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Preparation of Nanocomposite Magnetic Compounds Based on Layered Semiconductors by Means of Electrochemical Intercalation in a Gradient Magnetic Field

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In this paper we propose a method of intercalation of layered single crystals with atoms of 3*d*-metals in a magnetic-field gradient. We report on structure properties of $\mathrm{Co}_x\mathrm{InSe}$ and $\mathrm{Co}_x\mathrm{In}_2\mathrm{Se}_3$ layered crystals intercalated by cobalt. It was established that ferromagnetic ordering at room temperature is observed in the intercalated crystals. The crystals are a nanocomposite material that consists of a layered matrix and arrays of Co nanoformations on the van der Waals surfaces of InSe and $\mathrm{In}_2\mathrm{Se}_3$ layers.

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1. Introduction

In recent years many efforts are directed to have implanted magnetism into the semiconductor architecture of modern electronic devices. One of the approaches for solving this problem consists in the preparation of materials able to combine properties of a ferromagnetic and a semiconductor [1, 2]. Because of progress in the technology and methods for preparation of semiconductor materials, along with investigations of single crystals (ferromagnetics and diluted magnetic semiconductors) the growing attention is concentrated on nanocomposite and granular semiconductor systems, films, layered structures and quasi-one-dimensional systems [3–8].

One of the methods having being used for the formation of systems with reduced dimensionality, including magnetic ones, is intercalation of various impurities into the interlayer spaces of the compounds with layered crystal structure [9, 10]. Layered semiconductor crystals InSe and $\mathrm{In}_2\mathrm{Se}_3$ belong to the binary III–VI compounds and are characterized by the existence of two types of chemical bond — strong covalent within a separate layer and weak van der Waals between the layers [11, 12]. As a result, there is a possibility to insert foreign atoms and even molecules into the interlayer spaces forming thereby layered structures with new properties. Intercalates are appropriate model objects to study physics of two-dimensional states and find applications as accumulators, thermoelements, solar cells, detectors and sources of IR radiation, etc. [13–15].

Layered semiconductors intercalated with atoms of 3*d*-metals are new nanocomposite structures with the alternate layers of a magnetoactive intercalant and a nonmagnetic semiconductor. The interaction of intercalated atoms with atoms of the lattice can lead to its deformation, changed conductivity, appearance of different magnetic states, decrease of the effective magnetic moment of inserted magnetic atoms. At present as the most studied layered compounds intercalated with 3*d*-metals we can consider dichalcogenides of transition metals TX_2 (T = Ti, Mo, W; X = S, Se) [16–20]. The preferable technique for their obtaining is high-temperature thermal treatment of a mixture of μm-sized powders of an intercalant and a layered compound. In this case there is a possibility to have formed incidental phases of both the intercalant and the initial layered compound. Besides, the intercalant can also inserted into the structure of separate layers. In addition, layered crystals are very sensitive to any deformations. On the contrary, electrochemical insertion needs single crystalline samples and the process occurs at room temperature. The aim of this work is to establish the possibility of the electrochemical intercalation of layered III–VI crystals with impurities of 3*d*-transition metals and to study the influence of magnetic-field gradient at the *crystal–electrolyte* interface on the intercalation process and properties of intercalates.

2. Experimental

2.1. Electrochemical intercalation

Intercalation of layered semiconductors from a liquid is heterogeneous process, which consists of several phases: diffusion of intercalating atoms or molecules to the crystal's surface, their adsorption and surface diffusion to the van der Waals gaps, formation of complexes between intercalating atoms and the crystal's atoms, transfer through the interface and electron–ion processes at elastic deformation of the lattice structure, in-plane diffusion of intercalated species through crystals till the formation of an equilibrium intercalate [21]. When we deal with electrochemical intercalation, the motion of interacting electrons or ions has a directed ordered character that is accompanied by their transition through the

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*corresponding author; e-mail: `chimsp@ukrpost.ua` *crystal-electrolyte* interface. A sketch of electrochemical intercalation is shown in Fig. 1. There $j_1(\tau)$ is the flow of intercalating particles, which defines the transfer from a liquid phase to the interface, $j_2(\tau)$ describes the intensity of insertion into some sites of the interlayer space, $j_3(\tau)$ characterizes the diffusion of particles in the crystal periodic field under concentration gradient and τ is the time [22].

