Magnetic Properties of Co$_{0.1}$Sb$_2$Te$_3$, Ni$_{0.1}$Bi$_2$Te$_3$ and Ni$_{0.2}$In$_4$Se$_3$ Compounds

V.B. Boledzyuk*, M.Z. Kovalyuk, V.I. Ivanov

*I.M. Frantsevych Institute for Problems of Materials Science, NAS of Ukraine,
Chernivtsi Branch, 5, I. Vilde St., 58001 Chernivtsi, Ukraine*

The properties of layered transition metal dichalcogenides intercalated with 3d metal ions are investigated. The influence of the gradient magnetic field at the intercalation front on the properties of intercalants is studied. It is shown that Co$_{0.1}$Sb$_2$Te$_3$, Ni$_{0.1}$Bi$_2$Te$_3$ and Ni$_{0.2}$In$_4$Se$_3$ intercalates have ferromagnetic properties at room temperature. The dependences of the magnetic moment on the magnetic field strength along and across the layers of Co$_{0.1}$Sb$_2$Te$_3$, Ni$_{0.1}$Bi$_2$Te$_3$ and Ni$_{0.2}$In$_4$Se$_3$ intercalates have the hysteresis loop. The obtained values of the coercive force of the studied samples are typical for hard ferromagnets. The properties of the obtained intercalates are determined by the crystal structure of layered crystals, localization and magnetic interaction of intercalant atoms between the layers of the crystal matrix and the influence of the magnetic field on the processes of exchange interaction between them.

Keywords: Bi$_2$Te$_3$, Sb$_2$Te$_3$, In$_4$Se$_3$, Intercalates, Magnetic properties, 3d metals.

1. INTRODUCTION

Monochalcogenides are layered compounds that have aroused great interest in recent years as initial materials for two-dimensional crystals [1]. A characteristic difference of layered semiconductor crystals from other semiconductors is their ability to reversible intercalation of the intercalant into the interlayer space. Intercalants can be ions, atoms, molecules and even whole organic complexes [2-4]. Since interlayer distances are several angstroms, there is a possibility of realization of impurity layers and controlled insertion of the intercalant at the molecular level.

The insertion of ferromagnetic elements into layered crystals makes it possible to form a hybrid ferromagnetic-semiconductor nanosystem with matrix insulation of layers. This creates additional opportunities to modify the properties of layered semiconductors, fabricate two-dimensional magnets [5-8], create new semimagnetic compounds and nanocomposite materials based on semiconductors and ferromagnetic metals [9], etc. In addition, intercalated layered semiconductors are convenient model systems for studying the contributions of the thermodynamic functions of the electronic subsystem of the intercalant in the thermodynamic functions of the layered semiconductor.

The aim of this work is to investigate the magnetic properties of Sb$_2$Te$_3$, Bi$_2$Te$_3$ and In$_4$Se$_3$ single crystals electrochemically intercalated by cobalt and nickel atoms.

2. EXPERIMENTAL

Sb$_2$Te$_3$ and Bi$_2$Te$_3$ single crystals were grown by the Bridgman method, and In$_4$Se$_3$ single crystals were grown by the Czochralski method. The obtained single crystals have a pronounced layered structure. The crystal lattice of Sb$_2$Te$_3$ and Bi$_2$Te$_3$ is formed by periodically ordered layers perpendicular to the axis of symmetry of the third order (C_3) and corresponds to a rhombohedral structure with the point group $R\bar{3}m$. The crystal structure of In$_4$Se$_3$ corresponds to the point group $Pnnm(D_{2h}^{12})$. The chemical bond within the layer is covalent-ionic. The distance between the layers is relatively large and the bond is weak, which is provided by the van der Waals forces and determines the anisotropy of the properties of single crystals. The ionic radii of Ni and Co intercalants are an order of magnitude smaller than the interlayer distances in Sb$_2$Te$_3$, Bi$_2$Te$_3$ and In$_4$Se$_3$. This enables the efficient intercalation of the samples without their destruction.

The samples for research were obtained from monocrystalline ingots by simple cleaving along the plane of the layers. The intercalation was performed by electrochemical method [10]. Saturated aqueous solutions of the corresponding salts were used as the electrolyte. The insertion of the intercalant was carried out in the galvanostatic mode, which prevents separation and deposition of the inserted impurity on the samples or electrodes of the cell, the density of the insertion current did not exceed 0.4 mA/cm². The concentration of the inserted impurity was determined by the amount of electricity that passed through the cell. The controlled parameters during the intercalation reaction were the electric current density and the duration of the process. Cobalt and nickel are 3d metals with ferromagnetic properties. The intercalation of Sb$_2$Te$_3$, Bi$_2$Te$_3$ and In$_4$Se$_3$ samples was carried out with and without applying a constant magnetic field. The magnetic field was created by permanent neodymium magnets, its value at the intercalation front was 4 kOe [11]. The magnetic properties of Co$_{0.1}$Sb$_2$Te$_3$, Ni$_{0.1}$Bi$_2$Te$_3$ and Ni$_{0.2}$In$_4$Se$_3$ intercalates were studied by magnetometry using a Vibrating Magnetometer 7404 VSM. The sensitivity of the magnetometer was of the order of 10^{-7} emu. The measurements of the magnetic moment along and across the plane of the layers were carried out at room temperature.

