DISORDER ORIGIN OF NONMAGNETIC KONDO-LIKE BEHAVIOUR IN ACTINIDE COMPOUNDS*

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It is shown that crystals of some uranium and thorium compounds, grown in off-stoichiometric composition, show single-ion Kondo type behaviour of the resistivity, thermoelectric power and the Hall coefficient. The data for off-stoichiometric crystals of uranium monoantimonide (antiferromagnet) and thorium arsenosulphide (diamagnet) are presented. The behaviour is discussed in terms of the two-level-system Kondo model.

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This work is a continuation of our studies of off-stoichiometry effect on conduction electron scattering in some thorium and uranium pnictides and pnictochalcogenides. Motivation for this study comes from the earlier observation of the single-ion-Kondo-like behaviour of the electrical resistivity in ferromagnetic state of the uranium arsenoselenide [1,2]. Usually, the ferromagnetism should block out the magnetic Kondo effect [3,4]. But magnetoresistivity examination [5] has shown that the observed Kondo scattering is of a nonmagnetic origin. Furthermore, the electron microscope as well as neutron and X-ray diffraction examination [6–8] have given strong indication that this Kondo-like scattering originates from a disorder of anions that presumably form scattering centres of Two-Level System (TLS). This hypothesis allowed us to predict and then prove the Kondo-like behaviour of another ferromagnet — UPS [9]. It also has turned our attention to off-stoichiometry effect on properties of the antiferromagnet — USb (the Néel temperature $T_{\mathrm{N}} = 215$ K) and diamagnet — ThAsS.

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The thorium arsenosulphide crystals have been grown by the chemical vapour transport method. X-ray examination showed that the crystals have tetragonal structure of the PbFCl-type and the Th:As:S atomic composition ratio equal to $1 : 1.23 : 0.77$ instead of $1 : 1 : 1$, as it is for stoichiometric composition. Details on the crystal growing and electrical properties examination will be given elsewhere [10]. The uranium monoantimonide is the well investigated semimetallic uranium compound. Its single crystals of U_xSb composition ($0.985 \leq x \leq 1$) were grown by a modified van Arkel method. Details on the crystal growing and their electrical properties examination are given elsewhere [11]. The temperature dependent electrical resistivity, $\rho(T)$, thermoelectric power, $S(T)$, and Hall coefficient, $R_{\rm H}(T)$, have been determined in the temperature range between 2 K and the room temperature. All these data will be presented here to demonstrate their Kondo-like features.

The temperature dependence of the electrical resistivity for no. 1 and no. 2 single crystals of thorium arsenosulphide is shown in Fig. 1. The most intriguing feature of $\rho(T)$ for the thorium arsenosulphide is a shallow valley around about 200 K. A similar behaviour of the resistivity has been also

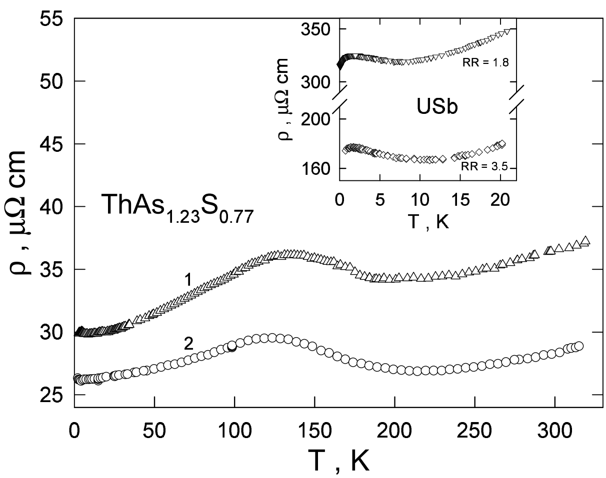

Fig. 1. Temperature dependence of the *ab* plane resistivity for two thorium arsenosulphide single crystals. The inset presents low-temperature resistivity data for two USb single crystals with different resistivity ratio, $RR (RR = R_{300\,{\rm K}}/R_{4.2\,{\rm K}})$.

observed for the off-stoichiometric crystals of uranium monoantimonide (see the inset of Fig. 1). However, in the case of U_xSb the valley-like anomaly is observed at about 10 K. This type behaviour of $\rho(T)$ is known for a Kondo system, *i.e.* for nonmagnetic metals containing magnetic impurity [3]. Moreover, we have found that $\rho(T)$ for $ThAs_{1.23}S_{0.77}$ down to 140 K can be very well approximated by the sum of residual, phonon and Kondo components if in the latter case a Kondo temperature of $T_{\mathrm{K}} = 22$ K is assumed. In turn a good approximation of $\rho(T)$ for U_xSb crystals between 2 K and 22 K has been obtain for $T_{\mathrm{K}} = 37$ K. Obviously, the total resistivity could be completed involving also the magnon contribution.

