

# Evidence for charge Kondo effect in superconducting Tl-doped PbTe

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## ABSTRACT

We report results of low temperature thermodynamic and transport measurements of  $\text{Pb}_{1-x}\text{Tl}_x\text{Te}$  single crystals for Tl concentrations up to the solubility limit of approximately 1.5 %. The material superconducts for  $x > 0.3$  %, with a maximum  $T_c$  of 1.5 K for the highest Tl concentrations. All superconducting samples exhibit an anomalous resistivity upturn at low temperatures, whereas non-superconducting samples ( $x < 0.3\%$ ) do not. The temperature and field dependence of this resistivity upturn are consistent with a charge Kondo effect involving degenerate Tl valence states differing by two electrons, with a characteristic Kondo temperature  $T_K \sim 6$  K. The observation of such an effect supports an electronic pairing mechanism for superconductivity in this material and may account for the anomalously high  $T_c$  values.

Keywords: superconductivity, charge Kondo effect, thallium, mixed valence, disproportionation.

## 1. INTRODUCTION

PbTe is a small gap semiconductor. It has a rocksalt structure and has been treated with reasonable success using ionic models (i.e.,  $\text{Pb}^{2+}\text{Te}^{2-}$ ) [1]. The material can be doped to degeneracy by either vacancies or third-element dopants, with typical carrier concentrations in the range of  $10^{18}$  -  $10^{20}$   $\text{cm}^{-3}$  [2-4]. In comparison with similar semiconducting materials such as SnTe, GeTe, and InTe, it was previously anticipated that doped PbTe would only superconduct below approximately 0.01 K, if at all [5]. This has been found to be the case for all dopants with the notable exception of thallium, for which superconductivity was observed with critical temperatures up to 1.5 K [6], two orders of magnitude higher than anticipated given the modest carrier concentrations. Given the unexpected discovery of superconductivity in this system, there has been considerable discussion as to the role of the Tl impurities.

Thallium is one of several elements known to skip valences, such that only  $\text{Tl}^{1+}$  and  $\text{Tl}^{3+}$  are observed in ionic compounds, corresponding to electron configurations  $6s^2$  and  $6s^0$  respectively. Compounds that one would otherwise expect to contain divalent Tl are found to disproportionate. For example,  $\text{TlBr}_2$  is more specifically  $\text{Tl}^+\text{Tl}^{3+}\text{Br}_4$ , and  $\text{TlS}$  is likewise  $\text{Tl}^+\text{Tl}^{3+}\text{S}_2$  [7]. This effect is driven by the stability of a filled shell in conjunction with the polarizability of the material [8]. In this case,  $\text{Tl}^{2+}$  can be characterized by a negative effective  $U$ , where  $U_n = (E_{n+1} - E_n) - (E_n - E_{n-1}) < 0$  and  $n$  labels the valence state [8-10]. As discussed in subsequent sections, there is considerable evidence from both thermodynamic and transport measurements that Tl impurities in PbTe can indeed be characterized by a negative effective  $U$ , and that for concentrations beyond a critical value are present as both  $\text{Tl}^+$  and  $\text{Tl}^{3+}$ ; i.e. as a mixed valence. Is it possible that quantum valence fluctuations associated with these Tl ions provide the pairing interaction that leads to superconductivity in this material?

To examine this question we have performed a systematic study of the normal state properties of single crystals of Tl-doped PbTe. We find that a critical concentration of Tl impurities ( $x_c$ ) is required for superconductivity in this system. For lower Tl concentrations the impurities act as acceptors ( $\text{Tl}^{1+}$ ), but for  $x > x_c$  additional Tl impurities appear to act in a self-compensating manner, indicating that they are present as a mixed valence ( $\text{Tl}^{1+}$  and  $\text{Tl}^{3+}$ ). Furthermore, all

superconducting samples up to the solubility limit ( $x_c < x < 1.5\%$ ) exhibit an anomalous low-temperature upturn in the resistivity, whereas non-superconducting samples ( $x < x_c$ ) do not. The temperature and field dependence of this resistivity anomaly are consistent with a charge Kondo effect – that is, a Kondo effect arising from the interaction of the conduction electrons with the two degenerate valence states of the Tl impurities. This observation directly attests to a fluctuating Tl valence, and as such implies that quantum valence fluctuations may indeed play a role in the superconductivity of Tl-doped PbTe. These results recently appeared in ref [11] – here we amplify our basic arguments and present further supporting data. The theoretical model for superconductivity in charge Kondo systems, and particularly worked out for the case of Tl-doped PbTe, can be found in ref [12].

