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$3d$ magnetism in $ThCo_2Sn_2$ single crystals

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Abstract. Intense efforts have been made in order to synthesize new tetragonal ternary intermetallic compounds with low-temperature ground states on the border of magnetism. Here we report the synthesis of $ThCo_2Sn_2$ single crystals, which crystallize in the tetragonal $CaBe_2Ge_2$-type structure, using the flux technique. Further investigation of the physical properties by magnetic susceptibility and pressure-dependent electrical resistivity measurements confirm the presence of antiferromagnetic ordering associated with the Co ions, but with a higher ordering temperature of $T_N = 78$ K when compared to $T_N = 65$ K of the polycrystalline counterpart. Our results show that both Cu-substitution and applied pressure up to 22 kbar are not able to induce superconductivity in this system. Nevertheless, our analyses point out to a putative quantum critical point at higher pressures.

1. Introduction

A rich variety of interesting low-temperature ground states is hosted by tetragonal ternary intermetallic compounds with the general formula AT_2X_2, where A is a rare-earth, actinide, alkali or alkaline earth metal, T is a d-electron transition metal, and X is a IIIA-IVA metalloid. For instance, $YbRh_2Si_2$ displays non-Fermi-liquid behavior [1], $SmMn_2Ge_2$ presents complex magnetic ordering [2], and unconventional superconductivity can be found in $CeCu_2Si_2$ at ambient pressure and in $BaFe_2As_2$ upon chemical substitution and/or applied pressure [3, 4].

In this regard, it is highly desirable to further investigate compounds which crystallize in the 122 tetragonal structure in order to search for the realization of such interesting properties. In particular, since low-dimensional materials often display anisotropic responses on their physical properties, the synthesis of such compounds in single crystalline form is greatly preferred. Nevertheless, reports on tetragonal stannide compounds (A = e.g., La, Ce, Th, U; T = e.g. Co, Ni, Cu, and X = Sn) are rather scarce and, to the best of our knowledge, have been restricted to polycrystalline samples prepared by the arc-melting technique [5, 6, 7, 8]. In addition, most of these previous studies have focused on the antiferromagnetic ordering due to the A = Ce or U ions and their heavy fermion behavior.

On the other hand, the complex $3d$ Co magnetism in ACo_2Pn_2 (A = Ca, Sr, Ba, and rare-earth elements; Pn = P, As) systems, as well as the related ACoPnO compounds, have been investigated extensively previously. For instance, $LaCo_2P_2$ exhibits ferromagnetism below $T_c = 125$ K while $CaCo_2P_2$ orders antiferromagnetically below $T_N = 113$ K [9, 10, 11]. Neutron diffraction data indicate that the magnetic moments of the cobalt atoms lie perpendicularly to the c-axis and order ferromagnetically within the basal plane and antiferromagnetically along the c-axis with stacking sequence +-+-. Interestingly, even though $BaCo_2As_2$ does not exhibit

magnetic order above 1.8 K, local-density approximation (LDA) calculations reveal the presence of in-plane ferromagnetic correlations [12].

In this paper, we report the physical properties investigation of the intermetallic antiferromagnetic (AFM) single crystal $ThCo_2Sn_2$. The polycrystalline compound has been reported to crystallize in the tetragonal $CaBe_2Ge_2$-type structure (a = 4.4302(6) Å and c = 9.7376(8) Å) which contains layers of Th ions separated by $[Co_2Sn_2]$ layers along the crystallographic c-axis. Unlike its polycrystalline counterpart, the field-dependent magnetic susceptibility for our single crystals shows an anisotropic response with respect to the crystallographic orientation below $T \sim 200$ K followed by an antiferromagnetic (AFM) ordering at T_N = 78 K, which is considerably higher than the previous reported T_N of 65 K [5]. Interestingly, a metamagnetic transition in the $M_{||}(H)$ data was observed at the critical field H_c = 3.4 T. Moreover, transport measurements under pressure revealed a suppression of the magnetic ordering in the parent compound hinting for a possible tuning towards a magnetic instability at higher pressures. In addition, our combined study of chemical Cu-substitution and applied pressure suggest that the Co 3d electrons remain rather localized in the studied pressure range.

