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Deformation effects in electronic spectra of the layered semiconductors $TlGaS_2$, $TlGaSe_2$ and $TlInS_2$

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Abstract

The deformation effects in electronic spectra of the ternary layered semiconductors $TlGaS_2$, $TlGaSe_2$ and $TlInS_2$ are considered. It is shown that the influence of hydrostatic pressure, thermal expansion and variation of composition in solid solutions on the band gap of the crystals investigated can be described in the framework of one common model of deformation potentials. This model appears to be close to that of layered semiconductors of the A_3B_6 group, attesting to 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 semiconductors $TlGaS_2$, $TlGaSe_2$ and $TlInS_2$ have layered crystalline structure and, according to existing data [1–5], all three compounds crystallize in the same monoclinic structure. It is shown that the monoclinic structure of these crystals is very close to tetragonal and, due to the absence of anisotropy in the layers, planar elastic and thermal properties can be treated even in the framework of hexagonal structure [6, 7].

The majority of investigations of ternary compounds concentrate on phase transitions, which are observed clearly in at least $TlGaSe_2$ and $TlInS_2$ [5, 8]. It is known that each of these crystals undergoes a phase transition with lowering of the temperature from the paraelectric phase to the incommensurate phase ($T_i = 216$ K for $TlInS_2$ and $T_i = 120$ K for $TlGaSe_2$) and then to the ferroelectric phase ($T_c = 202$ K for $TlInS_2$ and $T_c = 107$ K for $TlGaSe_2$) with quadrupling of the 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 is difficult to interpret the results obtained because of the lack of a model explaining the deformation effects in ternary layered semiconductors (TLS). The construction of such a model is a main goal of the present work.

2. The model of the deformation potential in the ternary layered semiconductors $TlGaS_2$, $TlGaSe_2$ and $TlInS_2$

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

(1) In [11], unusual behaviour of the exciton absorption peak with temperature was observed in $TlGaS_2$: the energy position of the exciton peak (E_{exc}) was shifted to higher energies with increasing temperature in the 4.2–200 K range in which the exciton absorption peak was observed (figure 1).

Because of the lack of appropriate deformation potentials it was not possible to evaluate the contribution of lattice deformation to the temperature dependence of the energy gap (E_g) in $TlGaS_2$. In figures 1 and 2 the temperature dependences of the exciton positions in $TlGaSe_2$, $TlGaS_2$ [11] and $TlInS_2$ [10], which reflect the $E_g(T)$ dependences, and the linear expansion coefficients parallel ($\alpha_\parallel$) and perpendicular ($\alpha_\perp$) to the layer plane for all three crystals [7, 12, 13] are shown. As is seen from figure 1 and as is shown in other investigations (see, for example, [14]) the $E_{exc}(T)$ dependences of $TlGaSe_2$ and $TlInS_2$ are quite different from that of $TlGaS_2$. At the same time, the $\alpha_\parallel(T)$ and $\alpha_\perp(T)$ dependences are very close in, for example, $TlGaS_2$ and $TlInS_2$ in the temperature region far from the phase transition point of $TlInS_2$ (figure 2).

(2) In our previous work [8] the influence of hydrostatic pressure on the absorption edge for all three TLS was investigated at room temperature; the results are presented in figure 3. In our investigations, pressure effects were restricted to up to 1.27 GPa. In [15] the effect of hydrostatic pressures up to 12 GPa on the lowest-energy gaps in $TlGaSe_2$ has been investigated. At small pressures ($P \leqslant 0.5$ GPa), which are the most interesting for our purposes, the results of the two investigations are very close. Some discrepancies between published data are concerned with the pressure-induced phase transitions, which may occur at higher pressures. However, this problem is beyond the scope of the present paper.

