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Ferromagnetism in Cobalt-Intercalated In₂Se₃ Layered Crystals

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We report on the impact of cobalt intercalation on properties of In₂Se₃ layered crystals. It is shown that electrochemical intercalation of Co atoms into the In₂Se₃ layered crystals does not cause any changes in structural type of the crystals and is accompanied by a decrease in the lattice constant in the direction perpendicular to the base plane. In the case of the Co_{0.15}In₂Se₃ intercalation compound, obtained by intercalation in constant magnetic field, we manifested ferromagnetic properties at room temperature. The dependence of magnetic moment on magnetic field strength has a shape of hysteresis loop. This dependence was not observed in the case of Co intercalation into In₂Se₃ without magnetic field.

Keywords: In₂Se₃, layered crystals, cobalt, intercalation, ferromagnetism.

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Introduction

In₂Se₃ is a semiconductor compound that belongs to the A₂^{III}B₃^{VI} type of crystal group and crystallizes as a layered structure [1]. A distinctive feature of the compounds of this class is a pronounced defectiveness, i.e. one-third of cation positions remain vacant, that are chaotically disordered in fact. A large number of structural modifications and complex low-temperature phases are characteristic of this class of compounds [1, 2]. In addition, layered semiconductors are the so-called “intercalation materials”, i.e. guest objects (atoms, molecules and even fragments of crystal lattices of other materials) can be intercalated into their crystal lattice [3].

The study of intercalated layered semiconductors is a pressing task because of the possible application of these materials as convenient model systems for the study on the contribution of thermodynamic functions of electron subsystem to the total thermodynamic functions of the material and formation of its phase diagram. This is forwarded by the possibility to control the type of embedded impurity and variation of the value of its concentration within a fairly wide range without changing crystal structure of the basic compound. It allows to obtain materials with “programmable” properties.

With the development of nanomagnetism and spintronics, considerable attention has been focused on investigations on intercalation of layered semiconductors by 3d-transition elements. It opens up a possibility to modify their magnetic properties and create quasi-two-dimensional magnetics [4, 5]. The interest in semiconductors with magnetic properties based on layered crystals is caused by their strong anisotropy and,

hence, the possibility of nonuniform dopant distribution in crystal lattice. Different states of magnetic impurity can lead to the formation of ferromagnetic domains, and that is of considerable interest for practical application.

I. Experimental details

The In₂Se₃ single crystals were grown by the Bridgman method from a stoichiometric melt with a temperature gradient of 15 K/cm at the crystallization front and growth velocity of 1 mm/h. The obtained materials possessed a clearly pronounced layered structure over the entire ingot length. The carried out X-ray analysis showed that they possessed α -phase structure, which is described by R3mH space group of trigonal system. The lattice constants of the obtained In₂Se₃ crystals are: $a = 4.05 \text{ \AA}$, $c = 28.771 \text{ \AA}$, which is consistent with known published data [6, 7]. Moreover, it should be noted that, according to Ref. 8, α -In₂Se₃ exhibits domain structure.

The intercalation of In₂Se₃ layered crystals was carried out by electrochemical method in saturated water solution of CoSO₄. Schematic diagram of the setup for electrochemical intercalation of layered crystals is shown in fig. 1. The intercalation process of In₂Se₃ single crystal samples was carried out by the method of sweeping electric field [9] using the P-5827M potentiostat in the galvanostatic mode (current $\leq 0.4 \text{ mA/cm}^2$). The electrochemical cell was made of chemical- and heat-resistant glass. The cell is a three-electrode system: reference (4), main (3) and additional (5) electrodes. Platinum wires were used as additional and reference electrodes. In order to study influence of magnetic field on the intercalation process, permanent neodymium

