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### Electron-Deformational Phase Transitions in a TlGaSe<sub>2</sub> Layered Crystal

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We investigate the self-consistent localized electron states which are related to charge carrier inhomogeneities in a TlGaSe<sub>2</sub> crystal, in the framework of the continuum and the deformational potential approaches. For this purpose a nonstandard dispersion law for charge carriers following from the *ab initio* band structure calculation of the considered crystal is utilized. It is shown that a formation of stable localized electron states with different bond energy, which are separated by the potential barrier, takes place. These states can be responsible for the occurrence of the deformational phase transition in the presence of the non-equilibrium charge carriers in TlGaSe<sub>2</sub>.

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### 1. Introduction

Recently, a ternary layered TlGaSe<sub>2</sub> crystal has attracted considerable interest due to its ferroelectric and semiconducting properties as well as sequences of the structural phase transition [1, 2]. In this crystal transitions from the high temperature paraphase to the incommensurate phase at  $T_i = 118$  K, and then to the commensurate ferroelectric phase at  $T_{\rm c} = 108$  K, as well as the existence of additional metastable phases [2] have been identified. Additionally, based on experimental investigations, it has been shown that TlGaSe<sub>2</sub> possesses unusual electrical and optical characteristics [3–6]. Specifically, the nonlinear effects in the I-V characteristics, which is accompanied by the negative differential resistance, memory effects, unusual temperature dependence of the conductivity and photoconductivity, anomalous behavior of relaxation time in the temperature region 145–190 K, and the anomalous optical absorption edge have been observed for the TlGaSe<sub>2</sub> crystal. It has been suggested [6] that the above mentioned peculiarities of the physical parameters in the temperature interval quite far from the known phase transition temperatures can be related to the non-equilibrium electron phase transitions. However, a theoretical description of these transitions for TlGaSe<sub>2</sub> is still absent.

According to a theory, the electron phase transition takes the place in the multi-valley semiconductors [7], or in the initially inhomogeneous single-valley ones with the fluctuating concentrations of charge carriers [8], as a consequence of the collective interactions. In our opinion, the observed nonlinear effects in the TlGaSe<sub>2</sub> monoclinic crystal, similar to those in the In<sub>4</sub>Se<sub>3</sub> one [8, 9], can be caused by the instability of the electron subsystem due to the electron-phonon interaction. The present report is devoted to the investigation of the self-consistent localized electron states, which are connected with charge carrier inhomogeneities in the TlGaSe<sub>2</sub> crystal. For this purpose, we use the developed deformational theory of phase transitions [7, 8], in which the interaction between electrons and phonons is taken into account within the deformational potential. A nonstandard dispersion law for charge carriers which follows from the *ab initio* band structure calculation of the TlGaSe<sub>2</sub> crystal is a decisive factor for the localization phenomenon of the electron states.

# 2. Crystalline structure and peculiarities of the band spectrum in the TlGaSe<sub>2</sub> layered crystal

TlGaSe<sub>2</sub> is a A<sup>III</sup>B<sup>III</sup>C<sub>2</sub><sup>VI</sup> group semiconductor possessing a layered structure which is described by the C12/c1( $C_{2h}^{6}$ ) space symmetry group from the monoclinic system [10]. Its crystalline structure (Fig. 1) consists of the metal-chalcogen layers formed by Ga<sub>4</sub>Se<sub>10</sub> complexes which are combinations of four elementary GaSe<sub>4</sub> tetrahedra. The Tl<sup>+</sup> ions are located along the [110] and [ $\overline{110}$ ] directions. Two separated atomic layers within the elementary crystal cell are rotated relative to each other by 90°. The lattice parameters of TlGaSe<sub>2</sub> are the following: a = 10.772(3) Å, b = 10.771(5) Å, c = 15.636(8) Å,  $\beta = 100.06(3)^{\circ}$  [10].

The band structure of the TlGaSe<sub>2</sub> layered crystal has been calculated initially by means of the semi-empirical pseudopotential method [11, 12], and next by *ab initio* methods [13], however in an inappropriate Brillouin zone. Our recent *ab initio* DFT-based calculations within a relevant BZ of the monoclinic base-centered lattice [14] have revealed that the band structure of TlGaSe<sub>2</sub> exhibits a complicated form in the vicinity of the energy gap, see Fig. 1, right.

