P H Y S I C A L   R E V I E W   L E T T E R S

Evidence for Charge Kondo Effect in Superconducting Tl-Doped PbTe

Y. Matsushita,[1] H. Bluhm,[2] T. H. Geballe,[3] and I. R. Fisher[3]

[1]*Department of Materials Science and Engineering and Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California 94305-4045, USA*
[2]*Department of Physics and Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California 94305-4045, USA*
[3]*Department of Applied Physics and Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California 94305-4045, USA*

We report results of low-temperature thermodynamic and transport measurements of $Pb_{1-x}Tl_xTe$ single crystals for Tl concentrations up to the solubility limit of approximately $x = 1.5\%$. For all doped samples, we observe a low-temperature resistivity upturn that scales in magnitude with the Tl concentration. The temperature and field dependence of this 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.

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The Kondo effect arises from the interaction of conduction electrons with degenerate degrees of freedom in a material and is usually associated with dilute magnetic impurities in a nonmagnetic host. In such cases, the two degenerate states correspond to the impurity spins oriented up or down. Second order scattering processes involving virtual intermediate states lead to the well-known logarithmic increase in resistivity at low temperatures, which saturates in the unitary scattering limit below a characteristic Kondo temperature [1]. However, other systems comprising two degenerate degrees of freedom can also lead to Kondo-like phenomena [2]. In particular, a "charge Kondo effect," corresponding to dilute impurities with two degenerate charge states, has been proposed in the negative-U Anderson model [3], though to date there has not been an experimental realization of such an effect. Significantly, the quantum valence fluctuations implicit in such a model, which involve pairs of electrons that tunnel on and off impurity sites, also provide an electronic pairing mechanism for superconductivity [4–7].

Thallium is one of several elements that is known to skip valences, such that only Tl^{1+} and 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, $TlBr_2$ is more specifically $Tl^ITl^{III}Br_4$, and TlS is likewise $Tl^ITl^{III}S_2$ [8]. This effect is driven by the stability of a filled shell in conjunction with the polarizability of the material. In this case, 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 [9–11]. For this reason, valence-skipping elements provide experimental access to negative-U behavior and are therefore suitable candidate impurities for realizing a charge Kondo effect in a bulk material.

In this Letter we describe measurements of PbTe doped with small amounts of Tl. The material exhibits a Kondo-like upturn in the resistivity in the absence of magnetic impurities and superconducts at low temperatures. We make the case that this behavior originates from a charge Kondo effect involving degenerate valence states of the Tl impurities. This is the first evidence for such an effect and is especially significant in substantiating claims that the superconducting pairing mechanism in Tl-doped PbTe derives principally from negative-U effects.

PbTe is a small gap semiconductor. It has a rocksalt structure and has been treated with reasonable success using ionic models (i.e., $Pb^{2+}Te^{2-}$) [12]. The material can be doped to degeneracy by either vacancies or third-element dopants, with typical carrier concentrations in the range of $10^{18}–10^{20}$ cm^{-3} [13–15]. 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 [16]. This has been found to be the case for all dopants except thallium, for which superconductivity was observed with critical temperatures up to 1.5 K [17], 2 orders of magnitude higher than anticipated given the modest carrier concentrations. Given the anomalously high T_c values for Tl-doped PbTe, there has been considerable discussion as to the role of the Tl impurities in this material, whether they act as negative-U centers, and specifically whether such impurities can enhance an incipient tendency towards superconductivity [4–6,18,19].

Single crystals of $Pb_{1-x}Tl_xTe$ were grown by an unseeded physical vapor transport method as described elsewhere [20]. The thallium content was measured by electron microprobe analysis (EMPA). Resistivity measurements were made at 77 Hz and with current densities in the range of 25 mA/cm^2 (corresponding to a current of 10 μA for low-temperature measurements) to 1 A/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.

T_c values estimated from the midpoints of superconducting transitions in the resistivity are shown as a function of Tl concentration in Fig. 1 and agree with published data for polycrystalline samples [21] and for thin films [22] for high Tl concentrations. By measuring T_c for the lowest Tl concentrations, we find that there is a critical concentration of ~0.3% below which the material does not superconduct above 20 mK. The inset to Fig. 1 shows the sharp resistive transitions for representative samples.