## 2. EXPERIMENTAL METHODS

Single crystals of  $\text{Pb}_{1-x}\text{Tl}_x\text{Te}$  were grown by an unseeded physical vapor transport method with Tl concentrations up to the solubility limit  $x \sim 1.5\%$ . Samples were prepared using two different Tl sources to check for extrinsic impurity effects:  $\text{Tl}_2\text{Te}$  and elemental Tl. Each vapor growth produced several well-formed crystals up to a few millimeters in size that could be cut and cleaved to prepare bars for thermodynamic and transport measurements. The thallium content was measured by Electron Microprobe Analysis (EMPA) using PbS, Te, and  $\text{Tl}_2\text{Te}$  standards.

Electrical contact was made to transport bars using Epotek H20E silver epoxy on sputtered or evaporated gold pads, with typical contact resistances of 1-4  $\Omega$ . Resistivity measurements were made at 16 Hz and with current densities in the range of 25  $\text{mA}/\text{cm}^2$  (corresponding to a current of 10  $\mu\text{A}$  for low-temperature measurements) to 1  $\text{A}/\text{cm}^2$  at higher temperatures. To check for heating effects, resistivity data were taken for different current densities and for warming and cooling cycles for each sample. Several samples were measured for each Tl concentration to increase confidence in absolute values of the resistivity. Magnetization measurements were made for larger crystals in an applied field of 1000 Oe using a commercial Quantum Design SQUID magnetometer.

## 3. RESULTS

Representative resistivity data showing sharp superconducting transitions for various Tl concentrations are shown in panel (a) of Figure 1.  $T_c$  values estimated from the midpoints of these transitions are shown as a function of Tl concentration in panel (b). These data agree well with values obtained from heat capacity measurements of crystals taken from the same growth batches [13] and, for the higher Tl concentrations, with published data for polycrystalline samples [14] and for thin films [15]. Significantly, by measuring  $T_c$  for the lowest Tl concentrations, we find that there is a critical concentration  $x_c \sim 0.3\%$  below which the material does not superconduct above 20 mK (our base temperature).

The temperature dependence of the normal-state resistivity of the Tl-doped crystals is shown on an expanded scale for temperatures below 10 K in Figure 2 (for  $x < x_c$ ) and Figure 3 (for  $x > x_c$ ). Data for the non-superconducting samples do not show a resistivity upturn at low temperatures (the sample with  $x = 0$  is metallic due to a small concentration of Pb vacancies). However, for  $x > x_c$  the resistivity shows a distinct upturn for temperatures below approximately 9 K, which appears to scale in magnitude with the Tl concentration, and follows a form characteristic of the Kondo effect. These results were repeated using two different Tl sources to rule out extrinsic impurity effects. Similar results were observed previously by Andronik and co-workers for temperatures above 4.2 K for a smaller subset of two Tl concentrations [16]. A crude estimate for the magnitude of this effect, neglecting any additional temperature dependence below 10 K, can be made from the quantity  $\rho_0 - \rho_{min}$ , where  $\rho_0$  is the residual resistivity measured at our lowest temperatures and  $\rho_{min}$  is the value of the resistivity at the resistance minimum. As shown in Figure 4, for  $x > x_c$  this quantity scales approximately linearly with the Tl concentration  $x$ . Insets to Figures 3(c) and 3(d) show the resistivity as a function of  $T^2$  for the two lowest Tl contents that superconduct,  $x = 0.3$  and  $0.4\%$ , for which  $T_c$  is less than 0.3 K. The resistivity clearly follows a  $T^2$  temperature dependence, as expected for Kondo-like behavior, for temperatures below approximately 4 K.