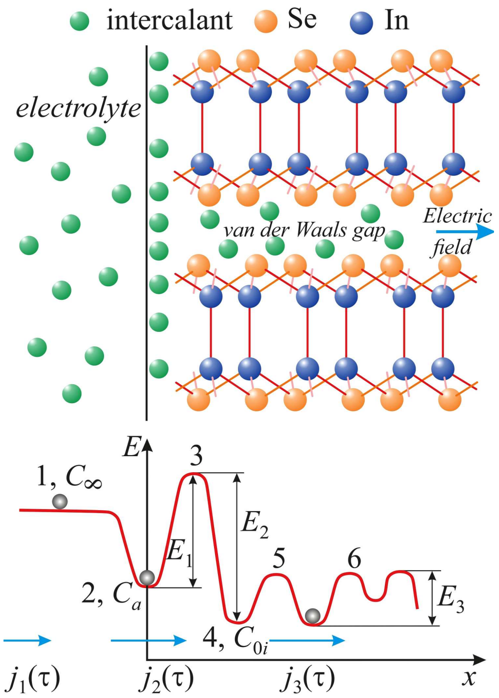

Fig. 1. Scheme drawing of an electrochemical intercalation into a layered crystal (top) and an energy diagram of the process (bottom). Energy levels intercalated particles (1), adsorption (2), transition of liquid–solid interface (3), diffusion in emptiness interlayer spaces (4,…,n); $j_{1,2,3}(\tau)$ — flux particles; $C_{\infty,a,0i}$ — particle concentration, respectively.

Each of the above-mentioned stages is determined by the conditions of insertion and can create some restrictions for this process. From an analysis of the components of an insertion process one can conclude that the transition processes at the interface and the diffusion of intercalated atoms between the layers give the biggest restrictions for intercalation into layered crystals. In the case of electrochemical intercalation from a liquid solution the activation energy of a transition through the interface decreases because of applying of a "drawing" electric field of appropriate polarity. The processes of the transfer of intercalated particles under a concentration gradient are described by the Fick laws and the diffusion flow is $j_D = -D(\mathrm{d}C/\mathrm{d}x)$, where D is the diffusion coefficient. When electrochemical intercalation is used, besides the diffusion component in a flow of particles along the layers the drift component $j_D = c_i u_i E$ (c_i is the concentration of particles, u_i is their mobility, E is the electric field strength) appears, which is less than the diffusion component as it is limited by electric field magnitude (below the appearance of thermal breakdown).

Ions of all chemical elements are diamagnetic or paramagnetic. Ions with open electron shells have no compensation of the magnetic moments of isolated electrons in the shell. Atoms with such the structure, including those of $3d$ transition metals, have a magnetic moment and are paramagnetic. Being in a magnetic field, the magnetic moments become oriented along its field lines. The force acting on a magnetic ion in a gradient magnetic field is

$$F = m\chi H \frac{\mathrm{d}H}{\mathrm{d}z}, \tag{1}$$

where m is the mass of an ion, χ is the atomic magnetic susceptibility, H is the magnetic field strength and $\mathrm{d}H/\mathrm{d}z$ is its gradient. Taking into account that m and χ are constant, the maximum value of F corresponds to the maximum of $H(\mathrm{d}H/\mathrm{d}z)$. Obviously, the gradient of the external magnetic field because of the force F will increase the concentration of magnetic ions at the *crystal–electrolyte* interface.

2.2. Samples and measurements

Single crystals of the III–VI binary compounds InSe and In_2Se_3 used in the experiment were grown by the Bridgman method from stoichiometric melts. The fabricated materials have layered crystal structure along all the length of the grown ingots. The carried out X-ray analysis has shown that the obtained InSe crystals have a rhombohedral γ-polytype structure (space group C_{3V}^5) whereas the In_2Se_3 single crystals have an α-polytype structure (space group D_{3d}^5). The determined lattice parameters are the following: $a = 4.003$ and $c = 24.9553$ Å for InSe and $a = 4.05$ and $c = 28.771$ Å for In_2Se_3.

Then the ingots were cut with a circular saw into disks 5 mm thick. Samples for the measurements of the same dimensions have been cleaved from the same disks. The electrochemical intercalation was carried out by the method of "drawing" electric field [13]. A saturated aqueous solution of $CoSO_4$ was used as the electrolyte.

