

## OPTICAL, ELECTRICAL, AND ELECTROCHEMICAL PROPERTIES OF INDIUM MONOSELENIDE INTERCALATED WITH IODINE

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We have investigated electrical, optical, and electrochemical properties of layered single crystals of InSe intercalated with iodine ions. By the method of X-ray electron-probe microanalysis, it is found that the insertion of iodine in near-surface layers is more intense than into the bulk of the samples under study. It is established that the intercalation of indium selenide with iodine leads to a shift of the excitonic maximum to the high-energy region by  $\sim 9$  meV and to an increase of the half-width of the excitonic absorption band by  $\sim 3$  meV. The model of the formation of spatial chains of the intercalant in layered crystals is confirmed.

The discovery of the ability of layered compounds  $A^3B^6$  for the intercalation by ions of alkaline and alkaline-earth metals [1, 2], by hydrogen [3], and by metals [4, 5] led to the appearance of a number of works on the study of properties of the produced intercalates [6, 7]. Of a certain interest is the study of the possibility to intercalate semiconductors of the  $A^3B^6$  type with the electronegative element, iodine, and to determine a change of properties of input crystal matrices due to the intercalation of a given intercalant. The solution of the posed problem has not only the scientific meaning, but can help in various practical applications: semiconductive materials with preassigned properties, heterogeneous catalysts, electrodes fuel cells and secondary current sources, etc.

Here, we present the results of studies of electrochemical, electrokinetic, and optic properties of layered single crystals of InSe intercalated by ions of iodine. Actual is the use of the method of optic excitonic spectroscopy which is intensively applied the recent years to the investigation of properties of "pure" and intercalated layered semiconductors [8].

Single crystals of indium monoselenide were grown by the Bridgman modified method. Intercalation was performed by the electrochemical method in the course of the anodic reaction of intercalation with the help of a potentiostat P-5827M in the galvanostatic mode. A 1-N aqueous solution of LiI was taken as an electrolyte. By allowing the passage of an electric current of the necessary magnitude through the electrochemical

cell, we realized the intercalation of ions of iodine into a layered crystal (under its anodic polarization). The concentration of the intercalated impurity was determined by the amount of change which has passed through the cell (the controlled parameters in the process of intercalation were the electric current density and the process duration). The influence of the concentration of intercalated iodine on the properties of InSe was studied on the same group of specimens by means of deintercalation. During the process of intercalation of layered semiconductor InSe, we carried out the measurement of the concentration and time (chronopotentiograms) dependences of the electrode potential  $\varphi$  of intercalation compounds  $I_x\text{InSe}$ , ( $0 < x \leq 1$ ,  $x$  – the number of iodine ions per one formula unit of the crystalline matrix). The measurement of the electrode potential were performed in a three-electrode cell relative to a reference chlorine-silver electrode. In experiments, we used specimens of  $5 \times 5 \times 0.5$  mm<sup>3</sup> in size. The measurement of electrical conduction was carried out in the directions along and normally to the hexagonal axis  $c$  of a crystal. The process of measurement of the concentration dependences of the electrical conduction of the layered semiconductor includes the measurement of parameters of a "pure" crystal and the stage-by-stage measurement of the electrical conduction of an intercalate after the attainment of the required concentration of an impurity. As input specimens, we took single crystals of InSe of  $10 \times 2 \times 0.5$  mm<sup>3</sup> in size. We deposited the electric contacts on specimens according to [9]. The concentration dependences of the electrical conduction for the intercalated compound  $I_x\text{InSe}$  were determined in the directions along and normally to the hexagonal axis (the intercalant content  $0 < x \leq 1$ ).

