ELECTRICAL PROPERTIES OF In_2Se_3 INTERCALATED LAYERED CRYSTALS

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The anisotropy and the electrical properties of In_2Se_3 layered crystals and their lithium and hydrogen intercalates are studied in the temperature range 80÷400 K. It is established that, with increase in the temperature, the electrical conduction and the mobility along layers decrease, whereas the free electron concentration remains practically invariable. The obtained temperature dependence of the electron mobility is explained by the interaction of electrons with homopolar optical phonons. A change of the electrical conduction of hydrogenated In_2Se_3 crystals depending on the annealing time is due to the formation of new levels in the forbidden band and the effect of intercalated hydrogen on the deformation potential of a crystal. The established decrease of the anisotropy for the $Li_{1.5}In_2Se_3$ intercalate as compared with that of In_2Se_3 in the temperature interval 250÷400 K is caused by the prevailing reduction of the electrical conduction normally to layers over a slight decrease of the conduction in parallel to them.

1. Introduction

One of the layered compounds which are of interest both in the scientific and applied aspects is In_2Se_3 semiconductor. This crystal as well as intercalation compounds on its basis can be used to produce primary and secondary current sources with high specific characteristics and sensitive elements of strain gauges. The published results of studies of the physical properties of these crystals [1–3] considerably differ, which is explained both by the strong imperfection of the material structure and the presence of various (α, β, and γ) crystal phases. The aim of this work is to study the electrical properties of In_2Se_3 layered crystals and their lithium and hydrogen intercalates.

2. Experimental Technique

In_2Se_3 single crystals were grown by the Bridgman technique from a stoichiometric melt at a temperature gradient at the crystallization front equal to 15 deg/cm and a growth rate of 1 mm/h. The obtained materials are characterized by a pronounced layered structure over the whole length of a sample. The performed X-ray analysis demonstrates that they have a structure of the α-phase with the lattice parameters $a = 4.031$ Å, $c = 19.2$ Å. The In_2Se_3 layered crystals were intercalated by the electrochemical method using a 1M solution of $LiClO_4$ in propylene carbonate. The effect of the concentration of intercalated lithium ions on the properties of In_2Se_3 was studied on the same group of samples by means of the deintercalation. The process of intercalation of In_2Se_3 single crystals was realized within the the the method of "pulling" electric field [4] in the galvanostatic mode. Lithium ions were intercalated into the layered crystal by allowing the passage of the electric current of the necessary magnitude through the electrochemical cell. The concentration of the intercalated impurity x ($0.1 \leq x \leq 1.5$, where x is the number of intercalated lithium ions per one formula unit of the crystalline matrix) was determined by the charge which has passed through the cell, i.e. the controlled parameters in the process of the intercalation reaction were the electric current density and the duration of the process. The use of the optimal technological parameters of the intercalation process (current density below 10 μA/cm^2) allowed us to obtain homogeneous intercalated samples.

The intercalation of hydrogen into In_2Se_3 (hydrogenation) was performed according to the thermal exposure method used for the intercalation of layered semiconductors with metals [5, 6]. For this purpose, the initial In_2Se_3 samples were placed in quartz ampoules evacuated to a residual pressure of 10^{-3} Torr through a nitrogen trap in order to prevent the formation of a vapor with carbon compounds. The evacuated ampoules were filled with hydrogen at the liquid-nitrogen temperature and then sealed off. Molecular hydrogen was introduced by keeping the samples in the hydrogen medium at a temperature of 600 °C and a pressure of ~ 0.3 MPa. Moreover, the first group of the samples was kept during 24 h, while the second one — during 48 h. According to the Sieverts law, in the case of diffusion of a diatomic gas decaying into separate atoms when entering a solid body, the amount of intercalated hydrogen is proportional to

