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Crystallization of $(Th_{1-x}U_x)_3As_4$ ferromagnetic semiconductor from the Ga flux

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Crystals of n- or p-type heavily doped ferromagnetic semiconductor $(Th_{1-x}U_x)_3As_4$ (x = 0.67 and 0.80) were grown using a mineralization process in the Ga flux. An excess of As corresponding to $MeAs_2$ composition was necessary to grow the Me_3As_4 phase at temperature cycled between 1000 ºC and 1060 ºC. Dilution of U_3As_4 ferromagnet (Curie temperature T_C = 198 K) with 20% of Th_3As_4 semiconductor (energy gap of 0.39 eV) reduced T_C by 19%.

Key words: *ferromagnetic semiconductor; crystallization; actinide compounds*

1. Introduction

The discovery of ferromagnetism in zinc blende III–V and II–VI Mn-based compounds (see [1] and references therein) allows one to explore the physics of previously unavailable combinations of quantum structure and magnetism in semiconductors. Studies of magnetic and semiconducting properties in solid state systems served as an important test for understanding basic physics and discovering new applications in spintronics [2, 3]. During last decades, the anomalous Hall resistivity and anisotropic magnetoresistance in sd electron systems were experimentally investigated to great extent, motivated by the technological importance of both effects. On the other hand, these effects originate from anisotropy of the density of states and spin-orbit interaction [4] which can be fairly high in f electron systems, as it is in U_3As_4 ferromagnet [5] and therefore we have proposed research on spintronic properties of its semiconducting thorium derivatives [6].

Both U_3As_4 and Th_3As_4 crystallize in Th_3P_4 type structure, which belongs to the space group $I\bar{4}3d$. U_3As_4 is a low-carrier ferromagnet (Curie temperature T_C = 198 K)

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showing giant anomalous Hall resistivity and high anisotropic magnetoresistance [6, 7]. Th_3As_4 is an indirect gap semiconductor with energy gap of 0.39 eV [8]. Crystals of U_3As_4 could be grown by the conventional vapour transport method in a quartz ampoule [9]. This method could not be used for growing Th_3As_4 crystals because of a strong reaction with the quartz ampoule. Therefore a modified van Arkel method [10] has been developed. This method allowed growing either n- [11] or p-type [12] Th_3As_4 crystals, presumably due to their specific off-stoichiometry. These possibilities indicated $(Th_{1-x}U_x)_3As_4$ system to be more attractive for spintronic studies. Hitherto Th-rich n-type $(Th_{1-x}U_x)_3As_4$ solid solutions (up to $x = 0.15$) grown by the modified van Arkel method [10] remained non-ferromagnetic semiconductors down to 4 K. However, the modified van Arkel method is complicated and requires high amounts of Th and U for effective preparation of samples of examined system. Expecting coexistence of semiconducting and ferromagnetic properties, promising interesting spintronics-oriented features in U-reach $(Th_{1-x}U_x)_3As_4$ solutions [6], we look for easier and cheaper methods of preparation of such solid solutions. In this work, a possibility of growing such solid solutions using the Ga flux method has been examined.

2. Experimental

Thorium, uranium, arsenic and gallium elements in proper atomic ratios were placed in covered alumina crucibles and closed in quartz ampoules, under 150 mm Hg of argon. Then they were heated and cooled in three different ways. In experiments I, II and III the Th:U:As:Ga elements were taken with atomic ratios 1:2:4:50, 1:2:6:50 and 1:2:6:50, respectively. In the case of experiments I and II, the ampoules were heated up to 1080 ºC, annealed for 10 h, cooled down to 860 ºC at the rate 1 ºC/h, next to 500 ºC at the rate 2 ºC/h and then quickly placed in ambient temperature. In the experiment III, the ampoule was heated up to 1080 ºC, annealed for 10 h and then for two weeks repeatedly cooled down to 1000 ºC at the rate of 5 ºC/h and heated to 1060 ºC at the rate of 20 ºC/h, and then quickly placed in ambient temperature, directly from the furnace (1000 ºC). Liquid gallium was removed with a syringe, its remains washed out with mercury and diluted HCl. Remains of mercury were distilled out in vacuum. The obtained material was cooled down with liquid nitrogen and the ferromagnetic phase was extracted with a strong permanent magnet.

