

The Study of Electrical Properties of Cobalt Intercalated InSe

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The investigation of the electrical properties of InSe crystals and Co_xInSe ($x = 0.05; 0.1; 0.15$) intercalates as well as the effect of permanent magnetic field on the intercalation processes and parameters of the obtained structures was carried out. It was established that the dependence of the change of the electrical resistance is not stable with the increase in the concentration of the intercalated cobalt. We have shown that the magnetic field effects on the properties of the intercalated compounds based on InSe crystals during the intercalation process. The properties of the obtained intercalates depend on the crystal orientation in the magnetic field.

Keywords: Indium selenide, Impedance, Intercalation, Cobalt, Magnetic field, Ferromagnetism.

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1. INTRODUCTION

Indium monoselenide is a representative of the class of layered semiconductors which are characterized by a strong anisotropy of the electronic properties conditioned by the specific character of their crystal structure and also by the presence of structural defects (vacancies and dislocations) which leads to a high density of states localized near the Fermi level [1, 2]. Moreover, layered semiconductors are the so-called “intercalated materials”, i.e. compounds with foreign objects, such as atoms, molecules and even fragments of crystal lattices of other materials, which can be incorporated in a reverse way into their crystal lattice [3]. The relevance of the study of intercalated layered semiconductors is defined by their use as suitable model systems for the exploration of the contribution of thermodynamic functions of an electron subsystem to the total thermodynamic functions of the material and formation of its phase diagram. This is facilitated by the possibility of a wide variation of concentration and nature of the incorporated component while maintaining the basic structural motive of the initial compound that allows to obtain materials with the desired properties. Intensive development of spintronics and nanomagnetism attracts the attention to the materials with magnetic atoms both in the composition of a compound-matrix and intercalated into it [4, 5]. Change in the degree of localization of electrons can influence the magnetic moment of such atoms and, correspondingly, the character of the interaction with charge carriers.

Among the methods used for the study of the state and behavior of the impurity-defect structure in semiconductor materials, the capacitive (impedance) investigation methods, which allow to determine both the nature of energy levels in the semiconductor band gap and their properties, occupy an important place. The aim of the present work is to establish the influence of incorporation of $3d$ -element atoms (in particular, cobalt) on the electrical properties of indium monoselenide and their dependence on the magnetic field.

2. EXPERIMENTAL TECHNIQUE

InSe monocrystals were grown by the Bridgeman

method from the melt of stoichiometric composition. Samples were found to be n -type with electron concentration of $p = 10^{14} \div 10^{15} \text{ cm}^{-3}$ at $T = 300 \text{ K}$, electron mobility was equal to $\mu = 500\text{-}800 \text{ cm}^2/\text{V}\cdot\text{s}$. It was established by the Weissenberg method that crystals had the γ -InSe structure (the $P6_3/mmc$ space group). Crystal structure and parameters of InSe are described in detail in the work [6]. For the investigations we have used samples cleaved from one washer. Incorporation of cobalt into gallium selenide was performed electrochemically by the “sweeping field” method. CoSO_4 saturated aqueous solution was used as the electrolyte. Since d -elements have a low deposition potential, intercalation was carried out in the galvanostatic mode by the currents whose density did not exceed 0.4 mA/cm^2 . And in this case, extraction of the incorporated impurity or its salts on the sample and cell electrodes was not observed. Concentration of the incorporated impurity per one formula unit of the matrix was determined by a quantity of electricity passed through the sample during incorporation. In order to define the influence of the magnetic field on the incorporation of d -elements, intercalation was carried out both in the absence of the magnetic field and when applying it parallel and perpendicular to the crystallographic c -axis of the crystal. Magnetic field was generated by permanent neodymium magnets, and its value in the sample placement was equal to 4 kE .