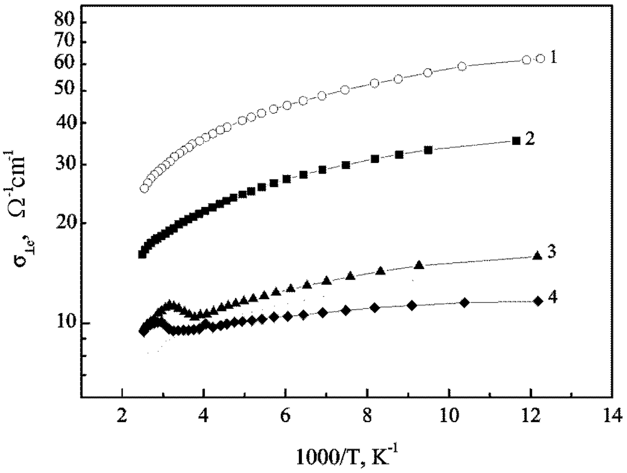

Fig. 1. Temperature dependence of the layer-parallel electrical conduction $\sigma_{\perp c}$ for In_2Se_3 layered crystal (*1*) and intercalation compounds $Li_{0.1}In_2Se_3$ (*2*), $Li_{1.0}In_2Se_3$ (*3*), and $Li_{1.5}In_2Se_3$ (*4*)

$\sqrt{P}$ (where P is the partial gas pressure in the system) [7]. The weak van der Waals bond between layer packets in In_2Se_3 and the strong ion-covalent bond inside the layers enable one to intercalate hydrogen into the interlayer space. The relation between the interlayer distance in In_2Se_3 (3.55 Å) and the gas-kinetic diameter of a hydrogen molecule (2.89 Å) testifies to the validity of such an assumption. An increase of the time of keeping the samples in the hydrogen atmosphere must result in a rise of the amount of introduced hydrogen and its ordering in the crystal system of the sample. The ampoules with samples were cooled in a switched-off furnace for 24 h. The described procedure yielded hydrogenated samples $\langle H\rangle In_2Se_3$.

The temperature dependences of the Hall coefficient R_H, ($B \parallel \mathbf{c}$), the electrical conductions in parallel and normally to layers ($\sigma_{\perp c}$ and $\sigma_{\parallel c}$, respectively), and the Hall mobility $\mu_{\perp c}$ were studied in the temperature range 80÷400 K. The experiments were performed at a constant current using the samples $10 \times 2.3 \times 0.6$ mm^3 in size in a magnetic field. Indium contacts were deposited in the classical configuration. The electrical conduction $\sigma_{\parallel c}$ was measured by the four-probe technique with contacts placed at the opposite cleaved surfaces: two of them were used as current ones and the other two — as probe ones. The electrical properties of the hydrogenated In_2Se_3 samples were investigated the next day after the completion of annealing, as there exist data [8] on the 15–20% decrease of the effect of intercalated hydrogen on the properties of layered crystals kept in air at room temperature during 80–100 days.

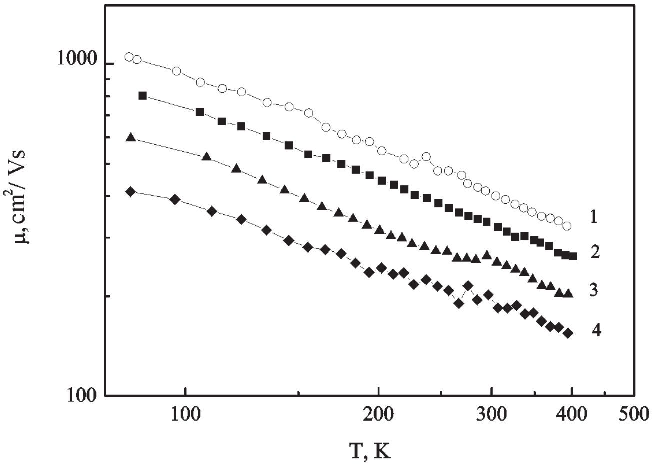

Fig. 2. Temperature dependence of the free carrier mobility $\mu_{\perp c}$ for In_2Se_3 layered crystal (*1*) and intercalation compounds $Li_{0.1}In_2Se_3$ (*2*), $Li_{1.0}In_2Se_3$ (*3*), and $Li_{1.5}In_2Se_3$ (*4*)

