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Physical properties of layered $FeIn_2Se_4$ single crystals

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Single crystals of $FeIn_2Se_4$ having a hexagonal structure and mirror-like cleaved surfaces were grown by the Bridgman method. X-ray spectroscopic analysis of the grown crystals was carried out. The morphology of their surface $FeIn_2Se_4$ was investigated by means of atomic-force microscopy. Temperature dependence of conductivity was measured in the range of 80 - 385 K. It was established the existence of the hysteresis loop of the layered crystals $FeIn_2Se_4$ at the room temperature.
Keywords:layered crystal, surface morphology, conductivity, magnetism

Методом Бриджмена выращены монокристаллы $FeIn_2Se_4$ с гексагональной структурой и зеркальной поверхностью. Проведен рентгеноспектральный анализ. При помощи атомно-силовой микроскопии исследована морфология поверхности образцов $FeIn_2Se_4$. Построена температурная зависимость электропроводимости. Установлено наличие петли гистерезиса в слоистых кристаллах $FeIn_2Se_4$ при комнатной температуре.

Фізичні властивості шаруватого монокристала $FeIn_2Se_4$. *В.Б.Боледзюк, З.Д.Ковалюк, З.Р.Кудринський, В.І.Іванов, А.Д.Шевченко.*

Методом Бріджмена отримано монокристали $FeIn_2Se_4$ з гексагональною структурою та дзеркальною поверхнею. Проведено рентгеноспектральний аналіз. За допомогою атомно-силової мікроскопії досліджено морфологію поверхні зразків $FeIn_2Se_4$. Побудовано температурну залежність електропровідності. Встановлено наявність петлі гістерезису у шаруватих кристалах $FeIn_2Se_4$ при кімнатній температурі.

1. Introduction

Semimagnetic semiconductor compounds $II–III_2–VI_4$ (II = Mn, Fe, Co, NI; III = Ga, In; IV = S, Se, Te) having layered crystal structure are promising materials for modern electronics. The components of the transition metals enable to receive desirable magnetic properties. These compounds are also interesting because of their optical properties. They have high photosensitivity, strong photoluminescence, and a very wide range of optical transmission [1].

Earlier $FeIn_2Se_4$ crystals were studied in the papers [2–8]. It was found that in the high-temperature range the magnetic susceptibility χ of $FeIn_2Se_4$ obeyed to the Curie-Weiss law $\chi = C/(1 - \theta)$ that indicated on dominant antiferromagnetic interaction. The asymptotic Neel temperature found in [2] is $\theta = -183$ K. At the same time in [7] the values of θ established at two different orientation of magnetic field **H** with respect to the crystallographic **c** axis are $\theta = -195$ K for **H**||**c** and $\theta = -220$ K for **H**⊥**c**. The latter value was explained as to be due to the anisotropy of exchange interaction that is stronger in the magnetic field direction **H**⊥**c**. It was also detected that $FeIn_2Se_4$ crystals demonstrated properties typical for spin glass [2, 7].

2. Experimental

Single crystals of $FeIn_2Se_4$ were grown by the Bridgman method in double quartz ampoules. Temperature gradient at the melt — crystal interface was 20 deg/cm at a rate of the crystal growth about of 1.2 mm/h. The grown ingots were 14 mm in diameter and 35–40 mm long.

The structure and lattice parameters of the crystals were established from X-ray diffraction measurements in CuKα radiation by means of DRON-2.0 installation assembled according to the Bragg-Bertano scheme. The obtained X-ray diffraction patterns were processed by using LATTIK-KARTA software. The morphology of the samples cleaved surface of was investigated by means of atomic-force microscope Nanoscope IIIa Dimension 300SPM microscope" (Digital Instrument, USA) in the tapping mode.

Conductivity of the crystals was measured in the temperature range of $T = 80$–385 K by using the four-probe method. Magnetization of the samples was measured by means of Vibrating Magnetometer 7404 VSM in magnetic field **H** with strength up to 3000 Oe. Its sensitivity being of the order of 10^{-7} emu makes it possible to measure the magnetic moment for the samples with the mass of several milligrams. The mass of the $FeIn_2Se_4$ samples under investigation was established by means of electronic balance AB135-S/FAST (sensitivity 10^{-5} g). Measurements of the magnetic moment were carried out at the temperature $T = 300$ K at the directions of **H** along and across the crystallographic **c** axis.