The intercalation was carried out in a three-electrode electrochemical cell (Fig. 2), where the investigated samples of the layered crystals were used as the working electrode. The internal cell volume containing the samples, electrolyte, electrodes and magnets was hermetically isolated from the environment and kept at a temperature $T = 293$ K. The samples were placed between two magnets separated by 10 mm. The special design of the cell provided a contact of the samples with an electrolyte by means of a micrometric screw able to move samples. The magnetic field strength H during the intercalation was perpendicular to the C axis. In the presence of a magnetic-field gradient, the magnetic force pulls the paramagnetic Co^{2+} ions into the interlayer space of the crystals. In this case, the intercalant becomes localized in the van der Waals gaps between the Se planes of adjacent layers whereas the structure of the layers remains unchanged.

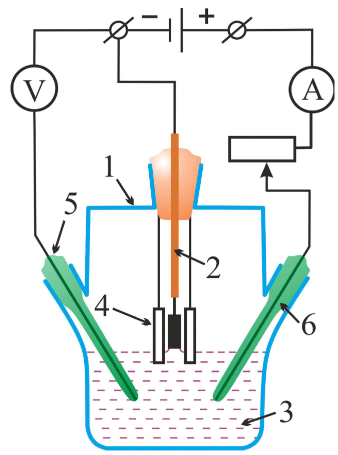

Fig. 2. Block diagram of plant for electrochemical intercalation materials in layered crystals. 1 — electrochemical cell, 2 — working electrode with a sample, 3 — electrolyte, 4 — $Nd_2Fe_{14}B$-magnets, 5 — reference electrode, 6 – auxiliary electrode.

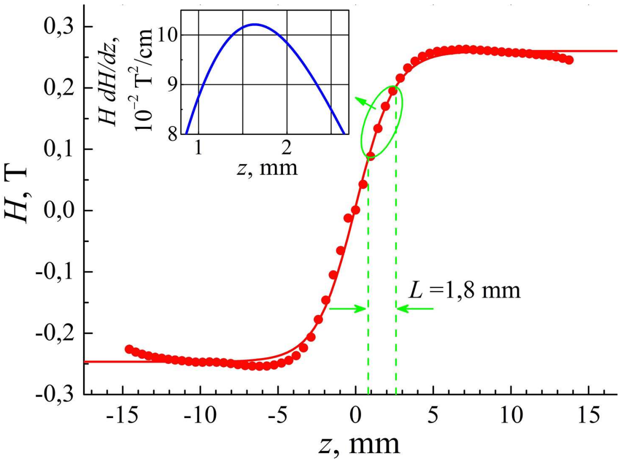

Fig. 3. Profile of magnetic field H along a direction z in a plane parallel to the magnets (symbols — measured data, line — calculated dependence) for a system of two neodymium magnets used in the electrochemical cell at intercalation of Co^{2+} ions into InSe and In_2Se_3. Inset — values of $H(dH/dz)$ within the isodynamic range L.

As transitions d-metals have a small reduction potential, to prevent a deposition of the intercalant or its salts on the samples and electrodes of the cell the intercalation was carried out under galvanostatic conditions at a current density below 0.4 mA/cm^2. The concentration x of intercalated Co was determined as the amount of inserted Co^{2+} ions per a formula unit of the III–VI compounds and calculated according to the Faraday law. Current density and duration of the insertion are characteristics of the intercalation process. A control of intercalant's insertion has been performed by using an auxiliary electrode.

In the experiment $Nd_2Fe_{14}B$-magnets were used to create a constant magnetic field. These magnets have an elongate form and are made in such the way that in their middle range there is the line with the zero magnetic field ($H = 0$). In two opposite directions, normal to this line, there is a magnetic field gradient with an isodynamic range ($dH/dz = \text{const}$), directed along a direction z in a plane parallel to the magnets' plane (Fig. 3). It was established from the experiment that a use of the system consisting of two magnets placed against each other enables to increase the magnetic field strength affecting the magnetoactive ions of the intercalant. The measured values of the magnetic field were approximated by means of the χ^2 method with the fitted function $f(z) = a\tanh(bz) + c$. To have obtained the maximum effect of the force F on intercalant Co^{2+} ions it is necessary to match the range of the maximum force acting on magnetic ions with the intercalation front (the inset in Fig. 3).

To determine the effect of magnetic-field gradient on the process of intercalation of Co^{2+} ions into the layered crystals, the intercalation was carried out in and without a magnetic field using the samples with the same geometric dimensions and intercalation conditions. It was experimentally found that in the presence of a magnetic system, which consists of two magnets placed against each other, the magnetic-field gradient increases, and therefore the force affecting magnetoactive intercalant's ions increases, too. The value of the magnetic-field gradient at the intercalations front was ≈ 0.7 T/cm, and the value of $H(dH/dz)$ changed from 0.08 to 0.12 T^2/cm.

