Correlation of anomalous normal state properties with superconductivity in $Pb_{1-x-y}Tl_xIn_yTe$

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Recent evidence for a charge-Kondo effect in superconducting samples of $Pb_{1-x}Tl_xTe$ has brought renewed attention to the possibility of negative U superconductivity in this material, associated with valence fluctuations on the Tl impurity sites. Here, we use indium as an electron donor to counterdope $Pb_{.99}Tl_{.01}Te$ and study the effect of changing the chemical potential on the Kondo-type physics and the superconductivity. We find a clear correlation between these two effects, providing further evidence that both are induced by the same source, as anticipated in the charge-Kondo model.

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I. INTRODUCTION

When doped with more than $x_c=0.3\%$ T1 atoms, the degenerate semiconductor $Pb_{1-x}Tl_xTe$ superconducts,[1] with T_c reaching 1.4 K at the solubility limit, $x=1.4\%$,[2,3] an order of magnitude higher than other materials of similarly low hole concentration, $n_H \sim 10^{19}-10^{20}$ cm^{-3}.[4] Thallium is the only element known to induce superconductivity in this host, though it can be tuned to similar carrier concentrations with other dopants.[5] For Tl concentrations for which superconductivity is observed, a low-temperature resistance upturn is also found, with a temperature dependence consistent with the Kondo effect. Initial estimates of the Kondo temperature based on the low-T resistivity gave $T_K \sim 6$ K (Ref. 1) but more recent thermopower measurements yield higher estimates closer to 50 K.[6] Magnetic impurities were ruled out as the source of this effect based on susceptibility measurements.[1] Significantly, Tl is a valence-skipping element, preferring +3 and +1 filled-shell valence states to the $6s^1$ configuration of the +2 valence state.[7] Measurements of the Hall coefficient have shown that, for low Tl concentrations, Tl impurities in PbTe have a +1 formal valence, doping holes and moving the chemical potential deeper into the valence band.[2,8] When the Tl concentration is increased beyond the critical value for superconductivity, $x_c=0.3\%$, the Hall number is found to vary much less rapidly with x, indicating a pinning of the Fermi level and an average Tl valence of +2 for the additional dopants. Due to the valence skipping nature of Tl, a mixed-valence state is likely for $x > x_c$.[9] Results from preliminary core-level photoemission spectroscopy are consistent with this expectation.[10]

Valence skipping impurities can be described by a Hubbard model with a negative value of the parameter, U, the charging energy for having two electrons on the same impurity site,[7,11] and indeed Tl impurities in PbTe have been described in this manner by a number of authors.[9,12–14] If one allows the quasilocal impurity states to interact with the valence band of the host, the resulting model must be formulated in the grand canonical ensemble, in which case it is easy to see that the energy difference between the empty shell Tl^{+3} and the filled-shell Tl^{+} state depends on the chemical potential, μ.[13,14] If the energy difference between these two states is small, it may be possible to adjust the chemical potential through doping to a particular value, $\mu=\mu_c$, for which the energy difference between these two states vanishes. It has been suggested that this is exactly what happens in Tl-doped PbTe when the Tl concentration reaches x_c.[1,14] For Tl concentrations beyond this value the chemical potential remains pinned at μ_c, yielding a mixture of +1 and +3 valence states,[9] consistent with the Hall data described above.

With degenerate impurity charge states differing by two electrons, pairwise scattering of charge carriers from negative U impurities is strongly favored. The resulting charge fluctuation at the impurity site constitutes a change of the formal valence between the two resonant charge states and can be described in terms of a pseudospin flip in an analogous model to that which describes the traditional Kondo effect associated with dilute magnetic impurities in a metal.[15] In addition to contributing a Kondo-type behavior through the pseudospin flip scattering channel,[12,14,15] which yields an associated resistance minimum and peak in the density of states at the Fermi level, this resonant two-electron scattering can further serve as a mechanism of forming Cooper pairs between valence-band holes, providing a possible realization of negative-U superconductivity. We have previously used this charge-Kondo model to describe the correlation between the onset of superconductivity in Tl-doped PbTe with the associated anomalous low-temperature scattering.[1,14] Here we further test the correlation between these two effects by deliberately tuning the Fermi level for a given Tl concentration by use of an additional counterdopant, indium.