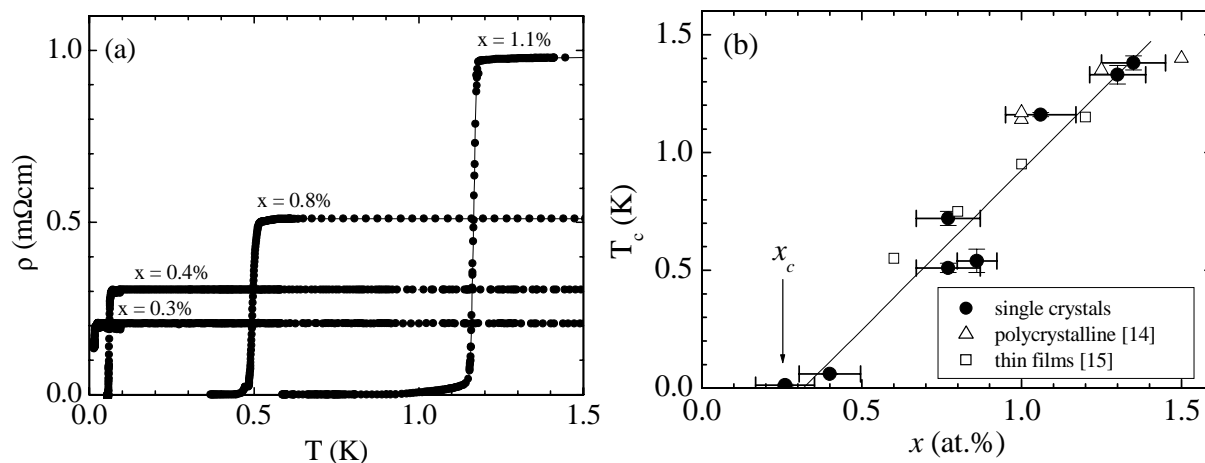


Figure 1: (a) Representative resistivity data as a function of temperature for superconducting samples of  $\text{Pb}_{1-x}\text{Tl}_x\text{Te}$  (i.e.  $x > x_c$ ) showing the superconducting transition. (b) Variation of  $T_c$  with  $x$ . Line shows linear fit. Arrow indicates the critical concentration,  $x_c$ .

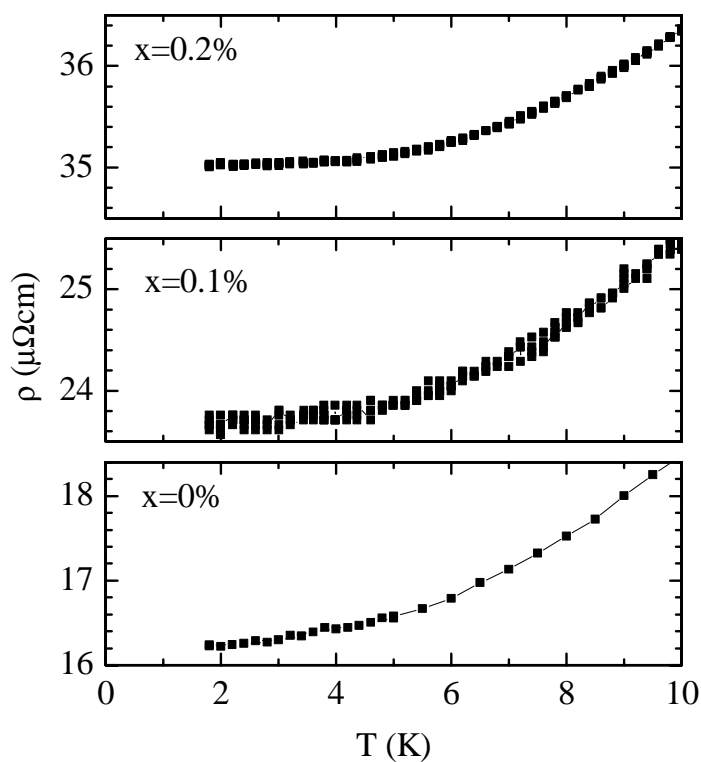


Figure 2: Low temperature resistivity of  $\text{Pb}_{1-x}\text{Tl}_x\text{Te}$  for  $x = 0, 0.1$  and  $0.2\%$  (i.e.  $x < x_c$ ).