2. Experimental Details

Single crystalline samples of $ThCo_2Sn_2$ were grown using the In-flux technique. The mixture of high purity elements was placed in an alumina crucible and sealed in a quartz tube under vaccum. The sealed tube was heated up to 1150 °C for 2 h, cooled down rapidly to 800 °C at 20 °C/h, and finally cooled down slowly to 650 °C. The flux was then removed by centrifugation. The single crystals with dimensions $\sim 1 \times 1 \times 0.25$ mm^3 were grinded and their crystal structure was checked by X-ray powder diffraction on a diffractometer with Cu $K\alpha$ radiation at room temperature. The obtained lattice parameters (a = 4.4302(6) Å and c = 9.7376(8) Å) are in very good agreement with previous reports on polycrystalline samples [5]. Several single crystals from different batches were also submitted to elemental analysis using a commercial Energy Dispersive Spectroscopy (EDS) microprobe coupled to a FEG SEM microscope. From the EDS analysis, we obtain the composition $ThCo_{1.76(5)}Sn_{1.96(4)}$, indicating a slight Co-defficiency in this compound. It is noteworthy that non-stoichiometric (U,Th)$T_{2-x}Sn_2$ compounds have been reported previously with $x = 0.4 - 0.6$.

Magnetization measurements were performed using a superconducting quantum interference device (SQUID) commercial magnetometer. The in-plane resistivity was measured using a standard four-probe method. Electrical-resistivity measurements under hydrostatic pressure were carried out in a clamp-type cell using Fluorinert as pressure transmitting medium. Pressure was determined by measuring the superconducting critical temperature of Pb.

3. Results and Discussion

Figure 1 presents the temperature dependence of the magnetic susceptibility, χ (T), for an applied magnetic field of H = 1 kOe parallel ($\chi_{||}$) and perpendicular ($\chi_{\perp}$) to the c-axis. At high temperatures ($T > 200$ K), $\chi(T)$ can be well fitted by a Curie-Weiss (CW) law plus a T-independent Pauli term, $\chi(T) = \chi_0 + C/(T - \theta_{CW})$ (solid lines). From the Curie constant C, we obtain an effective moment of $p_{eff} \approx 1.1\mu_B$/Co for $H||ab$ and of $p_{eff} \approx 1.3\mu_B$/Co for $H||c$. Our result is particularly similar to recent reports on $CaCo_2As_2$ single crystals for which the effective moment of Co was calculated to be $\approx 1.0\mu_B$ for $H||ab$ and $\approx 1.4\mu_B$ for $H||c$ [13, 14]. We note that free Co ions have seven eletrons in the 3d shell ($3d^7$ configuration), which may contribute to the magnetic moment. However, the tetrahedral crystal field to which the Co ions are subjected in $ThCo_2Sn_2$ lifts the $3d^{10}$ degeneracy into a low energy doublet (e_g) and an excited triplet (t_{2g}) level. Since the experimental moment is small, it is reasonable to infer that the Co ions are in a low-spin configuration, i.e., that there is only one unpaired spin corresponding to a theoretical

value of $p_{eff} \approx 1.7\mu_B$. The fact that our experimental value is smaller than the theoretical one suggests that the unpaired spin may be slightly compensated.

As the temperature is further lowered, χ (T) becomes anisotropic, consistent with an easy-axis along the c-direction, and $\chi_{||}$ presents a sharp drop at the onset of the antiferromagnetic (AFM) order. At $T_N = 78$ K, the ratio $\chi_{||}/\chi_{\perp} = 1.3$ indicates that $ThCo_2Sn_2$ is an uniaxial antiferromagnet with low anisotropy, which in turn may be caused by the tetragonal CEF and the low-T Co^{2+} single ion anisotropy. From the CW fits, we are also able to extract the θ values of $\theta_{||} = 75$ K when the magnetic field is applied along the c-axis and $\theta_{\perp} = 89$ K when H is perpendicular to the c-axis. We again emphasize the similarity with $CaCo_2As_2$ ($T_N = 76$ K), which shows $\theta_{ab} = 98$ K for $H||ab$ and $\theta_c = 65$ K for $H||c$. This result indicates (i) the presence of ferromagnetic interactions, due to the positive sign of θ; (ii) that the main CEF parameters responsible for the tetragonal anisotropy is finite but rather small, in agreement with the also small value of the ratio $\chi_{||}/\chi_{\perp}$. We note that the presence of the anisotropy associated with the CEF tetragonal symmetry indicates that the Co orbital angular momentum is only partially quenched in this compound. In this case, the Co ions are subjected to an intermediate ligand field where CEF and spin-orbit effects are comparable. In order to average out the CEF anisotropy effects, the inverse of the polycrystalline averaged susceptibility is shown in the lower inset of Fig. 1. The linear Curie-Weiss fit for $T > 150$ K yields an effective magnetic moment $p_{eff} = 1.1\mu_B$/Co and a paramagnetic Curie-Weiss temperature $\theta_p = 83(1)$ K. It is worth noting that we subtracted the Pauli temperature independent term $\chi_0 = 3.2 \times 10^{-4}$ emu/mol.Oe from $\chi_{poly}(T)$ before taking the inverse in order to avoid the curvature observed in Ref. [5].