As is seen from figure 3, at small pressures ($P \leqslant 0.5$ GPa) the behaviour of the band gap with pressure is the same for all crystals: the baric coefficient, $\mathrm{d}E_g/\mathrm{d}P$, is negative, which is typical for almost all semiconductors with layered structure [16–19]. With increasing pressure, however, the behaviour of the baric coefficients in TLS becomes different. For $TlInS_2$, $\mathrm{d}E_g/\mathrm{d}P$ changes sign at pressures $P \geqslant 0.59$ GPa and remains positive up to $P \sim 0.9$ GPa. At higher pressures, $\mathrm{d}E_g/\mathrm{d}P$ for $TlInS_2$ again changes sign and becomes negative, but the absolute value of $\mathrm{d}E_g/\mathrm{d}P$ increases: $\mathrm{d}E_g/\mathrm{d}P \approx -22 \times 10^{-11}$ eV Pa^{-1} ($\mathrm{d}E_g/\mathrm{d}P = -8.5 \times 10^{-11}$ eV Pa^{-1} at $P < 0.59$ GPa). According to [20–22], the phase transitions takes place in $TlInS_2$ at pressures $P \sim 0.59$ GPa and $P \sim 1.0$ GPa.

For $TlGaSe_2$, the baric coefficient remains negative up to $P \sim 0.92$ GPa, $\mathrm{d}E_g/\mathrm{d}P = -12.5 \times 10^{-11}$ eV Pa^{-1}. At $P > 0.92$ GPa, $\mathrm{d}E_g/\mathrm{d}P$ stay negative, but $|\mathrm{d}E_g/\mathrm{d}P|$ increases drastically: $\mathrm{d}E_g/\mathrm{d}P = -20 \times 10^{-11}$ eV Pa^{-1}.

For $TlGaS_2$, $\mathrm{d}E_g/\mathrm{d}P \approx -7.2 \times 10^{-11}$ eV Pa^{-1} and remains practically unchanged in all ranges of pressures investigated.

As was mentioned above, we will restrict ourselves to constructing a deformation potential model for TLS in the low-pressure region.

(3) In [23] the influence of uniaxial pressure, perpendicular to the layer plane, on the exciton absorption peak position for $TlGaS_2$ and $TlGaSe_2$ was investigated at low temperatures,

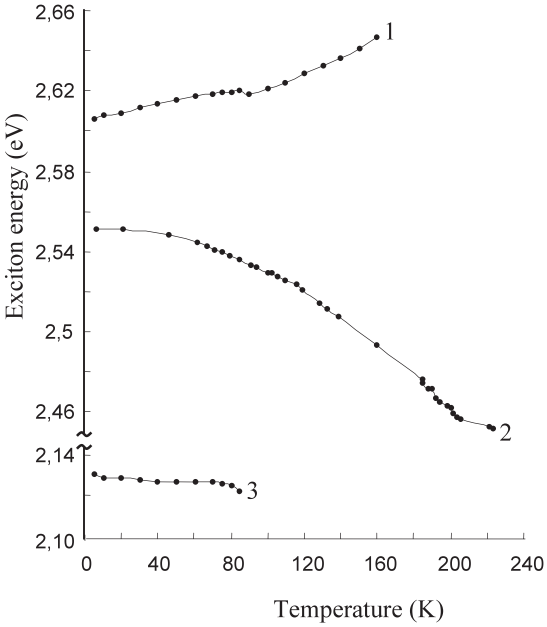

Figure 1. Temperature dependences of the exciton energies in $TlGaS_2$ (1) [11], $TlInS_2$ (2) [10] and $TlGaSe_2$ (3) [11].

$4.2\,K < T < 100\,K$. The baric coefficients appeared to be approximately the same for the two crystals: $dE_g/dP \approx -3 \times 10^{-11}$ eV Pa^{-1} in the range of temperatures investigated.

We tried to explain all the 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 the deformation is: $\Delta E_g = D_\perp U_\perp + 2D_\parallel U_\parallel$, where $U_\parallel$ and $U_\perp$ are the deformations in the layer plane and in the perpendicular direction, respectively. This model allowed us to explain the deformation phenomena of all types in layered semiconductors of the A_3B_6 group [16].

