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OPTICAL AND ELECTRICAL PROPERTIES OF InSe AND GaSe LAYERED CRYSTALS INTERCALATED WITH ETHANOL

Structural, optical, and electrical properties of InSe and GaSe single crystals diffusely intercalated with ethanol have been studied. The X-ray analysis confirmed that ethanol molecules become introduced into the interlayer space of samples. The dependences of the energy position of the main exciton maximum and a half-width of the excitonic absorption band on the holding time of InSe and GaSe single crystals in ethanol are found to be non-monotonous. The temperature dependences of the conductivity, concentration, and mobility of electrons along the layers in InSe are obtained. The change in the conductivity of InSe crystals intercalated with ethanol and its dependence on the holding time are explained by the formation of new levels in the energy gap and the influence of intercalated alcohol molecules on the deformation potential in a crystal.

Keywords: InSe and GaSe single crystals, intercalation.

1. Introduction

According to the modern viewpoint, the intercalation is a reverse chemical process, at which guest molecules (atoms, ions) are introduced into the crystallographic matrix of a solid [1, 2]. Interest to such processes is associated with a capability of synthesizing the new compounds with a set of physical and chemical properties that are either difficult or, sometimes, impossible to be obtained with the use of conventional synthesis techniques. A considerable number of works devoted to studying the intercalation systems containing various two-dimensional matrices (hosts) and guest molecules testify that a characteristic feature of the intercalation process in layered structures is the introduction of impurities into the space between layers. Semiconducting crystals A^3B^6 with a layered structure belong to compounds, in which the introduced molecules can be located not only in the interlayer space, but sometimes in the layers themselves as well. Single crystals of InSe and GaSe belong to layered compounds with drastically anisotropic properties [3]. The chemical bond in such crystals is of mixed type: it is covalent between the atoms in every layer and of the Van der Waals type between four-layer packets. The strongly pronounced layered structure with weak coupling between layer packets in InSe and GaSe allows atoms or molecules to diffuse into the space between the packets to form an intercalated compound—a layered structure, in which the layers of introduced impurity alternate with four-layer packets Se–Ga(In)–Ga(In)–Se. As was shown in works [4, 5], the electrochemical intercalation of impurities from organic solvents results in that not only intercalant atoms, but also the solvate shell and OH complexes are introduced. In order to distinguish between the influences of intercalant atoms and organic solvent molecules, it seems important to study a possibility of introducing the pure organic solvents into layered crystals A^3B^6, as well as the properties of obtained intercalates.

In this work, we report the results of our researches concerning the optical and electric properties of InSe and GaSe single crystals intercalated with ethyl alcohol.

2. Experimental Technique

Specimens of InSe and GaSe single crystals for experimental researches were grown from highly pure components using the Bridgman method. Following the Weissenberg method, we found that the crystals obtained had either the γ-InSe or the ϵ-GaSe struc-

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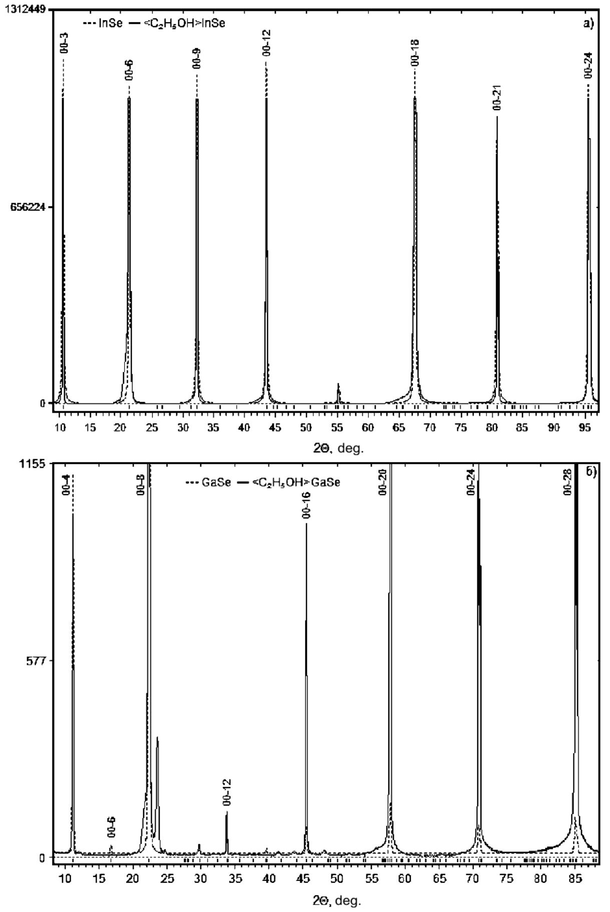