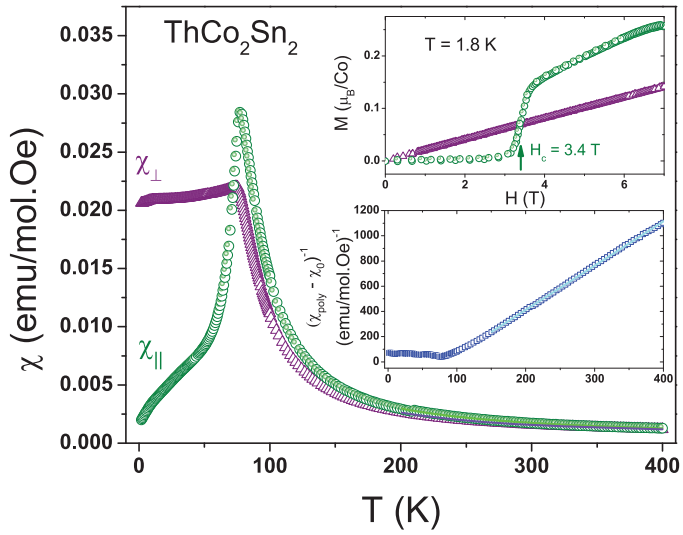

Figure 1. T-dependence of the magnetic susceptibility for the $ThCo_2Sn_2$ single crystals measured with a magnetic field of $H = 1$ kOe applied parallel $\theta_{||}$ (open circles), and perpendicular $\theta_{\perp}$ (open triangles) to the c-axis. The solid lines represent Curie-Weiss fits. The upper inset shows the magnetization as a function of the applied magnetic field in a $ThCo_2Sn_2$ single crystal at $T = 1.8$ K for both in-plane and out-of-plane orientations. The arrow indicates the spin-flop transition at $H_c = 3.4$ T when H is applied along the easy-axis. The lower inset displays the inverse of the polycrystalline averaged susceptibility as well as the linear fit for $T > 150$ K (solid line).

Despite the antiferromagnetic ground state displayed by $ThCo_2Sn_2$ at low fields, its $M_{||}(H)$ curve at 1.8 K undergoes a steep jump at $H_c = 3.4$ T, as shown in the upper inset of Fig. 1. On the other hand, a linear change in magnetization up to $H = 7$ T is observed when the field is applied perpendicular to the c-axis (triangles). We note that, besides playing a role in determining the anisotropic paramagnetic susceptibility, the single-ion anisotropy also provides a sizeable contribution to the macroscopic magnetocrystalline anisotropy, which in turn underlies the phenomenon of metamagnetism. We note that, despite the obtained paramagnetic moment

$p_{eff} \approx 1.2(1)\mu_B$, the maximum measured magnetization saturation is 0.25 μ_B/Co ($\sim$ 20% of p_{eff} at high temperatures), indicating that the ordered moments are far from the saturated regime or in an intermediate regime between local and itinerant magnetism. Thus, all the above suggests that a complex magnetic structure takes place in $ThCo_2Sn_2$, as suggested by previous neutron diffraction measurements [15].

Nevertheless, the presence of the transition-metal metamagnetism in a 122 system indicates that the Co 3*d* electrons have a significant local character in this material. As such, to further investigate the local moment behavior in $ThCo_2Sn_2$ we now turn our attention to pressure dependent electrical resistivity measurements. Fig. 2 displays $\rho(T)$ at several selected pressures offset by 0.05 mΩ.cm. At high temperatures ($T > 200$ K), $\rho(T)$ decreases linearly, as typically found in metallic systems. However, $\rho(T)$ becomes considerably curvilinear as the temperature is further lowered, which may be due to the interband scattering present in compounds containing transition metals, which arises from the scattering of electrons between $s-$ and $d-$ type bands. Nonetheless, one cannot rule out non-trivial magnetic scattering associated with the Co^{2+} ions. Ongoing angle resolved photoemission spectroscopy (ARPES) measurements will shed light on the possible multi-band character of this material.