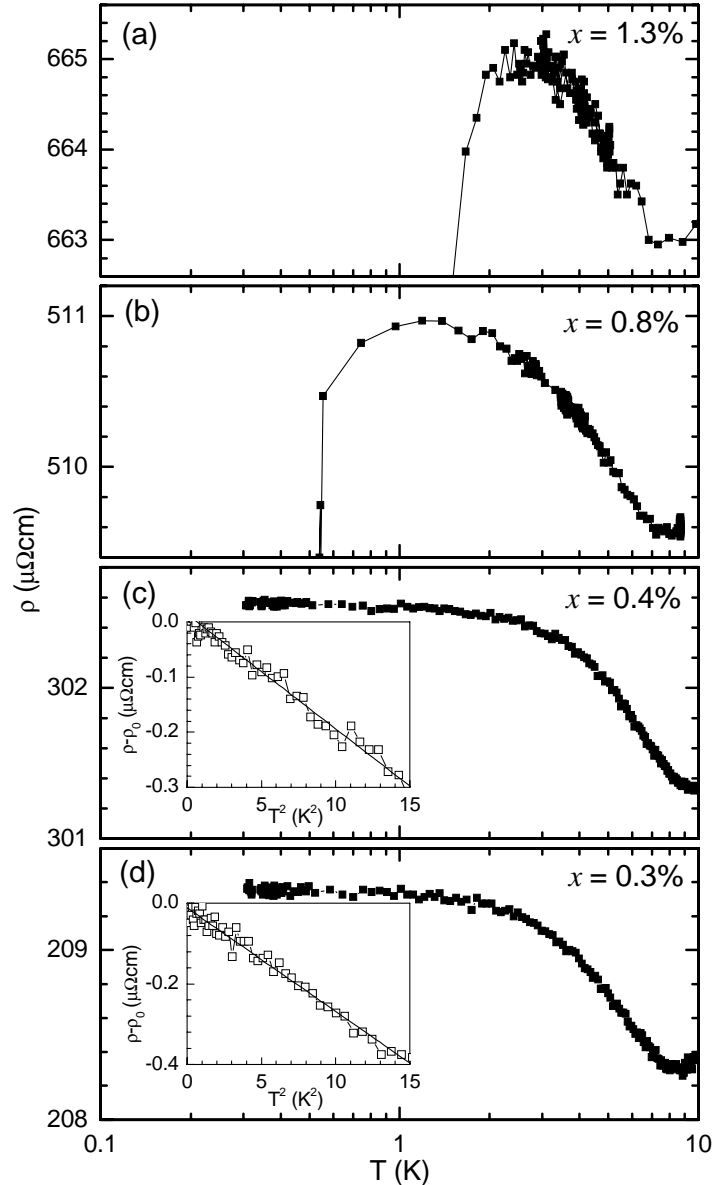


Figure 3: Low temperature resistivity of  $\text{Pb}_{1-x}\text{Tl}_x\text{Te}$  for  $x = 0.3, 0.4, 0.8$  and  $1.3\%$  (i.e.  $x > x_c$ ). Insets to panels (c) and (d) show  $T^2$  behavior at low temperatures for the smallest Tl concentrations.

The transverse magnetoresistance of the Tl-doped PbTe is shown in Figure 5 for the case of  $x = 0.4\%$  (representative of the lower Tl concentrations that superconduct). The magnetoresistance is positive and follows a  $B^2$  field dependence. The  $B^2$  coefficient does not appear to have a strong temperature dependence, and indeed the temperature dependence of the resistivity in our largest applied field (5 T) is identical to that in zero field, shifted to a higher value.

The susceptibility for representative Tl-containing samples is shown in Figure 6. The susceptibility is diamagnetic, with a weak temperature dependence that has previously been attributed to the temperature dependence of both the band gap and effective mass of PbTe [17]. The susceptibility becomes less diamagnetic with increasing Tl concentration, presumably due to an increased density of states. Significantly, the lack of a Curie-like paramagnetic contribution is consistent with the absence of divalent Tl (corresponding to  $6s^1$ ) and magnetic impurities down to  $< 5$  ppm, limited by the resolution of the measurement.

