Proceedings of the 16th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 13–17, 2016

Characterization of New U–Ni–X_2 Splats and Study of their Physical Properties

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We explored the crystal structure, magnetic, and transport properties of $UNiX_2$ (X = Ge, Si) materials, which were prepared by a conventional metallurgical technique and by rapid solidification — splat cooling. The $UNiSi_2$ splat is mostly single phase, containing only small traces of a minority phase. Magnetic and electrical properties of the splat resemble properties of samples, which were prepared by conventional methods, exhibiting a ferromagnetic transition at about 91 K and similar temperature dependence of resistivity. The coercive field of $\mu_0 H_c = 4.25$ T is much enhanced due to the magnetic anisotropy introduced by the sample preparation technique. The Barkhausen jumps were observed on the hysteresis loop. Magnetization of the sample does not saturate in fields up to $\mu_0 H = 9$ T. The phase structure of $UNiGe_2$ splat is not completely solved and will be subject of our study in future. Our preliminary results indicate the presence of completely new phase with tetragonal crystal structure and antiferromagnetic ordering below 54 K.

DOI: 10.12693/APhysPolA.131.994

PACS/topics: 61.82.Bg, 75.50.Kj, 75.30.–m, 72.15.–v

1. Introduction

The splat cooling technique can facilitate stabilization of selected polymorphous modifications. It was successfully used for retention of high temperature γ-uranium phase to room temperature [1]. It can be expected that the rapid solidification can stimulate preparation of single phase from non-congruently melting materials. The uranium compound $UNiSi_2$ melts incongruently, however single crystals of this compound were grown by the Czochralski method [2] and in a gallium flux [3]. The sample with the composition $UNiGe_2$ has not been prepared yet. In the present paper we report on synthesis, characterization, electrical and magnetic properties of samples with nominal compositions $UNiSi_2$ and $UNiGe_2$, which were prepared by the splat cooling technique.

The ternary uranium intermetallic $UNiSi_2$ crystallizes in the orthorhombic $CeNiSi_2$-type layered structure (space group *Cmcm*) [4], which is constructed from deformed fragments of the $CeGa_2Al_2$ and α-$ThSi_2$ structures. $UNiSi_2$ exhibits ferromagnetism with local uranium moments below the Curie temperature T_C = 95 K [5–7], while a Kondo lattice behaviour was reported at higher temperatures [3, 5, 6]. The residual resistance can be enhanced by high pressure of about 5.5 GPa [3]. A strong magnetic anisotropy was observed on the single crystal with the easy magnetization direction in the *ac*-plane [2]. The electronic coefficient γ is small in comparison with uranium heavy fermion compounds [6].

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Although $UNiGe_2$ sample has not been prepared yet, UNiGe and UNi_2Ge_2 have been studied intensively. UNiGe crystalizes in the orthorhombic TiNiSi (space group *Pnma*) structure and undergoes magnetic phase transitions at 41.5 K and 51 K into the antiferromagnetic ground state [8]. UNi_2Ge_2 adopts the tetragonal $ThCr_2Si_2$ structure (space group *I4/mmm*) and orders magnetically as a simple (long-range) antiferromagnet below $T_N = 80$ K [9].

2. Experimental details

In the first step, polycrystalline samples of $UNiSi_2$ and $UNiGe_2$ were prepared by arc melting from the starting constituents in argon atmosphere. Subsequently the sample was placed in the ultrafast splat cooling system, remelted and rapidly solidified. The phase analysis of the prepared samples was performed by X-ray diffraction (Bruker D8 Advance) from the surface of the splats and from powder sample on Rigaku Ultima IV using Cu K_α radiation. Additional analysis was performed by TESCAN VEGA3 scanning electron microscope (SEM) using secondary electron and back scatter electrons imaging as well EDX analysis. X-ray diffraction patterns were analyzed using the Match!3 and Fullprof software. Thompson-Cox-Hastings pseudo-Voigt profile was used to resolve peak broadening.

The magnetic measurements were carried out by SQUID magnetometer in MPMS and by VSM magnetometer in DYNACOOL equipment in applied magnetic fields up to 5 T or 9 T, respectively. In both cases all measurements were performed in the temperature range 2–300 K. The electrical resistivity was measured in the temperature range 5–380 K by the PPMS and DYNACOOL equipment.

