LAYERED CHARACTER OF DIELECTRIC FUNCTION DEFINED BY THE METHOD OF EXCITON SPECTROSCOPY IN $TlGaSe_2$ AND $TlInS_2$ CRYSTALS AT PHASE TRANSITIONS

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It is shown that within the temperature region, corresponding to paraphasia - ferroelectric phase transition, the dielectric constant of layered crystals $TlGaSe_2$ and $TlInS_2$ can be considered as consisting of two slabs with different dielectric constants ϵ_1, ϵ_2 and thickness d_1 and d_2 ($d_1+d_2=c$, c is the lattice vector projection in the direction normal to layer). So, the dielectric anomaly and spontaneous polarization occurring at phase transition takes place only in one of the slabs. This model is confirmed by some experimental results, such as dielectric function anisotropy and spectroscopy of excitons at temperatures corresponding to phase transition.

KEYWORDS: exciton, phase transition, layered crystal, spatial dispersion, dielectric anomaly.

INTRODUCTION

Some layered crystals A^3B^6, A^4B^6 and their ternary compounds exhibit at temperature fall the structural phase transitions (PT) from high symmetric paraphase to lower symmetric ferroelectric phase [1-5]. Such a PT is accompanied by appearing of spontaneous polarization in low symmetric commensurate and incommensurate (IC) phases [6]. Anomalies of physical parameters of a crystal take place near the critical temperatures T_i and T_c. For example, the order of value of the dielectric function ϵ_0 in $TlGaSe_2$ and $TlInS_2$ increases more than two times reaching the value up to 10^3 and more in IC phase. This anomaly is believed due to the appearing of spontaneous polarization in layer plane as a result of small positional shifts of T_l atoms situated inside prisms. This second order PT takes place only in monoclinic modification of these crystals which have numerous polytypes with different lattice parameters $c=c'$, $2c'$, $4c'$, $8c'$ ($c' \approx 15$Å).

Wannier and intermediate type exceptions were observed in these layered crystals [7]. The order of ionization energy and effective Bohr radius are the following

$$\varepsilon_i \sim m^* \cdot Ry \cdot \epsilon_0^{-2}, \qquad r_B^* \sim r_B^* \sim \varepsilon_i^{-1} \epsilon_0^{-1}, \qquad (1)$$

where m^* is electron-hole reduced effective mass, Ry-hydrogen Ridberg. The value of ε_i is ~20meV for Wannier type and about 100meV for intermediate type excitons. It is seen from (1) that excitons should be sensitive to change of ϵ_0. So, they are to be destroyed at such increase of ϵ_0 due to screening of Coulomb interaction between electron and hole. Therefore it is natural to expect disappearance of appropriate lines in excitons spectra at temperatures near $T_{i,c}$. However, some experimental works concerning temperature dependence of band edge excitons line shape, including PT region witnesses the existence of excitons lines at PT temperatures [8,9]. Another surprising fact, to our mind, follows from the dielectric measurements. Being almost isotropic at temperatures far from PT the dielectric function ϵ_0 became strongly anisotropic at PT. So, the dielectric anomaly takes place only for $\epsilon_{\parallel}$ in all directions in layer plane, having remained practically unchanged for $\epsilon_{\perp}$ in direction normal to layers.

In this work the exciton spectroscopy method is applied for more detailed studying of PT in $TlGaSe_2$ and $TlInS_2$. The lines shapes of three excitons at quantum energies E_1=2.13eV, E_2=2.21eV, E_3=2.37eV (hereafter labeled as *A*, *B* and *C* correspondingly) in $TlGaSe_2$ with different Bohr radius are investigated at PT temperatures (107-120K). The comparative analysis of temperature dependences of the excitons lines shapes and dielectric function has been made. Excitons lines shapes were detected with standard methods of photoconductivity (PC) and absorption spectra, using monochromator MDR-23 and spectrometer DFS-24 respectively. PC spectra was registered as a conductivity change

$$\Delta\sigma(\lambda) = e\Delta n\mu_n + e\Delta p\mu_p, \qquad (2)$$

(Δn, Δp- carriers concentrations changes and $\mu_{n,p}$ - their mobilities) of samples under the monochromatic radiation with wavelength λ by cross-modulation method with modulation frequency 12-1200Hz. The PC spectra are normalized to equal number of quantum. For this purpose the thickness h of the samples was chosen more than the value of reciprocal absorption coefficient for the band edge *A*-exciton ($h > \alpha_A^{-1} \approx 3\cdot10^{-3}$cm). For capacitance measurements alternate current bridge E7-12 (at frequency 100Hz) was used.