Investigations of the properties of the initial and intercalated InSe monocrystals are carried out by the dielectric spectroscopy method using impedance spectrometer “Solartron 1255 FRA” and potentiostat “Solartron 12860” (the frequency range is $1\text{-}10 \text{ MHz}$, amplitude of the sinusoidal signal is $10\text{-}100 \text{ mV}$). Frequency dependence of the complex permittivity was analyzed by the graphoanalytical method using the software ZView 2.8 (Scribner Associates). Monocrystalline InSe samples in the form of plane-parallel plates with the average sizes of $10 \times 5 \times 1 \text{ mm}^3$ were used for the investigation. Ohmic contacts were deposited on the natural freshly cleaved surfaces perpendicular to the crystal c -axis using silver conductive paste, their area was $0.06 \div 0.07 \text{ cm}^2$. Similarly to the intercalation process, study of the properties of InSe and Co_xInSe samples ($x = 0.05; 0.1; 0.15$) was

carried out both in the case of $B = 0$ and at $B \perp c$ and $B \parallel c$ ($B = 4$ kE).

The frequency and temperature dependences of the impedance of pure and cobalt intercalated InSe monocrystals, and also the influence on these characteristics of the constant magnetic field, have been studied in the present work. All measurements have been performed without protective atmosphere.

3. RESULTS AND DISCUSSION

In Fig. 1 we illustrate the frequency dependence of the impedance of pure InSe and Co_xInSe monocrystals ($x = 0.05; 0.1; 0.15$) intercalated by cobalt atoms without the magnetic field. Incorporation of cobalt atoms into the layered matrix of the initial InSe leads to a significant decrease in the resistance. It was shown in the works [7, 8] that Co_xGaSe intercalates obtained by electrochemical intercalation [9] monotonously decreased their resistance with increasing concentration of the incorporated cobalt. When reaching higher concentrations of cobalt ($x = 0.15$) in Co_xGaSe samples, changes in the conductivity were small compared with the changes at lower concentrations [8]. In our case, it is seen from Fig. 1 that the decrease in the electrical resistance of intercalated samples under the introduction of the intercalate is not a monotonous – for the concentration of $x = 0.1$ at. % one observes the increase in the impedance value compared with $\text{Co}_{0.05}\text{InSe}$ samples and further decrease in the electrical resistance at $x = 0.15$ at. %. Such non-monotonous dependences can be explained by the unequal overlap of the wave functions of the cobalt electron states with atoms of the layered structure [10] that can also depend on the distance between separate InSe layers. Non-monotonous change in the parameter c of the InSe crystal lattice was observed in the work [11] during the incorporation of nickel which, as well as cobalt, belongs to the iron group elements.

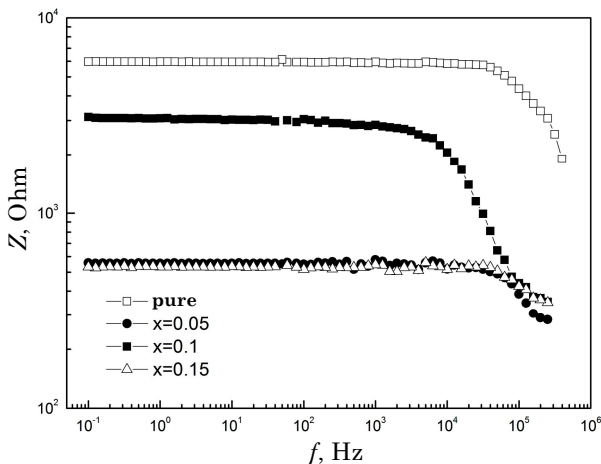


Fig. 1 – Frequency dependence of the impedance of Co_xInSe sample at different concentrations of cobalt atoms

Influence of the magnetic field on the process of cobalt intercalation into the layered InSe structure does not make significant qualitative differences to the obtained dependences.

Increase in the impedance values of $\text{Co}_{0.1}\text{InSe}$ samples compared with $\text{Co}_{0.05}\text{InSe}$ (Fig. 2) is also observed at the cobalt concentration of $x = 0.1$ at. %. As seen from

the dependences, ohmic characteristics between $\text{Co}_{0.1}\text{InSe}$ and $\text{Co}_{0.05}\text{InSe}$ differ less during intercalation in the magnetic field than in its absence (Fig. 1). More ordering of cobalt atoms in the interlayer space under the action of the constant magnetic field during intercalation is a possible reason of this fact.

