*JOURNAL OF NANO- AND ELECTRONIC PHYSICS*
Vol. **7** No 1, 01027(4pp) (2015)

*ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ*
Том **7** № 1, 01027(4cc) (2015)

# Room Temperature Ferromagnetism in InTe Layered Semiconductor Crystals Intercalated with Cobalt

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(Received 16 November 2014; published online 25 March 2015)

The magnetic properties of $Co_xInTe$ layered crystals electrochemically intercalated with cobalt in constant gradient magnetic field and the morphology of the van der Waals surfaces of layers of these crystals were studied. It was established that impurity clusters consisting of cobalt nanoparticles are formed in the intercalates under investigation of the van der Waals planes in the interlayer space. It was revealed that at room temperature the investigated $Co_xInTe$ intercalates exhibit magnetic properties characteristic for magnetically hard ferromagnetic materials.

**Keywords:** Layered crystals, InTe, Intercalation, Ferromagnetism, Semiconductors, Cobalt.

PACS numbers: 61.43.Dq, 75.50.Pp, 75.60Ej

## 1. INTRODUCTION

Modern development of materials science requires the elaboration of controlled synthesis methods of binary semiconductor compounds with the necessary structure, composition and, as a consequence, electrophysical properties predicted in advance. Layered compounds of the $A^{III}B^{VI}$ group (A – In, Ga; B – Se, Te) find application in different fields of semiconductor engineering, namely, piezoelectrics, infrared and radiation detectors, photosensitive heterojunctions, spintronics, solid-state hydrogen storages, etc. [1-8]. We should also note that significant interest of researchers to the crystals of this group during last years is associated with the prospects of research of two-dimensional (2D) semiconductor crystals and creation of 2D functional devices on their basis [9-13].

Moreover, these compounds using intercalation can absorb and localize in the interlayer space atoms and ions of different elements [14, 15] maintaining the initial crystal structure. Investigation of layered semiconductors intercalated with magnetic elements of the iron group (Fe, Co, Ni) is especially important [16-19]. The obtained compounds-intercalates combine both semiconductor properties inherent to the initial compounds and magnetic properties of intercalated impurities.

Indium monotelluride InTe is crystallized as TlSe, space group I4/mcm [20]. It takes a special place among layered semiconductors of $A^{III}B^{VI}$ due to more complex crystallographic structure compared with other compounds of $A^{III}B^{VI}$. $In^{3+}$ ions are tetrahedrally coordinated to $Te^{2+}$ ions forming $InTe_{4/2}$ chains of the SiS type, while $In^{+}$ ions form an octuple tetragonal antiprism coordination to $Te^{2-}$ ions. $In^{3+}$ and $In^{+}$ ions, which are chemically different, occupy two different crystallographic positions (Fig. 1) and prevent the free electron transfer from $In^{+}$ to $In^{3+}$. Investigation of InTe monocrystals is, mainly, focused on the study of the structural [21, 22] and electrical properties [23, 24]. Data on the investigation of the intercalates based on InTe is currently absent.

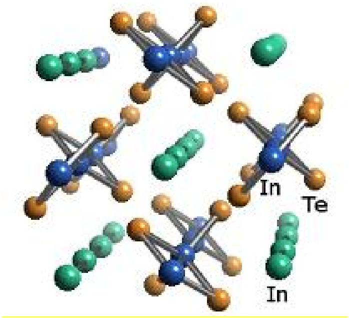

**Fig. 1** – Crystal structure of InTe. $In^{+}$ and $In^{3+}$ atoms which are crystallographically different are shown, respectively, by green and blue spheres. Te atoms are illustrated in yellow

## 2. EXPERIMENTAL

It is known [20] that indium monotelluride is crystallized at the temperature of 969 K in the tetragonal system, and with increasing temperature and pressure it is transformed into NaCl cubic modification. Monocrystalline InTe ingots were obtained by the Bridgeman method from the solution of the stoichiometric composition. Stoichiometry of the obtained crystals, their single-phase state and uniformity were controlled by the X-ray diffraction method. Structural characteristics of the obtained crystals were equal to $a = 8.455$ Å and $c = 7.136$ Å (space group I4/mcm) and correspond to the literature data of [25]. Samples of the sizes of $5 \times 5 \times 1 mm^3$ were used for the experiments.