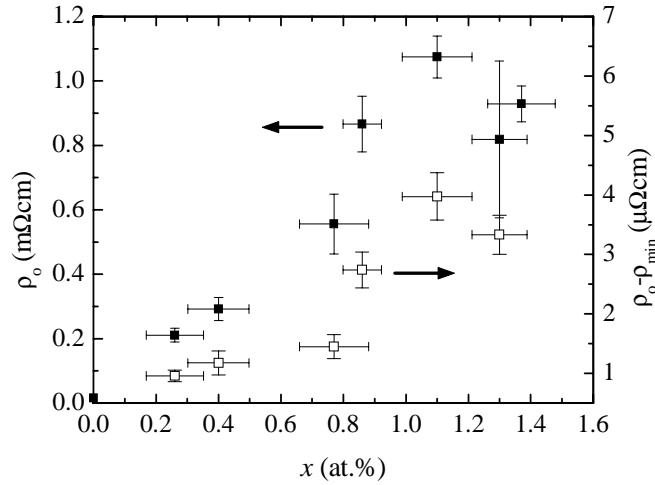


Figure 4: Residual resistivity  $\rho_0$  (left axis, solid symbols) and  $\rho_0 - \rho_{\min}$  (right axis, open symbols) as a function of Tl concentration  $x$ .

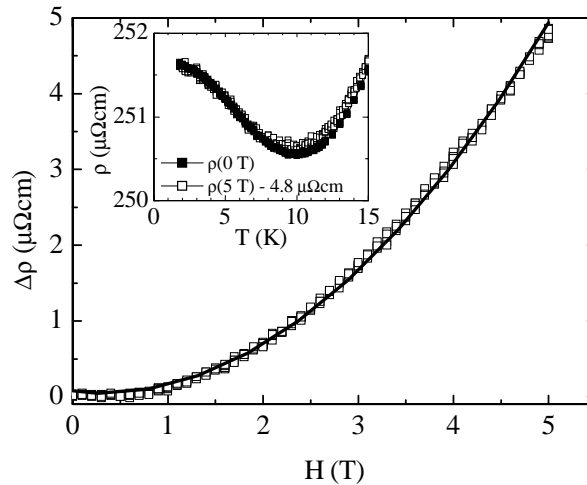


Figure 5: Magnetoresistance  $\Delta\rho = \rho(H) - \rho(H = 0)$  at 1.8 K for  $x = 0.4\%$ . Inset shows the temperature dependence of the resistivity in fields of 0 and 5 T. The data for 5 T have been shifted down by  $\rho_0(5\text{ T}) - \rho_0(0\text{ T})$ .

#### 4. DISCUSSION

Our results show that superconductivity in Tl-doped PbTe requires a critical concentration of Tl impurities,  $x_c$ . Associated with the superconductivity we find an anomalous upturn in the resistivity at low temperatures. Non-superconducting samples ( $x < x_c$ ) do not show this effect. For the lowest Tl concentrations that cause superconductivity ( $x = 0.3\%$  and  $0.4\%$ ) this upturn is reminiscent of the Kondo effect, even following a  $T^2$  behavior at the lowest temperatures. For higher Tl concentrations the onset of superconductivity masks the normal state temperature dependence. It is likely that this unusual normal state behavior is intimately linked to the occurrence of superconductivity in Tl-doped PbTe. Here we discuss the origin of the resistivity anomaly, and make the case that it is due to a charge Kondo effect associated with degenerate valence states of the Tl impurities. This effect, which emerges naturally from a negative- $U$  model, has previously been predicted [18] but to date has not been observed in a bulk material.