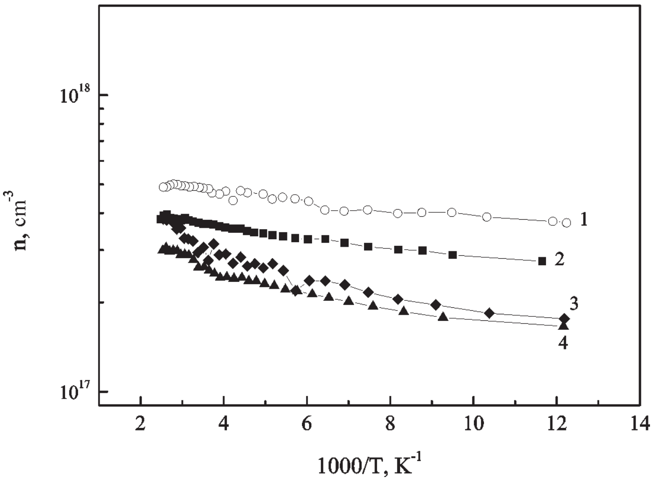

Fig. 3. Temperature dependence of the free carrier concentration n for an In_2Se_3 layered crystal (*1*) and intercalation compounds $Li_{0.1}In_2Se_3$ (*2*), $Li_{1.0}In_2Se_3$ (*3*), and $Li_{1.5}In_2Se_3$ (*4*)

3. Results and Their Discussion

The electrical properties of an In_2Se_3 layered crystal and its intercalates were investigated in the temperature range 80÷400 K. Figures 1–3 show the temperature dependences of the electrical conduction $\sigma_{\perp c}$ and the electron mobility $\mu_{\perp c}$ in parallel to layers, as well as the free electron concentration n for the initial In_2Se_3 crystal (curve *1*) and its lithium intercalates (curves *2*–*4*) with various lithium concentrations. Experimental data are also presented in Table 1. The temperature dependence of the electrical conduction anisotropy of the initial In_2Se_3 samples and the intercalation compound

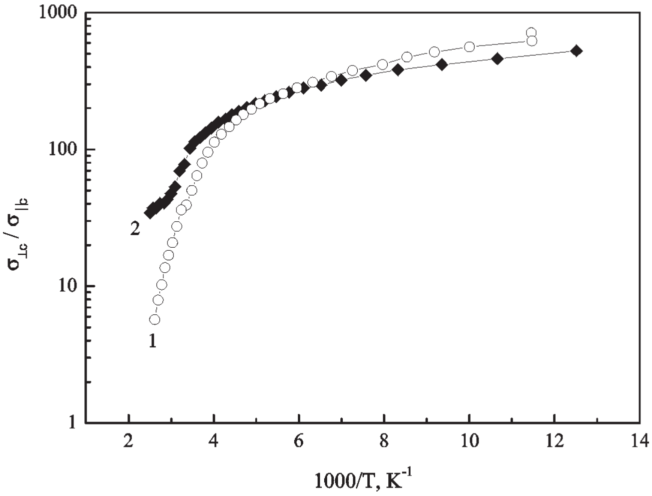

Fig. 4. Temperature dependence of the electrical conduction anisotropy for a In_2Se_3 layered crystal (*1*) and the intercalation compound $Li_{1.5}In_2Se_3$ (*2*)

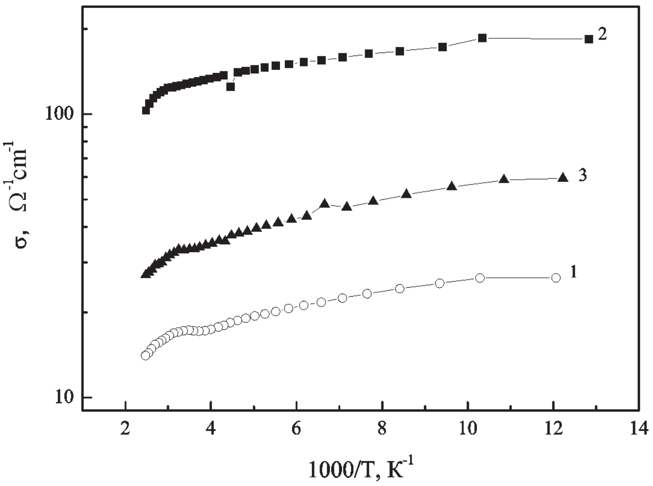

Fig. 5. Temperature dependence of the layer-parallel electrical conduction $\sigma_{\perp c}$ for In_2Se_3 layered crystal (*1*) and In_2Se_3 crystals annealed in the hydrogen atmosphere during 24 (*2*) and 48 (*3*) h

$Li_{1.5}In_2Se_3$ are depicted in Fig. 4. The experimental dependences $\sigma_{\perp c}(T)$ and $n(T)$ for the hydrogenated In_2Se_3 crystals are depicted in Figs. 5–6.