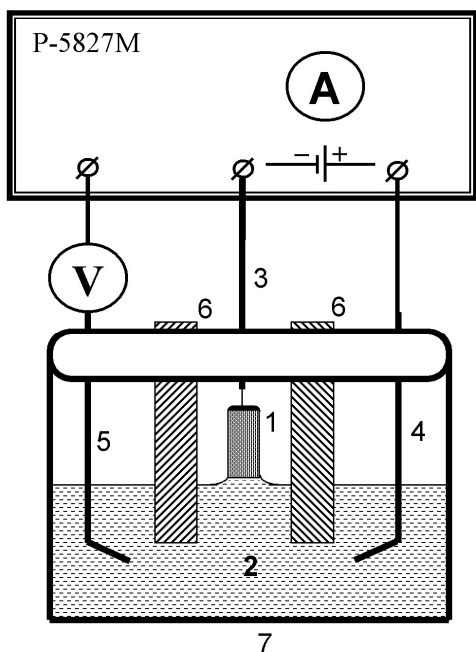


Fig. 1. Schematic diagram of the setup for electrochemical intercalation of layered crystals.

magnets (6) were put into the cell. The samples were intercalated under magnetic field of these magnets, which was applied perpendicularly or in parallel to the crystallographic axis \vec{C} of the crystal. A copper wire from the sample was soldered to the main electrode (1). The sample was contacting the electrolyte (2).

Small current was used in order to prevent deposition of free metal on the samples and electrodes. Co^{2+} ions were intercalated into the layered crystal by passing electric current of the required magnitude through the electrochemical cell. The concentration of intercalated impurity x ($0.01 \leq x \leq 0.15$; x – amount of intercalated Co ions per formula unit of the crystal) was determined

from the quantity of electricity which had passed through the cell, i.e. current density and process duration were the control variables in the process of intercalation reaction.

To see how constant magnetic field B influences Co intercalation in In_2Se_3 , we conducted two types of intercalations: with the magnetic field applied perpendicular to the crystallographic axis \vec{C} of the crystal and without magnetic field. The magnetic field was generated by permanent neodymium magnets. The magnetic field strength was 4 kOe at the sample.

An X-ray diffraction analysis of the grown crystals was performed using a DRON-3 diffractometer in CuK_α radiation. The obtained diffraction patterns were analysed with LATTIK-KARTA software.

Magnetic characteristics of the $\text{Co}_{0.15}\text{In}_2\text{Se}_3$ intercalation compound were studied by the magnetometry method on “Vibrating Magnetometer 7404 VSM” (Lake Shore Cryotronics Inc., USA) in magnetic field with the strength up to 3000 Oe. The magnetometer sensitivity was $\sim 10^{-7}$ EMU, which allowed to measure magnetic moment of the samples weighing several milligrams. We used an electronic microbalance AB135-S/FACT with automatic compensation (sensitivity 10^{-5} g) to measure the mass of the sample. The mass of the $\text{Co}_{0.15}\text{In}_2\text{Se}_3$ sample was 0.11796 grams. Magnetic moment was measured along and across the \vec{C} axis of the crystal.

II. Results and discussion

The diffraction patterns of the In_2Se_3 single crystals, both pure and cobalt intercalated ($x_{\text{Co}} = 0.15$), are shown in fig. 2. The presence of the $00l$ reflections ($l = 3, 6, 9, 12, 15, 18$) of the In_2Se_3 and $\text{Co}_{0.15}\text{In}_2\text{Se}_3$ samples suggests that structural type and space group of the $\text{Co}_{0.15}\text{In}_2\text{Se}_3$ samples remain unchanged. Intercalation