Usually the Kondo effect is associated with dilute magnetic impurities in a non-magnetic host. Given the remarkable resemblance of the measured resistivity to such magnetic Kondo systems, we have been very careful to rule out the possibility of magnetic impurities in these samples. We can be confident of this for the following reasons. First, the magnetic susceptibility clearly shows that there are no magnetic impurities down to a 5 ppm level for all Tl concentrations, limited only by the resolution of the measurement. Second, the magnitude of the resistivity upturn scales with the amount of Tl (Figure 4), so if it is an impurity effect then it is clearly associated with the Tl source, but we observe exactly the same resistivity upturn for crystals prepared using two very different Tl sources (elemental Tl and  $\text{Tl}_2\text{Te}$ , as described in the experimental methods section). Third, crystals grown using the same Tl sources but with  $x < x_c$  do not have a resistivity upturn (Figure 2). And finally, the magnetoresistance for the lower Tl concentrations with  $x > x_c$  is substantial and positive (Figure 5), whereas one would expect a significant negative contribution if the upturn were due to magnetic impurities. Our resistivity data, therefore, have a temperature dependence that is reminiscent of the Kondo effect, but in the absence of discernible magnetic impurities. We will go on to suggest that this behavior is due to a charge Kondo effect associated with the Tl impurities. First, we address the possibilities that the anomaly is due to either localization or a structural effect.

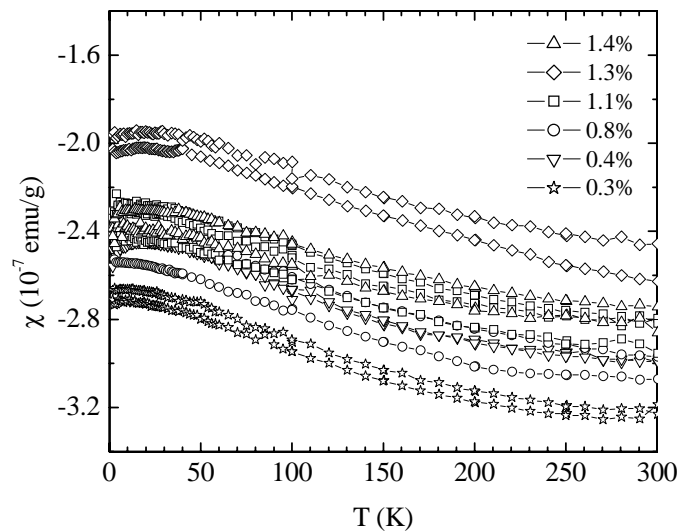


Figure 6: Temperature dependence of the susceptibility for representative Tl concentrations, in an applied field of 1000 Oe.

Thallium impurities cause a rapid increase in residual resistivity of PbTe, characterized by approximately  $0.8 \text{ m}\Omega\text{cm}$  per at.% Tl, as shown in Figure 4. Taking  $x = 0.4 \%$  as representative of the lower Tl content samples, and assuming that the Tl impurities do not substantially alter the band structure of PbTe [3,4], the measured hole concentration of  $7 \times 10^{19} \text{ cm}^{-3}$  (from Hall effect measurements) implies that there are holes in both the light and heavy bands located at the  $L$  and  $\Sigma$  points in the Brillouin zone, and that the Fermi level lies approximately 180 meV below the top of the valence band. This allows an estimate of the Fermi velocity, which has an average value of  $10^6 \text{ m/s}$  for holes in the anisotropic  $L$  pockets and  $10^5 \text{ m/s}$  for holes in the heavier  $\Sigma$  pockets. Based on these estimates, the mean free path  $l$  is relatively large at around  $130 \text{ \AA}$ . Resulting values of  $k_F l$  are also large, being approximately 7 for  $x = 0.4\%$  and falling to approximately 2 for the highest Tl concentrations. It is therefore very unlikely that the low-temperature upturn in resistivity is due to localization effects, at least for the lowest Tl concentrations. Furthermore, the observed  $T^2$  temperature dependence of the resistivity is not readily identified with such a scenario.