As one can see from the data presented for the $Li_xIn_2Se_3$ (Fig. 1) and $H_xIn_2Se_3$ (Fig. 5) crystals, an increase of the temperature results in a monotonous decrease of $\sigma_{\perp c}$. It is worth paying attention to the nonmonotononic character of the temperature behavior of $\sigma_{\perp c}$ for the $Li_{1.0}In_2Se_3$ and $Li_{1.5}In_2Se_3$ intercalated samples in the temperature range 250÷400 K. Thus, the performed measurements testify to the fact that the electrical conduction along layers decreases from 63.2 Ohm^{-1}cm^{-1} ("pure" In_2Se_3) to 14.6 Ohm^{-1}cm^{-1} ($Li_{1.5}In_2Se_3$) at $T = 80$ K and from 25.3 Ohm^{-1}cm^{-1} ("pure" In_2Se_3) to 9.5 Ohm^{-1}cm^{-1} ($Li_{1.5}In_2Se_3$) at $T = 400$ K. A somewhat opposite picture is observed in the hydrogenated intercalates $\langle H\rangle In_2Se_3$: the electrical conduction of the samples hydrogenated during 24 h increases approximately sevenfold as compared to the initial In_2Se_3 sample. With the following twofold increase of the time of keeping (which is expected to induce an increase of the amount of introduced hydrogen), the electrical conduction decreases thrice.

As follows from the temperature dependence of the Hall mobility of electrons along layers $\mu_{\perp c}$ (Fig. 2), curves *1–4* monotonously decrease in the temperature interval 80÷400 K without any changes of the slope angle with respect to the temperature axis. Analyzing the obtained data (see Table), one can see that the parameter $\mu_{\perp c}$ at $T = 80$ K decreases from 1050 cm^2/(V·s) ("pure" In_2Se_3) to 413 cm^2/(V·s) ($Li_{1.5}In_2Se_3$), while, at $T = 400$ K, the Hall mobility along layers decreases from 325 cm^2/(V·s) ("pure" In_2Se_3) to 155 cm^2/(V·s) ($Li_{1.5}In_2Se_3$).

According to the temperature dependence of the free carrier concentration n for $Li_xIn_2Se_3$ (Fig. 3) and $\langle H\rangle In_2Se_3$ (Fig. 6), the given parameter undergoes insignificant changes (see Table). That is why the temperature behavior of $\sigma_{\perp c}$ must be mainly determined by that of $\mu_{\perp c}$.

Analyzing the dependence $\sigma_{\perp c}(10^3/T)$ for In_2Se_3 and its lithium intercalates (Fig. 1), one can see that $\sigma_{\perp c}$ decreases, as the temperature increases, which testifies to the partially "metal" type of conduction of these compounds. The nonmonotonic behavior (partial growth) of $\sigma_{\perp c}$ for the $Li_{1.0}In_2Se_3$ and $Li_{1.5}In_2Se_3$ intercalation compounds in the temperature interval 250÷400 K is possibly related to the activation of a shallow donor level [9, 10], which is also confirmed by a partial increase of the free carrier concentration on the experimental dependence $n(10^3/T)$ (Fig. 3, curves *3, 4*). A decrease of $\sigma_{\perp c}$ and n at a fixed temperature with increase in the lithium concentration (Figs. 1, 3) is due most probably to the fact that the intercalation of lithium ions can result in the formation of deformation defects that induce, in turn, the generation of acceptor levels in the forbidden band of the In_2Se_3 crystal.

