

ON TWO-LEVEL-SYSTEM KONDO STATE FORMATION IN THORIUM PNICTOCHALCOGENIDES

Z. HENKIE, R. WAWRYK, D. GNIDA, A. WOJAKOWSKI, AND C. MARUCHA

*W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences
P.O. Box 1410, 50-950 Wrocław 2, Poland*

Abstract: Resistivity minimum at $T_M \sim 15$ K as well as logarithmic singularity and negative magnetoresistivity ($\sim 0.2\%$ at 14 Tesla) were observed below T_M for resistivity both along a -axis, ${}^a\rho(T)$, and along c -axis, ${}^c\rho(T)$, of ThAsSe – tetragonal structure diamagnet. This behaviour is ascribed to the Kondo effect of structural defects producing scattering centres of two-level-system. Another anomaly, of an unclear origin, was observed for ThAsSe at temperature increasing above ~ 60 K; metallic-like increase of ${}^c\rho(T)$ is accompanied by a Kondo-like decrease of ${}^a\rho(T)$. The ${}^a\rho(T)$ for isostructural ThPS shows typical metallic behaviour. Room temperature thermoelectric power, equal to $3.4 \mu\text{V/K}$, $5.4 \mu\text{V/K}$ and $7.7 \mu\text{V/K}$ for a - and c -axis of ThAsSe and a -axis of ThPS, respectively, indicate metallic state of both compounds.

1. INTRODUCTION

This work continues the study of uranium and thorium pnictochalcogenides that are motivated by the discovery of the Kondo effect in ferromagnetic state of UAsSe compound [1, 2]. Coexistence of the ferromagnetism and the Kondo state is possible due to nonmagnetic origin of the latter. UAsSe crystallise into tetragonal structure the PbFCl-type where, As and Se should occupy two different sublattices. A disorder in the occupation of the anion sublattices leads to structural defects that form of two-level system (TLS) scattering centres [2, 3]. Their interaction with conduction electrons causes the TLS-Kondo effect [4]. The TLS-Kondo effect may thus be also possible in ThAsSe, which is diamagnetic, compound isostructural with UAsSe.

It has been proved recently [5] that the diamagnetic crystals of ThAsSe show the TLS-Kondo effect characterized by the Kondo temperature $T_K \approx 5$ K and the TLS energy splitting $\Delta \approx 1$ K. Below T_K a non-Fermi-liquid behaviour of the resistivity was observed, in consistency with theoretical prediction [4, 5]. The same mechanism of electron scattering was also observed by means of the spectroscopy of point contacts formed by Cu nanoscale junctions [6] and the resistivity of the Co/M/Co (M, nonmagnetic spacer layer) trilayers of nanoscale thickness [7].

However, ThAsSe is the TLS Kondo system better defined than any nanosystem. It is also a member of a large family of thorium and uranium pnictochalcogenides crystallising in tetragonal, PbFCl-type structure, all being potential TLS-Kondo systems. Therefore, they should offer various possibilities of research of the TLS-Kondo problem as well as of verification of different theoretical models. To increase our knowledge in this field we have extended our examination of ThAsSe to its anisotropy of the resistivity (ρ), magnetoresistivity (MR) and thermoelectric power (S), examined hitherto along a -axis only. The a -axis resistivity and thermoelectric power of ThPS crystal, grown for the first time, were determined as well.

2. EXPERIMENTAL

Both ThPS and ThAsSe were grown by the chemical vapour transport method in silica ampoules covered inside with a layer of pyrolytic carbon. Thorium phosphorosulphide crystals were grown from ThPS substrate with I_2 transporting agent (3 mg per cm^3 ampoule volume) in temperatures $700 \rightarrow 780^\circ C$. After about ten days of the growing we could obtain ThPS crystals of the form of about 0.6 mm-long pillar along a -axis with a cross section of the order of 0.01 mm^2 . Thorium arsenoselenide crystals were grown from ThAsSe substrate with bromine (3 mg per sample volume), in temperatures $1040^\circ C \rightarrow 990^\circ C$. ThAsSe crystals grew typically in a thin plate-like form. Accidentaly, we have grown the ThAsSe crystal as thick as 1.08 mm. It allowed us to determine the anisotropy of their $\rho(T)$, $S(T)$, and $MR = \{\rho(H, T) / \rho(0, T)\} / \rho(0, T)$.

