}$. Below we'll explain the results of other deformation experiments on the basis of obtained values of D_{\parallel} and D_{\perp} .

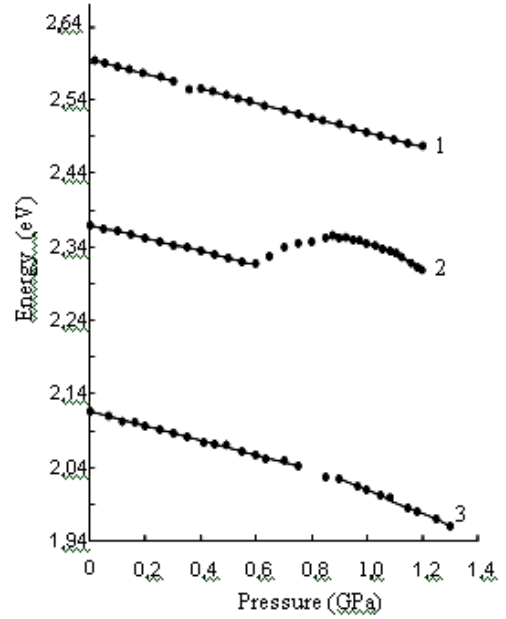


Fig.3. Pressure dependences of energy gaps obtained from absorption edge behavior with pressure at 300K in TlGaS₂ (1), TlInS₂ (2) and TlGaSe₂ (3) [8].

Using the thermal expansion curves (fig.2) the contribution of thermal expansion to $E_g(T)$ dependences can be obtained for all three crystals:

- in TlGaS₂ this contribution gives $\Delta E_g \approx +20 \text{ meV}$ in 4.2÷100K temperature range;
- in TlGaSe₂ this contribution must lead to $\Delta E_g = +25 \text{ meV}$ due to small linear expansion in the layers plane, α_{\parallel} ;
- the positive shifts of $\Delta E_g = +25 \text{ meV}$ with temperature must be in TlInS₂ in the same temperature region.

As it is seen from experimentally measured E_{exc} dependences (fig.1) the results of calculations are appeared to be true only for TlGaS₂ - in TlGaSe₂ and TlInS₂ E_{exc} decreases with temperature. However, it can be shown, that this discrepancy between calculations and experiment are not due to the method used for the calculation of D_{\parallel} and D_{\perp} . Really, as it was noted above, unlike TlGaS₂, both TlGaSe₂ and TlInS₂ are in ferroelectric phase at 4,2-100K due to phase transitions, which they underwent when temperature became lower. It is shown in [11] that addition of sulfur into TlGaSe₂ in TlGaSe_{2(1-x)S_{2x}} solid solutions leads to $E_g(T)$ dependences which are typical for TlGaS₂ beginning from $x=0,1$. At the same time there are no evidences of phase transition typical for TlGaSe₂ in solid solutions TlGaSe_{2(1-x)S_{2x}} at $x \geq 0,25$ [18].

Thus, unusual behavior of $E_g(T)$ in TlGaS_2 and $\text{TlGaSe}_{2(1-x)}\text{S}_{2x}$ with $x \geq 0,1$ are typical for crystals without phase transitions and deformation potentials D_{\parallel} and D_{\perp} obtained above are true for TlGaS_2 and paraelectric phases of TlInS_2 and TlGaSe_2 .

The other type of deformation effects is the change of band gap in $\text{TlGaSe}_{2(1-x)}\text{S}_{2x}$ solid solutions, where the changing of lattice parameters can be interpreted as effective lattice deformation. Using the lattice parameters of TlGaSe_2 and TlGaS_2 (table 1) and deformation potentials D_{\parallel} and D_{\perp} , the change of E_g very close to experimental value can be found: $\Delta E_g = 450 \text{ meV}$. Thus, deformation potentials D_{\parallel} and D_{\perp} , obtained above, can describe the results of at least four independent deformation experiments.

Table 1.

Lattice parameters and elastic constants in TlGaS_2 , TlGaSe_2 and TlInS_2 .

Crystals	Lattice parameters, Å [1-3]			Values of elastic constants, 10^{10} Pa [6]			
	a	b	c	C_{11}	C_{12}	C_{33}	C_{44}
TlGaS_2	10,29	10,29	15,28	-	-	-	-
TlGaSe_2	10,77	10,77	15,64	6,42	3,88	4,37	0,5
TlInS_2	10,95	10,95	15,14	4,49	3,05	3,99	0,5

As it was shown in [14] the deformation potentials obtained at room temperatures and low pressures cannot be used determining the energy shifts at low temperatures, and high pressures in layered crystals of A_3B_6 group. The same seems to be true also for TLS. For example, using the D_{\parallel} and D_{\perp} obtained above the values $dE_g/dP \approx 34 \times 10^{-11} \text{ eV} \times \text{Pa}^{-1}$ for TlGaSe_2 and $dE_g/dP \approx 41 \times 10^{-11} \text{ eV} \times \text{Pa}^{-1}$ for TlInS_2 are obtained for uniaxial perpendicular to the layers plane pressures instead of experimentally obtained value $dE_g/dP \approx 3 \times 10^{-11} \text{ eV} \times \text{Pa}^{-1}$ for low temperatures. To explain the significant changes of baric coefficients with pressure in TlInS_2 and TlGaSe_2 one must also suppose that deformation potentials strongly depend on pressure. As in the case of layered crystals of A_3B_6 group to explain the discrepancy between experimental results and calculations, it should be assumed that deformation potential D_{\perp} , describing the energy shifts at deformations perpendicular to the layers plane decreases (or even changes its sign from positive to negative) with the lowering of the temperature or pressure increasing.