3. RESULTS AND DISCUSSION

---

* boledvol@gmail.com

Layered III-VI semiconductors are paramagnetic. Insertion of atoms of transition elements of the iron group into their structure affects the magnetic properties of the initial compound regardless of their location between layers or in the structure of the layer. Cobalt and nickel are ferromagnetic. Thus, in particular, hysteresis of the magnetic properties, which is characteristic of ferromagnetic materials, was observed in layered InSe and GaSe crystals intercalated with cobalt [11, 12].

Table 1 – The specific magnetic moment and coercive force measured in different crystallographic directions for $Co_{0.1}Sb_2Te_3$ and $Ni_{0.2}In_4Se_3$ intercalates

Measurement direction	$Co_{0.1}Sb_2Te_3$		$Ni_{0.2}In_4Se_3$	
	m_S, emu/g	H_C, Oe	m_S, emu/g	H_C, Oe
Along the plane of the layers	0.2216	170.8	6.98×10^{-3}	48.88
Across the plane of the layers	0.2887	120.99	5.62×10^{-3}	101.03
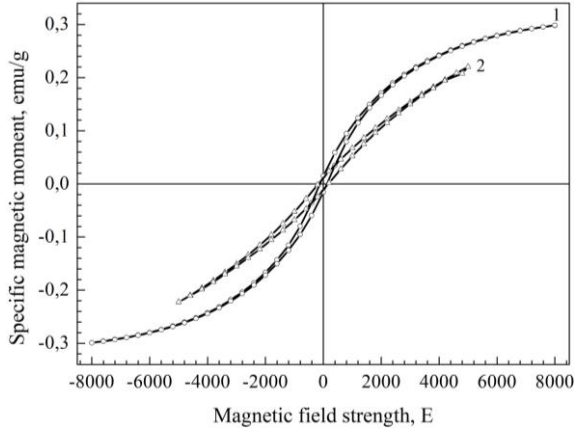
Fig. 1 – Dependence of the specific magnetic moment on the magnetic field strength for $Co_{0.1}Sb_2Te_3$ samples intercalated in the magnetic field: 1 – across the plane of the layers; 2 – along the plane of the layers
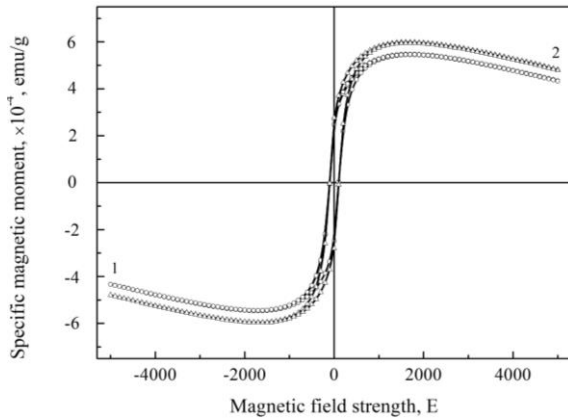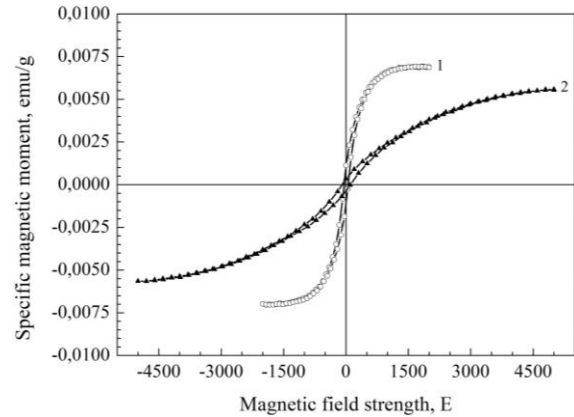

Fig. 2 – Dependence of the specific magnetic moment on the magnetic field strength for $Ni_{0.1}Bi_2Te_3$ samples: 1 – intercalation in a magnetic field; 2 – intercalation without a magnetic field (2)