Fig. 1. Diffraction patterns of InSe (*a*) and GaSe (*b*) layered crystals: initial and kept in alcohol for four months

ture. Ethyl alcohol (C_2H_5OH) of 96% was used as an impurity for the introduction. The introduction was carried out using the diffusion method, namely, by holding the specimens in alcohol at the constant temperature $T = 50$ °C. The holding time was 1, 2, and 5 months for InSe and 1, 2, and 4 months for GaSe. The crystalline structure of intercalated specimens was monitored with the help of X-ray analysis on a DRON-2.0 installation in CuK radiation. The results of measurements were processed using the Rietveld analysis. The transmission spectra of the initial and intercalated InSe and GaSe specimens were studied at $T = 77$ K near the edges of fundamental and excitonic absorptions; more specifically, in an interval of 1.32–1.45 eV for InSe and 2.08–2.15 eV for GaSe. Optical measurements were carried out on a spectrometric installation constructed on the basis of a monochromator MDR-23 (in the configuration when light propagated normally to the basic crystal plane) and a cryostat system UTREKS-RTR. The resolution of the device in the examined spectral range amounted to 0.5 MeV. Specimens 10–20 μm in thickness were used for optical measurements. The temperature dependences of the Hall coefficient R_{H} ($\mathbf{B} \parallel \mathbf{c}$), the electric conductivities along, $\sigma_{\perp c}$, and perpendicular, $\sigma_{\parallel c}$, to the layers, and the Hall mobility $\mu_{\perp c}$ were studied in a temperature interval of 80–400 K. The experiments were carried out, by using the direct current and the dc magnetic field. The specimens were parallelepipeds $10 \times 2.3 \times 0.6$ mm^3 in dimensions. Indium contacts were deposited in the classical configuration following the technique described in work [6].

3. Results and Their Discussion

The analysis of diffraction patterns obtained for InSe and GaSe single-crystalline specimens, initial and kept in alcohol, showed that the specimens kept in alcohol demonstrate a broadening (smearing) of diffraction peaks (Fig. 1) and a reduction in the reflection intensity. It is known [7] that the broadening of diffraction reflections is associated with microdeformations or packing defects in the crystal structure, the shape and the intensity of reflections depend on atomic shifts, and their shift testifies to a variation of crystal lattice parameters. Taking into account that an alcohol molecule has a plane structure, and its dimensions are comparable with the magnitude of Van der Waals gap, we may admit that alcohol molecules diffuse into the interlayer space in specimens to form interstitial compounds of the $[C_2H_5OH]A^3B^6$ type. The appearance of an intercalant in the interlayer space and its further localization give rise to the emergence of deformation stresses in the Van der Waals gap and the variations of crystallographic structure parameters; all that, in its turn, results in a broadening of diffraction peaks. It should be noted that the observed broadening of diffraction reflections is more substantial for GaSe single crystals kept in alcohol than for InSe ones, which may be governed by the magnitude of Van der Waals gap in those compounds. The interlayer distance in GaSe amounts to 4.199 Å against 3.84 Å in InSe [8], and alcohol molecules diffuse more readily into the crystalline matrix of GaSe layered crystal.

The introduction of alcohol molecules into the interlayer space of examined specimens is confirmed by the transmission spectra (in the excitonic absorption interval) of InSe (Fig. 2) and GaSe (Fig. 3) single crystals kept in alcohol. The authors of works [9, 10] showed that the appearance of an intercalant in the Van der Waals space of layered crystals results in the emergence of a pressure between the layers and a modification of the deformation potential in the crystal lattice. In addition to the above-mentioned smearing of diffraction reflections, the described processes induce the changes in the energy position of the main excitonic maximum ΔE_{ex} and the half-width of the excitonic absorption band ΔH. From the obtained spectral dependences, we determined those optical characteristics and their dependences on the holding time t (Table), because the concentration of an intercalant that has diffused into the crystal increases with t.