In Fig. 3 we illustrate the Nyquist diagrams of InSe and Co_xInSe crystals obtained for the electrical current direction along the crystal c -axis, which are the reflection of the total impedance in the complex plane with coordinate axes of its real (Z') and imagine (Z'') parts. View of the obtained diagram has the form corresponding to the equivalent scheme of series connection of the sample resistance which takes into account the resistance of the crystal, contacts and wires and also parallel circuit with shunt resistance and barrier capacity. It is seen from Fig. 3 that deformation of the impedance hodograph is typical for pure InSe and $\text{Co}_{0.01}\text{InSe}$, which are characterized by a much larger value of the electrical resistance in comparison with the concentrations of $x = 0.05$ and 0.15 at. %. For a pure sample at high and medium frequencies, the presence of an auxiliary arc responsible for the frequency-dependent part of the impedance is observed. Similarly, although in a less degree,

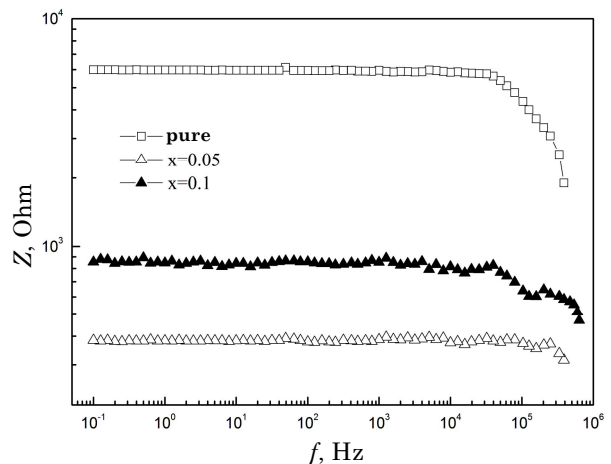


Fig. 2 – Frequency dependence of the impedance of Co_xInSe sample intercalated in the magnetic field with the parallel direction to the c -axis

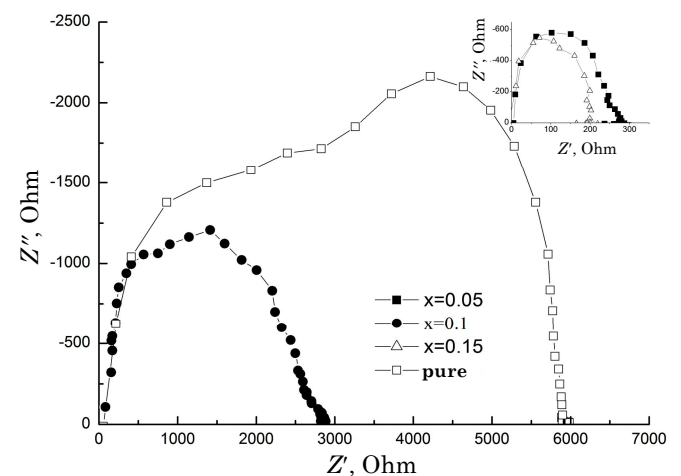


Fig. 3 – Nyquist diagrams obtained in the direction perpendicular to the layers of intercalated InSe for different concentrations of cobalt

one additional arc, which is not strongly expressed, is present on the impedance hodograph in the range of high and medium frequencies that also corresponds to the frequency-dependent part of the impedance. These phenomena can be explained by the dominance of the hopping mechanism of current flow over the levels localized near the Fermi level [12].

For two other concentrations (0.05 and 0.15 at. %), at which frequency-dependent part of the impedance is considerably less, the hodograph travel is usual and is close to a semi-circle. In the low-frequency region for all cases of concentrations of cobalt atoms the hodograph travel has classical decay behavior.

Except the study of the frequency dependence of the impedance at room temperature (Fig. 1, Fig. 2), investigation of the change of these dependences with temperature was performed. By the investigation results we have plotted the temperature dependences of the impedance values at the frequency of 1000 Hz for three compounds of $\text{Co}_{0.05}\text{InSe}$ incorporation obtained at different conditions of incorporation, namely, orientations of the applied magnetic field $\vec{B} = 0$, $\vec{B} \parallel \vec{c}$ and $\vec{B} \perp \vec{c}$.

