

# Band structure and the model of a disorder in the $\text{In}_4\text{Se}_3$ crystal

M. SZNAJDER<sup>1\*</sup>, D. M. BERCHA<sup>1,2</sup> and L. YU. KHARKHALIS<sup>2</sup>

<sup>1</sup>Institute of Physics, Pedagogical University, Rzeszów, Poland

<sup>2</sup>Department of Physics, Uzhgorod State University, Uzhgorod, Ukraine

*Our study of the band structure for the  $\text{In}_4\text{Se}_3$  crystal led to an unconventional dispersion law for electrons and holes with low-energy unparabolicity caused by large values of fourth power terms. We showed that it was possible to find in this crystal a special state for an electron, the so called condenson, which has been found only for the one-dimensional case so far. We used a variational procedure and a deformation potential approximation. The knowledge of the density of states function and isoenergetic surfaces allowed us to describe more accurately other parameters of the condenson and to investigate its nature. Owing to an electron – phonon interaction the condenson exists in the  $\text{In}_4\text{Se}_3$  crystal as a soliton. Such identification explains thermal conduction in this crystal in a wide temperature range. We showed that the condition for a phase transition to the disordered phase is fulfilled, due to the existence of the density of state function.*

## 1. Compounds of the In – Se system

Recently, a great attention has been paid to the properties of thin films of the In – Se system due to their importance in photovoltaic applications [1]. Compounds of the In – Se system are low-dimensional. Crystals exhibit layered structure ( $\sim 10^6$  layer/mm), in small volume they have a large, active surface ( $\sim 2 \times 10^3 \text{ m}^2/\text{cm}^3$ ). Practical application of such a surface is achieved by means of intercalation. In – Se system compounds are phases of a variable composition and they originate in the slow peritectic reaction. Phase diagrams foresee the existence of the following compounds:  $\text{InSe}$ ,  $\text{In}_2\text{Se}_3$ ,  $\text{In}_4\text{Se}_3$ ,  $\text{In}_6\text{Se}_7$  [2]. The  $\text{InSe}$  compound is the most examined one and possesses the simplest crystallographic structure. However this structure is less thermally stable than that of the  $\text{In}_2\text{Se}_3$  compound. The  $\text{In}_2\text{Se}_3$  compound is a semiconductor which is characterized by a large number of structural

modifications and complicated low-temperature phases [3]. The  $\text{In}_4\text{Se}_3$  compound was described for the first time by Hogg [4] and afterwards by Likformann [5]. It is the least known compound. Initially it was incorrectly described as  $\text{In}_2\text{Se}$ . Later investigations have shown that the correct formula of the rhombic phase is not  $\text{In}_2\text{Se}$  but  $\text{In}_4\text{Se}_3$  and for the monoclinic phase it is not  $\text{In}_5\text{Se}_6$  but  $\text{In}_6\text{Se}_7$  [4, 6]. The basic phases and some of their characteristics are presented in Tab. 1.

Table 1. The data for the rhombic  $\text{In}_4\text{Se}_3$  crystal.

Component	Symmetry space group	Lattice parameters
$\text{In}_4\text{Se}_3$	$D_{2h}^{12}(\text{P}_{\text{nm}})$	$a = 15.297$ $b = 12.308$ $c = 4.085$

Thin films of the In – Se system have wider applications in the solar energetics than bulk crystals. The effectiveness of the photovoltaic effect is enhanced in thin films. The photovoltaic effect in bulk crystals of the  $\text{In}_4\text{Se}_3$  (known as a transversal Dember effect) is of the order of mV [7] and in layers of In – Se system it is of the order of  $\sim 1.3 - 2.5$  V, besides the intercalation with, e.g., lithium may increase this effect [8]. This is

\* corresponding author: Malgorzata Sznajder Institute of Physics, Pedagogical University, 16a Rejtana Str, 35-310 Rzeszów. tel. (48-17) 625-628 1017 fax: (48-17) 8522-044 e-mail: sznajder@univ.rzeszow.pl

the indication of the existence of spatial charges of both signs in the samples of this system. It means a distinct inhomogeneity. However the X-rays experiments confirm that the  $\text{In}_4\text{Se}_3$  compound occurs in the proper crystallographic form and that there is a one-dimensional disorder in the direction of the weak bond in some samples of this crystal [9].