The specific character of the crystalline structure in layered crystals manifests itself as a difference between the contributions of deformations in the layers and between them to a reconstruction of the crystal energy spectrum when intercalant molecules are introduced. The deformation of the crystal lattice stemming from the variation of interlayer elastic constants is accompanied by an increase of the energy gap width E_g in the crystal [11] and the growth of the exciton binding energy [8], which provokes a shift of E_{ex} into the high-energy spectral region. The reverse behavior of the dependence $\Delta E_{\mathrm{ex}}(T)$ is mainly driven by the prevailing variation of elastic constants in the layer (as a result, E_g decreases [8]) and the variation of the density of states near the forbidden gap edge induced by the impurity potential. The latter gives rise to the emergence of a "tail" in the density of states [12] in the forbidden gap of the intercalated crystal. The half-width of the excitonic band changes, when alcohol molecules penetrate into the crystal lattice of InSe or GaSe, owing to an aperiodic character of the potential relief in the intercalated crystals, which directly affects the radius of excitons and their scattering [12].

In Figs. 4 to 6, the temperature dependences of the electric conductivity $\sigma_{\perp c}$, free electron concentration n, and electron mobility $\mu_{\perp c}$ along the layers, respectively, obtained for InSe specimens, initial and kept in alcohol, are depicted. One can see that the conductivity along the layers in InSe crystals intercalated with alcohol for three months decreases, the concentration of free electrons becomes lower, whereas the electron mobility remains practically constant. As the time of specimen holding in alcohol and, accordingly, the concentration of introduced alcohol molecules increase, an inverse process is observed, i.e. the values of $\sigma_{\perp c}$ and n start to grow. The reduction of those parameters at a fixed temperature as the intercalant concentration increases may be a result of the pressure that emerges between the layers and deformation-induced defects that emerge during the introduction of alcohol molecules. As was shown in work [4], the introduced molecules of ethyl

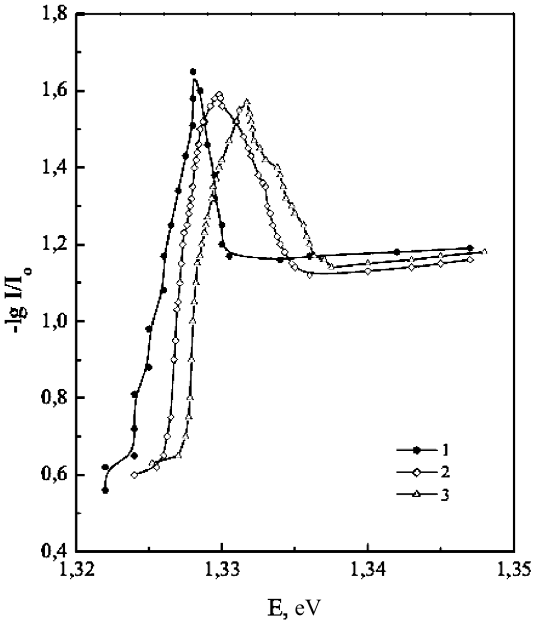

Fig. 2. Optical density spectra for InSe layered crystals: initial (*1*) and kept in alcohol for two (*2*) and five (*3*) months

Changes in the position of the main excitonic maximum E_{exc} and the half-width of the excitonic band ΔH for InSe and GaSe single crystals kept in ethyl alcohol

Time of specimen holding in C_2H_5OH	InSe		GaSe	
	ΔE_{ex}, meV	ΔH, meV	ΔE_{ex}, meV	ΔH, meV
1 month	2.6	1.7	2.8	1.9
2 months	5.6	3.6	6.1	4.8
5 months	6.8	4.3	4.0	2.8

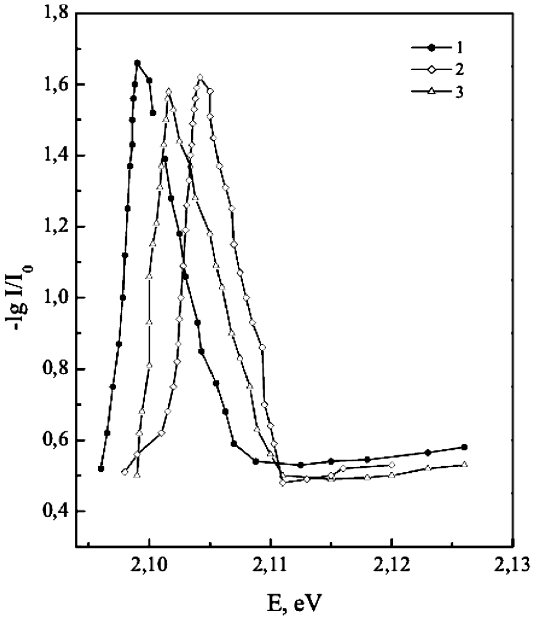

Fig. 3. Optical density spectra for GaSe layered crystals: initial (*1*) and kept in alcohol for two (*2*) and four (*3*) months