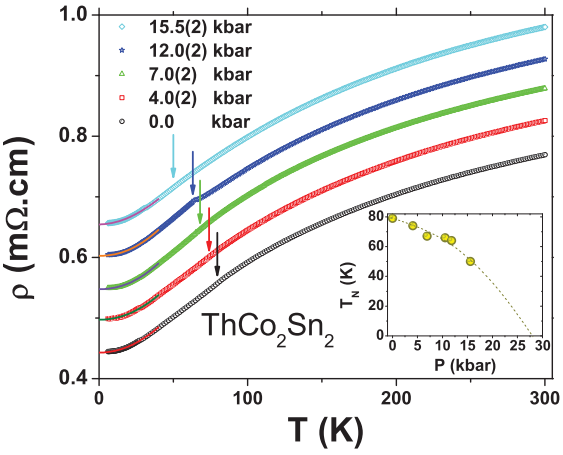

Figure 2. Temperature dependence of the in-plane electrical resistivity for several applied pressure in $ThCo_2Sn_2$ single crystals. The inset shows the phase diagram as a function of pressure.

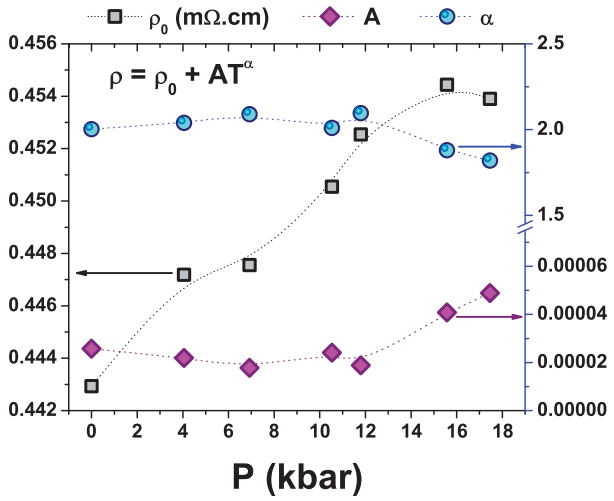

Figure 3. Extracted parameters from the fits to equation $\rho(T) = \rho_0(T) + AT^{\alpha}$.

At lower temperatures, a small kink is observed in $\rho(T)$ due to the magnetic ordering. Here, we define the AFM transition temperature, T_N, as the peak in first derivative of $\rho(T)$. Interestingly, we observe a decrease in T_N as a function of applied pressure, as indicated by the arrows in Fig. 2. This decrease in the ordering temperature as a function of pressure is consistent with the increase in the hybridization of the Co *d*-electrons.

In the magnetically ordered state, $\rho(T)$ can be well described by a simple power law expression $\rho(T) = \rho_0(T) + AT^{\alpha}$, where ρ_0 is the residual resistivity. We note that for $\alpha = 2$, this term describes the electron-electron scattering within the Fermi liquid theory. The solid lines in Fig. 2 for $T < 40$ K are the best fits to the above equation. The extracted values of ρ_0, A, and α are displayed in Fig. 3. Remarkably, the exponent $\alpha = 2.05(5)$ remains close to the Fermi liquid regime in the pressure range from ambient pressure up to 12 kbar. However, for $P > 12$ kbar, α starts to decrease and reaches $\alpha = 1.8$ at 17 kbar. We note that, at AFM quantum critical points

(QCP), spin-fluctuation theories predict $\alpha = 1.5$ for 3D-spin fluctuations [16, 17]. In addition, the coefficient A is often enhanced near the QCP, reflecting the divergence of the quasiparticle mass at the QCP itself. In fact, one can observe that A starts to increase in the same pressure range as α starts to decrease. Moreover, the increase of ρ_0 also indicates the proximity to a magnetic stability, although in this case one cannot rule out the effects of disorder. The slope dT_N/dP is relatively small and yields an estimate of $T_N \to 0$ at $P_c \sim 30$ kbar, as shown by the phase diagram in the inset of Fig. 2. High pressure measurements are in progress to determine whether there is another magnetic ordering with increasing pressure or T_N is suppressed toward a quantum critical point.