The correlation between chemical potential pinning and superconductivity has previously been studied in the cases of $Pb_{1-x-y}Tl_xLi_yTe$ (Ref. 16) and $Pb_{1-x-y}Tl_xNa_yTe$,[17,18] where Li and Na counterdopants were used to inject additional holes, while keeping a fixed Tl concentration. In those cases, moving the chemical potential away from the critical value, μ_c, resulted in a suppression of T_c,[16,17] consistent with the expectations of the negative-U picture described above. However, the associated anomalous charge-Kondo behavior was not explored in this regime and it remains an outstanding question as to whether the low-T resistivity upturn observed

TABLE I. Composition of $Pb_{1-x-y}Tl_xIn_yTe$ samples used in this study, determined by EMPA measurements. Error bars are standard deviations of 4–6 data points, taken in different locations on two separate samples.

x (at. %)	1.1(2)	1.0(4)	0.7(4)	1.0(2)	1.0(4)	1.0(4)	1.1(4)
y (at. %)	0	0.5(1)	0.8(1)	1.2(1)	1.4(1)	2.1(1)	3.1(1)

for superconducting Tl-doped PbTe is suppressed simultaneously. If this is found to be the case, it would be further evidence for the applicability of the charge-Kondo model to this system, and by extension, for the validity of a negative-U pairing interaction.

Before considering the mixed case of $Pb_{1-x-y}Tl_xIn_yTe$, it is first worth briefly reviewing the behavior of indium impurities in the simpler system $Pb_{1-y}In_yTe$ since In itself is also a valence-skipping element. For very low concentrations, In impurities in PbTe act as a donors, indicating a +3 formal valence. However, the carrier concentration is almost immediately pinned at around 8×10^{18} cm^{-3}, even though the indium concentration can reach up to 20%.[19] This has been explained by the presence of a quasilocal impurity level at an energy of 0.07 eV above the bottom of the conduction band.[20] X-ray photoelectron spectroscopy measurements have revealed a mixed In valence for $0.5\%<y<1.1\%$.[21] The energy of indium impurity levels in $Pb_{1-y}In_yTe$ is independent of indium concentration up to 2% doping, indicating that the radius of s-shell electron wave functions is less than 15 Å.[19] This highly local nature of indium impurity states suggests that hybridization with conduction-band electrons is weak.[19] Thus the charge disproportionation is thought to be static, not resulting in a fluctuating valence state, and indeed superconductivity is not observed in this system. This behavior is, however, intimately linked to the observation of an extremely long-lived photoconductivity; the barrier to recombination of nonequilibrium carriers presumably reflecting the two-electron nature of In traps in this material.[13,22] Hence, it appears that In and Tl impurities in PbTe are two sides of the same coin—both lead to disproportionation for concentrations beyond some critical value but in the case of In one finds a static heterogeneous mixed valence whereas in the case of Tl evidence points toward a dynamically fluctuating homogeneous mixed valence.

In the present case, we use In as a counterdopant to tune the chemical potential in $Pb_{0.99-y}Tl_{0.01}In_yTe$, for a fixed Tl concentration, $x=1.0(3)\%>x_c=0.3\%$. Since the Fermi level is well below the bottom of the conduction band, the indium impurities are anticipated to act as donors so long as $y<x$. In practice, the presence of Pb vacancies, and uncertainty in the actual Tl concentration, means that somewhat higher In concentrations still appear to act as donors, moving the Fermi level first higher in the valence band, and eventually up in to the conduction band. For indium concentrations below a critical value y_c of approximately 1%, the Fermi level appears to be pinned at a value typical for Tl-doped PbTe with $x\geq x_c$, and these samples are found to superconduct. Larger values of the indium concentration result in a suppression of the superconductivity and samples with $y\geq1.2\%$ do not superconduct above 50 mK. This is similar to the action of Na and Li counterdopants[16–18] but in this case In acts as an electron donor rather than Na and Li which are electron acceptors. Significantly, we also find a suppression of the low-temperature resistance upturn, and an increase in the residual resistance ratio, $\text{RRR}=\rho(300K)/\rho(0)$, as y increases beyond y_c, further demonstrating the correlation between superconductivity and the anomalous low-temperature scattering previously attributed to the charge-Kondo effect.[1]