All the crystals of monoclinic modification of $TlGaSe_2$ and $TlInS_2$ used in this work had been grown by Bridgmen method. Samples were prepared from different ingots with different residual impurity concentrations. *X*-ray investigations show the existence of the different polytypes of monoclinic structure. The value of dielectric constant at IC phase depends on crystal polytype and impurity concentration. In this work we did not identified the residual impurities and polytypes of samples investigated.

EXCITON SPECTROSCOPY RESULTS

For the most of $TlGaSe_2$ investigated samples the behavior of excitons line shape temperature dependence is not adequate to the results of dielectric measurements. Investigating various samples there were obtained three types

of the line shape temperature dependence. For the first type samples *C*-exciton line indicated in fig.1 disappear completely in absorption as well in PC spectra. The absorption coefficient for *A*-exciton line indicated in fig.2 (which is not resolved from B line in absorption spectra at T>80K) decreases about 2 times for these samples in IC region. Also strong decrease of PC signal takes place. At *C*-line the signal lowers up to noise values but for lines *A* and *B* it decreases about two order of magnitude. Any shift of excitons lines to the violet region of spectra as it would be expected from (1) was not observed. In contrast the small shift (~meV) of *A*-line to the red side of spectra occurs [8]. For these samples the capacitance measurements show the drastic anomaly of dielectric function reaching the value of $\in_0 \approx 1100$ for $TlGaSe_2$ and $\in_0 \approx 1800$ for $TlInS_2$.

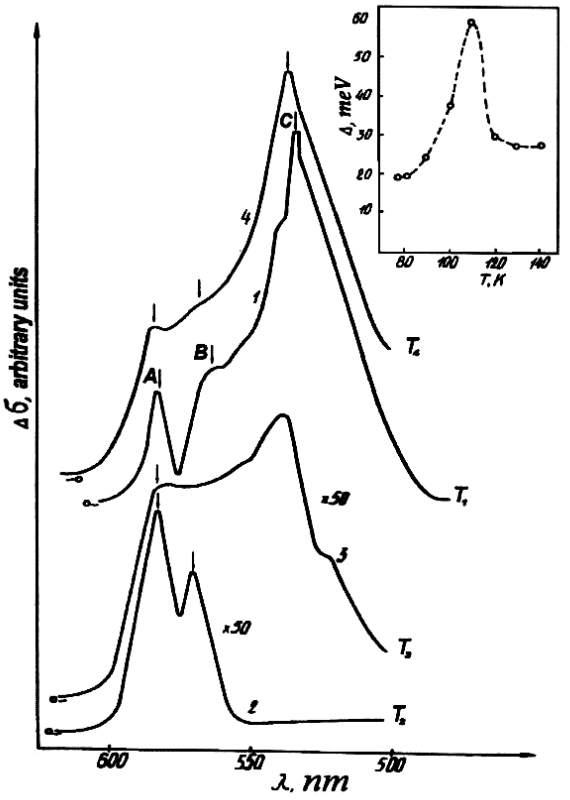

Fig.1. PC distribution against wavelength at different temperatures for first type samples of $TlGaSe_2$. 1-T_1=80K; 2-T_2=115K; 3-T_3=120K; 4-T_4=140K; insert-line width dependence on temperature.