The spectra of transmission of single crystals of InSe and  $I_x\text{InSe}$  ( $0 < x \leq 1$ ) were studied on a spectrometric setup constructed on the base of a modified spectrometer IKS-31 (the light propagation direction was

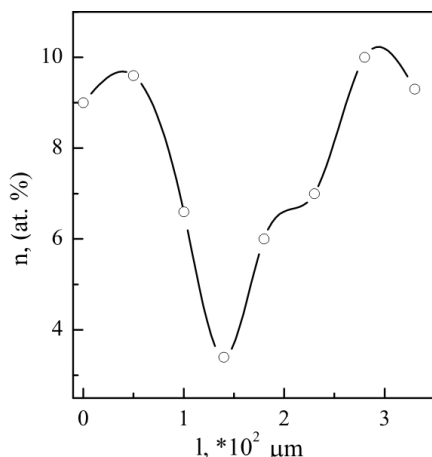


Fig. 1. Distribution of intercalated iodine (in at.%) in  $I_x\text{InSe}$  along the  $c$  axis of a crystal

perpendicular to the base plane of a crystal). The spectral resolving power of the setup in the region of excitonic absorption was  $1 \div 2$  meV (a 600-lines/mm diffraction grating). By using a cryostat system "UTREKS-RTR", the transmission spectra were studied in the temperature range 77–200 K. As a result of optical studies, we determined the concentration dependences of the energy position of the excitonic maximum  $E_{\text{ex}}(x)$  and a half-width of the excitonic band  $\Delta H(x)$ .

The identification and the quantitative analysis of the intercalated impurity (I) in a crystal were performed by the method of X-ray electron-probe microanalysis on an X-ray microanalyzer "Superprobe-733". In this case, we established that the measured concentration of the intercalated impurity with a high accuracy (0.5 at.%) agrees with that calculated by the Faraday law. In addition to the identification of the intercalant in a matrix, the application of the method of X-ray electron-probe microanalysis allows one, in some cases, to determine the distribution of an intercalated impurity in a crystal. For the compound  $I_x\text{InSe}$ , we determined (Fig. 1) that, like the case of the intercalation by methods in [10, 11], the intercalation into near-surface ("basic") layers of the matrix occurs more intensively than that into the bulk of a specimen. Thus, analogously to metallic intercalates of compounds  $\text{InSe}$  and  $\text{GaSe}$  [8, 10], there appear "near-surface" layers with a thickness of several tens of microns enriched by the intercalant.

The measurements of the concentration dependences of the electrode potential of the iodine intercalate of  $\text{InSe}$  (Fig. 2, curve 1) revealed the presence of a number of peculiarities on the curve  $\varphi(x)$ . At  $x=0 \div 0.1$ , there occurs some decrease of  $\varphi$ . Then we observe the region

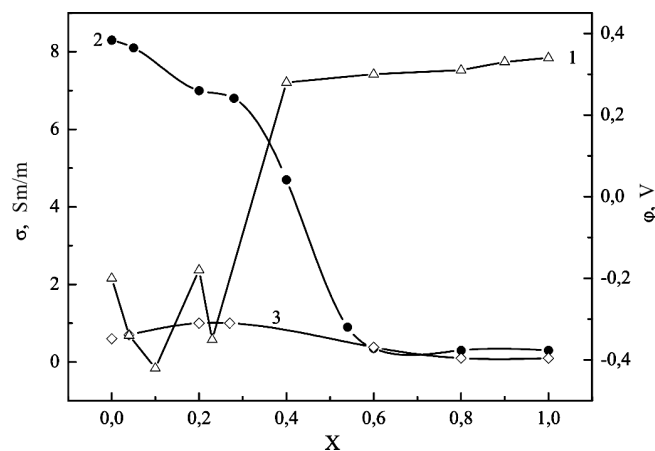


Fig. 2. Concentration dependences of the electrode potential (curve 1) and the electrical conduction along (curve 2) and normally (curve 3) to the plane of layers for compound  $I_x\text{InSe}$