It follows from Fig. 1 that the top of the valence band is located in the  $\Gamma$  point. The absolute minimum of

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Fig. 1. Left: conventional unit cell of the  $TIGaSe_2$  crystal. Right: band structure of  $TIGaSe_2$  near the energy gap.

the conduction band is observed in the  $\Gamma$ - $F_1$  direction and the additional minima are found in the center of the Brillouin zone. These two conduction band minima are situated both in a near  $\mathbf{k}$ -space and energetic distances. The obtained results indicate an abnormal dispersion of the lowest conduction band in the direction  $F_1$ - $\Gamma$ - $Q_1$  which, in our opinion, can be caused by a lowenergy non-parabolicity of the dispersion relation  $E(\mathbf{k})$ of this band. A similar situation is observed in the case of several indium selenides [8, 15]. Now we estimate a curvature of this dispersion relation near  $\Gamma$  point in the direction  $\Gamma$ - $F_1$  within the quadratic approximation, by restricting ourselves to a small distance in the  $\mathbf{k}$ -space. As a result, the following dependence is obtained:

$$E(\mathbf{k}) = A + Bk^2 + Ck^4 + Dk^6,$$
(1)

with parameters: A = 0.7964 eV, B = -0.64043 eV, C = 6.55473 eV, D = -5.78826 eV. For a more precise description of this dispersion relation in the vicinity of the Brillouin zone center it is necessary to take into account higher order of the wave vector components. However, in order to analyze the localized electron states in the TlGaSe<sub>2</sub> crystal, the chosen accuracy is good enough.

## 3. Investigations on the self-consistent localized electron states in $TIGaSe_2$

As it is known [7, 8], a functional of the total energy of a system can be determined in the framework of the continuum and the deformational potential approaches by the following expression:

$$E[\psi, u_{ij}] = E_0 + E_{\text{int}} + E_{\text{pot}}, \qquad (2)$$

where  $E_0 = \int \psi^* \hat{H}_0 \psi d\mathbf{r}$  describes the kinetic energy of a charge carrier,  $E_{\text{int}} = \int \sum_{ij} b_{ij} \varepsilon_{ij} |\psi|^2 d\mathbf{r}$  is the interaction energy of an electron with crystal lattice,  $E_{\text{pot}} = 1/2 \sum_{ijkl} C_{ijkl} \varepsilon_{ij} \varepsilon_{kl}$  is the energy of a local elastic deformation of crystal,  $C_{ijkl}$  are the elastic moduli, and  $b_{ij}$ ,  $\varepsilon_{ij}$  denote tensor components of the deformation potential and the deformation, respectively. Utilizing the variational procedure and the nonstandard dispersion law of electrons in TlGaSe<sub>2</sub> defined by Eq. (1), we obtain the following functional:

$$E(\psi) = \int \left[ B\left(\frac{\partial\psi}{\partial x}\right)^2 + C\left(\frac{\partial^2\psi}{\partial x^2}\right)^2 + D\left(\frac{\partial^3\psi}{\partial x^3}\right)^2 \right] d\mathbf{r} - \tilde{A} \int |\psi|^4 d\mathbf{r},$$
(3)

where the electron-deformational interaction parameter  $\tilde{A}$  depends on the elastic moduli and the deformation potential. Here we consider only the interaction of an electron with the longitudinal acoustic vibrations in the TlGaSe<sub>2</sub>. For this purpose we adapt the following values of the elastic moduli tensor components and the deformation potential tensor components:  $C_{11} = C_{22} = 64.2$  GPa,  $C_{12} = 38.8$  GPa,  $C_{13} = 15$  GPa,  $C_{33} = 43.7$  GPa,  $b_{\perp} = -7.3$  eV,  $b_{\parallel} = 11.9$  eV [16]. Applying to Eq. (3) a probe function in the from used by us in [8, 9], we obtain the following dependence of electron energy versus the variational parameter  $\mu$ :

$$E(\mu) = B\pi \left(\frac{\mu}{a}\right)^2 + 3C\pi^2 \left(\frac{\mu}{a}\right)^4 + 15D\pi^3 \left(\frac{\mu}{a}\right)^6 - \tilde{A}\frac{\mu^3}{a^2c},$$
(4)

where a and c denote crystal's lattice parameters. The energy dependence of an electron interacting with longitudinal acoustic phonons in the TlGaSe<sub>2</sub> crystal versus the variational parameter  $\mu$  is presented in Fig. 2.