Fig. 1, Fig. 2 and Fig. 3 show the dependences of the specific magnetic moment on the magnetic field strength for Sb_2Te_3 (Fig. 1), Bi_2Te_3 (Fig. 2) and In_4Se_3 (Fig. 3) layered crystals intercalated with Co^{2+} and Ni^{2+} ions in a magnetic field. The vector of the magnetic field strength **H** lies in the base plane of the crystal samples during intercalation. Layered crystals are anisotropic compounds, so the measurements of the magnetic moment were carried out in the directions of the magnetic field perpendicular (**H**⊥*c*) and parallel (**H**∥*c*) to the *c*-axis. As can be seen from the obtained data,

the dependences $m = f(H)$ differ depending on the direction of the magnetic field relative to the plane of the layers. In the first case, the dependence $m = f(H)$ is typical for the ferromagnetic interaction between 3d metal atoms, and in the second case, the dependence $m = f(H)$ is determined by the ferromagnetic interaction between the layers. The values of the specific magnetic moment (m_S) and coercive force (H_C) for $Co_{0.1}Sb_2Te_3$ and $Ni_{0.2}In_4Se_3$ intercalated in magnetic fields up to 8 kOe are listed in Table 1. The values of the magnetic moment for $Ni_{0.1}Bi_2Te_3$ intercalates were 5.47×10^{-4} and 5.97×10^{-4} emu/g for intercalation with and without applying a magnetic field (Fig. 2). The obtained values of H_C for the studied samples are typical for hard ferromagnets.

Fig. 3 – Dependences of the specific magnetic moment on the magnetic field strength for $Ni_{0.2}In_4Se_3$ samples intercalated in the magnetic field: 1 – across the plane of the layers; 2 – along the plane of the layers

The difference in the dependences $m = f(H)$ along and across the layers is determined by many factors, including the crystal structure of layered crystals, the localization of the intercalant between the layers of the crystal matrix, the influence of magnetic fields on Co and Ni atoms and other. The use of a magnetic field during intercalation causes the magnetization of the intercalant.

In the case of antimony and bismuth tellurides, the intercalant accumulates around point defects and dislocation wells in the (0001) Sb_2Te_3 and Bi_2Te_3 planes in the intercalation process. Initially, the number of intercalated atoms is small, and they occupy a small part of the interlayer surface, i.e., the intercalated atoms are concentrated in small quantities. As the intercalation process continues, their concentration increases, and

they combine into nanoparticles which are capable of forming nanoscale intercalant islands on van der Waals surfaces of semiconductor crystal layers in electric and magnetic fields. These nanoinclusions are characterized by a domain structure. In the future, due to the processes of self-organization and the influence of an external magnetic field, it is possible to form enlarged areas of the intercalant and merge them into large clusters, which are localized on van der Waals surfaces of interlayer crystal space. The presence of an external constant magnetic field in the intercalation process leads to the appearance of a magnetic exchange interaction between the nanoinclusions of the intercalant and, accordingly, to the ferromagnetism of the magnetic clusters of the intercalant. The situation is similar in the case of $Ni_{0.2}In_4Se_3$. At the beginning of intercalation, nickel atoms are far from each other and do not interact with each other. As their concentration increases, they may appear next to each other, forming a nanoinclusion of metallic nickel.

The presence of a magnetic field during intercalation leads to the insertion of some nickel atoms into the structure of the In_4Se_3 layer packet. In this case, the formation of Ni-Se-Ni pairs is possible, in which one of the nickel atoms is localized in the interlayer space and the other in the layer structure. Under the action of a magnetic field, the interaction of atoms with each other in the plane of layers and exchange magnetic interaction through the Se atom perpendicular to the plane of layers is possible, similarly between atoms in the layered III-VI semiconductor doped with Mn [13, 14].

4. CONCLUSIONS

It is shown that the use of a gradient magnetic field at the interface (intercalation front) in electrochemical intercalation of Sb_2Te_3, Bi_2Te_3 and In_4Se_3 layered crystals with ions of 3d metals (cobalt, nickel) leads to changes in the magnetic properties of the starting compounds. It is found that $Co_{0.1}Sb_2Te_3$, $Ni_{0.1}Bi_2Te_3$ and $Ni_{0.2}In_4Se_3$ intercalates have ferromagnetic properties at room temperature. The dependences of the magnetic moment on the magnetic field strength along and across the layers for $Co_{0.1}Sb_2Te_3$, $Ni_{0.1}Bi_2Te_3$ and $Ni_{0.2}In_4Se_3$ intercalates have the form of hysteresis loops. In the case of $Co_{0.1}Sb_2Te_3$ and $Ni_{0.2}Bi_2Te_3$, the magnetic properties are determined by the formation of intercalant nanoinclusions at the chalcogen vacancy sites and the influence of the magnetic field on the processes of exchange interaction between these nanoinclusions. For $Ni_{0.1}Bi_2Te_3$ intercalates, this is due to the interaction of nickel atoms in the layer plane and the exchange magnetic interaction through the Se atom perpendicular to the layer plane.