The nature of such a behavior of deformation potential D_{\perp} is due to peculiarities of the band structure of layered crystals of A_3B_6 group. According to band structure calculations [14] interlayer interaction leads to splitting of the top of valence band and bottom of conduction band of layer crystal. Under deformation when interlayer distances decrease, splitting increases and leads to decrease of E_g . On the other hand the compression of layers in both directions leads to increase of E_g . Thus the final change of band gap depends on two competitive parts having opposite signs. Since the interlayer forces increase faster than intralayer ones with temperature lowering or pressure increasing the baric coefficient may decrease by absolute value or even change the sign from negative to positive with temperature or

pressure. For example, the baric coefficients for direct gaps in A_3B_6 group layered crystals change the signs from negative to positive with temperature lowering ($T \leq 77 \text{ K}$) and pressure increasing ($P \geq 0,5 \text{ GPa}$). At the same time the baric coefficients for indirect gaps in A_3B_6 group crystals do not change the signs and remain negative but the absolute values of baric coefficients decrease significantly as described above for TLS for uniaxial pressures at low temperatures. So, as it's seen from obtained results the deformation phenomena in TLS and layered crystals of A_3B_6 group have many common features.

3. Conclusion

The deformation potentials D_{\parallel} and D_{\perp} obtained above for TLS TlGaSe_2 , TlInS_2 and TlGaS_2 have allowed making following conclusions:

1. Deformation effects in TLS are very close to that observed in layered semiconductors of A_3B_6 group:

a) deformation potentials D_{\parallel} and D_{\perp} have the opposite signs, and behavior of band gap E_g under pressure depends on two competitive contributions: positive one due to contraction of layers and negative one due to contraction of interlayer distances ;

b) deformation potential D_{\perp} depends on pressure and temperature due to different behavior of elastic constants determining the deformation of layered crystals parallel and perpendicular to the layers plane.

The similarity of deformation effects in TLS and A_3B_6 group crystals leads to the conclusion that the band structures of these two types of crystals have the following common feature: E_g decreases when the interlayer distances decrease and E_g increases when intralayer distances decreases.

2. At low pressures ($P < 0,5 \text{ GPa}$) and room temperature all three investigated crystals have the close band structures and deformation potentials. The differences in contribution of thermal expansion to $E_g(T)$ dependences in TlInS_2 and TlGaSe_2 on one hand, and in TlGaS_2 on the other hand are due to phase transitions, which take place in TlInS_2 and TlGaSe_2 with temperature. The different behavior of baric coefficients with pressure may be due to different degree of elastic anisotropy and also to the phase transitions in TlInS_2 and TlGaSe_2 at high pressures.

3. It was mentioned above in introduction that according to the literature phase transitions that take place with temperature in TlInS_2 and TlGaSe_2 have the same natures. However, as it can be seen from fig.2 the deformation of lattices with temperature in the layers plane is quite different and phase transitions reveal itself in different way in TlGaSe_2 and TlInS_2 . The analogous conclusion was made in [19] investigating the temperature dependences of elastic constants in TlGaSe_2 and TlInS_2 : near phase transition points the elastic constants in TlInS_2 and TlGaSe_2 behave in somewhat different way. The pressure dependences of baric coefficients in TlGaSe_2 and TlInS_2 also demonstrate differences at pressures when phase transitions in both crystals take place. Though it's difficult to interpret the nature of such differences, one can conclude that baric coefficients behavior with pressure also testifies the differences in the nature of phase transitions in TlInS_2 and TlGaSe_2 .

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TlGaSe₂ TIPLİ KRİSTALLARININ ELEKTRON SPEKTRLƏRİNƏ TƏZYİQ VƏ TEMPERATURUN TƏSİRİ

TlGaS₂, TlGaSe₂ və TlInS₂ üçqat laylı yarımkəçiricilərin elektron spektrlərində deformasiya effektlərinə baxılmış və göstərilmişdir ki, hidrostatik təzyiğin, temperatur genişlənməsinin və bərk məhlulların tərkibinin dəyişilməsinin tədqiq olunan kristalların qadağan olunmuş zonasına təsiri deformasiya potensialının ümumi modeli çərçivəsində təsvir oluna bilər.

Məlum olmuşdur ki, göstərilən model A₃B₆ qrupun laylı yarımkəçiriciləri üçün deformasiya potensialları modelinə yaxındır. Bu isə onu göstərir ki, hər iki qrup laylı kristalların zona strukturlarının əsas formalaşması prinsipləri eynidir.

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ВЛИЯНИЕ ДАВЛЕНИЯ И ТЕМПЕРАТУРЫ НА ЭЛЕКТРОННЫЕ СПЕКТРЫ КРИСТАЛЛОВ ТИПА TlGaSe₂

Рассмотрены деформационные эффекты в электронных спектрах тройных слоистых полупроводников TlGaS₂, TlGaSe₂ и TlInS₂. Показано, что влияние гидростатического давления, температурного расширения, изменения состава твердых растворов на ширину запрещенной зоны исследуемых кристаллов может быть описано в рамках общей модели деформационных потенциалов.

Оказалось, что указанная модель близка к модели деформационных потенциалов для слоистых полупроводников группы A₃B₆. Это свидетельствует о том, что основные принципы формирования зонной структуры этих двух групп слоистых кристаллов одни и те же.

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