Two-Channel Kondo Effect in Glasslike ThAsSe

T. Cichorek,[1,2] A. Sanchez,[1] P. Gegenwart,[1] F. Weickert,[1] A. Wojakowski,[2] Z. Henkie,[2] G. Auffermann,[1] S. Paschen,[1]
R. Kniep,[1] and F. Steglich[1]
[1]*Max Planck Institute for Chemical Physics of Solids, 01187 Dresden, Germany*
[2]*Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wroclaw, Poland*
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We present low-temperature heat and charge transport as well as caloric properties of a ThAsSe single crystal. An extra $-AT^{1/2}$ term in the electrical resistivity, independent of magnetic fields as high as 14 T, provides evidence for an unusual scattering of conduction electrons. Additionally, both the thermal conductivity and the specific heat show a glass-type temperature dependence which signifies the presence of tunneling states. These observations apparently point to an experimental realization of a two-channel Kondo effect derived from structural two-level systems.

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Since the pioneering work by Noziéres and Blandin [1], the search for a two-channel Kondo (2CK) effect has been the subject of considerable scientific interest. However, its experimental realization requires a strict channel symmetry that is hard to achieve in the spin Kondo problem. As a viable alternative, one considers an equivalent Kondo effect that originates from scattering centers with orbital degrees of freedom instead of spin ones like, e.g., the quadrupole momenta in certain heavy-fermion systems [2]. In this so-called orbital Kondo effect, the spin of the conduction electrons plays the role of a silent channel index. The influence of a magnetic field on the orbital Kondo resonance must be very weak and, therefore, distinctly different from the destruction of the spin Kondo resonance by a comparatively low magnetic field [3].

As originally suggested by Zawadowski *et al.* [4,5], the interaction between structural two-level systems (TLS) and the conduction electrons may also lead to the orbital Kondo effect and hence to the 2CK problem. In the TLS Kondo model, a single tunneling center (e.g., an atom that quantum mechanically tunnels between two minima of a double-well potential) immersed in the Fermi sea is expected to behave like a spin-$\frac{1}{2}$ impurity coupled to the conduction electrons [6,7]. Since this is essentially a one-impurity Kondo problem, a considerably stronger effect on the transport properties rather than on the thermodynamic ones is anticipated [2]. On the other hand, it is still debatable whether the strong-coupling 2CK fixed point due to the TLS can be experimentally achieved or not. This is mainly because a Kondo temperature T_K as small as 10^{-3}–10^{-2} K is expected [2]. In addition, the contribution of higher excited states may reduce T_K by up to 3 orders of magnitude to negligibly small values [8,9]. Furthermore, even if the second vibrational level of the tunneling atom is just above the potential barrier, for a medium-heavy atom a T_K value below 0.5 K is predicted [10]. Nevertheless, various experimental observations obtained at liquid-helium temperatures are thought to be caused by an interaction between the conduction electrons and TLS [11–14]. For example, an orbital Kondo problem with large T_K value is inferred from the width of the Kondo resonance on the Cr(001) surface investigated by scanning tunneling microscopy [15]. Moreover, recent theoretical studies have shown that not all of the possible internal structures of the defect have been explored [16]. Finally, a significant enhancement of the Kondo temperature is suggested if the conduction electrons are coupled to the tunneling impurity via resonant scattering [17].

Recent work on the diamagnetic compound ThAsSe has demonstrated the importance of tunneling states to the charge transport on a macroscopic scale [18]: at temperatures lower than about 20 K, an additional term in the resistivity $\rho(T)$ was observed that frequently exhibited a complex temperature dependence. For other single crystals of ThAsSe, however, a simpler logarithmic increase of $\rho(T)$ upon cooling, followed by a saturation below $T_S \simeq$ 0.2–2 K, was found [18]. These peculiarities, together with their independence on both strong magnetic fields and high hydrostatic pressures, point to a Kondo effect derived from structural TLS. Furthermore, some tendency of $\rho(T)$ to pass from a logarithmic to a $-AT^{1/2}$ behavior was observed in a ThAsSe sample with $T_S \simeq 0.2$ K, hinting at the development of a possible 2CK state [19]. A crude comparison of the experimental results with the theoretical ones yielded a Kondo temperature of 4–5 K [19]. The presence of movable defects in single-crystalline ThAsSe was directly reflected by a quasilinear-in-T term of *non-electronic* origin in the low-T specific heat. Tunneling centers are apparently located in the structurally disordered As-Se sublattice, as suggested by x-ray and transmission-electron-microscopy studies [20]. According to our recent results on the related system $ZrAs_{1.40}Se_{0.50}$, a formation of TLS centers might be triggered off by empty places in the As (2*a*) layers and/or the mixed occupation of the 2*c* sites by arsenic and selenium [21].