Based on the obtained temperature dependences, we determined the anisotropy of the electrical conduction $N = (\sigma_{\perp c}/\sigma_{\| c})$ for initial In_2Se_3 crystals and their intercalates $Li_{1.5}In_2Se_3$: $N_{In_2Se_3} = 620$, $N_{Li_xIn_2Se_3} = 525$ at $T = 80$ K and $N_{In_2Se_3} = 5.7$, $N_{Li_xIn_2Se_3} = 35$ at $T = 400$ K. In other words, the anisotropies of the elec-

Experimental data on the electrical conduction, free carrier mobility, and concentration of a In_2Se_3 layered crystal and $Li_xIn_2Se_3$ intercalation compounds obtained at 80 and 400 K

Compound	$\sigma_{\perp c}$, Ohm^{-1}·cm^{-1}		$\mu_{\perp c}$, cm^2/(V·s)		n, cm^{-1}	
	80 K	400 K	80 K	400 K	80 K	400 K
In_2Se_3	63.2	25.3	1050	325	3.7×10^{-17}	4.9×10^{-17}
$Li_{0.1}In_2Se_3$	36.1	17.2	802	264	2.75×10^{-17}	3.82×10^{-17}
$Li_{1.0}In_2Se_3$	16.2	9.8	597	202	1.66×10^{-17}	3.10×10^{-17}
$Li_{1.5}In_2Se_3$	14.6	9.5	413	155	1.76×10^{-17}	3.82×10^{-17}

trical conduction for In_2Se_3 and $Li_{1.5}In_2Se_3$ almost coincide in the temperature range 80÷250 K. As the temperature increases (in the interval 250÷400 K), the value of N for $Li_{1.5}In_2Se_3$ exceeds the corresponding value for In_2Se_3 by a factor of six (Fig. 4). This relation can be explained with regard for the fact that, as compared to the initial In_2Se_3 crystals, the layer-normal electrical conduction $\sigma_{\parallel c}$ in the $Li_{1.5}In_2Se_3$ intercalation compounds decreases stronger (by one order of magnitude) than the layer-parallel one $\sigma_{\perp c}$ (by a factor of 3.5). In this case, it is possible that there arise potential barriers between the layers of the crystal lattice caused by the presence of an intercalator, whereas the electron motion along the axis **c** becomes spasmodic.

As for the electrical conduction of the hydrogenated In_2Se_3 crystals, its increase and subsequent decrease observed with varying the time of keeping the samples in the hydrogen atmosphere can be explained as follows. The initial increase of the electrical conduction is due to the growth of the free carrier concentration (Fig. 6) and can be related to the fact that a part of intercalated hydrogen occupies the H^+ state. In addition, it is worth paying attention to the possibility of the formation of new levels in the forbidden band of In_2Se_3. It is possible that, at small amounts of intercalated hydrogen, new levels are formed in the forbidden band of the layered crystal, which results in a rise of the electrical conduction. It is known that the interlayer interaction in layered crystals weakens at high temperatures, while the anisotropy of their elastic properties grows [11]. The increase of the annealing time of layered crystals in the hydrogen atmosphere results in a growth of the concentration of intercalated hydrogen in the van der Waals gap, which gives rise to an increase of the interlayer pressure and a deformation of the crystal structure due to the intercalation [8], which decreases, in turn, significantly the mobility of charge carriers as well as the value of $\sigma_{\perp c}$.

The temperature dependences of the layer-parallel Hall mobility $\mu_{\perp c}$ for In_2Se_3 and its lithium intercalates (Fig. 2) are stronger than the function $n(10^3/T)$ (Fig. 3), i.e. the dominant contribution to a change of the layer-parallel conduction is made by the electron mobility with a variation of the temperature or the free carrier concentration at a constant temperature. The temperature dependence of the layer-parallel mobility $\mu_{\perp c}$ in the considered interval is mainly determined by the interaction of carriers with thermal lattice oscillations (homopolar optical phonons) polarized normally to the layers [3, 12], which obeys the empirical dependence $\mu_{\perp c} = AT^p$, where $p = -1$ ($\hbar\omega = 14.3$ meV). High values of the mobility (Table), as well as the absence of the dominant electron scattering by ionized impurities at low temperatures, testify to the structural perfection of the studied crystals [13]. It is worth noting that the dependence $\mu_{\perp c} = AT^p$ ($p = -1$) does not exclude the existence of space charge regions in the crystal [14]. According to the studies performed for $Li_xIn_2Se_3$ compounds [3, 10], it is established that intercalated lithium ions occupy octahedral sites of the van der Waals gap forming Li_2Se inclusions (space charge regions). It is known that the interatomic bond inside the layers of In_2Se_3 has the ion-covalent nature, while the interlayer bond is the weak van der Waals one. In addition, there are one octahedral and two tetrahedral cavities per each Se atom