3. Results and discussion

Fig. 1 shows a photograph of grown $FeIn_2Se_4$ ingot. Because of its layered structure the surfaces obtained after cleaving normally to the **c** axis are mirror-like nearly ideal. It is seen from the figure that such surfaces cover a whole cross-section of the ingot what indicates the homogeneity of the obtained material.

Fig. 1. Photograph of grown $FeIn_2Se_4$ ingot.

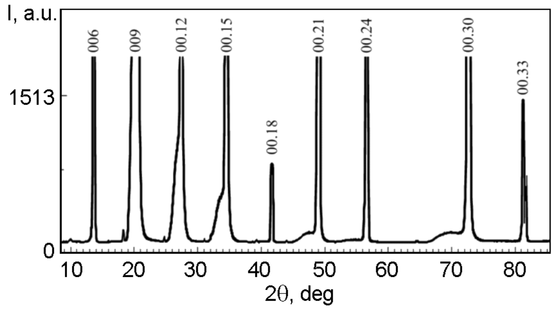

Fig. 2. X-ray diffraction pattern of $FeIn_2Se_4$ crystal.

X-ray spectrum analysis has shown that the $FeIn_2Se_4$ crystals have hexagonal structure with the lattice parameters $a = 4.0185$ and $c = 39.0594$ Å. These data are in a good agreement to those in [3]. The X-ray diffraction pattern of the $FeIn_2Se_4$ crystals registered from the cleaved surface is shown in Fig. 2 and demonstrates the $00l$ reflections ($l =$ 6, 9, 12, 18, 21, 24, 30, 33). The absence of additional peaks is evidence that composition of the grown $FeIn_2Se_4$ crystals corresponds to its formula.

Fig. 3 represents an AFM pattern of the $FeIn_2Se_4$ crystal surface (a) and redistribution of the deviation in height of this surface (b). From analysis of the obtained patterns the root-mean-square roughness Rms of the surface was established to be 0.046 nm. The radius r and the height h for roughnesses *1* and *2* shown in Fig. 3b are $r = 9.766$, $h = 0.127$ nm and $r = 13.672$, $h = 0.155$ nm, respectively. It is seen that the crystal has enough smooth surface without the presence of foreign phases or inclusions of other materials.

Temperature dependence of conductivity for the $FeIn_2Se_4$ crystals is shown in Fig. 4. In the high-temperature range ($T > 300$ K) the conductivity is due to activation process and the dependence obeys the law [9]

$$\sigma = \sigma_0 \exp(-\delta E / kT), \tag{1}$$

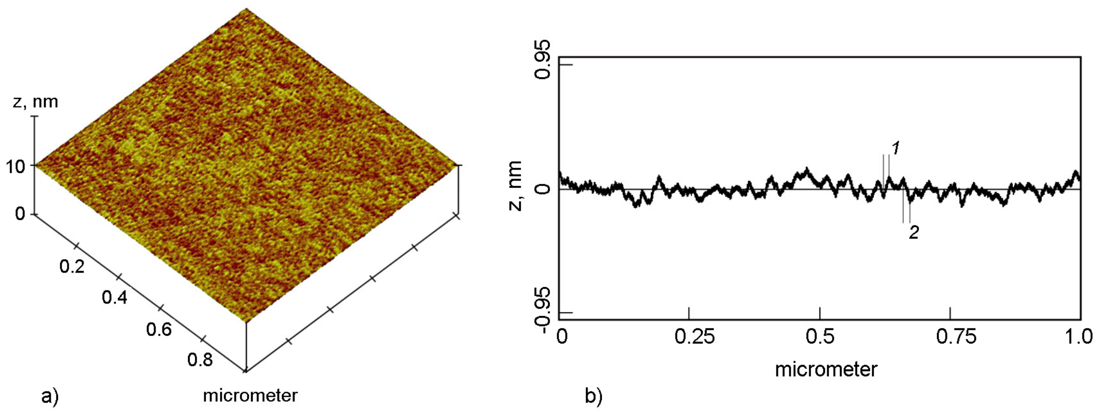

Fig. 3. AFM pattern of $FeIn_2Se_4$ crystal surface (a) and redistribution of deviation in height of this surface (b).

where δE is the activation energy and k is the Boltzmann constant. The dependence plotted as $\ln(\sigma \perp \mathbf{c})$ vs $10^3/T$ enables to determine the activation energy of donor levels from its slope. The found value of δE is equal 0.09 eV at the temperatures above 300 K. The decreased slope of the curve below 300 K indicates the presence of the shallower donors with $\delta E \approx 0.04$ eV.