This Letter reports the observation of a 2CK state originating from a scattering of the conduction electrons off structural TLS in ThAsSe. All experiments have been performed on the same single crystal. The synthesis procedure is described in Ref. [20]. Because of the platelike shape of the crystal, its transport properties have been investigated in the *ab* plane only. The thermal conductivity was measured in a ^{3}He-^{4}He dilution refrigerator utilizing a steady-state method. Specific heat measurements were made in a ^{3}He cryostat by means of a thermal-relaxation method. The electrical resistivity was studied in zero and applied magnetic fields up to 14 T using different equipment below and above 4 K.

It is well established that TLS determine the low-temperature thermal properties of matter with some kind of disorder [22]. This leads to anomalous terms in the temperature dependencies of both the thermal conductivity and the specific heat with comparable magnitude for various disordered materials. In the case of ThAsSe, the low-T thermal properties are remarkably similar to those of amorphous solids: Fig. 1(a) shows the temperature dependence of the thermal conductivity $\kappa(T)$ of ThAsSe. The electronic contribution $\kappa_{\mathrm{el}}^{\mathrm{WF}}$ was estimated from the electrical resistivity using the Wiedemann-Franz law. Since for $T \lesssim 1$ K, $\kappa_{\mathrm{el}}^{\mathrm{WF}}$ (dotted line) is distinctly smaller than the measured total $\kappa(T)$, the heat transport is dominantly carried by phonons. This becomes also evident by comparing the $\kappa(T)$ data of ThAsSe with the published ones for the dielectric glass As_2S_3 [23,24]—a prototype of pnictogenchalcogenide-based TLS materials. For $T < 0.7$ K, $\kappa(T)$ of As_2S_3 follows the relation $\kappa(T) = D(T/\alpha)^\delta$ with $\alpha = 1$ K, $\delta = 1.92$, and $D = 17 \times 10^{-4}$ W/K cm [24]. A universal power-law dependence of $\kappa(T)$ with $\delta = 1.9 \pm 0.1$ is characteristic for systems whose dominating phonon thermal conductivity is limited by scattering from TLS. For ThAsSe, $\kappa(T)$ can be well described, below 0.8 K, by the same relation with $\alpha = 1$ K, $\delta = 1.97$, and $D = 23 \times 10^{-4}$ W/K cm (cf. solid line). While the exponent δ fits perfectly into the narrow range 1.9 ± 0.1, the value of D is only slightly larger than that of vitreous As_2S_3 (part of this difference may be easily attributed to errors in the estimation of the geometric form factor of the ThAsSe crystal). Furthermore, phonon scattering off conduction electrons, leading also to a T^2 contribution to $\kappa(T)$, seems to be negligible in ThAsSe: the product of the mean free path of the charge carriers l_c and the wave vector of the phonon q_{ph} is estimated to be 0.5, i.e., below the so-called Pippard ineffectiveness condition $l_c q_{\mathrm{ph}} = 1$ [25]. Thus, the low-T thermal conductivity provides striking evidence for the TLS being the dominating scattering centers for the propagating phonons in ThAsSe.