of jump-like change of  $\varphi$ , and, at  $x \cong 0.25$ , the electrode potential increase sharply and attains the saturation at  $x > 0.3$ . The studies of chronopotentiograms of the  $I_x\text{InSe}$ –electrolyte system showed that the intercalate is stable for several tens of minutes. Then there occurs the intensive deintercalation of iodine from the matrix (Fig. 3). A specific feature of the intercalation of anions (e.g., I) into layered compounds is the electrical mismatch of the input crystal and the intercalated impurity, which apparently causes the jump-like change of the electrode potential. The sense of this mismatch consists in the following: the structure of crystals  $A^3B^6$  is a stack of microlayers  $\dots BAAB \dots BAAB \dots$  (along the  $c$  axis of the hexagonal lattice), and atoms of the chalcogen which are positioned in the plane on the edges of each microlayer attract somewhat the electron cloud to themselves, by forming some bulk charge along the van der Waals slit. Therefore, by finding itself in the interlayer space, iodine cannot create a complete stable bond with the matrix and try to leave the crystal or to fix itself on charged defects of the crystalline structure of a specimen. The mismatch of the intercalant and the matrix causes the strong deintercalation in the absence of the inflow of new ions.

The formation of a relatively stable intercalation phase in the  $I_x\text{InSe}$  system at  $x > 0.3$  cannot be explained by only the localization of the intercalant on defects of the matrix structure, because the concentration of the intercalated impurity exceeds significantly the amount of defects per unit volume. The duration of the existence of this phase is considerable (up to 4 h) and of the same order as that in the case of metallic intercalation [11]. As the concentration of an impurity in compounds

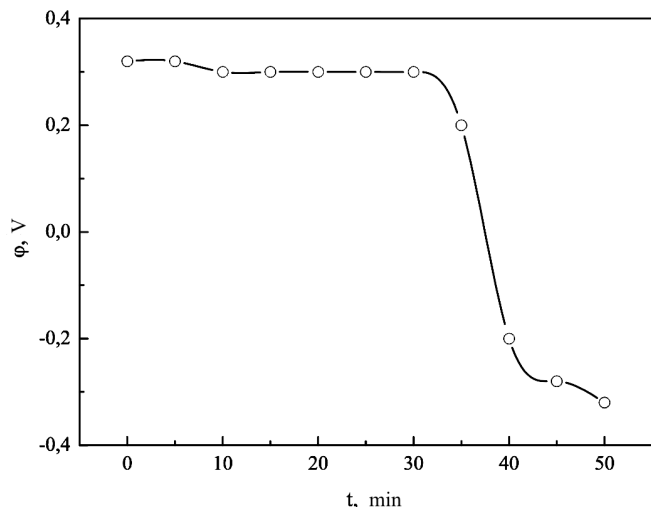


Fig. 3. Chronopotentiograms of the intercalation compound  $I_{1.0}\text{InSe}$  at  $T=293\text{ K}$

increases, there occurs, possibly, the ordering of the intercalant. As for the mean of ordering, we believe that spatial chains of the intercalant are, most probably, formed like the ordering of tellurium in  $\langle\text{Te}\rangle\text{InSe}$  [13]. It is worth noting that the stability of iodine intercalates on the basis of  $\text{InSe}$  depends on defects of the matrix structure, mobility of the intercalant, and its ordering.

The results of studies of the concentration dependences of the electrical conduction along and normally to the plane of layers of compounds  $I_x\text{InSe}$  (Fig. 2, curves 2 and 3) testify to a nonmonotone character of the curves  $\sigma_{\perp c}(x)$  and  $\sigma_{\parallel c}(x)$ . The dependence  $\sigma_{\parallel c}(x)$  is characterized by a break which separates conditionally the curve into two regions: at  $x=0\div 0.3$ , the electrical conduction normally to the layers increases monotonously (approximately by a half-order), whereas, at  $x>0.3$ , we observe a significant (by one order) decrease of the electrical conduction. For the first region, the impurity is localized on defects of the matrix structure. But, for the second region, the ordering of iodine in the form of spatial chains is dominant. Probably, due to a decrease of the concentration of free electrons, the electrical conduction along layers under intercalation decreases approximately by one order.