Intercalation of $Co^{2+}$ ions into the interlayer space of InTe was performed by the electrochemical method in the galvanostatic mode. Intercalation of 3-d transition metals into layered $A^{III}B^{VI}$ semiconductors is described in detail in [17, 19]. Structural investigation of the obtained $Co_xInTe$ ($x = 0.1$) intercalates was carried out by the atomic-force microscopy (AFM) method by using the microscope Nanoscope IIIa Dimension 3000SPM. Radius of the probe was not more than 10 nm, and all the mea-

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surements were performed *ex situ*. Magnetic characteristics of Co$_x$InTe intercalates were studied by magnetometry method on the magnetometer Vibrating Magnetometer 7404 VSM in magnetic fields with the strength to 3000 Oe.

## 3. RESULTS AND DISCUSSION

The performed X-ray structural analysis of the obtained Co$_{0.1}$InTe intercalates has shown that structural type and lattice parameters of intercalated InTe samples remain constant. This fact is typical for layered $A^{III}B^{VI}$ semiconductors and TiX$_2$ dichalcogenides (X-S, Se, Te) intercalated with magnetic impurities [16, 26, 27]. Such behavior of the crystallographic parameters is explained by the competing action of hybridization of 3d-orbitals of Co atoms with *p*-states of Te (formation of "tightening" Te-Co-Te bonds) and repulsion of Te atoms.

Due to their structure, layered InTe crystals are characterized by a higher density of defects on the van der Waals planes of the interlayer space in comparison with other layered crystals, in particular, InSe and GaSe. There is a possibility of adsorption of atoms or molecules of the intercalate and nucleation of impurity islands on the semiconductor surface on the given defects during the electrochemical intercalation. On account of such extended defects, formation of the intercalate nanostructures is possible that, in turn, will influence the properties of the initial crystals. In Fig. 2 we illustrate the AFM-images of the internal surfaces of Co$_{0.1}$InTe intercalates. These compounds are obtained by intercalation in the constant magnetic field of the value of 4 kOe. In this image one can observe a large amount of small nanoformations of the height of 10÷20 nm which are agglomerated into clusters with the lateral sizes of 1÷2 μm. Moreover, separate nanoformations of a pyramidal shape (see Fig. 2b, c) are also observed. Their height is about 50÷100 nm, though isolated nanoinclusions of the height of more than 100 nm exist. State of the van der Waals surfaces of the layered crystal can be the reason of the appearance of such different nanoformations. Probably, formation of clusters of the intercalate occurs in the places of defect localization on the van der Waals InTe planes, and formation of separate nanoformations – in nanocavities on the layer surface. To our opinion, nucleation and formation of cobalt clusters in the interlayer space of InTe occurs on account of the phenomenon of "self-organization" of intercalate atoms. Exchange magnetic interaction between cobalt atoms plays a key role in this process. We should also take into account the presence of the external constant magnetic field during intercalation. Its action promotes the formation both cobalt clusters and its separate pyramidal nanoformations.

As our previous investigations have shown, intercalation of the layered semiconductors with magnetic elements in the constant magnetic field [16, 19] changes the properties of the initial samples. After such intercalation, the so-called "ferromagnetic response" (when intercalated samples exhibit the ferromagnetic properties) is observed in the paramagnetic layered crystals. These properties consist in the appearance of the hysteresis magnetization curves typical for the ferromagnetic materials.

In Fig. 3 we present the dependences of the specific magnetic moment on the magnetic field strength for Co$_x$InTe intercalates with different concentrations of the introduced cobalt ($x = 0.1$; 0.15). We should note that for Co$_x$InTe intercalates obtained by electrochemical intercalation without application of a magnetic field, these properties were not observed. This fact implies the impact factor of a gradient magnetic field on the formation and properties of the intercalates of 3d transition metals based on layered semiconductors.