From the fact that the absorption coefficient for *C*-exciton (α_C~10^{-4} cm^{-1}) is more than for *A* one (α_A~$3\cdot10^2 cm^{-1}$) it follows that carriers exited at *C* are much closer to the surface of crystal and participate in surface PC. But despite this, as it is seen from figs.1 and 3 the PC signal at *C*- exciton at low temperature commensurate phase is much more than one for band edge *A*- exciton. From this fact and (2) it can be concluded that the mobility μ of carriers exited at *C*- line is much higher (or effective mass $m^*=e\tau/\mu$ is lower) than that of band edge carriers. Hence it follows from (1) that *C*-exciton has greater r_B^* than that of *A*.

The *C*-line for the second type samples in IC phase is barely seen in PC (fig.3) and absorption spectra. But the decrease of intensity for C- line in IC phase is more than one for *A* and B lines (especially in PC). The intensity of *A*-line also decreases in absorption (about 1.5 times) and in PC (10-20 times) spectra. For these types of samples the dielectric anomaly takes place with moderate values of $\in_0 (T) \sim 200 - 500$.

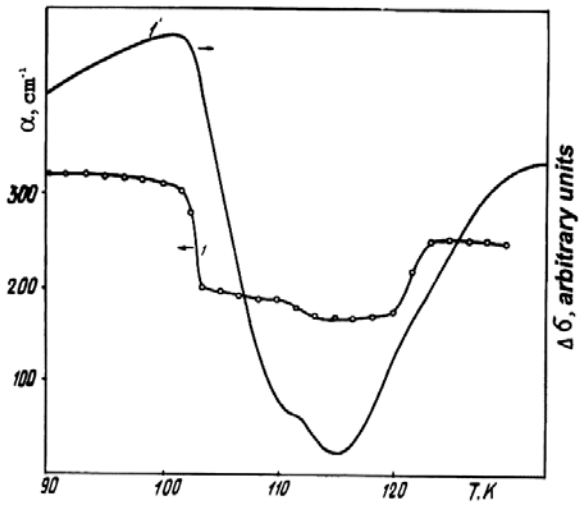

Fig.2. Absorption coefficient and PC dependence on temperature for *A*-exciton.

The rarely found samples of the third type have the usual excitons line shape dependence on temperature -gradual broadening and slight shifting to low energy, without any drastic change in PC and absorption spectra. Behavior of excitons line shape of such sample is in accordance with $\in_0 (T)$, because the capacitance measurements have shown no anomaly of $\in_0 (T)$ (cf. [6]). Probably PT for such samples hardly occurs.

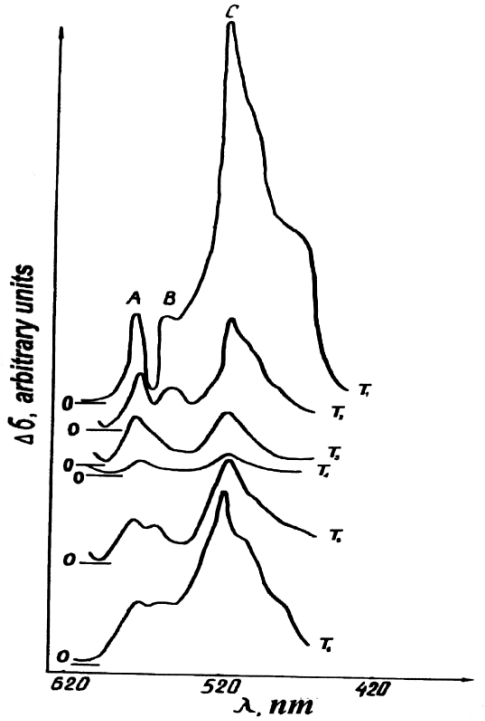

Fig.3. PC distribution against wavelength at different temperature for seconds type samples of $TlGaSe_2$ 1 - T_1=80K; 2 - T_2=105K; 3 - T_3=170K, 4 - T_4=115K; T_5=125K; T_6=140K.