II. EXPERIMENTAL METHODS

Single crystals of $Pb_{1-x-y}Tl_xIn_yTe$ were grown using the same physical vapor-transport method we have described previously.[8] The composition was measured by electron microprobe analysis (EMPA), using PbTe, In metal, and Tl_2Te standards. The results of these measurements are shown in Table I. Relatively large standard deviations for the Tl impurity concentration likely reflect slight inhomogeneity across any given sample. It should be noted, though, that it is difficult to measure such small concentrations of Tl accurately due to a combination of the proximity of strong Pb lines in the collected spectrum and also because the energies of thallium k- and l-shell lines happen to occur toward the edges of the x-ray photodetectors on the EMPA instrument. Thus, the count rate for thallium measurements is abnormally low, even considering the low dopant concentrations, and resulting standard deviations for Tl are particularly high, even when counting time is extended to two minutes. Since each batch was grown independently, it was not possible to maintain exactly equal Tl concentrations throughout the series. However, since all samples were within one standard deviation of the average value $x=1.0\%$, a Tl concentration of $x=1.0(3)\%$ will be assumed in the following analysis. As each sample has Tl concentrations, $x>x_c=0.3\%$ for each data point measured, we can confidently associate any change in the chemical potential away from μ_c to the effect of the additional In atoms. Even so, we can also anticipate some scatter when comparing closely spaced In concentrations.

Bars were cleaved from single crystals for electrical transport measurements. Resistivity data were obtained at frequencies of 13.5, 13.7, or 37 Hz, and current densities along the [100] direction of order 100 mA/cm^2 at temperatures above 1.8 K and 10 mA/cm^2 for data taken below 1.8 K, using a Quantum Design Physical Properties Measurement System (PPMS) system equipped with a He^3 insert. Measurements below 350 mK were performed using a He^3/He^4 dilution refrigerator. Data below 1.8 K were taken at a variety of current densities to check for heating effects. The Hall number at a temperature of 1.8 K was obtained from linear fits to the transverse voltage in fields from −9 to 9 T, aligned along the [001] direction. All electrical contacts were made by sputtering gold contact pads, then fixing platinum wire to the pads using Epotek H20E conductive silver epoxy, with

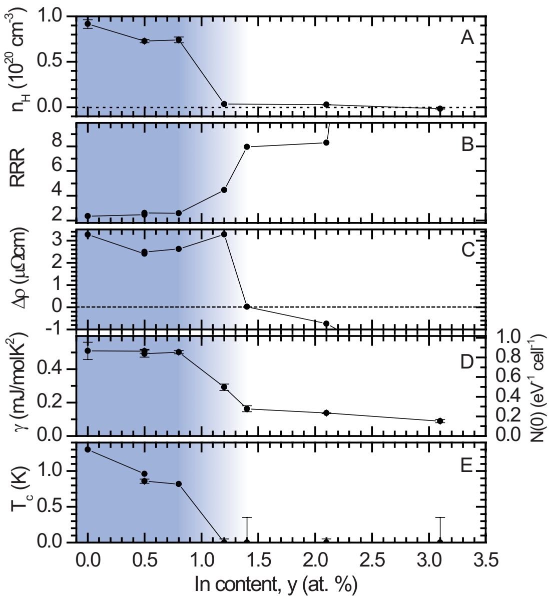

FIG. 1. (Color online) Effect of indium substitution in $Pb_{0.99-y}Tl_{0.01}In_yTe$ as a function of indium content y on (a) the Hall number, n_H; (b) the residual resistance ratio, $\mathrm{RRR}=\rho(300\ \mathrm{K})/\rho(1.8\ \mathrm{K})$; (c) an estimate of the magnitude of the low-temperature resistance upturn, $\Delta\rho=\rho(1.8\ \mathrm{K})-\rho(\mathrm{min})$; (d) the electronic coefficient to the specific heat, γ (left axis), and the corresponding density of states per spin at the Fermi level, $N(0)$ (right axis); and (e) the superconducting critical temperature, T_c, derived from heat-capacity measurements. Lines are drawn between data points as a guide to the eye. The data delineate two distinct regimes. For concentrations $y\leq 0.8\%$ (solid blue shading) samples have a large hole density, superconduct, and exhibit anomalous low-temperature scattering. For concentrations $y\geq 1.4\%$ (no shading) the Fermi level moves steadily up in to the conduction band, the material does not superconduct above 50 mK, and there is no resistivity upturn at low temperature (no shading). Crossover behavior between these two regimes (graded shading for $0.8<y<1.4\%$) is characterized by intermediate values of the RRR and γ.

typical contact resistances between 2 and 5 Ω.