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 on the influence of hydrostatic pressure on the optical absorption spectra (figure 3). The results of uniaxial deformation experiments, which are known for $TlGaS_2$ and $TlGaSe_2$ at low temperatures, cannot be used because, as was shown for A_3B_6-group layered crystals, the deformation potential $D_\perp$ may depend strongly on temperature and pressure.

Supposing that $TlInS_2$, $TlGaSe_2$ and $TlGaS_2$ have close deformation potentials and using the results on the hydrostatic pressure influence on E_g at low pressures ($P \leqslant 0.5$ GPa), the deformation potentials, $D_\parallel$ and $D_\perp$ were obtained. The data for $TlInS_2$ and $TlGaSe_2$ were used because only for these crystals are the values of the elastic constants known [6] (table 1). Calculating $D_\parallel$ and $D_\perp$ for $TlInS_2$ and $TlGaSe_2$, we used the value of $C_{13} = 1.5 \times 10^{10}$ Pa. This elastic constant takes values that are almost the same for the majority of layered crystals [16]. It was not measured for $TlInS_2$ and $TlGaSe_2$ because of the significant experimental difficulties that are always encountered when measuring it for layered crystals. Simple calculations give the values $D_\parallel = -7.3$ eV and $D_\perp = 11.9$ eV. Below, we will explain the results of other deformation experiments on the basis of the values of $D_\parallel$ and $D_\perp$ obtained.

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

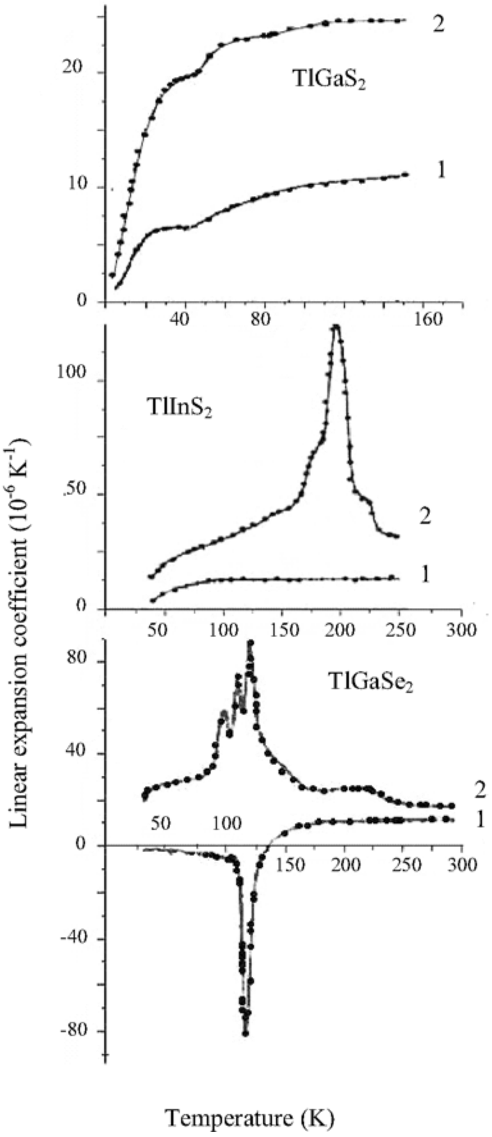

Figure 2. Linear expansion coefficients for $TlGaS_2$, $TlGaSe_2$ and $TlInS_2$ parallel (1) and perpendicular (2) to the layer plane [7, 12, 13].

Table 1. Lattice parameters and elastic constants of $TlGaS_2$, $TlGaSe_2$ and $TlInS_2$.