Strong anisotropy of the structural and electron characteristics along and perpendicular the layer plane is inherent to the layered semiconductor crystals. As seen from the represented dependences, curves $m = f(H)$ for both samples depend on the magnetic field direction with respect to the crystal layer plane and concentration of the introduced cobalt. The values of the coercive force $H_c$ determined from Fig. 3 are equal to 205.66 E and 177.57 E for Co$_{0.1}$InTe and 144.13 E and 145.26 E for Co$_{0.15}$InTe, respectively, for the direction of the field $H$ along and across the crystal layer plane that is typical for the hard ferromagnetic materials.

The values of the specific magnetic saturation moment $m_s$ in the $H \| c$ configuration for Co$_{0.1}$InTe and Co$_{0.15}$InTe samples differ slightly (respectively, $3.45 \times 10^{-3}$ and $3.396 \times 10^{-3}$ emu/g) in contrast to the values of $m_s$ for the $H \perp c$ configuration which are equal to, respectively, $2.79 \times 10^{-3}$ and $11.04 \times 10^{-3}$ emu/g. View of the hysteresis loops for the dependences $m = f(H)$ in the magnetic field direction along the layers implies the ferromagnetic interaction between cobalt atoms. As for the view of

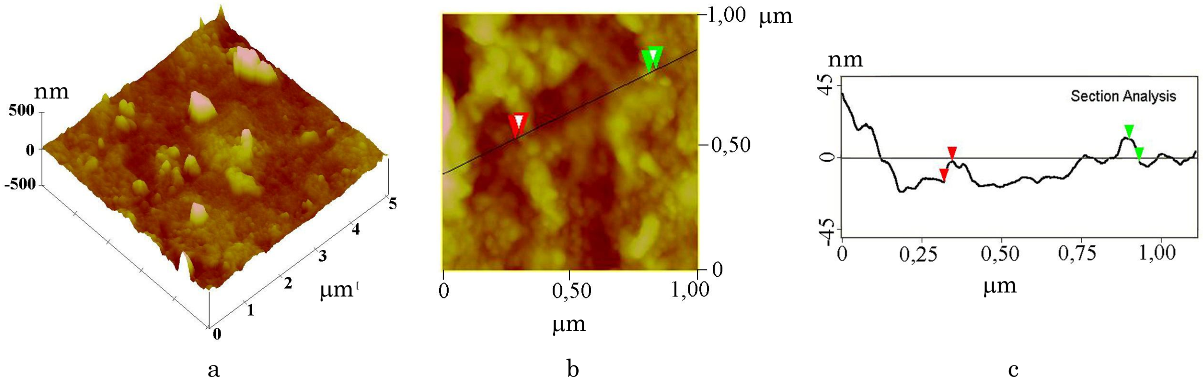

**Fig. 2** – Three-dimensional (a) and two-dimensional (b) AFM-images of the van der Waals surface of InTe intercalated with cobalt in magnetic field; distribution of nanoformations in height along the line is on the two-dimensional AFM-image