Nevertheless, it is possible to probe the $T_N \to 0$ region in the present pressure range by starting off with a smaller value of T_N at ambient pressure. To this end, we now combine chemical substitution and applied pressure. Fig. 4 shows the temperature dependence of the magnetic susceptibility of $Th(Co_{0.6}Cu_{0.4})_2Sn_2$, χ (T), for an applied magnetic field of $H = 1$ kOe parallel $(\chi_{||})$ and perpendicular $(\chi_\perp)$ to the c-axis. At high temperatures $(T > 200$ K), $\chi(T)$ can be well fitted by a Curie-Weiss (CW) law plus a T-independent Pauli term, $\chi(T) = \chi_0 + C/(T - \theta_{CW})$ (solid lines). From the Curie constant C, we obtain an effective moment of $p_{eff} \approx 1.2\mu_B$/Co for $H||ab$ and of $p_{eff} \approx 1.4\mu_B$/Co for $H||c$, which are only $0.1\mu_B$/Co higher than the values for the pure compound. At low temperatures, χ (T) is also consistent with an easy-axis along the c-direction, but it displays a much more anisotropic response with $\chi_{||}/\chi_\perp = 13$ at the transition temperature. Interestingly, $\chi_{||}$ presents a ferromagnetic response at low temperatures, whilst $\chi_\perp$ displays a drop at the onset of the magnetic order $(T_{\rm mag} \sim 36$ K), as typically found in antiferromagnets. The contrasting behavior between the two different field orientations is also evident in the M(H) data shown in the upper inset of Fig. 4. The $M_{||}(H)$ data reveal a typical ferromagnetic loop at 1.8 K with a small coercive field of 1.4 kOe and a saturation moment of 0.27 μ_B/Co for $H||c$. On the other hand, the $M_\perp(H)$ data display a linear behavior up to ~ 20 kOe followed by saturation at 0.26 μ_B/Co, as expected for the hard-axis. Microscopic measurements, such as neutron diffraction and/or Cu nuclear magnetic resonance (NMR) experiments, would be valuable to identify the nature of the magnetic ordering in these compounds.

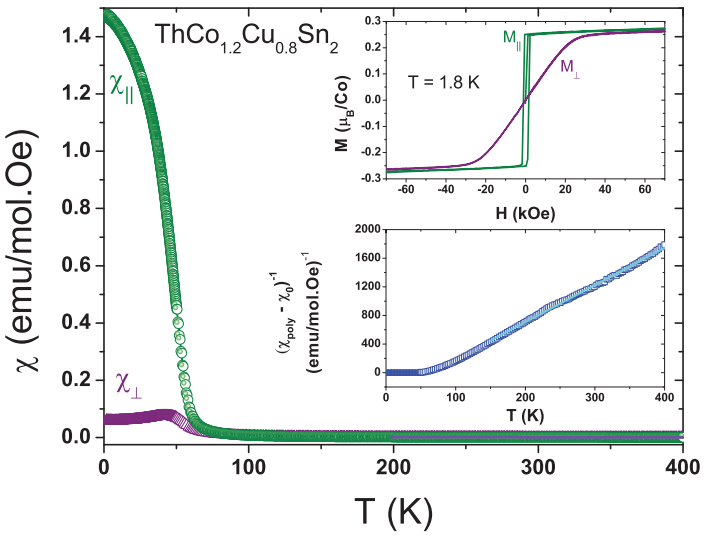

Figure 4. T-dependence of the magnetic susceptibility for the $Th(Co_{0.6}Cu_{0.4})_2Sn_2$ single crystals measured with a magnetic field of $H = 1$ kOe applied parallel $\theta_{||}$ (open circles), and perpendicular $\theta_\perp$ (open triangles) to the c-axis. The solid lines represent Curie-Weiss fits. The upper inset shows the magnetization as a function of the applied magnetic field in a $ThCo_2Sn_2$ single crystal at $T = 1.8$ K for both in-plane and out-of-plane orientations. The lower inset displays the inverse of the poly-crystalline averaged susceptibility as well as the linear fit for $T > 150$ K (solid line).

We now turn our attention to the pressure-dependence of the electrical resistivity of $Th(Co_{0.6}Cu_{0.4})_2Sn_2$. Fig. 5 shows $\rho(T)$ at several selected pressures for a Cu-substituted sample,