A presence of a peak-like component in $S(T)$, with a maximum near the Kondo temperature is another feature of the magnetic Kondo system [5]. Thus such a behaviour of $S(T)$ is also observed for the nonmagnetic system under investigation. Fig. 2 and its inset reveal this type of property for both the diamagnetic $ThAs_{1.23}S_{0.77}$ and the antiferromagnetic U_xSb, respectively. It is worth mentioning that the Kondo-like behaviour is displayed also by the temperature dependence of the thermoelectric power UPS [9] and

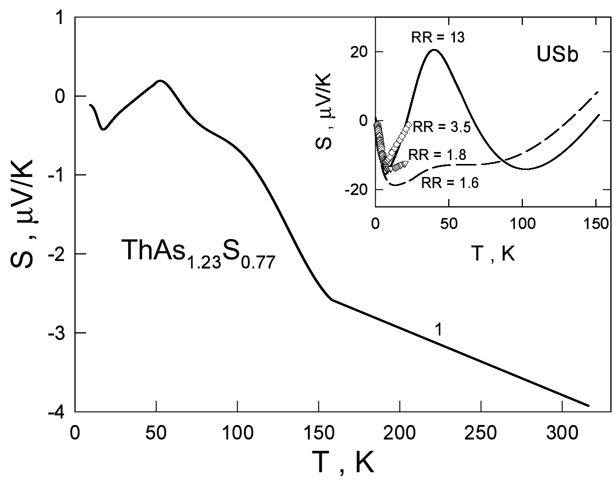

Fig. 2. Thermoelectric power *versus* temperature along the a-axis for no. 1 single crystal of $ThAs_{1.23}S_{0.77}$. The inset presents low-temperature thermoelectric power data for USb single crystals with different RR. The data presented by solid and dashed lines in the inset are taken from the paper [16].

UAsSe [12] in their ferromagnetic state. In the case of the Hall effect measured well above the Kondo temperature, the characteristic feature of the magnetic Kondo systems is the presence of the anomalous component in the Hall coefficient being an excess to the normal, temperature independent component. The anomalous component is proportional to the product of the Kondo resistivity and the magnetic susceptibility [13]. A very similar behaviour exhibits also the Hall coefficient of the diamagnetic $ThAs_{1.23}S_{0.77}$. Its Hall coefficient R_{H} is plotted *versus* $\rho_{\mathrm{K}}(T)/T$ ratio in Fig 3. There is observed a linear dependence of the R_{H} *versus* $\rho_{\mathrm{K}}(T)/T$ at the highest temperatures. Such behaviour is presumably due to the presence of the anomalous Hall component. This component behaves as if it was expected for the magnetic Kondo impurities for which the susceptibility fulfils the Curie law.

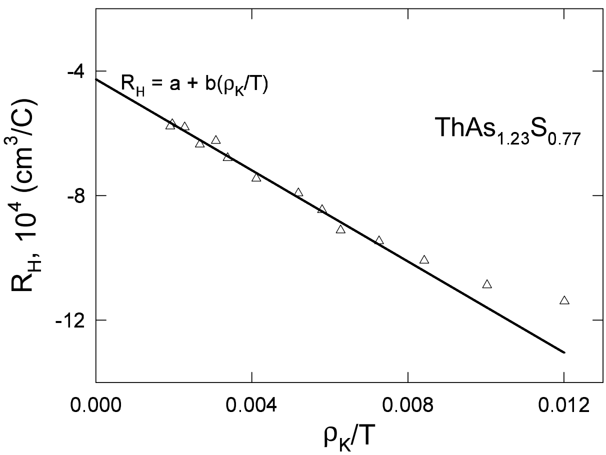

Fig. 3. Hall coefficient *versus* $\rho_{\rm K}/T$ for no. 1 thorium arsenosulphide single crystal. $\rho_{\rm K}$ is the Kondo resistivity component calculated in paper [10].

The appearance of the non-magnetic Kondo like behaviour, being observed for a given ferromagnet, antiferromagnet or diamagnet can be explained by the TLS Kondo model [14]. In the simplest realisation of the TLS an atom tunnels between two positions with an energy difference Δ in a double well potential. In the case of this model, the position of the atom in one of the metastable states corresponds to a pseudo-spin variable in the ordinary Kondo problem. Electrons may "flip" the spin by assisting in the quantum-mechanical tunnelling of the atom. Scattering of electrons by the TLS Kondo centre leads to similar consequences as the scattering by the magnetic Kondo impurity [14, 15]. A large Anisotropic Displacement Factor (ADF) is observed in the group of the Kondo like compounds. The ADF of As u_{11} reaches 0.03 Å^2 for ThAsSe, decreases through the $UAs_{1-x}Se_{1+x}$ series with decreasing x and falling down to 0.0073 Å^2 in UAsS. It was found that the decrease of ADF is accompanied by decrease the Kondo-like resistivity. This speaks forward for ascribing the origin of the Kondo like behaviour to the TLS Kondo mechanism [7, 8]. The ADF represents the average value of displacement of atoms vibrating around a given lattice position and equals to mean-square displacements along the Cartesian axes. We think that the off-stoichiometry is a natural source of the TLS centres.

As a conclusion we can state that small deviation from stoichiometry can lead to unusual behaviour of the transport properties in actinide compounds. Moreover, the same kind of behaviour is observed for the diamagnetic ThAsS, strongly uniaxial ferromagnetic UAsSe and UPS, and antiferromagnetic USb. We suppose, that such behaviour of the thorium and the uranium pnictochalcogenides as well as the uranium pnictide are a result of charge carrier scattering by the dynamic TLS centres, which classifies these compounds as being a novel Kondo system.

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