REFERENCES

1. K.S. Novoselov, A. Mishchenko, A. Carvalho, A.H. Castro Neto, *Science* **353**, aac9439 (2016).
2. M.S. Stark, K.L. Kuntz, S.J. Martens, S.C. Warren, *Adv. Mater.* **31** No 27, 1808213 (2019).
3. R. Shollhorn, *Physica B+C* **99** No 1, 89 (1980).
4. A,S Golub, Ya,V. Zubavichus, Yu.L. Slovokhotov, Yu.N. Novikov, *Russ. Chem. Rev.* **72** No 2, 138 (2003).
5. V.O. Vaskovskii, *Magnetism of Nanosystems Based on Rare Earth and 3d-Transition Metals*, 265 (Yekaterinburg: IONTS: 2007).
6. K. El-Sayeda, Z.K. Heiba, K. Sedeek, H.H. Hantour, *J. Alloys Compd.* **530**, 102 (2012).
7. A.R. de Moraes, D.H. Mosca, N. Mattoso, J.L. Guimaraes, J.J. Klein, W.H. Schreiner, P.E.N. de Souza, A.J.A. de Oliveira, M.A.Z. de Vasconcellos, D. Demaille, M. Eddrief, V.H. Etgens, *J. Phys.: Condens. Matter.* **18**, 1165 (2006).
8. K. Iordanidou, M. Houssa, J. Kioseoglou, V.V. Afanas'ev, A. Stesmans, C. Persson, *ACS Appl. Nano Mater.* **1**. No 12, 6656 (2018).
9. T. Dietl, *J. Appl. Phys.* **103**, 07D111 (2008).
10. Yu.I. Zhirko, Z.D. Kovalyuk, M.M. Pyrlja, V.B. Boledzyuk *Hydrogen Materials Science and Chemistry of Carbon Nanomaterials,* 325 (Netherlands: Springer: 2007).
11. V. Boledzyuk, A. Bakhtinov, Z. Kovalyuk, Z. Kudrynskyi, V. Ivanov, V. Slyn'ko, *Acta Phys. Pol. A* **130** No 3, 773 (2016).
12. Z.D. Kovalyuk, V.B. Boledzyuk, V.V. Shevchyk, V.M. Kaminskii, A.D. Shevchenko, *Semiconductors* **46**, 971 (2012).
13. V.V. Slynko, A.G. Khandozhko, Z.D. Kovalyuk, V.E. Slynko, A.V. Zaslonkin, M. Arciszewska, W. Dobrowolski, *Phys. Rev. B* **71**, 245301 (2005).
14. T.M. Pekarek, M. Duffy, J. Garner, B.C. Crooker, I. Miotkowski, A.K. Ramdas, *Appl. Phys.* **87**, 6448 (2000).

Магнітні властивості сполук Co_{0.1}Sb₂Te₃, Ni_{0.1}Bi₂Te₃ та Ni_{0.2}In₄Se₃

В.Б. Боледзюк, М.З. Ковалюк, В.І. Іванов

Інститут проблем матеріалознавства ім. І.М. Францевича НАН України, Чернівецьке відділення, вул. І. Вільде, 5, 58001 Чернівці, Україна

В роботі досліджено властивості шаруватих дихалькогенідів перехідних металів, інтеркальованих іонами 3d перехідних металів. Показано вплив градієнтного магнітного поля на фронті інтеркаляції на властивості інтеркалянтів. Встановлено, що інтеркалати Co_{0.1}Sb₂Te₃, Ni_{0.1}Bi₂Te₃ та Ni_{0.2}In₄Se₃ володіють феромагнітними властивостями при кімнатній температурі. Залежності магнітного моменту від напруженості магнітного поля вздовж і поперек шарів для інтеркалатів Co_{0.1}Sb₂Te₃, Ni_{0.1}Bi₂Te₃ та Ni_{0.2}In₄Se₃ мають вигляд гістерезисних петель. Отримані значення коерцитивної сили досліджуваних зразків характерні для магнітотвердих феромагнетиків. Властивості отриманих інтеркалатів обумовлені кристалічною будовою шаруватих кристалів, локалізацією і магнітною взаємодією атомів інтеркалянта між шарами кристалічної матриці та впливом магнітного поля на процеси обмінної взаємодії між ними.

Ключові слова: Bi₂Te₃, Sb₂Te₃, In₄Se₃, Інтеркалати, Магнітні властивості, 3d метали.