namely, $Th(Co_{0.6}Cu_{0.4})_2Sn_2$ with $T_{mag} = 36$ K at $P = 0$. Similarly to the parent compound, at high temperatures ($T > 200$ K), $\rho(T)$ decreases linearly and at low temperatures, a small kink is observed due to the AFM ordering. However, although T_{mag} is suppressed down to ~ 25 K at 13 kbar, no change in T_{mag} is observed at higher pressures, as indicated by the arrows in Fig. 5 and in the phase diagram displayed in its inset. In addition, from the fits of $\rho(T)$ data to $\rho(T) = \rho_0(T) + AT^{\alpha}$, we are again able to extract the parameters displayed in the inset of Fig. 6. However, in this case, there is no evolution of the parameters $\alpha \sim 2.18$ and $A \sim 3.4 \times 10^{-6}$ mΩcm$/K^{\alpha}$ as a function of pressure. Furthermore, contrary to the behavior observed in the pure compound, ρ_0 decreases with pressure for the Cu-substituted sample. This result suggests that the application of pressure in this case has the dominant effect of reducing the strain distribution associated with disorder. We note that the $Th(Co_{0.5}Cu_{0.5})_2Sn_2$ sample does not present magnetic ordering, indicating that $T_{mag} \to 0$ near the 40 % percolation limit for a two-dimensional lattice [18, 19]. Thus, it is reasonable to infer that chemical substitution in this structure suppresses the ordering temperature by magnetic dilution instead of changes in the hybridization of Co ions. All the above results strongly indicate that the Co 3*d* electrons remain rather localized in the studied pressure range. Ongoing ARPES measurements will help us to unveil the possible role of Co bands at the Fermi surface.

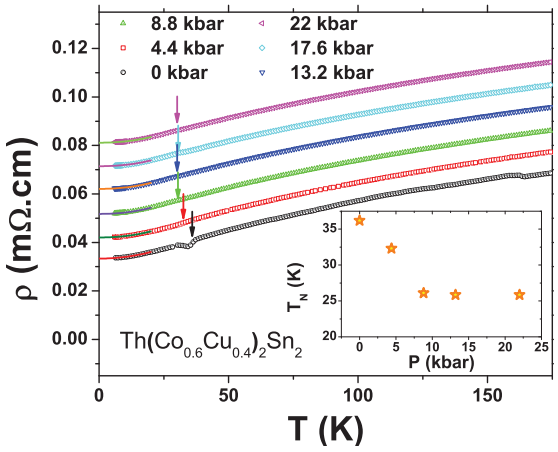

Figure 5. Temperature dependence of the in-plane electrical resistivity for several applied pressure in $Th(Co_{0.6}Cu_{0.4})_2Sn_2$ single crystals. The inset shows the phase diagram as a function of pressure.

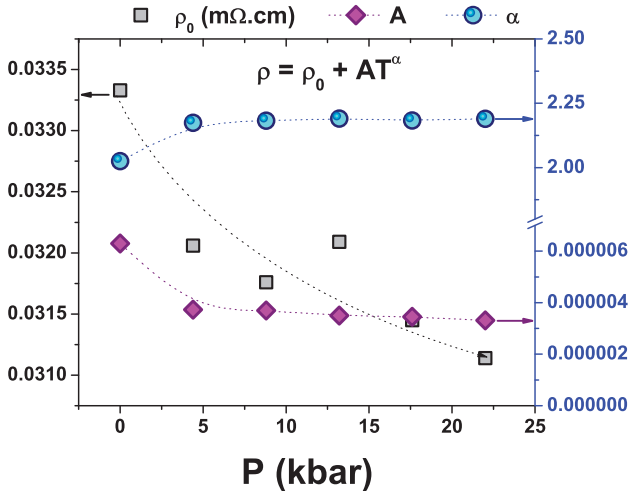

Figure 6. Extracted parameters from the fits to equation $\rho(T) = \rho_0(T) + AT^{\alpha}$.

4. Conclusions

In summary, we have successfully synthesized single crystalline samples of $ThCo_2Sn_2$ by the flux technique. Magnetic susceptibility measurements reveal that our single crystals order antiferromagnetically at $T_N \sim 78$ K, which is considerably higher than the value reported for polycrystalline samples ($T_N \sim 65$ K). Furthermore, we observe a metamagnetic transition at $H_c = 3.4$ T when the magnetic field is applied along the c easy-axis. Our pressure-dependent transport measurements reveal a suppression of T_N in the parent compound signaling to a possible magnetic instability at higher pressures. On the other hand, our combined study of chemical Cu-substitution and applied pressure reveals a slight decrease in T_{mag} followed by its saturation at ~ 25 K. Thus, our results suggest that the Co 3*d* electrons remain rather localized

in the studied pressure range. Further investigations by high pressure electrical resistivity and neutron diffraction measurements are needed to determine the magnetic structure of $ThCo_2Sn_2$ and to study a putative quantum critical behavior in this compound.

Acknowledgments
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