The temperature dependence of the normal-state resistivity of the Tl-doped crystals is shown on an expanded scale in Fig. 2 for temperatures below 10 K. The resistivity shows a distinct upturn for temperatures below approximately 9 K, following a form characteristic of the Kondo effect. Similar results were observed previously by Andronik and co-workers for temperatures above 4.2 K for a smaller subset of two Tl concentrations [23]. 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 ρ_0 is the residual resistivity measured at our lowest temperatures and ρ_{min} is the value of the resistivity at the resistance minimum. As shown in the inset to Fig. 2(a), this quantity scales approximately linearly with the Tl concentration x. Insets to Fig. 2(c) and 2(d) show the resistivity as a function of T^2 for the two lowest Tl contents, $x = 0.3$ 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. In the following paragraphs we argue that this behavior originates from a charge Kondo effect associated with degenerate valence states of the Tl impurities. First we demonstrate that the behavior is not due to localization or electron-electron effects.
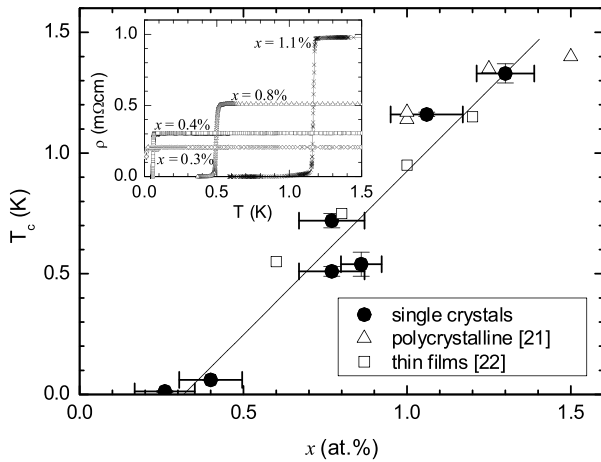
Thallium impurities cause a rapid increase in residual resistivity of PbTe, characterized by approximately 0.8 mΩ cm per at.% Tl, as shown in the inset to Fig. 2(a). Taking $x = 0.4\%$ as representative, and assuming that the Tl impurities do not substantially alter the band structure of PbTe [14,15], the measured hole concentration of 7×10^{19} cm^{-3} implies that there are holes in both the light and heavy bands located at the L and Σ 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 m/s for holes in the anisotropic L pockets and 10^5 m/s for holes in the heavier Σ pockets. Based on these estimates, the mean free path l is relatively large at 130 Å. With the large resulting values of $k_F l$, at approximately 7 for $x = 0.4\%$, it is very unlikely that the low-temperature
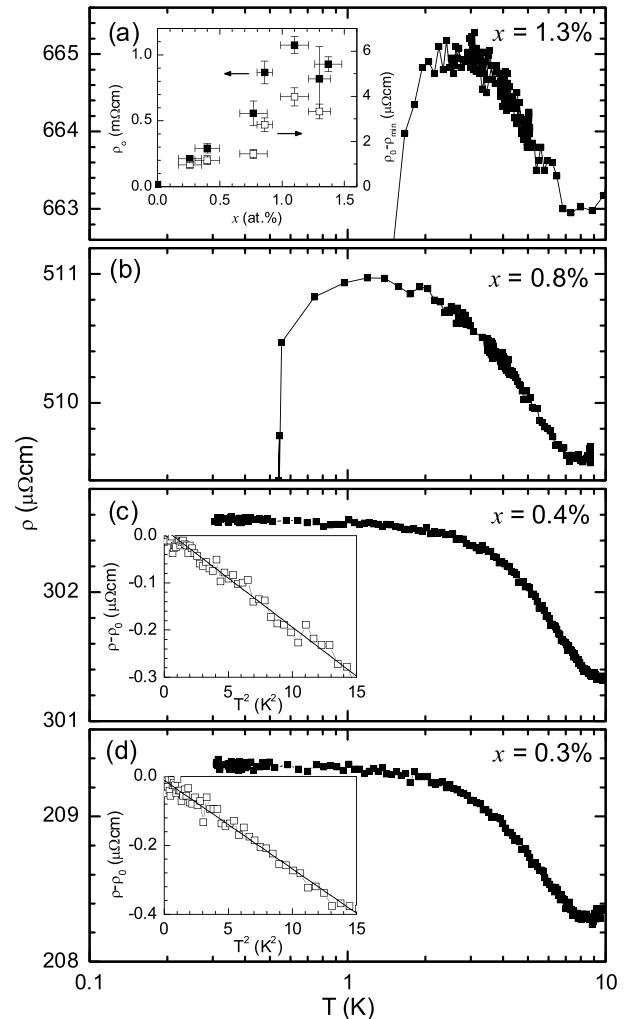