The executed studies of the dependence of the spectral position of the excitonic maximum ( $n=1$ ) and its half-width for the intercalation compound  $I_x\text{InSe}$  on the concentration of intercalated iodine ( $0 < x \leq 1$ ) and on the temperature (77–200 K) showed the following: with increase of the intercalant content, the coefficient of thermal shift of the excitonic maximum  $dE_{\text{ex}}(x)/dt$  varies from  $3.1 \times 10^{-4}$  (“pure”  $\text{InSe}$ ) to

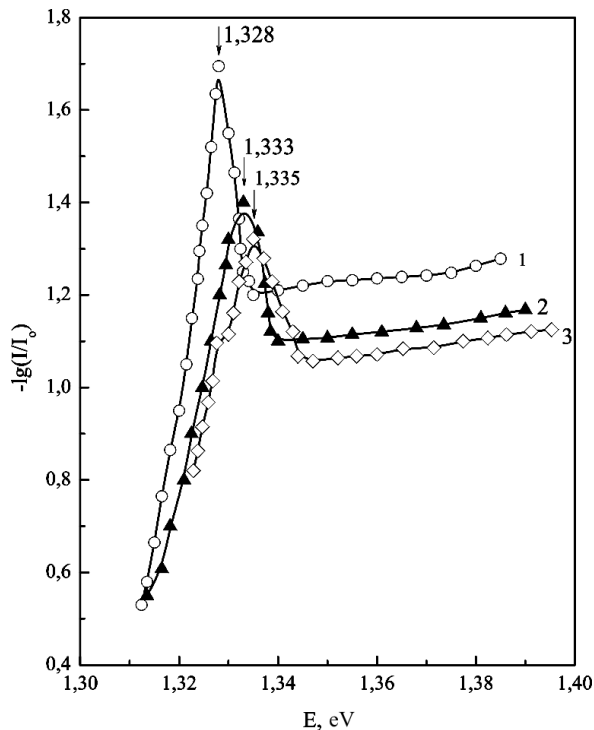


Fig. 4. Spectral dependences of the transmission of  $\text{InSe}$  (curve 1),  $I_{0.4}\text{InSe}$  (curve 2), and  $I_{0.9}\text{InSe}$  (curve 3) at  $T=77\text{ K}$

$3.8 \times 10^{-4}$  eV/degree ( $I_{1.0}\text{InSe}$ ), and the thermal coefficient for a half-width of the excitonic band  $dH/dT$  changes from  $3 \times 10^{-5}$  to  $6 \times 10^{-4}$  eV/degree, respectively, for  $\text{InSe}$  and  $I_{1.0}\text{InSe}$ .

It follows from the obtained transmission spectra for “pure”  $\text{InSe}$  (Fig. 4, curve 1) and intercalates  $I_x\text{InSe}$  (Fig. 4, curves 2 and 3) that the excitonic maximum shifts to the high-energy region in the process of intercalation. In this case, a gradual widening of the excitonic absorption band occurs. The concentration dependences of the energy position of the excitonic maximum  $E_{\text{ex}}(x)$  and a half-width of the excitonic absorption band  $\Delta H(x)$  of compound  $I_x\text{InSe}$  ( $0 < x \leq 1$ ) at  $T=77\text{ K}$  are presented in Fig. 5. We note that the curves of the dependences of the energy position and a half-width of the excitonic maximum on the content of the intercalant are not monotone: in the interval  $0.3 < x < 0.8$ , a horizontal section appears on the curves. This specific feature is also revealed at temperatures of 90–200 K, but manifests itself most clearly at 77 K.

To explain the obtained results, we take into account that, in the Wannier–Mott model of excitons (irrespective of their dimensionality), a high-energy shift of the spectral position of the excitonic maximum  $E_{\text{ex}}$