The magnetic properties of the $Co_{0.15}InSe$ and $Co_{0.15}In_2Se_3$ intercalates were studied by measuring the magnetization by means of a vibrating-coil magnetometer Vibrating Magnetometer 7404 VSM in magnetic fields up to 0.3 T. The sensitivity of the magnetometer was of the order of 10^{-7} emu. The mass of the samples was determined by using an electronic microbalance AB135-S/FACT (sensitivity 10^{-5} g). The measurements of the magnetic moment along and across the C axis were performed at room temperature. The structure of van der Waals surfaces of the samples InSe intercalated with Co^{2+} ions has been investigated by an *ex situ* method of atomic-force microscopy (AFM) by using a Nanoscope IIIa Dimension 3000SPM microscope in tapping mode. The radius of a probe spike was not more than 10 nm.

3. Results and discussion

The crystal structure of the initial samples of InSe and In_2Se_3 and their Co intercalates was established from X-ray diffraction measurements by means of a DRON-2.0 equipment in Cu K_α radiation. The obtained data show that the structural type and space group of the intercalated samples remain unchanged. The lattice parameters for the $Co_{0.1}InSe$ and $Co_{0.15}In_2Se_3$ intercalates are $a = 4.0020$ Å, $c = 24.9501$ Å and $a = 4.052$ Å, $c = 28.727$ Å, respectively. As compared to the data for the initial samples, one can see that the intercalation with

Co^{2+} ions is accompanied by decreasing the lattice parameters along the C axis whereas the in-plane lattice parameters are nearly unchanged. Such the behavior of the lattice parameters of layered crystals intercalated with ions of $3d$-metals was observed at different methods of intercalation [23, 24]. A decrease of the lattice parameter c at low intercalant's concentrations occurs due to hybridization of the $3d$-states of intercalant's atoms with the p-states of InSe [23], as well as because of the formation of the interlayer covalent bonds in intercalated crystals Co_xTiSe_2 [24]. Note that the observed changes are typical for the intercalated samples obtained by both the ways — in magnetic field and without it.

Layered semiconductors InSe and In_2Se_3 are paramagnetic. The electrochemical intercalation with cobalt in a gradient magnetic field causes a change of their magnetic properties. Figure 4 shows the dependence of the magnetic moment M on magnetic field for the $Co_{0.1}InSe$ and $Co_{0.15}In_2Se_3$ samples intercalated in a magnetic-field gradient. As it is seen from these dependences, they contain a hysteresis loop typical for ferromagnetics. For the $Co_{0.1}InSe$ and $Co_{0.15}In_2Se_3$ compounds obtained without magnetic field similar dependences were not observed. Thereby, it can be argued that these intercalates are magnetically indifferent.

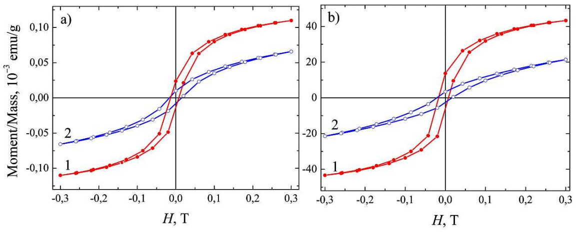

Fig. 4. The dependence of the specific magnetic moment on magnetic field for the $Co_{0.1}InSe$ (a) and $Co_{0.15}In_2Se_3$ samples (b) intercalated in the magnetic field: 1 — the magnetic field perpendicular to the C axis, 2 — the magnetic field parallel to the C axis. $T = 293$ K.

The layered semiconductors are strongly anisotropic due to peculiarities of their crystal structure. The measurements of the magnetic moment for anisotropic crystals InSe and In_2Se_3 were carried out in the directions of the magnetic field parallel ($H \| C$) and perpendicular ($H \perp C$) to the C axis. Figure 4 shows that the magnetic moment value in the case $H \perp C$ (curve 1) is higher than in the case $H \| C$ (curve 2). This fact may be explained as a result of the influence of a demagnetizing field of the sample. In our case, the magnetic field in the interior of the sample is the sum of external and demagnetizing magnetic fields: $H' = H_{ex} + H_d = H_{ex} - NI$ (I is the magnetization and N is the demagnetizing factor). The parameter N can be estimated considering the sample as an ellipsoid with the axes $a = b > c$: $N_a = N_b < N_c$. Therefore, the value of H_d along the layers is always higher than that across to them. Accordingly, the magnetic moment in the sample's plane is higher which is seen in Fig. 4. The values of the specific magnetic moment (m_S) and coercive force (H_C) in magnetic fields up to 0.3 T are listed in Table I. Such the values of H_C are typical for hard ferromagnets.