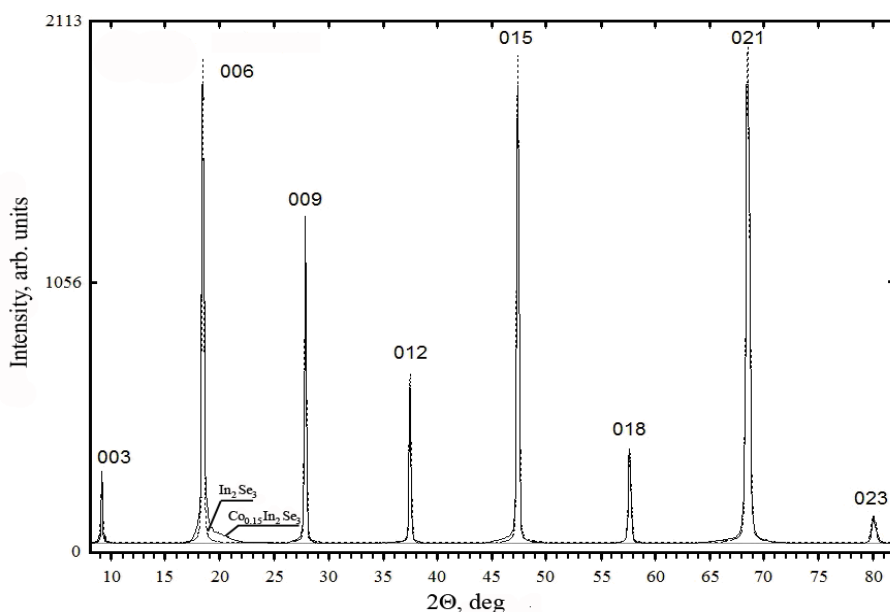


Fig. 2. Diffraction patterns of the In_2Se_3 and $\text{Co}_{0.15}\text{In}_2\text{Se}_3$ samples obtained by intercalation in constant magnetic field.

of cobalt into In_2Se_3 is confirmed by the broadening of the X-ray diffraction peaks of the intercalated samples in comparison with the pure compound. Unit cell parameters of the $\text{Co}_{0.15}\text{In}_2\text{Se}_3$ single crystals were measured as well: $a = 4.052 \text{ \AA}$, $c = 28.727 \text{ \AA}$. As can be seen, the intercalation of Co into In_2Se_3 causes reduction of the lattice constant in the direction of the crystallographic axis \vec{C} and insignificant variations of the lattice constant in the layer plane ($\perp \vec{C}$). Such behaviour of the crystallographic parameters is inherent to the layered semiconductors intercalated by 3d-transition elements [10-12]. Taking into account the structure and properties of the studied materials, this fact can be explained in the same way as in Refs. 10, 12. It is explained by a hybridization of the p-states of Se, which is located at the boundary of the five-layer packet ...Se-In-Se-In-Se..., with the 3d-orbitals of intercalant atoms (Co). As a result, it causes formation of covalent bonds In-Co-In between the intercalated atom and the In_2Se_3 crystal matrix system. These bonds constrict the crystal layers of the host lattice, which leads to the reduction of the lattice constant c .

Layered semiconductor crystals exhibit the properties of paramagnetics. Intercalation of such compounds by the atoms of 3d-transition metals, which exhibit ferromagnetic properties, can lead not only to the impact on the interaction of charge carriers, as it is in case of intercalation of alkaline metals ions [13], but also to the changes of magnetic properties of the crystal. The weak van der Waals bonds between layers of the crystal lattice encourage localization of intercalated atoms in octahedral and tetrahedral cavities of the interlayer space. Moreover, the constant magnetic field applied to the samples during intercalation process can influence on the intercalation of ferromagnetic atoms. The dependences of the specific magnetic moment of the $\text{Co}_{0.15}\text{In}_2\text{Se}_3$ samples intercalated in magnetic field are shown in fig. 3. These dependences have a shape of hysteresis loop [14]. It should be noted that these dependences were not observed in case of the $\text{Co}_{0.15}\text{In}_2\text{Se}_3$ samples intercalated

without magnetic field. In common with all $A^{III}B^{VI}$ layered semiconductors, the In_2Se_3 crystals are anisotropic. Hence, magnetic moment was measured in \parallel and \perp directions to the layers. As can be seen from fig. 3, the dependence $m=f(H)$, obtained along the layers of $\text{Co}_{0.15}\text{In}_2\text{Se}_3$ intercalant, is typical for ferromagnetic interaction between cobalt atoms, and specific saturation magnetic moment is $m_s = 0.043344 \text{ emu/g}$ at magnetic field strength $H = 3000 \text{ Oe}$. When measurements are conducted in the direction perpendicular to the layer plane, the behaviour of $m = f(H)$ corresponds with the ferromagnetic interaction between layers, and the magnetization is $m_s = 0.02146 \text{ emu/g}$. The coercive force is $H_c = 122.82 \text{ Oe}$ and $H_c = 188.72 \text{ Oe}$ along and across the layer plane of the $\text{Co}_{0.15}\text{In}_2\text{Se}_3$ samples, respectively, which is characteristic of the hard-magnetic ferromagnetics in both cases.