The crystals were examined by an X-ray diffraction (XRD) method and by scanning electron microscopy with energy dispersive X-ray (EDAX) microanalysis. Both ThAsSe and ThPS crystals have tetragonal structure of the PbFCl type ($P4/nmm$ space group) and their room temperature lattice parameters are given in Table 1. Crystals of both compounds were found to be stoichiometric in the limit of accuracy of the two X-ray methods applied.

Table 1. Some physical quantities characterising three thorium pnictochalcogenides crystallising with PbFCl-type structure

Compounds	Axis	ρ (300 K) $\mu\Omega\text{cm}$	ρ_{ph} (300 K) $\mu\Omega\text{cm}$	S (300 K) $\mu\text{V/K}$	Lattice parameters \AA
ThAsSe	a	200	⁽¹⁾ 59	5.3	4.084
	c	1791	⁽²⁾ 226	3.4	8.578
ThAs _{1.23} S _{0.77} *	a	32	⁽¹⁾ 16	3.7	4.022
	c				8.483
ThPS	a	64	⁽²⁾ 36.5	7.7	3.986
	c				8.178

*based on data of Ref. [10]; ⁽¹⁾ ρ_{ph} (300 K) = $\rho_{\text{B-G}}$ (300 K); ⁽²⁾ ρ_{ph} (300 K) = ρ (300 K) ρ_0

The a -axis electrical resistivity, ${}^a\rho(T)$, of ThPS has been measured by a conventional dc method and accuracy of the geometrical factor determination was about 35%. ThAsSe crystals show sample-dependent ${}^a\rho(T)$ behaviour [5]. Therefore, it was important to determine the anisotropy of the resistivity for the same sample. It was possible to do this by the Montgomery's method [8] that allow us to determine the mutually perpendicular components of resistivity tensor. In this case we have measured the resistivity with the ac technique to reduce heating the sample. Thermoelectric power has been measured by the method described in Ref. [9].

3. RESULTS

The ${}^a\rho(T)$ of examined ThPS crystal shows metal-like behaviour presented by the lowest curve in Fig. 1. Below 36 K the ${}^a\rho(T)$ data can be well approximated by expression ${}^a\rho(T) = \rho_0 + cT^n$ for $\rho_0 = 27.5 \mu\Omega\text{cm}$ and $n = 3$. For such behaviour it can be assumed that the Mattiessen's rule is fulfilled, ρ_0 is the temperature independent residual resistivity due to electron scattering by static impurities while phonon component to the resistivity is: ρ_{ph}

$(T) = \rho(T)$, ρ_0 . The same treatment has been given to the c -axis resistivity data for ThAsSe presented by the highest curve in Fig. 1. However, in this case the approximation was performed from the temperature range 20-40 K yielding $\rho_0 = 1565 \mu\Omega\text{cm}$. The $\rho_{\text{ph}}(300 \text{ K})$ values are given in Table 1.

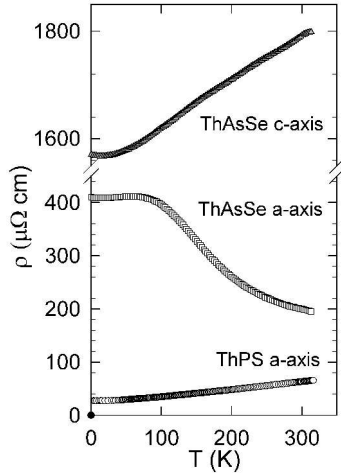


Fig. 1. Temperature dependence of resistivity for ThAsSe along c - and a -axis is shown by the highest and the middle curve, respectively. The lowest curve presents the a -axis resistivity data for ThPS