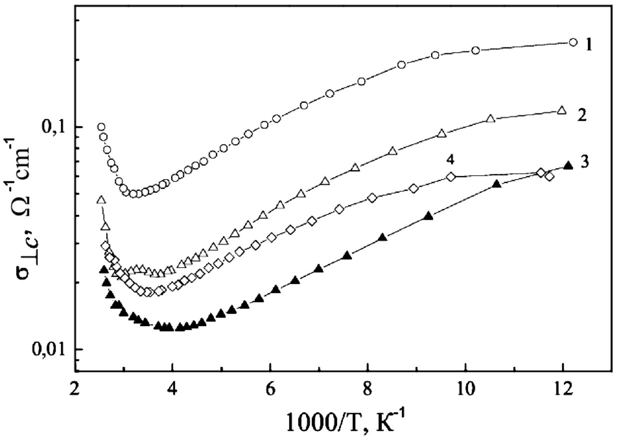

Fig. 4. Temperature dependences of the in-plane electric conductivity $\sigma_{\perp c}$ for InSe specimens: initial (*1*) and kept in alcohol for two (*2*), four (*3*), and five (*4*) months

alcohol are mainly located in the space between the layers and passivate point-like and spatial defects at the crystal sites, where the bonds are broken. At the beginning of the introduction, when the concentration of intercalated alcohol molecules is low, the intercalant forms additional structural defects in those regions. As a result, shallow acceptor levels emerge in the energy gap of InSe, and, as a consequence, the concentration of charge carriers and the in-plane conductivity in the layered crystals decrease. The InSe specimens kept in ethyl alcohol for five months demonstrate an increase in the charge carrier concentration and the corresponding growth of conductivity, which may be associated with increase in the inter-

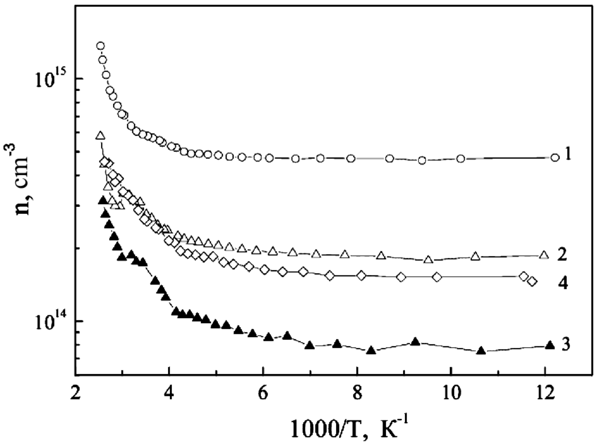

Fig. 5. The same as in Fig. 4, but for the free carrier concentration

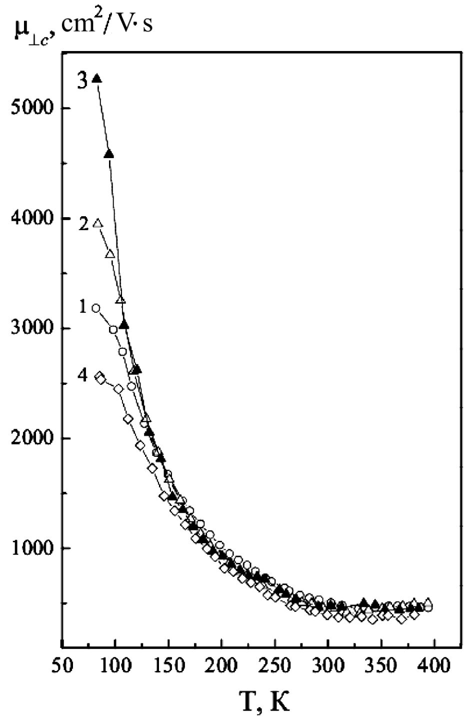

Fig. 6. The same as in Fig. 4, but for the mobility of free charge carriers $\mu_{\perp c}$

calant concentration and the following ordering of intercalant molecules in the interlayer space. In view of the structure of C_2H_5OH molecule and the structure of layered crystals, the ordering may probably occurs in the form of spatial chains, similarly to what takes place at the ordering of iodine atoms in InSe [13]. The results of researches of hydrogenated InSe crystals [14, 15] have also to be taken into consideration, because a characteristic feature of the hydroxyl group of alcohols consists in the mobility of a hydrogen atom, which is explained by the electron structure of a hydroxyl group [16]. In works [15, 17], it was shown that the growth of conductivity along the layers in hydrogen-containing layered crystals is associated with the fact that some part of the introduced hydrogen is in the H^+ state.