## 2. The kinetic properties of the $\text{In}_4\text{Se}_3$ crystal

The kinetic properties of the  $\text{In}_4\text{Se}_3$  crystal are similar to that of layered semiconductors, such as:  $\text{InSe}$ ,  $\text{GaSe}$ ,  $\text{GeSe}(\text{S})_2$ ,  $\text{SnSe}(\text{S})$ . The experiments carried out on the  $\text{In}_4\text{Se}_3$  compound have shown that the main peculiarity of the kinetic properties is an uncommon dependence of conductivity on temperature [10,11,12]. Some characteristic anomalies appear also for the Hall coefficient which changes the sign repeatedly (see Fig. 1) [10, 11].

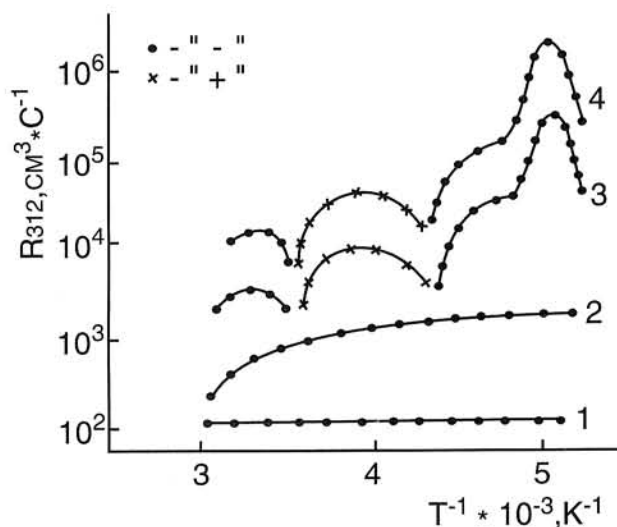


Fig. 1. The Hall coefficient for the  $\text{In}_4\text{Se}_3$  crystal.

The maximum of the  $R_{312}(T)$  dependence indicates that there occurs a switching from the band to jumping mechanism when the temperature is lowered [12].

The activation energies in the  $\text{In}_4\text{Se}_3$  crystal are different for directions perpendicular and parallel to the layers, which is the specific property of layered crystals. However the anisotropy of the conduction is not too large and it has different values depending on the concentration and the kind of the charge carriers [11]:

for  $n \sim 10^{15} \text{ cm}^{-3}$ :  $\sigma_{33}/\sigma_{22} = 5 - 10$ ,  $\sigma_{33}/\sigma_{11} = 1.5 - 3$ ,  
for  $p \sim 10^{14} \text{ cm}^{-3}$ :  $\sigma_{33}/\sigma_{22} = 20$ ,  $\sigma_{33}/\sigma_{11} = 1.2$ .

A different thermal dependence of the mobility for directions perpendicular and parallel to the layers

directions was observed. For the temperature in the range of  $T = 300 - 500 \text{ K}$  and for the activation energy  $E = 0.15 \text{ eV}$  (in the perpendicular direction), the mobility is proportional to  $\exp(-\Delta E/kT)$ . For the temperature less than  $200 \text{ K}$  the one hundred times increase of the concentration of impurities produces  $10^6$  times increase of the conduction. This property and the fact that the Mott law is fulfilled indicates that there occurs a switching from the band to jumping mechanism for temperatures lower than  $200 \text{ K}$  [13].