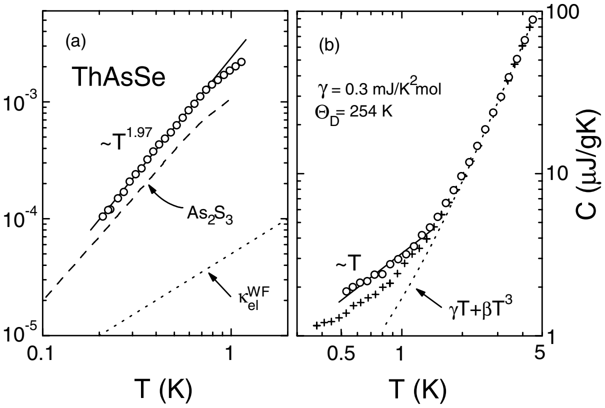

FIG. 1. Low-temperature thermal properties of the ThAsSe single crystal. (a) Total thermal conductivity (circles) and estimated electronic contribution $\kappa_{\mathrm{el}}^{\mathrm{WF}}$ (dotted line) as a function of temperature. The solid line is a fit to the data as described in the text. For comparison, $\kappa(T)$ of the noncrystalline insulator As_2S_3 is also shown [24]. (b) Specific heat in a double-logarithmic plot (circles). Crosses are the previous $C(T)$ data for a sample composed of several pieces [18]. The dotted line shows the $\gamma T + \beta T^3$ dependence with $\gamma = 0.3$ mJ/K^2 mol, the Sommerfeld coefficient of the electronic specific heat, and $\beta = 3 \times 1944/\Theta_D^3$ in units of J/K^4 mol. The parameters γ and β were determined from the fit in the temperature range 1.7–5 K. The solid line indicates the presence of an additional linear-in-T term due to TLS.

Additional evidence for tunneling centers in ThAsSe stems from the low-T specific heat results in Fig. 1(b). Here, we compare $C(T)$ of our ThAsSe crystal with $C(T)$ previously obtained for an ensemble of small single-crystalline pieces of this material [18]. Though quantitatively slightly different, the two sets of data confirm the

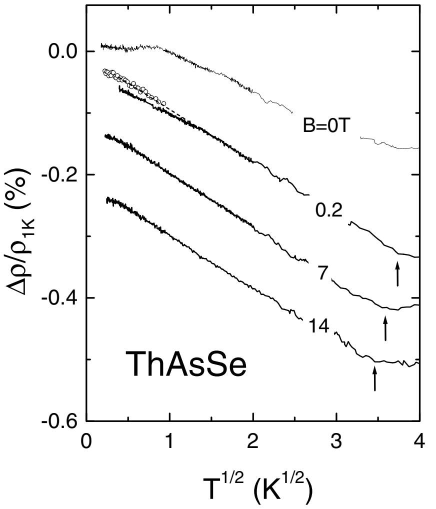

FIG. 2. Low-temperature electrical resistivity of ThAsSe as $\Delta\rho/\rho_{1K}$ vs $T^{1/2}$ in varying magnetic fields applied along the c axis. For clarity, the different curves in $B > 0$ were shifted subsequently by 0.1%. Circles display the $B = 1$ T data and the dashed line represents a $-AT^{1/2}$ behavior with $A = 0.38$ $\mu\Omega$ cm/K$^{1/2}$, independent of field at $B \geq 1$ T. Arrows indicate the upper limit of the square-root temperature dependence of the resistivity.

existence of an anomalous term, $\sim T$, to the specific heat. At low temperatures, this term adds to the specific heat due to charge carriers and phonons, $\gamma T + \beta T^3$, determined at $1.7\ \mathrm{K} < T < 5\ \mathrm{K}$. The additional low-$T$ contribution is ascribed to the presence of TLS.

Having established the glassy character of the ThAsSe single crystal studied, we now turn to the discussion of its electronic transport properties at low temperatures. As shown in Fig. 2, an additional contribution to $\rho(T)$ emerges at temperatures below 16 K. Here, we plotted the relative change of the resistivity normalized to the corresponding value at 1 K, $\Delta\rho/\rho_{1\mathrm{K}}$. For $T \lesssim 0.9$ K and $B = 0$, the resistivity levels off. If a magnetic field $B \geq 1$ T is applied then $\rho(T)$ depends strictly linearly on $T^{1/2}$ in a wide temperature window, i.e., from around 0.16 K to above 12 K at $B = 14$ T. The coefficient of the $-AT^{1/2}$ term amounts to $A = 0.38\ \mu\Omega\,\mathrm{cm/K}^{1/2}$ for all fields $B \geq 1$ T. [According to Ref. [26], we assumed $\rho_{\mathrm{ab}}(300\ \mathrm{K}) = 220\ \mu\Omega$ cm; see also Fig. 3(c).] Finally we note that, while the additional resistivity sets in at slightly lower temperatures with increasing B (cf. arrows in Fig. 2), $\rho(T)$ begins to saturate at very low temperatures. (This is apparently an intrinsic feature, although the heating effects that could still exist in our arrangement prevent us from discussing this point in detail.)