The samples were examined with electron microscope with EDAX analysis. Crystal structure of selected single crystals was analysed with 4-circle X-ray diffractometer and resolved using the SHELX-97 program with a final discrepancy factors, $R1$, given in Table 1 [13, 14]. The dc magnetic susceptibility, χ_{dc}, in fields of 2000 Gs was measured between 1.7 and 200 K using a SQUID magnetometer. The resistivity in longitudinal fields of 0 and 1 T was measured between 60 and 200 K by conventional 4-point ac technique in an electromagnet. Thermoelectric power was estimated with a home-made thermoelectric probe.

Table 1. Some physical data for $(Th_{1-x}U_x)_3As_4$ compounds

Sample	Composition	Lattice parameter [Å]	Discrepancy factor $R1$	Thermoelectric power [μV/K]
II-a, -ba	$(Th_{0.2}U_{0.8})_3As_4$	8.587	0.035	–20
II-bc	$(Th_{0.33}U_{0.67})_3As_4$	8.577	0.086	+35
III	$(Th_{0.33}U_{0.67})_3As_4$	8.573	0.055	–5

3. Results

Experiment I resulted in a small amount of ferromagnetic phase in the form of fine powder that was not examined here. Two characteristic forms of $(Th_{1-x}U_x)_3As_4$ phase were obtained in the experiment II, labelled here as samples II-a and II-b. The sample II-a consisted of small (≈0.05 mm in diameter) ferromagnetic $(Th_{0.2}U_{0.8})_3As_4$ isometric single crystals with rounded edges, partially immersed in a surface of large (ca. 2 mm) GaAs crystal (Fig. 1a). Temperature dependence of magnetization of the composite, shown in Fig. 2, yielded $T_C = 160$ K. The second form looked like pieces of broken crust of sphere, whose concave surface (sample II-bc) was formed of bigger $(Th_{0.33}U_{0.67})_3As_4$ crystals with sharp edges and thermoelectric power $S \approx 35$ μV/K. A cross-section of the crust is shown in Fig. 1b where one can see the structure of the convex surface of the crust formed of small crystals of Th_3P_4 type crystal structure, identical with that of the first form (II-a), and thermoelectric power $S \approx -20$ μV/K. After polishing out the bigger crystals from the convex surface, we obtained a sample (II-ba) of uniform S, for which temperature dependence of electrical resistance is shown in Fig. 3. It allowed us to determine $T_C = 150$ K.

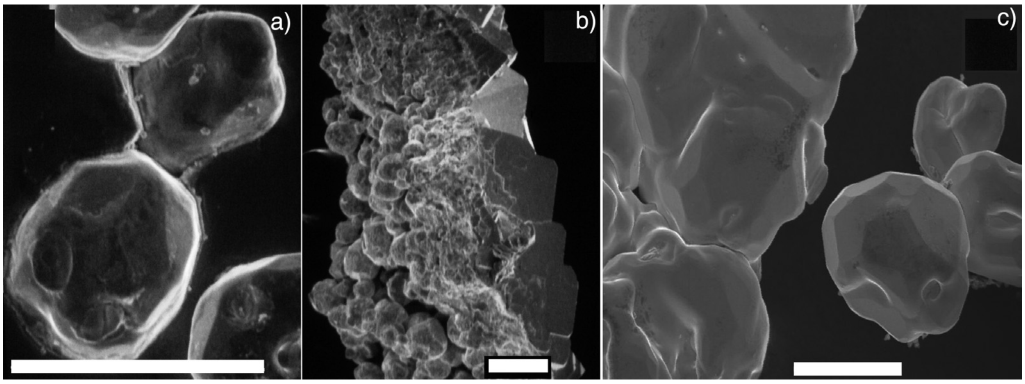

Fig. 1. SEM images: a) sample II-a immersed in GaAs surface, b) cross section of the crust surrounding U and Th and facing them with (bigger) crystals – sample II-bc and tiny crystals on the opposite side – sample II-ba, c) single (sample III) and polycrystalline $(Th_{0.33}U_{0.67})_3As_4$; all bars represent 0.1 mm

The experiment III gave $(Th_{0.33}U_{0.67})_3As_4$ isometric crystals, like those in sample II-a, but about twice as big and with sharper edges, as shown in Fig. 1c. The product of that experiment contained also small thin plates of GaAs. Some physical quantities describing the examined samples are collected in Table 1.