The frequency dependence of conduction also indicates such a jumping mechanism. Investigations of this relation offered a possibility to calculate the localized states density near the Fermi level  $N_f = 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$  and the characteristic phonon frequency. It appeared that there exist two regions of the  $\sigma$  on  $\omega$  dependence. In the low frequency region the characteristic frequency equals  $10^9 \text{ Hz}$  and for high frequencies the characteristic frequency corresponds to the frequency of the atomic vibrations in the  $\text{In}_4\text{Se}_3$  crystal and equals  $10^{13} \text{ Hz}$  [12, 14].

These data confirm that the jumping mechanism is caused by the localized states of a different nature. Localized and quasilocated states are conditioned by the electron - phonon interaction. A theoretical model of this interaction was proposed in [15]. The authors of this model assumed, that the multilayered crystal is composed of separate layers and the fluctuational excitations consist of parallel movements of layers at random distances. This excitation affects the crystalline potential by the means of the electron-phonon interaction. The non-linear equation leads to a self-consistent state -- a soliton-like object composed of clustered layers, which may be a possible cause of the observed disorder. However, the model proposed in [15] was only one-dimensional.

## 3. The kinetic properties of thin films of the $\text{In}_4\text{Se}_3$ system

Thin layers of the  $\text{In}_4\text{Se}_3$  are obtained by a vacuum vapourisation from polycrystalline materials on substrates maintained at different temperatures  $T_s$ . Thin layers grown for temperatures  $T_s < 440 \text{ K}$  are amorphous and for  $T_s > 400 \text{ K}$  possess a polycrystalline structure [16].

To determine the optic width of the forbidden band one has to investigate the fundamental edge of absorption. For thin layers, the fundamental edge  $E_g$  changes from  $1.44$  to  $1.48 \text{ eV}$  for different values of temperatures. The  $E_g$  is much lower for the  $\text{In}_4\text{Se}_3$  crystal. By means of spontaneous and stimulated emission and by

investigations of the kinetic properties the value of  $E_g$  was determined to be 0.6 – 0.8 eV [11, 17]. The exact determination of the  $E_g$  value was impossible because of the existence of an additional absorption band, which strongly overlaps the fundamental one.

There are two common mechanisms of conductivity in bulk crystal and thin films of  $\text{In}_4\text{Se}_3$ . These are band mechanism and the jumping between localized states. The intervals of straight lines in the graph of  $\ln(\sigma T^{1/2})$  on  $T^{-1/4}$  dependence [16] indicate an uncontinuous change of conduction for temperatures lower than 160 K. For the thin films grown at  $440 \text{ K} \leq T_s < 520 \text{ K}$  there appears an increase of the conductivity of more than two orders of magnitude. For the room temperature conductivity is of the order  $10^{-5} - 10^{-2} \Omega^{-1} \text{ cm}^{-1}$ . Such a difference of the conductivity is an evidence that the localized states density depends on the substrates temperature  $T_s$ .

The potential barrier model at the grains boundaries was proposed in [18], to explain the transport mechanism in polycrystalline thin films. The boundaries of the grains were established by the non-stoichiometric volumes. The height of the potential barrier was determined as  $U = 35 \text{ meV}$ , the concentrations of the doped states  $N_d = 1.5 \times 10^{17} \text{ cm}^{-3}$  and the size of the grains  $L = 23 \text{ nm}$  [16].

In contrary to the  $\text{In}_4\text{Se}_3$  crystal, for the thin films the frequency dependence of conductivity is approximated by only one expression  $\sigma(\omega) = A \omega^s$ ,  $s \sim 1$  [16]. The localized states density equal to  $N_f = 8.55 \times 10^{18} \text{ cm}^{-3} \text{ eV}^{-1}$ , appeared to be close to the value for the crystalline  $\text{In}_4\text{Se}_3$ .

The temperature dependences of conductivity and the Hall coefficient are much more complicated for crystals than for thin films. They cannot be explained

by a classical theory. Therefore, there was proposed a model of a partially – disordered crystal with the electron – phonon interaction.