Heat capacity was measured between 0.35 and 5 K on 5–12 mg single crystals using the relaxation method with a Quantum Design PPMS system equipped with a He-3 cryostat. Measurements were made in zero field and in an applied field of 1 T (aligned at an arbitrary angle to the crystal axes) to suppress the superconducting transition. The electronic contribution, γ, was calculated from linear fits to C/T vs T^2, for data taken below 1 K and in an applied field.

III. RESULTS

Although PbTe is a multiband semiconductor, the Hall number, $n_H=1/R_He$, can be used as a reasonable estimate of the carrier concentration because the mobilities of the two valence bands occupied at these carrier concentrations are similar.[8] Values of n_H measured at 1.8 K are shown as a function of y in Fig. 1(A). For In concentrations, $y\leq 0.8\%$, the carrier concentration is near 0.8×10^{20} cm^{-3}, indicating that the chemical potential is pinned at the critical value μ_c, as observed in $Pb_{1-x}Tl_xTe$, with $x>0.3\%$.[8] Above $y=0.8\%$, the carrier concentration decreases, indicating a movement of the chemical potential away from μ_c. This is consistent with the expected donor nature of In dopants in lead telluride, as described above. The initial change in carrier density as y varies from 0.8% to 1.2% is abrupt. Taking the average of these two indium concentrations gives an estimate of the critical indium concentration for depinning of the chemical potential of $y_c\sim 1\%$ but this value is necessarily poorly defined given the variation in the actual Tl concentration from batch to batch (Table I). At even higher In concentrations, between $y=2.1\%$ and 3.1%, the material becomes n-type. In the case that all Tl atoms are in the +1 formal valence, one would expect full compensation of holes introduced by Tl dopants for an In concentration equal to the concentration of Tl dopants. It is unclear why this happens at a slightly higher indium concentration, but this might suggest an increase in the number of lead vacancies, which add additional holes, with increasing In concentration.

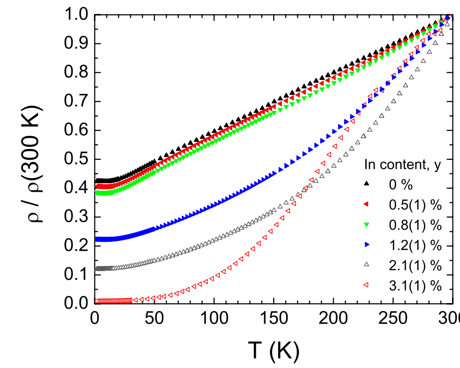

FIG. 2. (Color online) Representative resistivity data for $Pb_{0.99-y}Tl_{0.01}In_yTe$ between 1.8 and 300 K, normalized to the value at 300 K for clarity. Data are labeled by the In content. For In concentrations above 0.8% there is a substantial reduction in the residual resistivity and corresponding increase in the RRR.

Resistivity data for $Pb_{.99-y}Tl_{.01}In_yTe$ between 1.8 and 300 K (normalized to the value at 300 K for clarity) are shown in Fig. 2 for six representative In concentrations, including $y=0$. As can be seen, for In concentrations $y\leq 0.8\%$ the material is characterized by a large residual resistivity (indicative of a large scattering rate) and consistent with previous measurements of $Pb_{1-x}Tl_xTe$, with $x>0.3\%$.[6] The temperature dependence of the resistivity is modest and there is little variation between the three representative In concentrations shown in this range ($y=0$, 0.5, and 0.8%). However, as the In concentration is increased beyond 0.8%, the residual resistivity *decreases*, and the temperature dependence becomes much stronger. This behavior is qualitatively similar to that observed in $Pb_{1-x}Tl_xTe$, with $x<0.3\%$.[23] The trend can be characterized by the variation in the residual resistance ratio, $\mathrm{RRR}=\rho(300\ \mathrm{K})/\rho(1.8\ \mathrm{K})$ with y, which is shown in Fig. 1(B). Significantly, the abrupt increase in RRR (decrease in scattering rate) correlates with the "offset" of Fermi level pinning [Fig. 1(A)] that occurs as y is increased beyond $y_c\sim 1\%$. The decrease in scattering clearly outweighs the reduction in carrier density in terms of its effect on the conductivity.