FIG. 2.   Low-temperature resistivity of Pb$_{1-x}$Tl$_x$Te for $x = 0.3$, 0.4, 0.8, and 1.3%. Inset to panel (a) shows residual resistivity ρ_0 (left axis, solid symbols) and $\rho_0 - \rho_{min}$ (right axis, open symbols) as a function of x. Insets to (c) and (d) show T^2 behavior at low temperatures for the smallest Tl concentrations.

FIG. 1.   Variation of T_c with Tl content x for Pb$_{1-x}$Tl$_x$Te. Line shows linear fit. Inset shows representative resistivity data for single crystals.

upturn in resistivity is due to localization effects. Furthermore, the observed T^2 temperature dependence of the resistivity is not readily identified with such a scenario.

To further probe the origin of the normal-state resistivity anomaly, the transverse magnetoresistance of the samples was measured, taking care to avoid spurious Hall contributions. Representative data for $x = 0.4\%$ are shown in Fig. 3. In all cases, the magnetoresistance is positive, following a B^2 dependence for temperatures above T_c or fields above H_{c2}. Furthermore, the overall temperature dependence of the resistivity shows the same Kondo-like upturn even in an applied field (upper inset to Fig. 3) and is presumably shifted to a higher value due to a standard Kohler's rule type magnetoresistance. This behavior is consistent with the absence of both electron-electron effects and weak localization, which, even in the presence of strong spin-orbit scattering, would cause a $B^{1/2}$ field dependence at high fields. Furthermore, this behavior precludes a magnetic Kondo effect as the origin of the resistivity anomaly, for which a field of 5 T would cause a substantial negative magnetoresistance.

To verify the absence of magnetic impurities, susceptibility measurements for several samples of each Tl concentration were made for arbitrary crystal orientations in an applied field of 1000 Oe using a commercial quantum design SQUID magnetometer. Representative data are shown in the lower inset to Fig. 3 as a function of temperature. The susceptibility is diamagnetic for all Tl concentrations due to the small density of states and becomes less diamagnetic with increasing hole concentration. The weak temperature dependence arises from a temperature dependence of both the band gap and effective mass of PbTe [24]. Significantly, the lack of a Curie-like paramag-

netic term from the Tl dopants is consistent with the absence of magnetic impurities down to <5 ppm, limited by the resolution of the measurement. Hence, the low-temperature upturn in the resistivity of Tl-doped PbTe follows a temperature dependence characteristic of the Kondo effect in the absence of magnetic impurities.