#### 4. The structure of the rhombic $\text{In}_4\text{Se}_3$ crystal

The data for the rhombic  $\text{In}_4\text{Se}_3$  crystal (Tab. 2):

The main method to calculate the energy spectrum of the  $\text{In}_4\text{Se}_3$  crystal was the pseudopotential method. The band structure of this crystal (Fig. 2) [19]:

The band structure of the  $\text{In}_4\text{Se}_3$  is complicated especially in the  $\Gamma - Z$  direction. Both, the valence and the conduction bands are composed of many neighbouring subbands. The straight energy gap is localized in the  $\Gamma$  point. The central valley in the high-symmetry point  $\Gamma$  exhibits a low-energy unparabolicity with a negative curvature for small values of the wave vector  $k$ .

Small sub-bands distances in the valence and the conduction bands ( $\Delta E = 0.05 \text{ eV}$ ) and their interactions are the possible cause for an unusual dispersion law:

$$E(k) = -\alpha_1 k_x^2 - \alpha_2 k_y^2 - \alpha_3 k_z^2 + \beta_1 k_x^4 + \beta_2 k_y^4 + \beta_3 k_z^4 \quad (1)$$

with the following conduction band parameters:

$$\alpha_1 = 1.348 \cdot 10^{-18} \text{ eV} \cdot \text{m}^2, \alpha_2 = 1.996 \cdot 10^{-18} \text{ eV} \cdot \text{m}^2, \alpha_3 = 5.245 \cdot 10^{-20} \text{ eV} \cdot \text{m}^2,$$

$$\beta_1 = 2.697 \cdot 10^{-35} \text{ eV} \cdot \text{m}^4, \beta_2 = 2.092 \cdot 10^{-35} \text{ eV} \cdot \text{m}^4, \beta_3 = 8.452 \cdot 10^{-37} \text{ eV} \cdot \text{m}^4.$$

and for the valence band:

$$\alpha_1 = -5.445 \cdot 10^{-19} \text{ eV} \cdot \text{m}^2, \alpha_2 = 6.911 \cdot 10^{-19} \text{ eV} \cdot \text{m}^2, \alpha_3 = 5.68 \cdot 10^{-19} \text{ eV} \cdot \text{m}^2,$$

$$\beta_1 = -5.87 \cdot 10^{-36} \text{ eV} \cdot \text{m}^4, \beta_2 = 7.106 \cdot 10^{-36} \text{ eV} \cdot \text{m}^4, \beta_3 = 3.799 \cdot 10^{-37} \text{ eV} \cdot \text{m}^4.$$

Table 2. The basic phases of the In-Se system compounds.

Compound	Crystal symmetry	Unit – cell parameters, Å	$E_g$ , eV	$\sigma$ , $\Omega^{-1} \text{ cm}^{-1}$ (T = 300 K)	n, $\text{cm}^{-3}$	$\mu_H$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$
<b>InSe</b>	Rhombohedral R3m	a = 4.002 c = 8.75	1.29		$8.6 \times 10^{15}$	230
<b>In<sub>2</sub>Se<sub>3</sub></b> $\alpha - \text{In}_2\text{Se}_3$ $\beta - \text{In}_2\text{Se}_3$ $\gamma - \text{In}_2\text{Se}_3$	Hexagonal P6/mmm	a = 4.02 c = 19.23	1.356 1.308 1.812	$6 \times 10^{-2}$	$5 \times 10^{16}$	8.2
<b>In<sub>4</sub>Se<sub>3</sub></b>	Orthorhombic Pnnma	a = 15.297 b = 12.308 c = 4.085	0.7	$10^{-4} - 1$	$4 \times 10^{14}$ $5 \times 10^{16}$	< 200–500
<b>In<sub>5</sub>Se<sub>6</sub></b>	Monoclinic P2/ma	a = 17.65 b = 4.09 c = 9.45 $\beta = 101.10$	0.31	$10^{-2}$		