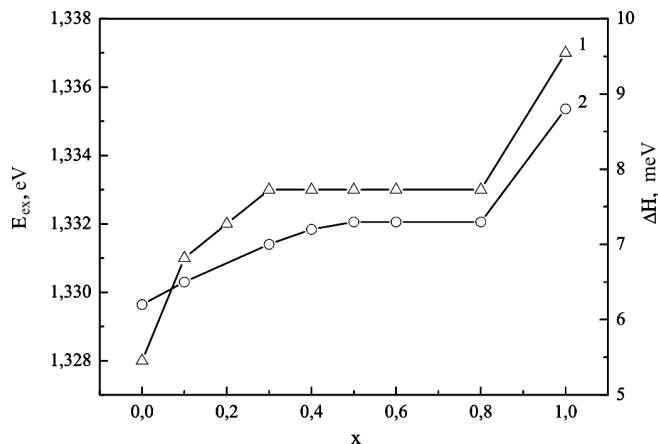


Fig. 5. Concentration dependences of the energy position  $E_{ex}$  (curve 1) and a half-width  $\Delta H$  (curve 2) of the excitonic absorption band of  $I_x$ InSe at  $T=77$  K

can be caused by a change of both the forbidden band width  $E_g$  and the binding energy of an exciton  $E_{bind}$ . We note that a significant change of the binding energy of an exciton under intercalation of indium selenide by iodine is possible only under an essential deformation of dispersion branches forming the allowed energy bands of the intercalated semiconductor, which seems to be improbable with regard for the experimental results obtained in the present work. Thus, we may assume that the influence of a change of the binding energy of an exciton on the dependence  $E_{ex}(x)$  is slight and cannot explain the observed shift to the high-energy region ( $\sim 9$  meV). In work [15], an analogous shift in  $I_x$ GaSe was explained within the charge transfer mechanism: the intercalant, I, accepts electrons in GaSe. This model [15] is valid, possibly, also in the case of  $I_x$ InSe: iodine, by localizing on defects of the structure, accepts electrons positioned near extrema of the allowed energy bands.

The nongradual change of the dependence  $E_{ex}(x)$  (Fig. 5), namely the appearance of a horizontal section at  $0.3 < x < 0.8$  agrees well with a model proposed in [13, 15] for the formation of spatial chains of the intercalant. Indeed, the acceptance of electrons stops in the given region of concentrations of the impurity, because the chain structures of iodine are neutral relative to the matrix. At a higher content of iodine ( $x > 0.8$ ), the intercalant “generates” structural defects of the matrix, which is accompanied by a further shift of the forbidden band width. The concentration widening of lines of excitonic absorption (Fig. 5) can be completely explained in the frame of the theory of disordered systems [16], i.e. by a decrease of the lifetime of an

exciton in the field of a “random” potential relief which is not characterized by a spatial periodicity.

Of interest is the detection of a dark emf in specimens of  $I_x$ InSe. We have studied the specimens with an input electrical conduction along the  $c$  axis of the order of  $10^{-5}$   $\text{Ohm}^{-1}\text{cm}^{-1}$ . After the intercalation (at  $x=0.45$ ), there appears the dark emf up to 500 mV which decreases in the course of time due to the deintercalation. The results of measurements showed that the dark emf depends strongly on the temperature: in the interval 230–365 K, it varies from 10 to 250 mV. This phenomenon can be interpreted if we take into account that its appearance depends significantly on the nonuniformity of the intercalation of the intercalant into the crystalline matrix of InSe along the  $c$  axis (Fig. 3).

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ОПТИЧНІ, ЕЛЕКТРИЧНІ ТА ЕЛЕКТРОХІМІЧНІ  
ВЛАСТИВОСТІ ЙОДНИХ ІНТЕРКАЛАТІВ  
МОНОСЕЛЕНІДУ ІНДІЮ

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Резюме

Досліджено оптичні, електричні, електрохімічні властивості шаруватих монокристалів InSe, інтеркальованих іонами йоду.

Методом електронно-зондового рентгенівського мікроаналізу для йодних інтеркалатів InSe виявлено, що впровадження йоду в приповерхневі ("базові") шари матриці відбувається інтенсивніше, ніж у внутрішній об'єм зразка. Встановлено, що впровадження йоду в селенід індію приводить до високоенергетичного зміщення положення екситонного максимуму  $\sim 9$  меВ і збільшення півширини екситонної смуги поглинання  $\sim 3$  меВ. Підтверджено модель створення просторових ланцюжків інтеркалянта в шаруватих кристалах.