The field-independent $T^{1/2}$ increase of $\rho(T)$ observed upon lowering the temperature can neither be attributed to weak localization [27] nor to electron-electron interactions in a three-dimensional disordered system [28]. In fact, both types of quantum corrections to the resistivity are highly sensitive to magnetic fields, which holds true even in the presence of strong spin-orbit coupling [27,28]. For example [29], the interference of the wave functions of the electrons moving along a closed loop is weakened or even destroyed by a magnetic field of the order of tens of an Oe only. We, therefore, attribute the field-independent $-AT^{1/2}$ term in the electrical resistivity to electron scattering off the TLS, whose existence is established by the thermal measurements described above. This is, to our knowledge, the first-ever observation of the 2CK state originating from TLS in a macroscopic system.

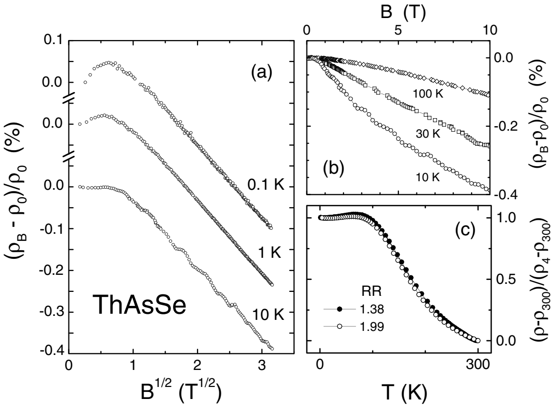

FIG. 3. (a) Magnetic field dependence of the electrical resistivity for ThAsSe at temperatures where a $-AT^{1/2}$ term is observed (see Fig. 2). (b) Magnetoresistivity at higher temperatures. (c) The normalized resistivity for ThAsSe with very different resistivity ratios $RR = \rho_{4\,\mathrm{K}}/\rho_{300\,\mathrm{K}}$ (see text for details).

At first glance, a deviation of the zero-field resistivity from the $-AT^{1/2}$ behavior below 1 K is reminiscent of a crossover to a Fermi-liquid state (cf. Fig. 2). However, its disappearance in a magnetic field as small as 0.2 T is surprising in the context of electron-TLS interaction [2]. Therefore, we suppose that the 2CK effect in the weak field limit is hidden by another phenomenon being suppressed already by $B \simeq 1$ T. To explore this possibility further, the isothermal response of the resistivity to a magnetic field was studied.

The magnetoresistivity (MR) data for ThAsSe are shown in Fig. 3(a) as $(\rho_B - \rho_0)/\rho_0$ versus $B^{1/2}$. The measurements were performed in the temperature window $0.1\ \mathrm{K} \leq T \leq 10$ K where the $-AT^{1/2}$ dependence was observed in $\rho(T)$. A positive MR whose magnitude gradually decreases with increasing temperature is found at $B < 1$ T only. At $T = 10$ K, $(\rho_B - \rho_0)/\rho_0$ is practically zero in this field range. This low-field effect hints at some quantum corrections. Most probably, the positive magnetoresistivity reflects spin-orbit scattering that rotates the spin of the conduction electrons and yields a destructive interference of the electron wave functions [29]. Consequently, the differences between the results obtained at $B \leq 0.2$ T and those obtained at $B \geq 1$ T, as depicted in Fig. 2, are tentatively ascribed to quantum corrections.

Further arguments against the interference effects in higher fields derive from the data at $B \geq 1$ T, where the MR is negative. Because of the T-independent slope of $(\rho_B - \rho_0)/\rho_0$ versus B curves displayed in Fig. 3(a) for $B \geq 1$ T, this negative MR cannot be ascribed to weak localization [29]. Furthermore, at fields of the order of $(2\mu_{\mathrm{B}}/k_{\mathrm{B}}T)^{-1}$, one should expect a deviation from the observed $B^{1/2}$ behavior due to the electron-electron interaction [27], which is not resolved in the data of Fig. 3(a).