In fact the higher radius *C*-exciton temperature dependence is more or less in accordance with dielectric function measurements, especially for the first type samples. But the situation is different for a smaller radius *A*-exciton, which exists at IC temperatures despite of drastic grow of ϵ_0. This allows one to suppose that in some parts of crystal's space the ϵ_0 remains practically unchanged, despite the dielectric anomaly for whole crystal. The size of these parts must be sufficiently large for a small radius *A*-exciton to be inserted inside it, but small for higher radius *C*-exciton. However, ϵ_0 being derived from measurements of capacitance has a value averaged over a whole unit cell. The unit cell of these crystals contains one or more layered blocks (with thickness 15Å) for different polytypes. [10-11]. The wave functions of conduction and valence bands are practically localized in separate blocks due to the weak Van der Waals interaction between the layers. At the same time the wave functions are free in the plane of a layer. As a result the excitons have a pancake- like shape. In other words, at least in IC region, it is possible to consider crystals as a medium with spatial dispersion in direction normal to layers $\epsilon_0\ (z)$, consisting from two (or more) slabs with thickness d_1 and $d_2 (d_1+d_2=c)$ and dielectric constants ϵ_1 and ϵ_2 respectively. According to this model the dielectric anomaly and spontaneous polarization appearing at IC phase take place only in the planes of Tl atoms. Appearance of the polarization laying in the plane of Tl^+ ions is due to shift of the Tl^+ [12]. The shift is taking place at PT inside prisms, which are included into a layered block. The ion radius of Tl^+ is about 1.3Å *A* layered block includes four Tl planes So, one can estimate the value of $d_2/d_1 \approx 2$.

For the first and second type samples strong broadening of excitons lines takes place at IC phase (inset in fig.1). The line width of *A*-exciton at IC phase is 3-4 and 2-3 times greater than one at low symmetric ($T<T_c$) and high symmetric ($T>T_i$) phase respectively. The given model allows one to consider the exciton line broadening mechanism as inhomogeneous broadening. The broadening arises due to fluctuations of exciton binding energy because of *z*-dependence of $\epsilon_0\ (z)$. The strong decrease of PC in IC phase (fig.2), which has been also observed at PT in $TlInSe_2$ [13], according to (2) is connected with change of μ as a result of carriers scattering mechanism alteration. For $TlInS_2$ crystals the result of excitons line shape investigations at PT temperatures 195-215K is practically the same. The exciton lines do not disappear completely in IC phase if the crystals are not doped specially. However, their intensities are lowered differently depending on ionization energy of excitons.

INTERPERETATION OF DIELECTRIC FUNCTION MEASUREMENTS RESULTS

The above given model of layered dielectric function in unit cell explains well the anisotropy of dielectric function anomaly at PT. To demonstrate this one can compare the effective dielectric constants in directions parallel and normal to layers $\epsilon_{ef}^{//}$ and $\epsilon_{ef}^{\perp}$. For this reason we consider two capacitors of cubic form with edge $d=d_1+d_2=c$ made as indicated in inset of fig.4. It is easy to obtain for $\epsilon_{ef}^{//}$ and $\epsilon_{ef}^{\perp}$ the following expressions:

$$\epsilon_{ef}^{//}=\frac{\epsilon_1 d_1+\epsilon_2 d_2}{d_1+d_2}, \qquad \epsilon_{ef}^{\perp}=\frac{\epsilon_1\cdot\epsilon_2\cdot(d_1+d_2)}{\epsilon_1\cdot d_2+\epsilon_2\cdot d_1},$$

(3) taking in the expression $\epsilon_{ef}=C/(d_1+d_2)$ C respectively as sequentially and parallel joint capacitors with ϵ_1, d_1 and ϵ_2, d_2.