Previously, a low-temperature resistivity upturn has been observed for Ge-doped PbTe [19, 20]. In that case, Ge concentrations above  $x = 0.5 \%$  lead to a structural phase transition, and it was suggested that the resistivity anomaly might be related to the small  $\text{Ge}^{2+}$  ions tunneling between degenerate sites (i.e. a Kondo-like effect arising from atomic motion [21]). Although we cannot completely rule out such a scenario for Tl-doped PbTe (and indeed it would be rather interesting if it were to be the case, especially with regard to the concomitant observation of superconductivity) nevertheless it seems unlikely for the following reasons. Firstly, Tl substitution in PbTe does not lead to a structural

phase transition, even for the highest Tl concentrations; secondly, the  $\text{Tl}^{1+}$  and  $\text{Tl}^{3+}$  ions are significantly larger than the  $\text{Ge}^{2+}$  ion thought to be responsible for the tunneling two level system; thirdly, other group III elements known to disproportionate when substituted in PbTe and which have even smaller ionic radii than Tl (specifically Ga and In) also do not cause such an effect. Nevertheless, is it possible that the superconductivity itself derives from proximity to a structural phase transition? Earlier reports of experiments investigating co-substitution of Tl-doped PbTe with small amounts of Ge, such as to cause further softening of the optic phonon without actually resulting in a structural phase transition, indicated that  $T_c$  is rapidly suppressed by even small amounts of Ge [22], which would argue against such a scenario.

Thallium substitutes on the Pb site in PbTe. Calculations by Weiser [1] indicate that  $\text{Tl}^{1+}$  has a lower energy than  $\text{Tl}^{3+}$  in the lattice. Tl impurities therefore initially act as acceptors, adding one hole per Tl to the valence band, as observed in Hall measurements [6]. However, the calculated energy difference between 1+ and 3+ impurity states, which can be modeled by  $\delta E = 2(\epsilon_0 - \mu) + U$  [12] (where  $\epsilon_0$  is the energy to remove an electron from the 6s orbital and  $U < 0$ ), is very small [1]. Indeed, for a finite concentration of Tl impurities, the chemical potential of holes in the system can reach the special value  $\mu^* = \epsilon_0 + U/2$  for which the two valence states become exactly degenerate ( $\delta E = 0$ ). A value of  $\mu^*$  larger than this would correspond to all of the impurities being 3+. However, additional Tl impurities beyond this critical value cannot increase  $\mu$  beyond  $\mu^*$  because conversion of all of the impurities to  $\text{Tl}^{3+}$  would add electrons to the valence band, which would act to reduce rather than increase  $\mu$ . Therefore, for Tl concentrations beyond a characteristic critical value, the chemical potential remains pinned at the special value  $\mu^*$ , and any additional Tl impurities act in a self-compensating manner such that both valence states are present in equilibrium. That is to say that the Tl impurities act in a very special manner; first doping holes, and then, beyond a certain critical concentration, self-tuning such that 1+ and 3+ valence states are degenerate. This behavior has been confirmed by Hall measurements, which show that for Tl concentrations beyond approximately 0.5% the Hall coefficient saturates to a constant value corresponding to approximately  $10^{20}$  holes per  $\text{cm}^3$  [12, 23]. Significantly, the Tl concentration at which this happens is remarkably close to the concentration  $x_c$  at which we observe the onset of superconductivity (Fig. 1). Furthermore, within such a scenario, it is natural to consider a charge Kondo effect, in which the conduction electrons interact with the two degenerate valence states of the Tl impurities, and pseudo-spin flip processes proceed via virtual excitations to the skipped valence state. In the absence of orbital degeneracy, the Kondo screening would proceed via a single channel, so the observation of a resistivity anomaly following a  $T^2$  dependence at low temperatures is strong evidence for such a state.

If we associate the observed resistivity upturn of Tl-doped PbTe with a Kondo-like mechanism, then we can estimate the characteristic Kondo temperature by fitting the data in the insets to Figures 3c and 3d to  $\rho_{\text{imp}}(T) \sim \rho_{\text{imp}}(0)[1-(T/T_K)^2]$  where  $\rho_{\text{imp}}(0)$  is the impurity contribution to the resistivity at  $T=0$ , approximated from the measured values of  $\rho_0 - \rho_{\text{min}}$ . This results in a value of  $T_K \sim 6$  K, with considerable uncertainty due to the crude estimate of  $\rho_{\text{imp}}(0)$ . Heat capacity measurements involving Na counter-doping allow an estimate for the range of  $\mu^*$  values for Tl impurities in PbTe, which is characterized by a width of 30 meV [6]. Assuming a Gaussian distribution of values of  $\mu^*$  centered at 200 meV and with a full width at half maximum of 30 meV, the fraction of Tl impurities for which the two valence states will be degenerate to within  $T_K = 6$  K is approximately 1%, corresponding to a concentration of  $6 \times 10^{17} \text{ cm}^{-3}$ .