As mentioned above, two different types of crystal binding in layered semiconductor encourage the fact that intercalated atoms can occupy only two different sets of positions in van der Waals space: octahedral and tetrahedral voids coordinated by chalcogen [15]. In our case, the intercalation of cobalt into octahedral voids of the interlayer space is energetically favorable. It is also necessary to take into account that the presence of different defects, which break translational symmetry of the crystal, initiates redistribution of the intercalated atoms and their localization at these defects. It leads to the formation of the clusters of the intercalated atoms. The applied magnetic field causes magnetization of the cobalt atoms and their intercalation into the layer structure under the action of the field. In addition, the magnetic field may cause direct interaction between the cobalt atoms in the direction of the layers and exchange interaction via Se atoms perpendicularly to the layer plane, similarly to the atoms interaction in MnA^3B^6 crystals [16, 17]. Such interaction causes magnetic ordering within the Co clusters, which can encompass several layers.

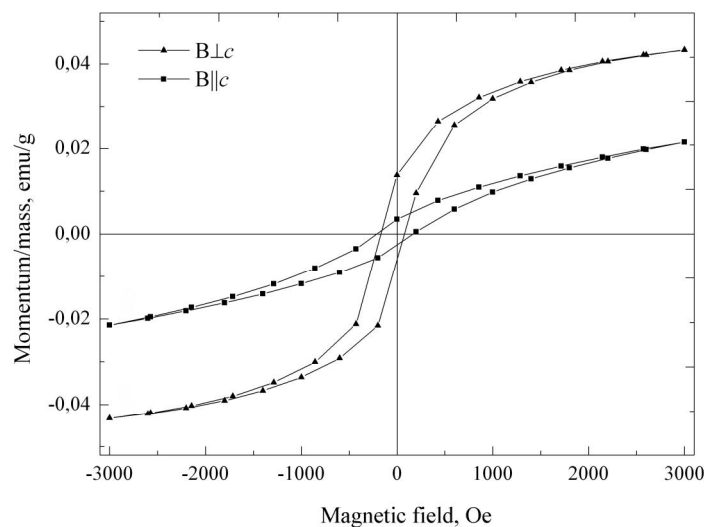


Fig. 3. Dependence of specific magnetic moment on magnetic field strength for the $\text{Co}_{0.15}\text{In}_2\text{Se}_3$ samples obtained by intercalation in constant magnetic field.

Conclusions

Electrochemical intercalation of Co atoms into the In_2Se_3 layered crystals does not cause any changes in structural type of the crystals and is accompanied by a decrease in the lattice constant in the direction perpendicular to the base plane. In the case of the $\text{Co}_{0.15}\text{In}_2\text{Se}_3$ intercalation compound, obtained by intercalation in constant magnetic field, we observed a dependence of magnetic moment on magnetic field strength at room temperature. The dependence had a shape of hysteresis loop. But we didn't observe such dependence in the case of Co intercalation into In_2Se_3 without magnetic field. We assume that this fact is

caused by the ferromagnetic exchange interaction of the Co atoms and formation of ordered ferromagnetic Co clusters.

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Ферромагнетизм в інтеркальованих кобальтом шаруватих кристалах In_2Se_3

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Досліджено вплив інтеркаляції кобальту на властивості шаруватих кристалів In_2Se_3 . Показано, що електрохімічна інтеркаляція атомів кобальту в шаруваті кристали In_2Se_3 не призводить до змін структурного типу кристалів та супроводжується зменшенням постійної ґратки перпендикулярно базовій площині кристалу. Виявлено прояви ферромагнетизму при кімнатній температурі в інтеркалатах $\text{Co}_{0.15}\text{In}_2\text{Se}_3$, отриманих інтеркаляцією в постійному магнітному полі. Залежність магнітного моменту від напруженості магнітного поля має вигляд петлі гістерезисну. Така залежність не спостерігається у випадку інтеркаляції атомів кобальту в шаруваті кристали In_2Se_3 без зовнішнього магнітного поля.

Ключові слова: In_2Se_3 , шаруваті кристали, кобальт, інтеркаляція, ферромагнетизм.