	Lattice parameters (Å) [1–3]			Values of elastic constants (10^{10} Pa) [6]			
Crystals	*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

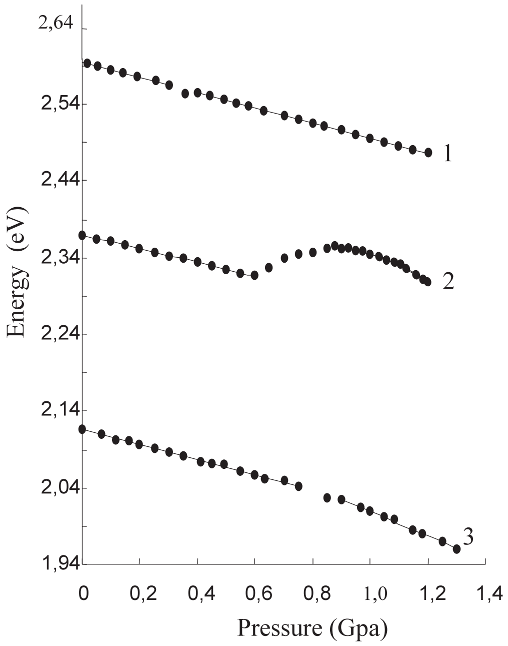

Figure 3. Pressure dependences of energy gaps obtained from absorption edge behaviour with pressure at 300 K in $TlGaS_2$ (1), $TlInS_2$ (2) and $TlGaSe_2$ (3) [8].

(a) for $TlGaS_2$ this contribution gives $\Delta E_g \approx +20$ meV in the 4.2–100 K temperature range;
(b) for $TlGaSe_2$ this contribution must lead to $\Delta E_g = +25$ meV due to the small linear expansion in the layer plane, $\alpha_{\|}$;
(c) the positive shifts of $\Delta E_g = +25$ meV with temperature must, for $TlInS_2$, be in the same temperature region.

As is seen from the experimentally measured E_{exc}-dependences (figure 1), the results of calculations appear to be correct only for $TIGaS_2$—for $TlGaSe_2$ and $TlInS_2$, E_{exc} decreases with temperature. However, it can be shown that this discrepancy between calculations and experiment is not due to the method which was used for the calculation of $D_{\|}$ and $D_{\perp}$. In fact, as was noted above, unlike $TlGaS_2$, both $TlGaSe_2$ and $TlInS_2$ are in a ferroelectric phase at 4.2–100 K due to phase transitions, which they underwent when the temperature was lowered. It is shown in [11] that addition of sulfur to $TlGaSe_2$ in $TlGaSe_{2(1-x)}S_{2x}$ solid solutions leads to $E_g(T)$ dependences which are typical for $TlGaS_2$ beginning from $x = 0.1$. At the same time there is no evidence of the phase transition typical for $TlGaSe_2$ in the solid solutions $TlGaSe_{2(1-x)}S_{2x}$ at $x \geqslant 0.25$ [24, 25]. Thus, the unusual behaviours of $E_g(T)$ for $TIGaS_2$ and $TlGaSe_{2(1-x)}S_{2x}$ with $x \geqslant 0.1$ are typical for crystals without phase transitions, and the deformation potentials $D_{\|}$ and $D_{\perp}$ obtained above are correct for $TIGaS_2$ and the paraelectric phases of $TlInS_2$ and $TlGaSe_2$.

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

As was shown in [16], the deformation potentials obtained at room temperature and low pressures cannot be used in determining the energy shifts at low temperatures and high pressures in the layered crystals of the A_3B_6 group. The same seems to be true also for TLS. For example, using $D_{\parallel}$ and $D_{\perp}$ obtained above, the values $\mathrm{d}E_g/\mathrm{d}P \approx -34 \times 10^{-11}$ eV Pa^{-1} for $TlGaSe_2$ and $\mathrm{d}E_g/\mathrm{d}P \approx -41 \times 10^{-11}$ eV Pa^{-1} for $TlInS_2$ are obtained for uniaxial pressures perpendicular to the layer plane instead of the experimentally obtained value $\mathrm{d}E_g/\mathrm{d}P \approx -3 \times 10^{-11}$ eV Pa^{-1} for low temperatures. To explain the significant changes of the baric coefficients with pressure for $TlInS_2$ and $TlGaSe_2$, one must also suppose that the deformation potentials strongly depend on pressure. As in the case of layered crystals of the A_3B_6 group, to explain the discrepancy between experimental results and calculations, one must suppose that the deformation potential $D_{\perp}$, describing the energy shifts for deformations perpendicular to the layer plane, decreases (or even changes sign from positive to negative) on lowering the temperature or increasing the pressure.