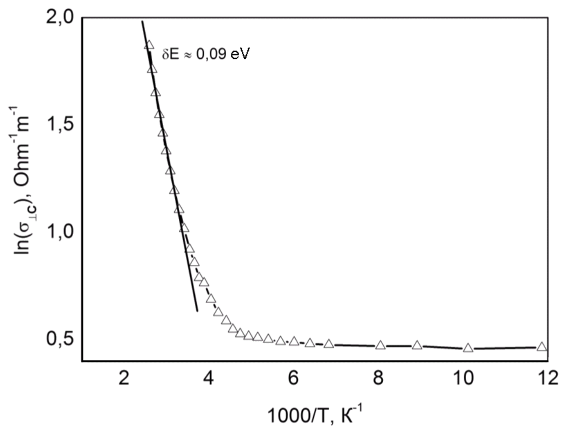

Fig. 4. Temperature dependence of conductivity of $FeIn_2Se_4$ sample.

Dependences of the specific magnetic moment m on magnetic field strength **H** measured at T = 300 K are shown in Fig. 5. The measurements of the magnetic moment for the anisotropic $FeIn_2Se_4$ crystals were carried out at the magnetic field directions along ($\mathbf{H} \perp$C) and normally ($\mathbf{H} \| \mathbf{c}$) to the **c** axis. It is seen from the figure that $m = f(H)$ curves are different for the different orientations of magnetic field. For the $m = f(H)$ dependence measured in the configuration $\mathbf{H} \perp \mathbf{c}$ the saturated value m_S of the specific magnetic moment at magnetic field strength H = 3000 Oe we have established to be 0.0386 emu/g. At $m = f(H)$ measurements in the configuration $\mathbf{H} \| \mathbf{c}$ it is found that m_S = 0.0384 emu/g. The values of the coercive force are 190.07 and 133.33 Oe in the configurations $\mathbf{H} \perp$c and $\mathbf{H} \| \mathbf{c}$, respectively, that is typical for hard-magnetic materials.

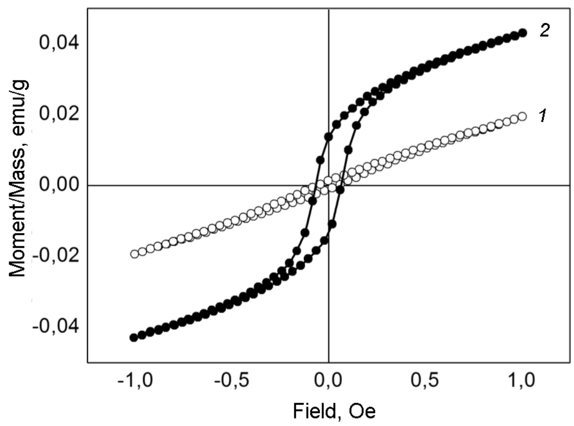

Fig. 5. Hysteresis loops for magnetization of $FeIn_2Se_4$ samples in configuration $\mathbf{H} \perp \mathbf{c}$ (curve *1*) and $\mathbf{H} \| \mathbf{c}$ (curve 2).

The structure features of the layered semiconductor crystals (the presence of two different types of bonding) result in the impurity atoms could both replace cations in a crystalline layer and be localized in the interlayer spacing during doping. The last mechanism is predominant owing to significantly lesser expenditure of energy. In addition, the layered crystals are characterized by different defects. These defects initiate redistribution of the impurity atoms and its localization in these defects with formation of the collective impurity atoms (clusters). The presence of the magnetic hysteresis in the $FeIn_2Se_4$ crystals (Fig. 5) is evidence of occurrence of three-dimensional ferromagnetic order in these clusters similarly to in $In_{1-x}Mn_xSe$ crystals [10]. This ferromagnetic ordering does not involve all crystal but it is formed in the isolated regions of the bulk, i.e., in the impurity atoms clusters. The presence of the magnetic hysteresis indicates the domain structure of these clusters.

4. Conclusions

Single crystals of $FeIn_2Se_4$ were grown by the Bridgman method. Their cleaved surfaces are enough smooth with the low root-mean-square roughness R_{ms} = 0.046 nm. It is found the presence of the shallow donor levels with activation energy <0.09 eV. The measured dependences of magnetization demonstrate hysteresis loops in the layered crystals of FeInSe at the room temperature. It is assumed that this fact is caused by formation of the clusters of ferromagnetic Fe and ferromagnetic exchange interaction of the impurity atoms.

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