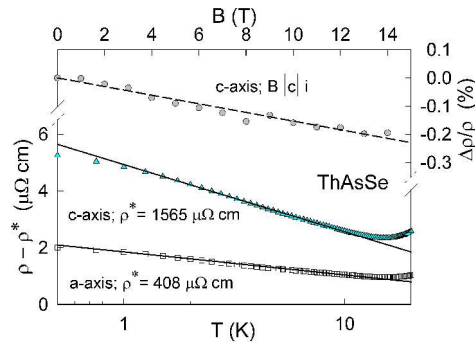


Fig. 2. Low temperature ${}^a\rho(T)$ and ${}^c\rho(T)$ data, decreased by a ρ^* , see text, and longitudinal magnetoresistivity along c -axis at 2.9 K (in the upper part)

Both ${}^a\rho(T)$ and ${}^c\rho(T)$ for ThAsSe behave similarly at the lowest temperatures. The resistivity decreases linearly with $\log T$ through one decade of temperature and reaches the lowest value at about the same temperature $T_M \sim 15 \text{ K}$. The resistivity data, decreased by a ρ^* , are plotted on semi-logarithmic scale in Fig. 2. The ρ^* is an arbitrary value we chosen for clear data presentation. The upper part of the Fig. 2 presents the longitudinal MR measured along c -axis at 2.9 K. The MR is low and negative, it reaches 0.2% at 14 Tesla. Low and negative MR was previously [5] observed for a -axis data also. Therefore, we may claim that ThAsSe reaches Kondo state below T_M . Previous close examination [5] showed that the logarithmic singularity of ${}^a\rho(T)$ below T_M is due to TLS-Kondo effect and the magnetic impurity origin of the observed Kondo effect is excluded.

The well-known Mott formula for diffusion thermoelectric power predicts linear dependence on T . The $S(T)$ either for a -axis, ${}^aS(T)$, of ThPS and c -axis ${}^cS(T)$ of ThAsSe and their values at 300 K are given in Table 1. Thus we think that we can use the Mott formula for the estimation of the Fermi energy E_F of the examined compounds in one-band approximation as it was previously done [10] for $\text{ThAs}_{1.23}\text{S}_{0.77}$. In this approach the ${}^aS(300 \text{ K}) = 7.7 \mu\text{V/K}$ for ThPS and ${}^cS(300 \text{ K}) = 3.4 \mu\text{V/K}$ for ThAsSe determine E_F equal to 2.9 eV and 6.5 eV, respectively. This is consistent with a metallic band structure.

4. DISCUSSION AND CONCLUSIONS

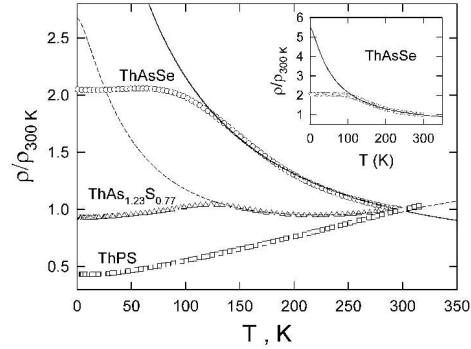
The resistivity of the examined compounds, that is especially high along c -axis of ThAsSe, may look as being inconsistent with metallic-like the $\rho(T)$ behaviour. However, the latter is consistent with estimated high, typical for metals, value of the E_F . This inconsistency is reduced if we take into account that the normal space volume of the unit cell, corresponding to Brillouine zone (BZ) volume, is by a factor of about 12 higher for copper than for ThAsSe. One unit cell of the latter contains two formula units. Thus the value of $\rho_{\text{ph}}(300 \text{ K}) = 226 \mu\Omega\text{cm}$ for ThAsSe (see in Table 1) may correspond to $\sim 20 \mu\Omega\text{cm}$ for a simple metal and does not exclude well filled metallic bands and Mattiessen's rule applicability for the case of the examined here thorium compounds.