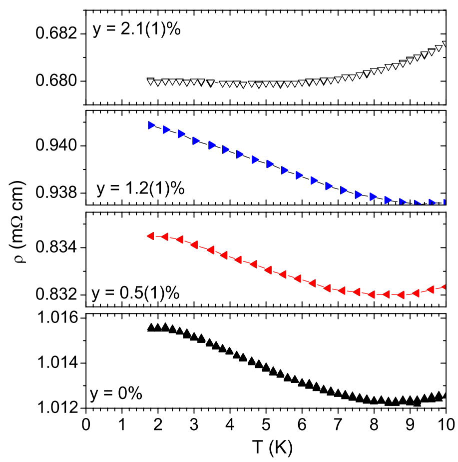

FIG. 3. (Color online) Temperature dependence of the resistivity of $Pb_{0.99-y}Tl_{0.01}In_yTe$ at low temperatures for four representative In concentrations. For $y \leq 1.2\%$ a low-temperature upturn is observed.

Further insight can be gained by more careful inspection of the low-temperature resistivity, representative examples of which are shown in Fig. 3. For $y \leq 1.2\%$, a low-temperature resistance upturn is observed, leading to a minimum $[\rho(\mathrm{min})]$ centered between 8.5 and 9 K, similar to that observed in $Pb_{.99}Tl_{.01}Te$ for $x > 0.3\%$.[1] Further increasing the In concentration beyond this value leads to a complete suppression of the low-temperature upturn, as observed for $Pb_{.99}Tl_{.01}Te$ with $x < 0.3\%$.[23] A crude estimate of the magnitude of the resistance upturn can be obtained by considering the difference $\Delta\rho = \rho(1.8\ \mathrm{K}) - \rho(\mathrm{min})$. This quantity is shown as a function of the indium content y in Fig. 1(C). It appears that the offset of Fermi-level pinning in $Pb_{.99-y}Tl_{.01}In_yTe$ as the indium concentration is increased beyond y_c is correlated with significant changes in the low-temperature scattering.

In addition to the transport measurements described above, heat-capacity measurements were used to determine both T_c (in zero field) and the density of states at E_F, $N(0)$ (in a field of 1 T, greater than H_{c2}). Considering first the measurements made in field, representative data for four In concentrations are shown in Fig. 4(B). Linear fits to C/T as a function of T^2, for $T < 1$ K yield estimates of the Sommerfeld coefficient, γ, which are shown as a function of y in panel D of Fig. 1 (left axis) together with the corresponding values of $N(0)$ (right axis). For $y < y_c$, $Pb_{0.99-y}Tl_{0.01}In_yTe$ shows an approximately constant value of $\gamma = 0.505(5)$ mJ/mol K^2, which is higher than the value of 0.4 mJ/mol K^2, expected for a Tl and In free sample of similar carrier concentration, based on previous calculations using the known PbTe band structure and made assuming a rigid band shift of the Fermi level.[8] For $y > y_c$, where superconductivity is not observed, the materials show a reduced value of $\gamma < 0.2$ mJ/mol K^2, much closer to the value expected for PbTe at those carrier concentrations.[8]

Representative heat-capacity data taken in zero field are shown in panel A of Fig. 4 for five In concentrations, including $y=0$. Samples with In concentration $y < 0.8\%$ show sharp superconducting transitions with T_c decreasing with increasing y. Estimates of the normalized heat-capacity jump, $\Delta C/\gamma T_c$, yield numbers close to the BCS value of 1.43