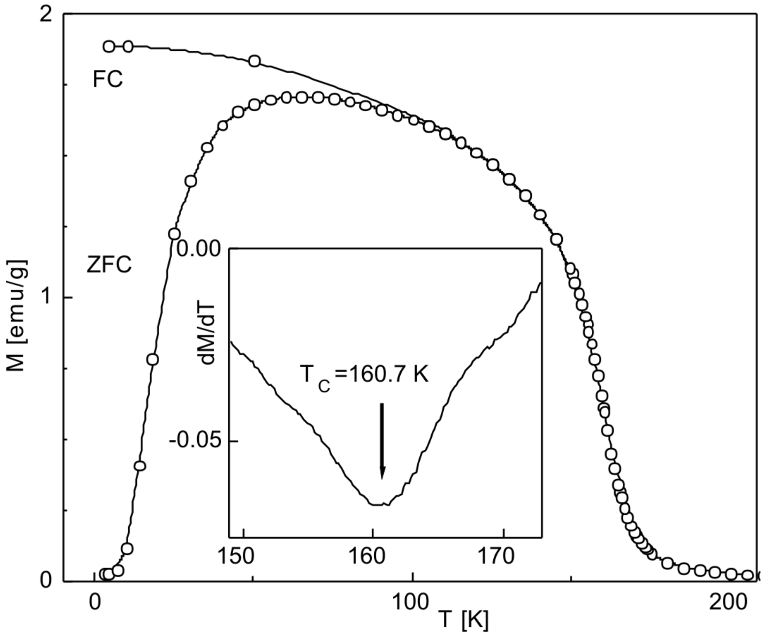

Fig. 2. Temperature dependence of magnetization of $(Th_{0.2}U_{0.8})_3As_4$, sample II-a, cooled in zero field (ZFC) and cooled in 0.2 T field (FC)

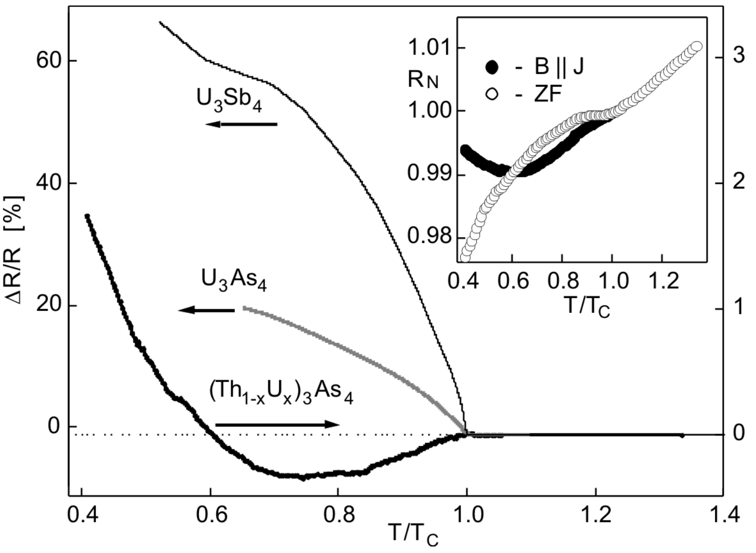

Fig. 3. Effect of longitudinal magnetic field on the resistivity of $(Th_{0.2}U_{0.8})_3As_4$ (sample II-ba) compared to the same effect for polycrystalline samples of U_3As_4 and U_3Sb_4. Inset: resistivity of the same sample II-ba at 0 T (empty circles) and 1 T (full circles) longitudinal magnetic fields ($R_N = R/R(T_C)$)

4. Discussion

MeAs, Me_3As_4 and $MeAs_2$ (Me denotes U or Th) were identified in Me–As phase diagrams. U_3As_4 is the only phases that becomes ferromagnetic. Upon heating $MeAs_2$ to higher temperature at low arsenic pressure P_{As} one gets Me_3As_4 and then congruently melting MeAs phase (above 2000 ºC). As there are T-P_{As} fields in the Me-As phase diagrams where these particular compounds exist, presumably there are also corresponding T-C_{As} fields where the same arsenides exists in the Me–As–Ga phase diagram (C_{As} denotes the concentration of As in liquid Ga). Solubility of As in Ga decreases from about 12.5 at. % at 1000 ºC to about 0.3 at. % at 500 ºC [15]. We should add also that substrate composition corresponded to Me_3As_4 + 50Ga in the experiment I and to $3MeAs_2$ + 50Ga in the experiments II and III.