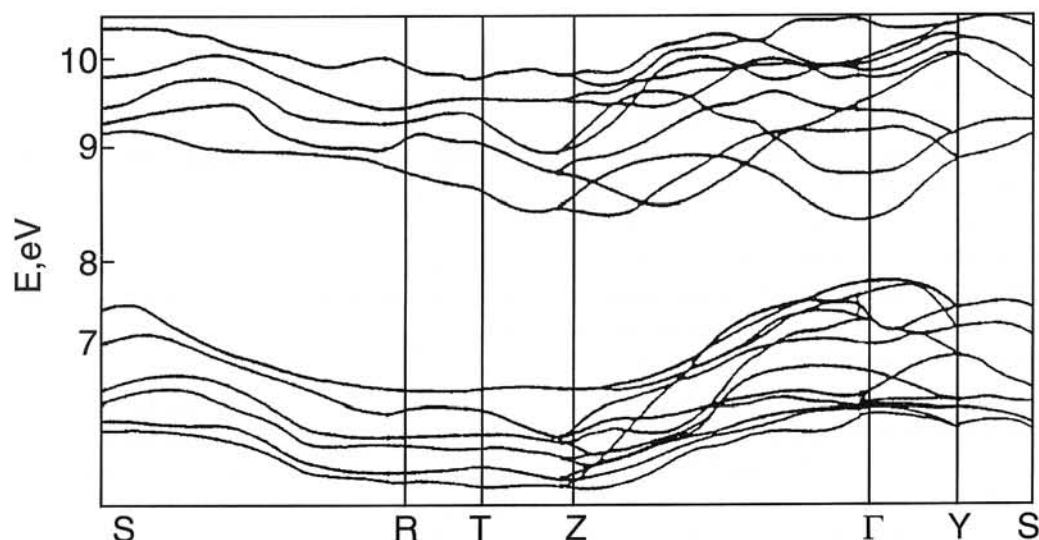


Fig. 2. The band structure of the  $\text{In}_4\text{Se}_3$  crystal.

## 5. A condenson (soliton) in the $\text{In}_4\text{Se}_3$ crystal

A condenson is a result of localization of an electron in the deformation field which is caused by this electron itself. Equations describing the condenson state in a three dimensional system may be obtained from the minimalization procedure applied to the following functional:

$$E(\mu) = a_1\mu^2 - a_2\mu^3, \quad (2)$$

where

$$\alpha_1 = \frac{\hbar^2}{2m^*} \int (|\nabla\Psi|^2) dr > 0$$

$$\alpha_2 = \frac{3b^2}{2(\chi_{11} + \chi_{12})} \int (|\Psi|^4) dr > 0,$$

where:  $b$  are the deformational potential constans,  $\lambda$  – elastic moduli,  $\mu$  – a variational parameter. The criterion obtained by Dejgen and Pekar [20] for the condenson to exist in a two- or three-dimensional system was not fulfilled in any known semiconductor, taking into account the quadratic dispersion law. However the existence of condenson states is possible in a three-dimensional system, in particular in the  $\text{In}_4\text{Se}_3$  crystal. The details of the interaction between charge carriers and acoustic phonons in the  $\text{In}_4\text{Se}_3$  crystal determine the form of the functional to be minimalized, as follows:

$$E(\mu) = -\pi \left[ \alpha_1 \left( \frac{\mu_1}{a_1} \right)^2 + \alpha_2 \left( \frac{\mu_2}{a_2} \right)^2 + \alpha_3 \left( \frac{\mu_3}{a_3} \right)^2 \right] + 3\pi^2 \left[ \beta_1 \left( \frac{\mu_1}{a_1} \right)^4 + \beta_2 \left( \frac{\mu_2}{a_2} \right)^4 + \beta_3 \left( \frac{\mu_3}{a_3} \right)^4 \right] - \tilde{\chi} \frac{\mu_1\mu_2\mu_3}{a_1a_2a_3}. \quad (3)$$