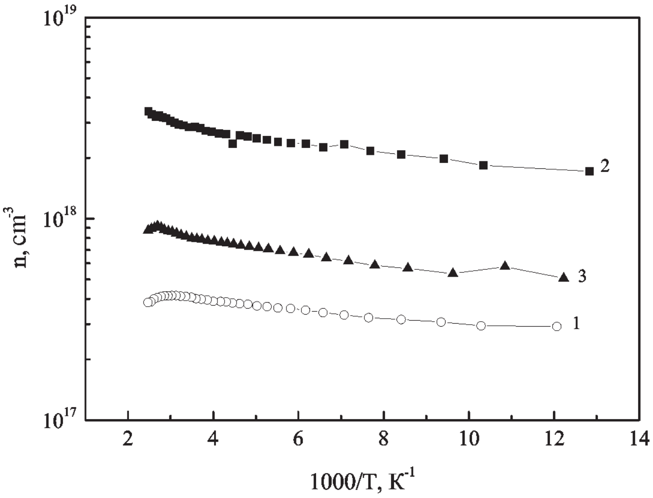

Fig. 6. Temperature dependence of the free carrier concentration n for In_2Se_3 layered crystal (*1*) and In_2Se_3 crystals annealed in the hydrogen atmosphere during 24 (*2*) and 48 (*3*) h

[15], i.e. there exists a possibility of the intercalation of Li^+ exactly to these sites. Assuming the possibility of the formation of Li_2Se inclusions in our crystals, this factor can result in considerable changes of the mobility (Fig. 2) at a fixed temperature due to insignificant changes of the concentration (Fig. 3), which will result in a noticeable decrease of $\sigma_{\perp c}$ (Fig. 1).

4. Conclusions

The electrical properties and the anisotropy of In_2Se_3 layered crystals, their lithium intercalates $Li_xIn_2Se_3$ ($0.1 \le x \le 1.5$), and In_2Se_3 crystals annealed in the hydrogen atmosphere are investigated. It is established that, with increase in the temperature, the electrical conduction and the mobility along the layers decrease, whereas the free electron concentration remains practically constant. The reduction of the anisotropy parameter for the $Li_{1.5}In_2Se_3$ intercalate as compared with In_2Se_3 in the temperature range 250÷400 K is related to the prevalence of the decrease of the layer-normal electrical conduction over the insignificant decrease of the layer-parallel one.

The growth of the electrical conduction for the In_2Se_3 crystals hydrogenated during 24 h is explained by the rise of the free carrier concentration (a part of hydrogen intercalated into the crystal occupies the H^+ state) and the formation of new levels in the forbidden band of the layered crystals at small amounts of intercalated hydrogen. An increase of the annealing time results in a growth of the interlayer pressure and a deformation of the crystal structure due to the intercalation, which significantly decreases the mobility of charge carriers, as well as the value of $\sigma_{\perp c}$.

Thus, the intercalation allows one to control certain electrical parameters of In_2Se_3 layered semiconductors depending on the nature, amount of intercalated impurity, and the way of intercalation. It is worth noting that the studied compounds represent effective model objects for fundamental investigations and are promising for their possible use as elements of energy and strain-sensing devices.

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ЕЛЕКТРИЧНІ ВЛАСТИВОСТІ ІНТЕРКАЛЬОВАНИХ ШАРУВАТИХ КРИСТАЛІВ In_2Se_3

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Резюме

У діапазоні 80–400 K досліджено електричні властивості, анізотропію шаруватих кристалів In_2Se_3, їх літієвих та водневих інтеркалятів. Встановлено, що зі зростанням температури електропровідність та рухливість вздовж шарів зменшуються, а концентрація вільних електронів практично не змінюється. Отримана температурна залежність рухливості електронів пояснена їх взаємодією з гомополярними оптичними фононами. Зміна електропровідності гідрованих кристалів In_2Se_3 залежно від часу відпалу пояснюється утворенням нових рівнів у забороненій зоні та впливом впровадженого водню на величину деформаційного потенціалу кристала. Встановлене зменшення анізотропії для інтеркаляту $Li_{1,5}In_2Se_3$ порівняно із In_2Se_3 в діапазоні температур 250–400 K пояснюється переважаючим зменшенням електропровідності перпендикулярно шарам над незначним зменшенням електропровідності вздовж шарів.