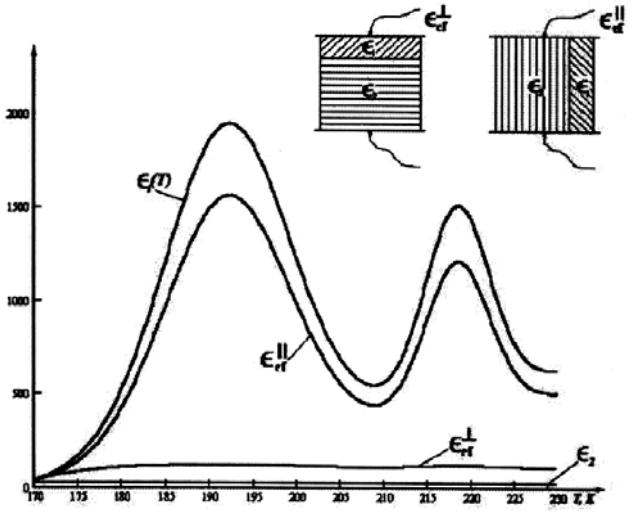

Fig.4. Calculated values of temperature dependence of $\epsilon_{ef}^{//}$ and $\epsilon_{ef}^{\perp}$; $\epsilon_2=\epsilon_0=10$; $d_2/d_1=2$.

The result of calculations of $\epsilon_{ef}^{//}$ and $\epsilon_{ef}^{\perp}$ are shown in fig.4. It is supposed that the dielectric anomaly takes place only for $\epsilon_1\ (T)$ which is represented as a superposition of ϵ_0 and two Gaussians centered at T_i=105K and T_c=115K (for $TlGaSe_2$) with different heights and widths so that $\epsilon_{ef}^{//}$ and $\epsilon_{ef}^{\perp}$ to be corresponded the results obtained from capacitance experiments. Just this kind of results shown in fig.4 is typical for capacitance measurement at PT. For $d_2/d_1=2$ the anomaly takes place only for $\epsilon_{ef}^{//}$ and is not seen for $\epsilon_{ef}^{\perp}$. At strong decrease of d_2/d_1 the week anomaly is seen for $\epsilon_{ef}^{\perp}$ also. Note that two-period nature of interference for some layered crystals is also in accordance with this model [14].

CONCLUSIONS

1. At least at IC phase $TlGaSe_2$ and $TlInS_2$ crystals can be considered as a naturally spatial dispersion mediums with periodic dielectric function $\epsilon(z+c)=\epsilon(z)$ in the direction normal to layers.

2. The same or similar effects should be observed in impurity spectroscopy (especially for shallow impurities). The impurity states disappearing or decreasing their density of states must take place at PT. This would lead to disappearing or decreasing of related line intensity in PC, photoluminicence and absorption spectra. The drastic decrease of donor–acseptor photoluminicence line, which was observed at PT temperatures in $TlGaS_2$ [15] can be explained by this model.

3. The small localization region of excitons in layered crystals makes the excitons spectroscopy diagnostic more informative in PT investigations in comparison with macroscopic parameters measurements, including dielectric constant measurements.

[1] *A.A.Volkov, U.G.Goncharov, G.V.Kozlov and R.M.Sardarly*. Zh. Eksper. Teor.Fiz.,Pisma 39, 1984, 293, (in Russian).

[2] *A.A. Volkov, U.G. Goncharov, G.V. Kozlov, K.R.. Allakhverdiev and R.M. Sardarly*. Fiz.Tverd. Tela, 1984, 26, 1754 (in Russian).

[3] *S.B. Vakhryshev, V.V. Zhdanova, B.E. Kvatkovskiy, N.M.Okuneva, K.R. Allakhverdiev, R.A. Aliev, R.M. Sardarly*. Zh. Eksper. Teor.Fiz., Pisma 39, 1984, 247, (in Russian).

[4] *K.R. Allakhverdiev, A.J. Baranov, T.G. Mamedov, D.A.Sandler, Y.R. Sharifov*. Ferroelectric Letter, 8, 1988, 125, (in Russian).

[5] *K.R. Allakhverdiev , N.D. Akhmedzade, T.G. Mamedov, T.S. Mamedov, M.Y. Seidov*. Fiz.Tverd. Tela, 2000, 26, 76, (in Russian).

[6] *R.M. Sardarly, O.A. Samedov, I.Sh. Sadykhov, E.I.Mardukhaeva and T.A. Gabilov*. Solid State Communications, 1991, 77, 453.