For the probe function we assumed:

$$\Psi(r) = \left( \frac{(\mu_1\mu_2\mu_3\sqrt{2})^{1/3}}{(a_1a_2a_3)^{1/3}} \right)^{3/2} \exp \left[ -\pi \left[ \left( \frac{\mu_1}{a_1} \right)^2 x^2 + \left( \frac{\mu_2}{a_2} \right)^2 y^2 + \left( \frac{\mu_3}{a_3} \right)^2 z^2 \right] \right]. \quad (4)$$

This functional may be written in a simpler form for the case of an isotropic system:

$$E(\mu) = -3\pi\alpha \left( \frac{\mu}{a} \right)^2 + 9\pi^2\beta \left( \frac{\mu}{a} \right)^4 + \tilde{\chi} \left( \frac{\mu}{a} \right)^3.$$

This functional exhibits a minimum and this is the main condition for a condenson to exist in the  $\text{In}_4\text{Se}_3$  crystal.

## 6. Collective conditions of an inhomogeneity in the electron – phonon system

The expression for the critical parameter  $A$ , which determines the possibility for the condenson to exist in



semiconductors at low temperatures, has the following form (for an isotropic case) [21]:

$$A = \frac{b^2 n}{\lambda \frac{2}{3} E(k_f(n))} = (r_e^3 n)^{1/3}, \quad (6)$$

where  $r$  is the condensation radius,  $E(k_f(n))$  – the Fermi energy level, which depends on the charge carriers concentration. The condition  $A > 1$  describes such density of states, for which the wave functions of condensation states overlap.

For an inhomogeneous system we have [21]:

$$A = \frac{b^2}{\lambda(\delta E_f/n, T)/\delta n}. \quad (7)$$

The dependence of the density of states on the concentration is inversely proportional to the shift of the Fermi energy level. Therefore, an increase of the density of states assure that the condition  $A > 1$  is fulfilled more easily. Our investigations of the topology of isoenergetic surfaces for the  $\text{In}_4\text{Se}_3$  crystal confirmed the anticipated changes of the function of the density of states. The shape of this function (see Fig. 3.) – the visible peak – attests the fulfillment of the  $A > 1$  condition, i.e. the formation of a multicondensation in the  $\text{In}_4\text{Se}_3$  crystal.

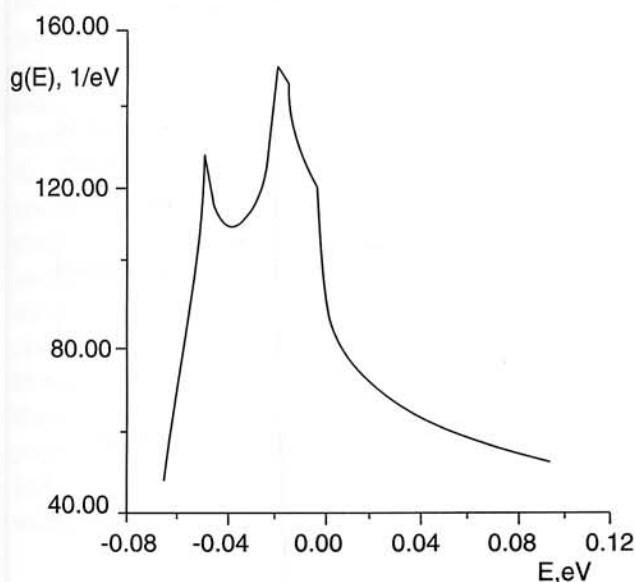


Fig. 3. The density of states function for the  $\text{In}_4\text{Se}_3$  crystal.

## 7. Conclusions

The specific form of the dispersion law for the  $\text{In}_4\text{Se}_3$  crystal determines that the inhomogeneity manifests itself in this crystal in a form of multicondensation. The formation of the multicondensation may be recognized in the specific kinetic properties of the  $\text{In}_4\text{Se}_3$  crystal.

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