It is seen from Fig. 4 that the obtained dependences have a non-monotonic behavior. At low temperatures, the impedance values for all the samples are almost the same. At temperatures close to 180 K the difference in the temperature dependences begins to appear. At temperatures close to room temperature, a sharp increase in the electrical resistance of the samples is observed. In the temperature range of 330-350 K, dependences reach their peak value and then begin to decay. We have to note that a similar situation of the magnetic field influence during electrochemical incorporation was observed for cobalt intercalates GaSe [7, 8]. View of the temperature dependences in Fig. 4 is typical for non-degenerate ferromagnetic semiconductors with a low concentration of donors [13], to which the maximum of the electrical resistance at the Curie temperature (CT) is inherent. InSe samples doped with vanadium selenide had a similar view of the temperature dependences [14].

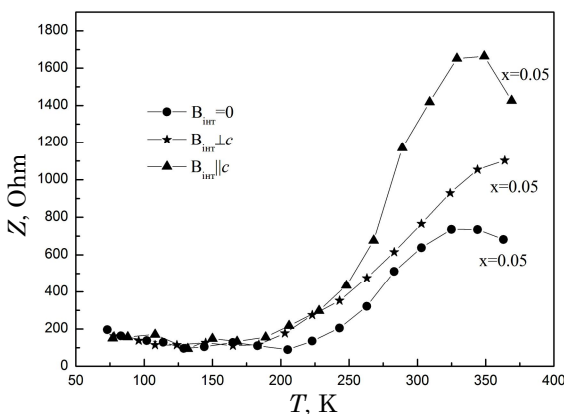


Fig. 4 – Temperature dependence of the impedance at the frequency of 1000 Hz for $\text{Co}_{0.05}\text{InSe}$ sample at different conditions of cobalt incorporation

In Fig. 5 we show the temperature dependences of Co_xInSe samples at different concentrations of incorporated cobalt. It is seen from the figure that only temperature curve for cobalt concentration of $x = 0.1$ at. % substantially differs. For concentrations of $x = 0.05$ and

$x = 0.15$ at. % the impedance values are close in magnitude. All temperature dependences obtained for Co_xInSe compounds have a metallic character.

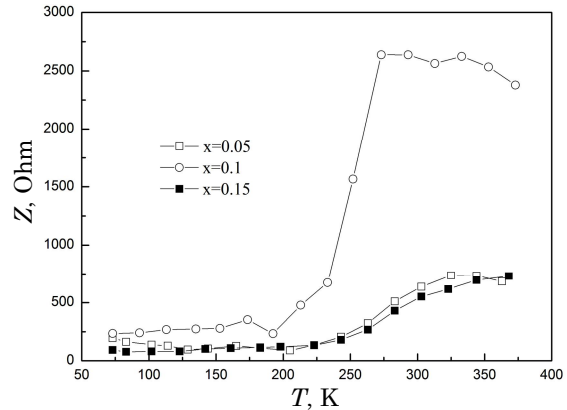


Fig. 5 – Temperature dependence of the impedance at the frequency of 1000 Hz for Co_xInSe samples at different concentrations of incorporated cobalt