Thallium substitutes on the Pb site in PbTe. Calculations by Weiser [12] indicate that Tl^{1+} has a lower energy than 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 [17]. However, the calculated energy difference between $1+$ and $3+$ impurity states, which can be modeled by $\delta E = 2(\epsilon_0 - \mu) + U$ [4] (where ϵ_0 is the energy to remove an electron from the $6s$ orbital and $U < 0$), is very small [12]. 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 μ larger than this would correspond to all of the impurities being $3+$. However, additional Tl impurities beyond this critical value cannot increase μ beyond μ^* because conversion of all of the impurities to Tl^{3+} would add electrons to the valence band, which would act to reduce rather than increase μ. Therefore, for Tl concentrations beyond a characteristic critical value, the chemical potential remains pinned at the special value μ^*, and any additional Tl impurities act in a self-compensating manner such that both valence states are present in equilibrium. 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 cm^3 [4,25]. Significantly, the Tl concentration at which this happens is remarkably close to the concentration 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 pseudospin 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 Fig. 2(c) and 2(d) to $\rho_{imp} \sim \rho_{imp}(0) \times [1 - (\frac{T}{T_K})^2]$ where $\rho_{imp}(0)$ is the impurity contribution to the resistivity at $T = 0$, approximated from the measured values of $\rho_0 - \rho_{min}$. This results in a value of $T_K \sim 6$ K, with considerable uncertainty due to the crude estimate of $\rho_{imp}(0)$. Heat capacity measurements involving Na counterdoping allow an estimate for the range of μ^* values for
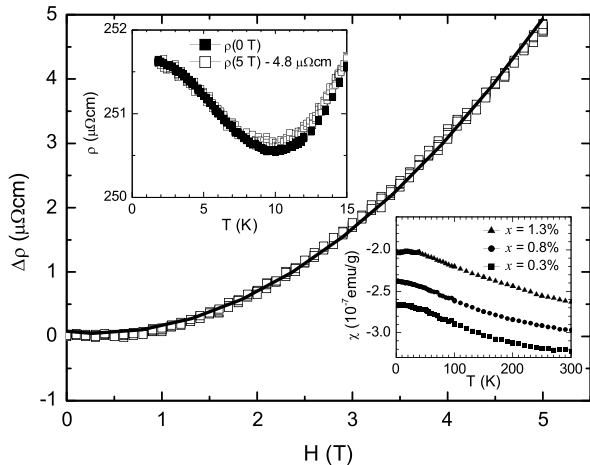

FIG. 3. Representative magnetoresistance, $\Delta\rho = \rho(H) - \rho(H = 0)$, for $x = 0.4\%$ at 1.8 K. Upper inset shows temperature dependence of the resistivity in fields of 0 and 5 T. The data for 5 T have been shifted down by $\rho_0(5\ T) - \rho_0(0\ T) = 4.8\ \mu\Omega$ cm. Lower inset shows temperature dependence of susceptibility for different Tl concentrations.

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Tl impurities in PbTe, which is characterized by a width of 30 meV [17]. Assuming a Gaussian distribution of values of μ^* 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 6×10^{17} cm^{-3}.

From the saturation value of the resistivity we are able to obtain an estimate of the concentration of Kondo impurities c_{imp} using the relation for unitary scattering [1], $\rho_{imp}(0) = 2mc_{imp}/[ne^2\pi\hbar g(E_F)]$, where n is the measured hole concentration (7×10^{19} 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 Σ band states ($m \sim 0.6m_0$) since this band contributes the majority of the density of states. The resulting estimated concentration of Kondo impurities of $c_{imp} \sim 2 \times 10^{17}$ cm^{-3} is consistent with the estimated concentration of Tl impurities for which the two valence states are degenerate, within the uncertainty.

In summary, we have measured the resistivity, magnetoresistance, and susceptibility of single crystals of Tl-doped PbTe, Pb$_{1-x}$Tl$_x$Te, in the range $0.3 < x < 1.5\%$. We observe an anomalous low-temperature upturn in the resistivity that scales in magnitude with the Tl concentration, with a temperature dependence that is consistent with the Kondo effect. We have demonstrated that this behavior does not arise from either magnetic impurities or from localization effects. 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 Pb^{2+}Te^{2-} host. Secondly, the large high-frequency dielectric constant of PbTe, approximately $30-40$ [17], presumably enables rapid, adiabatic tunneling of pairs of electrons on and off impurity sites. Most importantly, the observation of charge Kondo behavior directly attests to an electronic pairing mechanism for superconductivity in Tl-doped PbTe, which potentially accounts for the anomalously high T_c value of this material.

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