The above finding seems to be consistent with the following scenarios of the crystallization experiments: in experiment I, no excess of As remained in flux over the Me_3As_4 composition and it is the most probable reason for negligible presence of the ferromagnetic phase in the product. In the case of experiments II and III, there was an excess of 2 As atoms per Me_3As_4 formula. This As excess led to C_{As} ~4 at. % at the end of the process, at high temperature (equal to the saturation solubility at about 780 ºC) enabling to form Me_3As_4 phase. At high temperature, the dissolving U and Th diffused to the flux and reacted with As forming a crust separating more and more tightly this area from the whole flux. Presumably due to a lower excess of As, the p-type $(Th_{0.33}U_{0.67})_3As_4$ (sample II-bc) grew on one side of the crust, whereas n-type $(Th_{0.2}U_{0.8})_3As_4$ (sample II-ba) grew on the other side. Even if the separating crust was formed at the beginning of the experiment III, it presumably disappeared due to the temperature cycling. Such a cycling usually favorises growth of bigger crystals at the expense of smaller ones. We expect that such process carried for 6 weeks would give crystals of sufficient size for thorough examination of physical properties.

Temperature behaviour of magnetization for sample II-a (Fig. 2) is characteristic of strongly anisotropic ferromagnets [16]. Here T_C decreased to 160 K from 198 K for U_3As_4. One can compare this decrease of T_C to a one observed in 3:4 uranium pnictide series and examined at external pressure. T_C vs. U–U distance (d) dependence for U_3P_4, U_3As_4 and U_3Sb_4 reaches a maximum for d corresponding to U_3As_4. The effect of the external pressure closely follows this $T_C(d)$ [17]. One can think that such a $T_C(d)$ behaviour results from competition between RKKY interaction, increasing T_C for decreasing d, and hybridisation, between f and conduction electrons, acting contrary to the RKKY interaction. For U_3As_4–U_3Sb_4 and U_3As_4–$(Th_{0.2}U_{0.8})_3As_4$ pairs, $\Delta T_C/\Delta a$ equals to 88 and 580 K/Å respectively (a is the lattice parameter proportional to d). Thus the dilution of the U_3As_4 with Th_3As_4 suppresses ferromagnetic ordering stronger than one could expect from the increase of d. $(Th_{0.2}U_{0.8})_3As_4$ remains ferromagnetic and shows metallic-type, linear resistivity vs. T dependence in the paramagnetic range (Fig. 3) and low thermoelectric power at room temperature. However, growing either n- or p-type crystals at the same Th:U ratio as in the case of $(Th_{0.33}U_{0.67})_3As_4$ (see Table 1) may speak in favour of heavily doped (viz. low thermoelectric power) ferromagnetic semiconductor doped with stoichiometry defects.

5. Conclusions

Crystals of either n- or p-type ferromagnetic semiconductor $(Th_{1-x}U_x)_3As_4$ could be grown using a mineralization process in the Ga flux. An excess of As corresponding to $MeAs_2$ composition was necessary to grow the Me_3As_4 phase at temperatures 1000–1060 ºC. It is expected that crystals of the size sufficient for an examination of physical properties could be grown if the process was carried for about 6 weeks. Dilution of U_3As_4 ferromagnet with Th_3As_4 semiconductor reduced T_C stronger than expected from T_C behaviour in 3:4 uranium pnictide series. Low room temperature values and sample dependent sign of thermoelectric power might suggest that $(Th_{0.33}U_{0.67})_3As_4$ is a semiconductor heavily doped with stoichiometry defects. The presented technology opens a new route to a closer examination of spintronic properties of this f electron system.

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