3. Results and discussion

SEM methods revealed that the polycrystalline sample $UNiSi_2$ contains, besides the main phase 1:1:2, also two minority phases, namely of the 1:2:2 and 2:1:2 type. The analysis from the surface of the $UNiSi_2$ and $UNiGe_2$ rapidly cooled samples (splats) indicates that the average composition corresponds to the nominal one. The detailed analysis of secondary phases in these splats was limited by the roughness of the surface. Also the X-ray diffraction taken from the surface of the splats revealed that $UNiSi_2$ contains only small traces of spurious phases. The main phase is indeed the orthorhombic $CeNiSi_2$-type structure (space group *Cmcm*) with lattice parameters $a = 4.006$ Å, $b = 16.084$ Å, $c = 4.007$ Å. On the other hand, the analysis of X-ray diffraction pattern taken from $UNiGe_2$ is not completely finished. Preliminary investigation indicates that this splat may consist of UNi_2Ge_2 secondary phase and dominant phase with tetragonal structure similar to $CeNiGe_2$. The strong indication of new phase comes from electrical resistivity measurements. The steep decrease in $R/R_{300}(T)$ curve of the $UNiGe_2$ below 54 K we associate with the dominant magnetic phase in the splat. The very flat dependence $R(T)$ points at a substantial disorder in the splat material, which cannot be assumed as e.g. simple macroscopic coexistence of the UNiGe and UNi_2Ge_2 phases. Magnetization measurements taken on the $UNiGe_2$ splat in zero field (ZFC) and field cooled (FC) regimes, and AC susceptibility revealed two magnetic phase transitions at 64 K and 53 K. We associate the second one transition with dominant magnetic phase in the splat. Our investigation indicates that there is completely new phase and the verification of our preliminary results will be the subject of intensive study in near future.

The temperature dependence of the relative electrical resistivity, $R/R_{300}(T)$, measured on the $UNiSi_2$ splat, is shown in Fig. 1. The resistivity curve resembles the resistivity curves of polycrystalline material [3, 5]. The irregular shape of the sample did not allow the determination of absolute values of resistivity. We associate the steep decrease of resistivity below 91 K with transition to the magnetically ordered state. The low temperature part of the curve can be fitted by an expression, containing an exponential term, attributed to electron-magnon scattering. For example, the expression

$$\frac{R}{R_{300}} = R_0 + cT^2 \exp\left(-\frac{\Delta}{T}\right),$$

gives the value $\Delta = 19.3$ K below 33 K, which is somewhat smaller than the value determined on a polycrystalline material [3, 5]. Parameter R_0 is dimensionless and c has dimension K^{-2}. Weakly decreasing resistivity at high temperatures, also observed in [3], is generic for a broad class of U compounds with sizeable magnetic moments. They lead to a large spin-disorder resistivity, amounting to weak localization phenomena [10].

The results of AC susceptibility measurements suggest that the $UNiSi_2$ polycrystalline sample has magnetic transition at 91 K (Fig. 2). This temperature shifts somewhat to 90.5 K and the maximum broadens by the fast cooling synthesis. The temperature dependence of inverse susceptibility can be fitted above 180 K to a Curie–Weiss (CW) law giving the effective moment $\mu_{\mathrm{eff}} = 2.82\ \mu_{\mathrm{B}}$ and $\theta_p = 14.3$ K for the splat. The effective moment is smaller than expected one for free uranium ion ($3.6\ \mu_{\mathrm{B}}$), but higher than the moment of polycrystalline sample or single crystal. The value of θ_p is much smaller than in those cases [2, 5, 7]. The susceptibility data follow the Curie–Weiss law above 150 K with the effective magnetic moment $\mu_{\mathrm{eff}} = 2.82\ \mu_{\mathrm{B}}$ and $\theta_p = 11$ K.

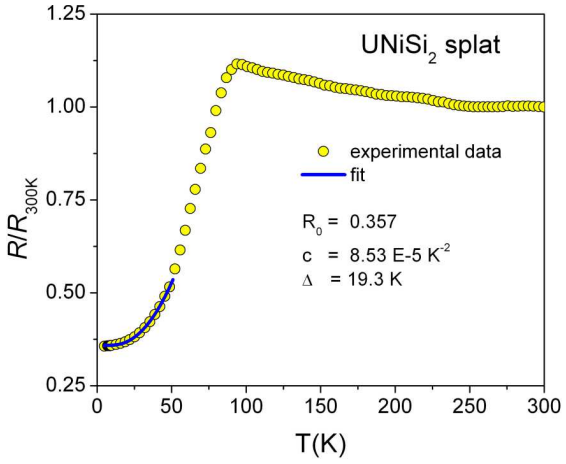

Fig. 1. Temperature dependence of resistivity for the $UNiSi_2$ splat.