The nature of such a behaviour of the deformation potential $D_{\perp}$ is due to peculiarities of the band structure of layered crystals of the A_3B_6 group. According to band structure calculations [26], interlayer interaction leads to splitting of the top of the valence band and the bottom of the conduction band of a layer crystal. Under deformation, when the interlayer distances decrease, splitting increases and leads to a decrease of E_g. On the other hand, the compression of the layers in both directions leads to increasing 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 on lowering the temperature or increasing the pressure, the baric coefficient may decrease in absolute value or even change sign from negative to positive with temperature or pressure changes. For example, the baric coefficients for the direct gaps in A_3B_6-group layered crystals change sign from negative to positive on lowering the temperature ($T \leqslant 77$ K) and increasing the pressure ($P \geqslant 0.5$ GPa). At the same time, the baric coefficients for indirect gaps in A_3B_6-group crystals do not change sign and remain negative, but the absolute values of the baric coefficients decrease significantly as described above for TLS for uniaxial pressures at low temperatures. So, as is seen from the results obtained, the deformation phenomena in TLS and layered crystals of the A_3B_6 group have many common features.

3. Conclusions

The deformation potentials $D_{\parallel}$ and $D_{\perp}$ obtained above for the TLS $TlGaSe_2$, $TlInS_2$ and $TlGaS_2$ allow us to draw the following conclusions:

(1) Deformation effects in TLS are very close to those observed in layered semiconductors of the A_3B_6 group:
  (a) the deformation potentials $D_{\parallel}$ and $D_{\perp}$ have opposite signs and the behaviour of the band gap E_g under pressure depends on two competitive contributions—a positive one due to contraction of the layers and a negative one due to contraction of the interlayer distances;
  (b) the deformation potential $D_{\perp}$ depends on pressure and temperature due to the different behaviours of the elastic constants determining the deformation of layered crystals parallel and perpendicular to the layer plane.

The similarity of the deformation effects in TLS and A_3B_6-group crystals leads to the conclusion that the band structures of these two types of crystal have the following common feature: E_g decreases when the interlayer distances decrease and E_g increases when intralayer distances decrease. This conclusion is in accordance with the qualitative description of energy shifts under pressure in $TlGaSe_2$ [15] based on the closed-shell interaction model [19, 27].

(2) At low pressures ($P < 0.5$ GPa) and room temperature, all three crystals investigated have close band structures and deformation potentials. The differences between the contribution of the thermal expansion to the $E_g(T)$ dependence in $TlInS_2$ and $TlGaSe_2$, on the 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 change. The different behaviours of baric coefficients with pressure may be due to the different degrees of elastic anisotropy and also to the phase transitions in $TlInS_2$ and $TlGaSe_2$ at high pressures.

(3) It was mentioned above in the introduction that, according to the literature, the phase transitions that take place with temperature change in $TlInS_2$ and $TlGaSe_2$ have the same nature. However, as can be seen from figure 2, the deformation of lattices with temperature change in the layer plane is quite different and phase transitions are revealed in different ways in $TlGaSe_2$ and $TlInS_2$. An analogous conclusion was reached in [28] from study of the phase transitions in $TlGaSe_2$ and in [29] from investigation of the temperature dependences of the elastic constants in $TlGaSe_2$ and $TlInS_2$: near phase transition points, the elastic constants of $TlInS_2$ and $TlGaSe_2$ behave in somewhat different ways. The pressure dependences of the baric coefficients of $TlGaSe_2$ and $TlInS_2$ also demonstrate differences at high pressures, when phase transitions possibly take place in both crystals. Although it is difficult to interpret the nature of such differences, one can conclude that the behaviour of baric coefficients with pressure also attests to the differences in nature of the phase transitions in $TlInS_2$ and $TlGaSe_2$.

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