The $\rho(T)$ of ThAsSe was measured for the first time by Schoenes *et al.* [11]. They noticed that the observed decrease of $\rho(T)$ is accompanied by the decrease of Hall coefficient corresponding to an increase of carrier density from 0.16 e/BZ below 100 K, to 1.2 e/BZ at room temperature. The latter was ascribed to braking of local As-As disordered dimers. Their presence within (001) planes was anticipated from the observed highly structured 'lines' of diffuse streaking in addition to the strong parents Bragg reflections in the electron diffraction patterns taken either at 30 K or at 100 K [12]. However this kind of resistivity anisotropy where the increase of temperature increases the resistivity for one crystallographic direction and decreases it for the another (Kondo-like anomaly – KLA), as we have found for ThAsSe, seem to rule out the interpretation based on a change of the carrier concentration.

An approach applied to interpret the KLA observed for $\text{ThAs}_{1.23}\text{S}_{0.77}$ [10] was consistent with above conclusion. It was assumed that the KLA is due to scattering of conduction electrons by dynamical centres that produce ρ_{KLA} contribution to the total resistivity. It was assumed in the Ref. [10] that $\rho_{\text{KLA}} = \rho_{\text{K}}$. We choose of the results of Arai [13] for ρ_{KLA} to make an explicit comparison. The total resistivity: $\rho(T) = \rho_0 + \rho_{\text{ph}}(T) + \rho_{\text{KLA}}(T)$ has been fitted to experimental resistivity data, in terms of $\rho(T)/\rho(300 \text{ K})$, either of $\text{ThAs}_{1.23}\text{S}_{0.77}$ and ThAsSe for temperature range $T > 130 \text{ K}$. The $\rho_{\text{ph}}(T)$ is the phonon resistivity here described by Bloch-Grünaisn function. We follow the fitting procedure described in Ref. [10] but we assumed here that $T_{\text{K}} = T_{\text{KLA}} = 22.4 \text{ K}$ are the same for both compounds. Broken and solid lines in Fig. 3 present the fitted dependences. In this approach the increase of the KLA when passing from ThPS through $\text{ThAs}_{1.23}\text{S}_{0.77}$ to ThAsSe is due to the increase of conduction electrons scattering by dynamical centres. Cooling the samples increases the scattering until it saturates below some temperature.

In general, a conductivity σ can be presented as product of charge of carries q , the density of carriers n and the carriers mobility μ : $\sigma = 1/\rho = |q|n\mu$. Any anisotropy of either σ or ρ may only come from anisotropy of μ . The n is a scalar therefore its increase or decrease must increase or decrease the σ for all crystallographic directions simultaneously. On the other hand, the mobility and its anisotropy depends either on effective mass of carriers and mechanisms of their scattering. It remains a question if there are possible such impurities that scatter conduction electrons like a static impurity along one crystal axis and as the dynamic one along another axis.

Fig. 3. The experimental data of the a -axis resistivity for ThPS, ThAs_{1.23}S_{0.77} and ThAsSe in terms of $\rho(T)/\rho(300\text{ K})$ plotted versus temperature. The broken and solid curves are calculated dependences fitted as described in text



Stoichiometric pnictochalcogenides have even number of valence electrons per BZ and they can develop either semimetallic structure or compensation metal multiband structure. In such case a cancellation effect may occur between electron and hole contribution in Hall effect and thermoelectric power. However, the off-stoichiometry in ThAs_{1.23}S_{0.77} system [10], isostructural with ThAsSe, can be treated as a hole doping (0.46 e⁺/BZ) which destroys the compensation metal case. Here, despite the dominant hole concentration, the observed Hall coefficient and thermoelectric power are still negative and close to those for ThAsSe and can be interpreted as the strong indication that the mobility of the electrons in ThAsS, and presumably in the other pnictochalcogenides, is considerably higher than that of the holes. Therefore, the single band approximation may be accepted for analysis of transport properties of the pnictochalcogenides.

It is concluded that the TLS-Kondo state in ThAsSe is formed at temperatures $T < T_M \sim 15\text{ K}$ and the Kondo-like anomaly observed, at temperatures $T > 60\text{ K}$ for basal plane only, is not any sign of a Kondo state.

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