Fig. 2. Dependence of the localized electron energy in TlGaSe<sub>2</sub> versus the variational parameter  $\mu$ .

### 4. Discussion and conclusions

The obtained dependence  $E(\mu)$  is characterized by the presence of two minima with a different energy depth. This feature indicates a possibility for the formation of stable localized electron states (polaron or condenson [7] type), with different bond energy, which are separated by the potential barrier. We estimate the energies and radii of these localized electron states to be  $E_1 \approx 0.01$  eV,  $r_1 \approx 20$  Å and  $E_1 \approx 0.003$  eV,  $r_2 \approx 36$  Å for a metastable state. Hence, it can be expected that even some small fluctuations in the system due to temperature or other factors, which change the potential shape, can lead to the occurrence of the deformational phase transition in  $TlGaSe_2$ , in the presence of the non-equilibrium charge carriers. Thus, owing to the dispersion law with lowenergy nonparabolicity, there exist favorable conditions for the charge accumulation in this crystal.

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#### References

- [1] A.M. Panich, J. Phys. Condens. Matter 20, 293202 (2008).
- [2] F.A. Mikailov, E. Basaran, E. Sentürk, L. Tümbek, T.G. Mammadov, V.P. Aliev, *Phase Transit.* 76, 1057 (2003).
- [3] M.H.Yu. Seyidov, R.A. Suleymanov, E. Balaban, Y. Sale, J. Appl. Phys. 114, 093706 (2013).
- [4] M.H.Yu. Seyidov, R.A. Suleymanov, Y. Sale, J. Appl. Phys. 112, 103106 (2012).
- [5] M.H.Yu. Seyidov, R.A. Suleymanov, Y. Sale, *Phys. Solid State* **50**, 1219 (2008).
- [6] F. Salehli, Y. Bakis, M.H.Yu. Seyidov, R.A. Suleymanov, *Semicond. Sci. Technol.* 22, 843 (2007).

- [7] V.A. Kochelap, V.N. Sokolov, B.Yu. Vengalis, *Phase Transitions in Semiconductors with Deformational Electron-Phonon Coupling*, Naukova dumka, Kiev 1984.
- [8] D.M. Bercha, L.Yu. Kharkhalis, A.I. Bercha, M. Sznajder, *Phys. Status Solidi B* 203, 427 (1997).
- [9] M. Sznajder, Y.S. Lim, K.E. Glukhov, L.Yu. Kharkhalis, D.M. Bercha, *Acta Phys. Pol. A* **122**, 1115 (2012).
- [10] W. Henkel, H.D. Hochheimar, C. Carlone, A. Werner, S. Ves, H.G. v. Schnering, *Phys. Rev. B* 26, 3211 (1982).
- [11] S.G. Abdullaeva, N.T. Mamedov, G.S. Orudzhev, *Phys. Status Solidi B* **119**, 41 (1983).
- [12] S.G. Abdullaeva, N.T. Mamedov, *Phys. Status Solidi B* 133, 171 (1986).
- [13] S. Kashida, Y. Yanadori, Y. Otaki, Y. Seki, A.M. Panich, *Phys. Status Solidi A* **203**, 266 (2006).
- [14] D.M. Bercha, K.E. Glukhov, M. Sznajder, *Phys. Status Solidi B* 248, 1446 (2011).
- [15] M. Sznajder, K.Z. Rushchanskii, L.Yu. Kharkhalis, D.M. Bercha, *Phys. Status Solidi B* 243, 592 (2006).
- [16] K.R. Allakhverdiev, T.G. Mammedov, R.A. Suleymanov, N.Z. Gasanov, J. Phys. Condens. Matter 15, 1291 (2003).