A small and negative MR appears to be characteristic for ThAsSe [Fig. 3(b)]. However, the MR decreasing as $B^{1/2}$ has been observed only at $T \leq 10$ K. Additionally, the slope of this isothermal $B^{1/2}$ dependence accounts for $0.77\ \mu\Omega\,\mathrm{cm/T}^{1/2}$ and is by a factor of 2 larger than the $A = 0.38\ \mu\Omega\,\mathrm{cm/K}^{1/2}$ coefficient obtained in constant B. Though not yet understood, this relationship between the negative MR and the occurrence of the extra $-AT^{1/2}$ term in $\rho(T)$ found for $T \lesssim 12$ K and $B \geq 1$ T (cf. Fig. 2) is very intriguing. Both observations, however, confirm the existence of a characteristic energy scale of a few K in ThAsSe. We note that a negative MR is also expected for a 2CK effect originating from electrical quadrupole moments [30].

Recent examinations of ThAsSe revealed a strong sample dependence of its resistivity in the high temperature region [18]. This is due to a different amplitude of the increase of $\rho(T)$ with decreasing temperature down to around 65 K. Indeed, all the $\rho(T)$ dependencies can be mapped to the same $\frac{\rho(T)-\rho_{300\,\mathrm{K}}}{\rho_{4\,\mathrm{K}}-\rho_{300\,\mathrm{K}}}$ curve, as demonstrated in Fig. 3(c). Here, we compare the normalized resistivity for the ThAsSe single crystal ($\rho_{4\,\mathrm{K}}/\rho_{300\,\mathrm{K}} = 1.99$, this study) with that one for the sample of lowest resistivity ratio (1.38) measured previously [18]. Since our treatment does not affect the temperature scale, the observed sample dependence in ThAsSe has clearly a quantitative character only.

The negative temperature coefficient of the resistivity above 65 K originates, most likely, from a gradual formation of covalently bonded dimers $(\mathrm{As\text{-}As})^{4-}$ [26], which are believed to be responsible for complex electron diffraction patterns of ThAsSe [31]. More importantly, virtually identical patterns obtained at 30 and 100 K point out that the gradual $(\mathrm{As\text{-}As})^{4-}$ dimerization is completed much above 16 K and hence does not directly affect the $-AT^{1/2}$ behavior of $\rho(T)$. Besides, the application of pressure alters the maximum resistivity at 65 K, leaving the low-T term completely unchanged [18]. This clearly indicates a different origin of both singularities.

As far as the formation of tunneling centers is concerned, it is, however, conceivable that some low-energy excitations of singular $(\mathrm{As\text{-}As})^{4-}$ dimers play an important role. A more exciting possibility concerns the fact that some pnictogen atoms As and chalcogen atoms Se become involved in a homopolar-to-heteropolar bond transformation, as discussed for $\mathrm{As_2Se_3}$ [32] and $\mathrm{As_2S_3}$ [33]. The latter scenario is even more plausible for nonstoichiometric samples [34]. In other words, we speculate that the movable particle is an electron, tunneling between As and Se, rather than an atom: T_K of a few K in ThAsSe would then be the consequence of the electron mass being smaller than the atomic masses by about 4 orders of magnitude.

In summary, we have investigated a ThAsSe single crystal whose low-temperature resistivity shows a $-AT^{1/2}$ behavior. Its origin was found to be very different from the frequently observed quantum interference [27–29], as highlighted by the independence of the resistivity on strong magnetic fields. Furthermore, the low-T thermal properties give clear evidence for the presence of tunneling centers in the sample studied. Our experimental findings lead to the suggestion of a two-channel Kondo effect originating from interactions between the conduction electrons and TLS. We hope that our results will have a significant impact on this interesting field of research, given the fact that the existence, in real matter, of a two-channel Kondo regime due to tunneling particles is still a matter of strong current controversy [9,17].

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[34] The chemical composition of various ThAsSe single crystals (1.5–2 mg each) were determined by the use of the ICP-OES (inductively-coupled-plasma–optical-emission-spectrometer) method. The analyses show a slight excess of As in the samples.