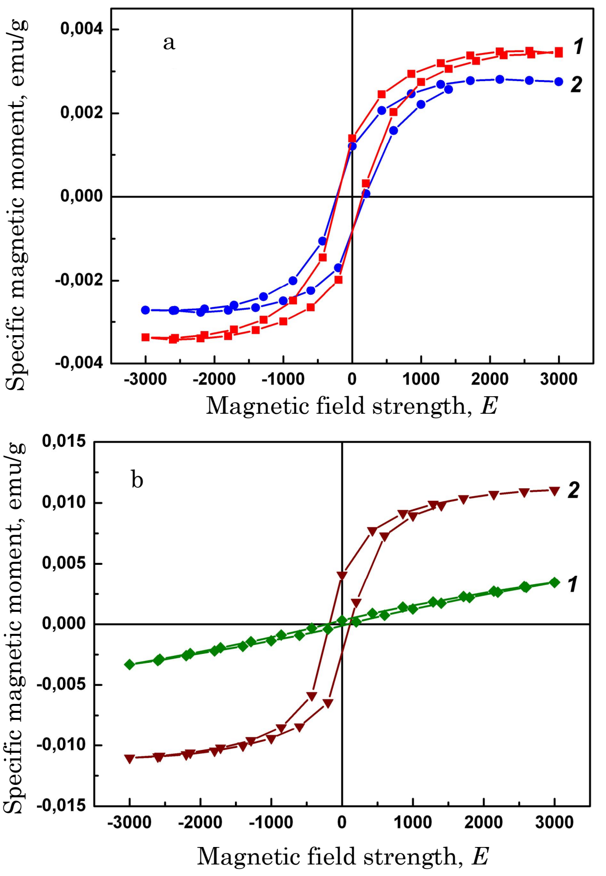

**Fig. 3** – Dependence of the specific magnetic moment on the magnetic field strength for Co$_{0.1}$InTe (a) and Co$_{0.15}$InTe (b) intercalates intercalated in magnetic field: 1 – magnetic field is directed perpendicular to the layer plane; 2 – magnetic field is directed along the layer plane

the dependences $m = f(H)$ for the field direction perpendicular to the layer plane, then in this case it is typical for the ferromagnetic interaction between layers.

Differences between the dependences $m = f(H)$ at different magnetic field directions of Co$_x$InTe intercalates can be explained taking into account the crystal structure of layered $A^{III}B^{VI}$ compounds and results the AFM-investigations presented below. During intercalation of the layered crystals, intercalate is localized in the van der Waals slots between chalcogen atoms. Structure of covalent …B–A–A–B… layers remains constant in this case. Depending on the concentration of the intercalated cobalt (value and amount of the formed clusters), interaction of clusters directly between each other in the layer plane is possible as well as the exchange interaction between layers through the Se atom. In particular, the authors of [28] have reported about such interaction through a chalcogen atom for layered Mn$A^{III}B^{VI}$ compounds. As seen from the analysis of the curves $m = f(H)$ for Co$_{0.1}$InTe and Co$_{0.15}$InTe (magnetic field direction is perpendicular to the layer plane), the values of the specific magnetic moment are almost the same. The value of the specific magnetic moment for the magnetic field direction along the layers is larger for Co$_{0.15}$InTe than for Co$_{0.1}$InTe. This implies the increase in the interaction between clusters in the layer plane on account of the increase in the concentration of intercalated cobalt.

Magnetic charges appear in cobalt clusters formed at intercalation when applying the external magnetic field. Their appearance induces a demagnetizing field directed opposite to the true magnetic field in a ferromagnetic cluster. This field is characterized by the demagnetizing factor, whose value depends on the external magnetic field direction. According to [29], the larger distance between magnetic charges, the less demagnetizing factor and, correspondingly, the less its counteraction to the true magnetic field. In our case, when external magnetic field is directed across the layers, demagnetizing field will have a greater influence on the dependence $m = f(H)$, since interaction between cobalt clusters is limited by the covalent layers of the initial InTe crystal. To our opinion, just this fact is the main reason of the differences in the behavior of $m = f(H)$ for the external magnetic field directions along and across the layer plane for Co$_x$InTe intercalates.

## 4. CONCLUSIONS

Use of the constant gradient magnetic field during electrochemical intercalation of the layered InTe crystals with cobalt leads to the formations of nanosized impurity inclusions (clusters) on the van der Waals planes of the interlayer space. This results in the change of the magnetic properties of Co$_x$InTe ($x = 0.1$; 0.15) intercalates compared with the non-intercalated samples. The obtained Co$_x$InTe compounds possess at room temperature the magnetic properties typical for the ferromagnetic materials, namely, the obtained dependences of the specific magnetic moment on the magnetic field strength have the shape of the hysteresis loops.

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