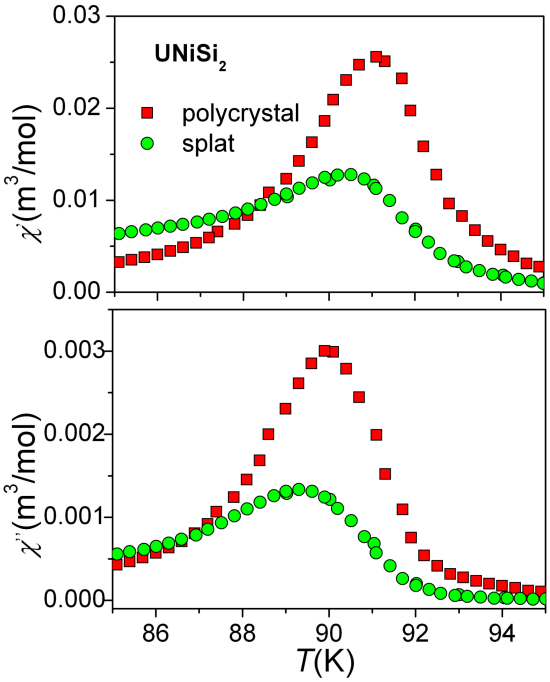

Fig. 2. Temperature dependence of AC susceptibility.

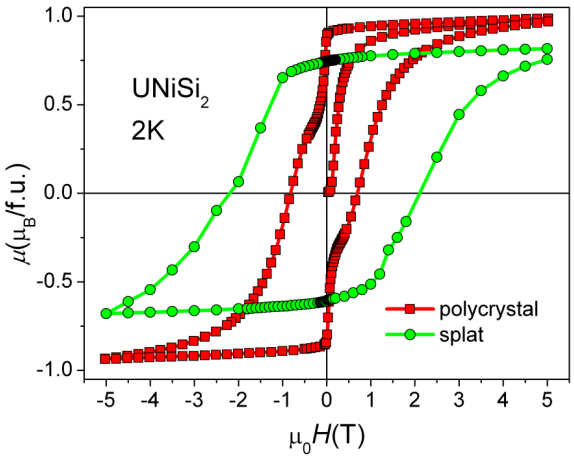

Fig. 3. Hysteresis loops for polycrystalline material and splat.

Very large coercive force $\mu_0 H_c = 4.25$ T, which is comparable with measurements along magnetic hard axis [7] and almost twice larger than on the polycrystalline sample ($\mu_0 H_c = 1.55$ T) is characteristic feature for the hysteresis loop of the $UNiSi_2$ splat (Fig. 3). Such enhancement of coercive force can be attributed to preferred orientation of crystallites along the hard magnetic axis and additional defects pinning domain walls, which were introduced by rapid solidification, in the conditions of high anisotropy, producing very narrow domain walls. The S-shape of hysteresis loop taken from polycrystalline sample indicates influence of hard magnetic axis as it is evident from measurements on single crystal [7]. The magnetization of the $UNiSi_2$ splat does not saturate up to 9 T (Fig. 4) and all presented results are typical for minority loops. The steps on the $UNiSi_2$ loop indicate magnetization processes in ferromagnetic material, which can be related to the Barkhausen jumps.

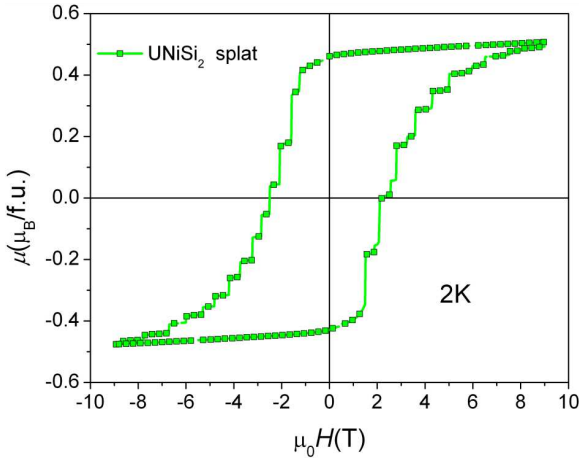

Fig. 4. Hysteresis loop was obtained from VSM measurement.

4. Conclusions

Rapid solidification of the $UNiSi_2$ splat resulted in very high coercive force, which cannot be explained only by magnetocrystalline anisotropy, but the anisotropy introduced by rapid solidification has to be taken into account. Temperature of magnetic transition determined from magnetization and resistivity measurements and the value of Δ resemble magnetic and electrical properties of polycrystalline $UNiSi_2$ sample. The $UNiGe_2$ splat contains two phases. Our investigation indicates the presence of completely new phase with tetragonal crystal structure and magnetic phase transition at about 54 K. Verification of our assumption will be subject of incoming investigation.

Acknowledgments

This work was supported by projects ERDF EU, No. ITMS26220120005, VEGA 2/0010/16, University Science Park TECHNICOM for Innovation Applications Supported by Knowledge Technology, ITMS: 26220220182.

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