By analyzing the temperature dependences $\sigma_{\perp c}(T)$ and $n(T)$, we may draw conclusion that the temperature growth is accompanied by an insignificant change of n and a monotonous decrease of $\sigma_{\perp c}$ in all examined specimens, which enables us to speak in this case about the "metallic" type of conductivity in them. At $T \geq 293$ K, the conductivity acquires a typical semiconducting character as a result of the drastic increase in the charge carrier concentration n.

The obtained experimental dependences of the electron mobility $\mu_{\perp c}$ on the temperature (Fig. 6) are, to some extent, typical of InSe layered crystals [18, 19] and intercalates on their basis [14, 20]. Curves *1* to *4* monotonously fall down in a temperature interval of 80–400 K, with a constant slope with respect to the temperature axis, so that the dependence $\mu_{\perp c}(T)$ is mainly determined by the interaction between charge carriers and thermal vibrations of the crystal lattice that are polarized along the normal to the layer plane [18]. The temperature dependences $\mu_{\perp c}(T)$ (Fig. 6) for pure and intercalated specimens can be explained with the help of the scattering by optical homopolar phonons ($\hbar\omega = 14.3$ meV).

InSe layered crystals are characterized by a critically high degree of bond ionicity [21, 22]. This circumstance brings about a high conductivity anisotropy, and the difference between its components in parallel and perpendicularly to the crystallographic axis **c** increases as the temperature diminishes [18]. We measured the conductivity anisotropy parameter at $T = 80$ K for initial InSe specimens and InSe specimens kept in alcohol for five months. This parameter was found to be two orders of magnitude smaller for intercalated crystals $[C_2H_5OH]$InSe, which resulted from a reduction of the in-plane component of the electric conductivity.

4. Conclusions

A research of structural, optical, and electric properties of InSe and GaSe layered crystals diffusely intercalated with ethyl alcohol has been carried out. It is found that holding the indicated compounds in alcohol for five months does not result in a violation of the structural properties and a change of the lattice parameters of initial crystals. We also found that intercalant molecules are localized in the space between layers of the crystal lattice. A shift in the energy position of the excitonic maximum $E_{\rm exc}$ and a change of the excitonic band half-width $H_{\rm exc}$ are revealed in the interval of the excitonic absorption for the interstitial compounds $[C_2H_5OH]$InSe and $[C_2H_5OH]$GaSe. Those changes are explained on the basis of ideas concerning the influence of an intercalation-induced deformation on the reconstruction of the energy spectrum in a layered crystal. The introduction of ethyl alcohol molecules within time intervals from 1 to 4 months is shown to decrease the concentration of free charge carriers and the in-plane electroconductivity, whereas the mobility of charge carriers remained almost invariable. The increase of the electric conductivity in InSe crystals kept in ethyl alcohol for five months is explained by an increase of the charge carrier concentration and the emergence of new levels in the energy gap of a layered crystal.

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ОПТИЧНІ ТА ЕЛЕКТРИЧНІ ВЛАСТИВОСТІ ШАРУВАТИХ КРИСТАЛІВ InSe I GaSe, ІНТЕРКАЛЬОВАНИХ ЕТИЛОВИМ СПИРТОМ

Резюме

Досліджено структурні, оптичні та електричні властивості монокристалів InSe та GaSe, дифузійно інтеркальованих молекулами етилового спирту. Рентгеноструктурним аналізом підтверджено впровадження молекул спирту в міжшаровий простір досліджуваних зразків. Встановлено немонотонні залежності енергетичного положення основного екситонного максимуму та півширини екситонної смуги поглинання від часу витримки монокристалів InSe та GaSe в етиловому спирті. Отримано температурні залежності електропровідності, концентрації та рухливості вільних електронів вздовж шарів зразків InSe. Зміна електропровідності інтеркальованих спиртом монокристалів InSe залежно від часу витримки в спирті пояснюється утворенням нових рівнів у забороненій зоні та впливом інтеркалювання молекул спирту на деформаційний потенціал кристала.