TABLE I

The specific magnetic moment and coercive force measured in the different crystallographic directions for $Co_{0.1}InSe$ and $Co_{0.15}In_2Se_3$ intercalates.

Measurement direction	$Co_{0.1}InSe$		$Co_{0.15}In_2Se_3$	
	m_S $[\frac{\text{emu}}{\text{g}}]$	H_C [mT]	m_S $[\frac{\text{emu}}{\text{g}}]$	H_C [mT]
$\|$ to the layers	0.117	11.668	0.043	12.282
$\perp$ to the layers	0.052	22.105	0.021	18.872

The investigations of the van der Waals surfaces of the interlayer space in the $Co_{0.1}InSe$ and $Co_{0.15}In_2Se_3$ intercalates were carried out by the method of AFM microscopy (Fig. 5). In a number of papers it was reported about the formation of ordered arrays of nanoparticles of $3d$-metals appeared due to magnetic field [25], as well as about the influence of magnetic field on the dimensions of nanoparticles [26] and the interaction between them [27]. In addition, 3D structures of intercalant's nanocrystals can be obtained by intercalation with $3d$-metal atoms from a liquid phase [28].

The AFM patterns of the van der Waals surfaces of the $Co_{0.1}InSe$ (a) and $Co_{0.15}In_2Se_3$ (b) samples intercalated in the magnetic field (Fig. 5) show many nanoinclusions or nanoformations of the intercalant. On these surfaces of the $Co_{0.15}InSe$ intercalate one can see separate pyramidal nanoformations with a height of about 10 nm. Height of nanoformations could be greater than van der Waals gap width since the incipient and the further nanoformations growth occurs in nanocavities of van der Waals surfaces. Increase of the crystal lattice constant during nanoformations growth with height greater than the width of the van der Waals gap does not take place because its small number compared to total area of van der Waals surfaces of InSe.

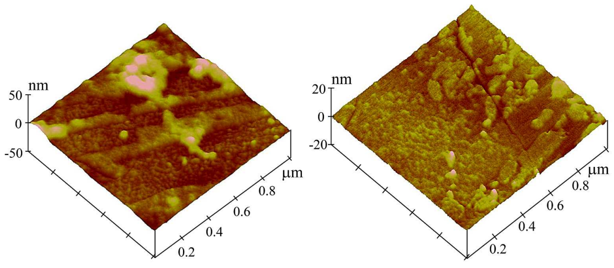

Fig. 5. AFM patterns of the surfaces of the $Co_{0.1}InSe$ (left) and $Co_{0.15}In_2Se_3$ (right) samples intercalated with Co^{2+} ions in the magnetic field.

We have also observed nanoscale aggregates of elongated form (nanowires) with a height about of 0.7 nm, which become joined and form the clusters up to 100 nm long (Fig. 5a). A similar situation takes place for the $Co_{0.15}In_2Se_3$ intercalate. The observed nanoformations have equilibrium pyramidal shape with a height about of 0.7–0.9 nm and an average lateral size ≈15 nm. These nanoformations create the arrays in the form of separated wires up to 100 nm long. We assume that the nanowires are formed along the lines of the dislocation grid in the plane (0001) (see Fig. 5a) and belong by the cobalt intercalated into the van der Waals space of the layered crystals.

4. Conclusion

In summary, we have found that the use of a magnetic-field gradient at the *crystal–electrolyte*interface (intercalation front) during electrochemical intercalation of InSe and In_2Se_3 crystals with ions of 3*d*-metals (cobalt, particularly) causes changes in the magnetic properties of the layered crystals. It is established that the $Co_{0.1}InSe$ and $Co_{0.15}In_2Se_3$ intercalates demonstrate ferromagnetic properties at room temperature. The dependences of the magnetic moment on magnetic field strength measured along and across the layers for the cobalt intercalates of InSe and In_2Se_3 have the form of hysteresis loops. This is caused by the ferromagnetic exchange interaction between the cobalt atoms. It is detected that during intercalation of the layered crystals with Co ions various nanostructures of the intercalant appear on the van der Waals surfaces of the layers.

The combination of electrochemical intercalation with gradient magnetic field offers the challenge to create magnetic nanocomposite structures consisting of a layered semiconductor matrix and interlayers of magnetic impurities which are perpendicular to the C axis.

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