[7] *O.Z. Alekperov, M.O. Godjaev, M.Z.Zarbaliev and R.A.Suleimanov*. Solid State Communications, 1991, 77, 65.

[8] *S.G. Abdullaeva, N.T. Mamedov*. Fiz.Tverd. Tela, 1986, 28, 894, (in Russian).

[9] *G.I. Abutalybov, L.S. Larionkina, N.A. Ragimova*, Fiz.Tverd. Tela, 1989, 31, 312, (in Russian).

[10] *Von Dieter Muller, H. Hahn*, Z. anorg. allg. Chem., 1978, 438, 258.

[11] *S. Kashida, K. Nakamura and S.Katayama*. J.Phys.: Condens. Matter, 1993, 5, 4243.

[12] *H.D. Hochhimer, E.Gmelin, B.Bauhofer*. Ch. von Schnering-Schwarz, H.G. von Schnering, J.Ihringer, and W. Appel, Z.Phys. B-Condensed Matter, 1988, 73, 257.

[13] *O.Z. Alekperov, M. Aljanov, E. Kerimova*. Tr. J. of Physics, 1998, 22, 1053.

[14] *O.Z. Alekperov, D.O. Gamzaev, A.M. Kulibekov and R.A. Suleimanov*. Fiz.Tverd. Tela, 1993, 35,184, (in Russian).

[15] *Kato, M. Nishigaki, N. Mamedov M. Yamazaki, S.Abdullayeva, H. Uchiki and S. Iida*. 13th International Conference on Ternary and Multinary Compaunds, Book of Abstracts, 2002, p.101, Paris.

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$IGaSe_2$ VƏ $TlInS_2$ KRİSTALLARININ FAZA KEÇİDİNDƏ EKSİTON SPEKTROSKOPİYASI METODU İLƏ TƏYİN EDİLMİŞ DİELEKTRİK FUNKSİYASININ LAYLI XARAKTERİ

Laylı və kristallarındp seqnetoelektrik faza keçidi temperatur oblastında dielektrik sabitinin laylara parallel iki (və çox), dielektrik nüfuzluğu ϵ_1 və ϵ_2 müvafiq olaraq qalınlığı d_1 və d_2 ($d_1+d_2=c$, c - гяфяс векторунун laylara perpendikulyar proyeksiyasıdır) təbəqədən ibarət olduğu göstərilmişdir. Fərz olunur ki, faza keçidi temperaturlarında dielektrik anomaliya və spontan polyarizasiyanın əmələ gəlməsi ancaq təbəqələrin birində (ϵ_1, d_1). Baş verir. Təklif olunan model faza keçidində dielektrik nüfuzluğunun anizotropiyası və bu kristallarda eksitonların spektroskopiyasından alınan eksperimental nəticələrlə uzlaşır.

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СЛОИСТЫЙ ХАРАКТЕР ДИЭЛЕКТРИЧЕСКОЙ ФУНКЦИИ, ОПРЕДЕЛЕННЫЙ МЕТОДОМ ЭКСИТОННОЙ СПЕКТРОСКОПИИ ПРИ ФАЗОВЫХ ПЕРЕХОДАХ В КРИСТАЛЛАХ $TlGaSe_2$ И $TlInS_2$

Показано, что по крайней мере в области температур, соответствующих сегнетоэлектрическому фазовому переходу (ФП) диэлектрическая постоянная слоистых кристаллов $TlGaSe_2$ и $TlInS_2$ может быть представлена методом двух (или более) пластинок с различными диэлектрическими постоянными ϵ_1, ϵ_2 и толшинами d_1 и d_2 ($d_1+d_2=c$, c- проекция вектора решетки в направлении нормальном к слоям). Предполагается, что диэлектрическая аномалия и появление спонтанной поляризации при ФП происходит только в пределах одной из пластинок. Данная модель подтверждается результатами экспериментов по анизотропному поведению диэлектрических измерений и экситонной спектроскопией указанных кристаллов при ФП.

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