From the saturation value of the resistivity we are able to obtain an estimate of the concentration of Kondo impurities  $c_{\text{imp}}$  using the relation for unitary scattering [24],  $\rho_{\text{imp}}(0) = 2mc_{\text{imp}} / (ne^2\pi\hbar g(E_F))$ , where  $n$  is the measured hole concentration ( $7 \times 10^{19} \text{ cm}^{-3}$  for  $x = 0.4$  %) and  $g(E_F)$  is the density of states at the Fermi level (estimated from the band structure to be 1.4 states/eV/unit cell). We use the effective mass of the  $\Sigma$  band states ( $m \sim 0.6 m_0$ ) since this band contributes the majority of the density of states. The resulting estimated concentration of Kondo impurities of  $c_{\text{imp}} \sim 2 \times 10^{17} \text{ cm}^{-3}$  is consistent with the estimated concentration of Tl impurities for which the two valence states are degenerate, within the uncertainty.

The data presented here and in ref [11] are compelling evidence for charge-Kondo behavior, but nevertheless do not constitute a “smoking gun”. Further experiments are in progress to directly and indirectly probe the valence of the Tl impurities in this material. However, if we are correct then this is dramatic evidence that for concentrations beyond  $x_c$  Tl impurities in PbTe behave as a dynamic mixed valence. Such impurities can naturally act as pairing centers for superconductivity, as previously envisaged in refs [12, 25-27], possibly accounting for the unexpected observation of superconductivity with such a high  $T_c$  in this system.

## 5. CONCLUSIONS

In summary, we have measured the resistivity, magnetoresistance, and susceptibility of single crystals of Tl-doped PbTe,  $\text{Pb}_{1-x}\text{Tl}_x\text{Te}$ , in the range  $0 < x < 1.5\%$ . We find that a critical concentration of Tl impurities,  $x_c \sim 0.3\%$ , is required for superconductivity. For concentrations  $x > x_c$  the resistivity has an anomalous upturn below approximately 8 K, which scales in magnitude with the Tl concentration and has a temperature dependence that is consistent with the Kondo effect. We have demonstrated that this behavior does not arise from magnetic impurities, and estimates of  $k_F l$  indicate that the effect is unlikely to be a manifestation of localization, at least for the lower Tl concentrations. Given the valence-skipping nature of thallium, and given that Tl impurities are known to pin the Fermi level in PbTe, these data are compelling evidence for charge Kondo behavior associated with degenerate valence states of the impurities. The effect, which is a unique property of the negative- $U$  Anderson model, has been predicted theoretically but to date has not been observed. It appears that PbTe is an ideal host for this effect for two reasons. Firstly, the special value of the chemical potential for which the two valence states are degenerate is accessible for relatively small Tl concentrations. This is likely a consequence of the requirement of charge balance upon doping Tl impurities into the largely ionic  $\text{Pb}^{2+}\text{Te}^{2-}$  host. Secondly, the large high-frequency dielectric constant of PbTe, approximately 30-40 [6], presumably plays a role in enabling rapid, adiabatic tunneling of pairs of electrons on and off impurity sites, avoiding self-trapping. Most importantly, the observation of charge Kondo behavior directly attests to an electronic pairing mechanism for superconductivity in Tl-doped PbTe, potentially accounting for the anomalously high  $T_c$  value of this material. Valence skipping elements are common in many other materials of current interest. Although it is difficult to predict with any certainty whether one would anticipate a dynamically fluctuating valence in a particular case, nevertheless our results do seem to motivate a reexamination of the valence states of heavy metal ions in a number of systems, including the charge reservoir layers of high- $T_c$  cuprates.

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