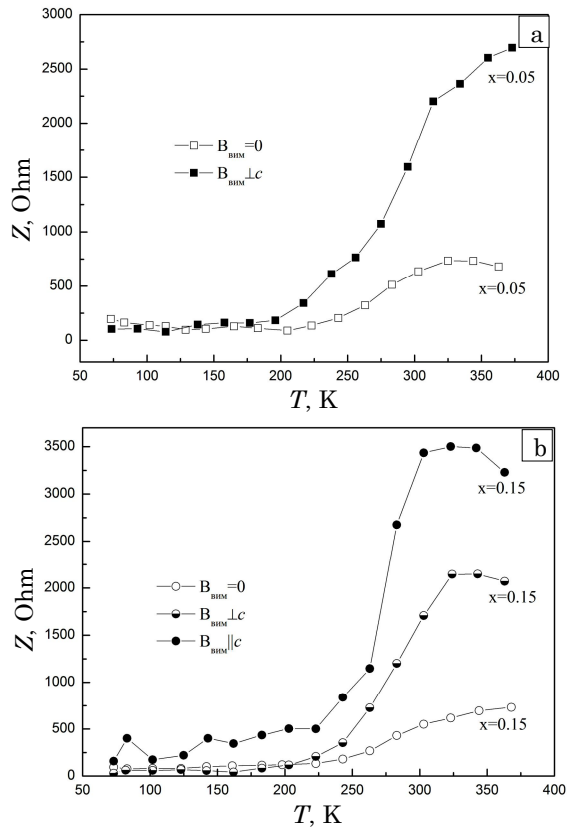


Fig. 6 – Influence of the magnetic field on the measurement results of the temperature dependences of the impedance at the frequency of 1000 Hz for Co_xInSe samples

Dependences illustrated in Fig. 6 characterize the magnetic field influence on the measurements results. In Fig. 6 we present the temperature study performed in the absence of the magnetic field and in its presence with different orientations of the magnetic field strength with respect to the crystallographic c -axis of the samples which were intercalated in the absence of the magnetic field. It is clearly seen from Fig. 6 that magnetic field has a substantial effect on the samples with both “low” ($x = 0.05$, Fig. 6a) and “high” ($x = 0.15$, Fig. 6b)

cobalt concentration. In the presence of the magnetic field with perpendicular orientation to the crystallographic c -axis ($\vec{B}_{meas} \perp \vec{c}$) of the crystal at low temperatures (up to 200 K) behavior of the curves on the temperature dependences is virtually identical to the behavior of the corresponding curves obtained in the magnetic field absence. With increasing temperature above 200 K differences between two concentrations begin to appear, and, as the temperature grows, difference in the values of the electrical resistance appears more significantly: electrical resistance of the samples with two different concentrations of incorporated cobalt at the alternating current frequency of 1000 Hz and application of the magnetic field with perpendicular orientation to the crystal c -axis increases approximately 5 times.

When applying the magnetic field with parallel orientation of the magnetic field vector to the crystal c -axis ($\vec{B}_{meas} \parallel \vec{c}$, Fig. 6b) one observes even more significant change in the electrical resistance than for the previous case ($\vec{B}_{meas} \perp \vec{c}$). Here, the difference begins to appear at 150 K, and as the temperature grows it appears even more in comparison with the dependence obtained in the absence of the magnetic field. When reaching "high" temperatures, the values of the electrical resistance for the given magnetic field direction increases more than 7 times. Thus, magnetic field leads to the increase in the sample electrical resistance, and it has the maximum effect when its orientation is parallel to the crystallographic c -axis of the crystal. Difference in the influence of the magnetic field of different orientation relative to the axis on the measurements of the electrical properties

of Co_xInSe can be explained based on the assumption that intensity of the interaction between magnetic field and cobalt atoms depends on the orientation of the former. It is seen from the obtained dependences (Fig. 6) that the maximum interaction of cobalt with magnetic field is observed for the orientation of the latter along the crystal c -axis. This may be caused by the increase in the dehybridization intensity of energy levels of orbitals of cobalt atoms and by the decrease in the number of conduction electrons [11].

4. CONCLUSIONS

It was revealed from the study of the electrical conduction of cobalt intercalates Co_xInSe in alternating electric fields that they have higher conduction compared with the initial InSe crystals, and concentration dependences of the electrical resistance of cobalt intercalates InSe have a non-monotonic behavior.

Non-monotonic temperature dependences of the electrical resistance of the investigated Co_xInSe samples ($0 \leq x \leq 0.15$) have the form typical for nondegenerate ferromagnetic semiconductors with a low concentration of donors.

It is shown that magnetic field during measurements leads to a substantial increase in the values of the electrical resistance of the samples for both the initial and higher concentrations of cobalt. Parallel direction of the magnetic field vector to the crystallographic c -axis of the crystal, into which the sample was placed, has more impact during both the incorporation process and measurements of the electrical parameters.

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