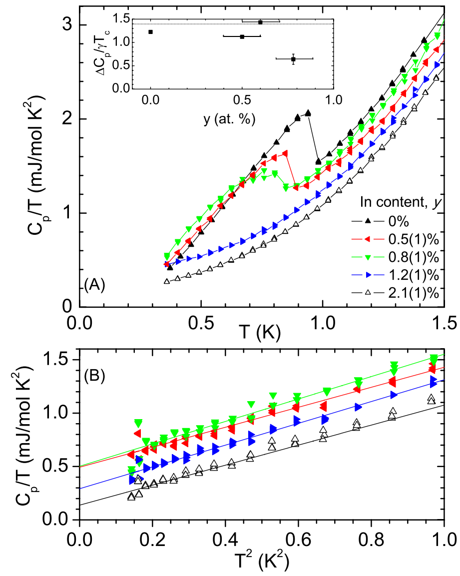

FIG. 4. (Color online) (a) Representative data showing the temperature dependence of the heat capacity of $Pb_{0.99-y}Tl_{0.01}In_yTe$ with $0 < y < 2.1\%$, shown as C_p/T. Inset shows the normalized heat-capacity jump, $\Delta C_p/\gamma T_c$, as a function of the indium concentration, y, as described in the main text. The horizontal line in the inset represents the BCS weak coupling prediction of $\Delta C/\gamma T_c = 1.43$. (b) C_p/T as a function of T^2, for the same samples shown in panel (a). Lines are linear fits to data taken below 1 K, from which the Sommerfeld coefficient, γ, is extracted.

for weak-coupled superconductors, indicative of bulk superconductivity in all of these samples (inset to Fig. 4; error bars were estimated by comparing linear extrapolations to C/T over different temperature ranges above and below T_c). For $y = 0.8\%$, the superconducting transition is significantly broadened, and for $y \geq 1.2\%$, samples do not show any evidence of a superconducting anomaly above 0.35 K (the base temperature of the He-3 cryostat used for these measurements). The broadened transition in the sample with $y = 0.8\%$, combined with the observation of a somewhat reduced value of $\Delta C/\gamma T_c$ for this sample, likely reflects the effect of inhomogeneity. While there is no reason to expect a greater degree of inhomogeneity in material with this particular In concentration, the effect of any given amount of inhomogeneity would be magnified in a sample with a composition near to a sharp transition between superconducting and nonsuperconducting behavior. Indeed, the doping dependence of T_c does appear to exhibit a sharp offset as the In concentration is increased above 0.8%. Estimates of T_c, obtained from the midpoint in the specific-heat discontinuity, are shown as a function of In content, y, in panel E of Fig. 1. Error bars are defined as 90–10 % of the full transition height. With increasing In counterdoping, T_c is reduced from a value of 1.1 K for $y=0$ to less than 0.35 K by an In concentration of $y = 1.2\%$. Resistivity data for two samples with this In concentration were also collected down to a temperature of 50 mK in a dilution refrigerator and were found to not superconduct.

IV. DISCUSSION

The results described above, and summarized in Fig. 1, paint the following general picture. First, In counterdoping in $Pb_{0.99-y}Tl_{0.01}In_yTe$ acts as an electron donor, as anticipated from previous studies of In-doped PbTe described in the Introduction. However, the Hall number n_H, reflecting the mobile carrier density, does not change significantly with increasing In concentration until y exceeds $y_c \sim 1\%$, consistent with the idea of Fermi-level pinning already developed by several authors for Tl-doped PbTe.[3,9,12,14] Second, associated with the offset of Fermi-level pinning as the indium concentration exceeds this threshold value, there is a substantial reduction in the residual resistivity (and corresponding increase in the RRR)—a quite remarkable effect given that this is achieved by adding more impurities to the material—and the low-temperature resistivity upturn disappears. Simultaneous with these effects, the electronic contribution to the heat capacity indicates that $N(0)$ is substantially reduced, and finally, the superconductivity turns off. These broad trends can be seen in Fig. 1 as the two regimes $y \leq 0.8\%$ (solid blue shading) and $y \geq 1.4\%$ (no shading), separated by a crossover region (graded shading).

The crossover region between the two classes of behavior is not perfectly distinct. In particular, samples with $y = 1.2\%$ exhibit a low-T resistive upturn with an intermediate value of γ and n_H, and did not superconduct down to 50 mK. Previously, Tl-doped PbTe, samples close to the critical Tl concentration $x_c = 0.3\%$ were only found to superconduct at very low temperatures (13 mK) (Ref. 1) and we cannot rule out a similarly low T_c in this case. Measurements were made for a variety of currents but it is also possible that heating or current-density effects suppressed T_c to below 50 mK. Equally, we cannot unambiguously rule out the possibility that this particular concentration results in a nonsuperconducting ground state. The inherent inhomogeneity in these doped samples may also play a role in obscuring the behavior in this crossover regime. Even so, there is a broad correlation between the presence of Fermi-level pinning, anomalous low-T scattering, and a superconducting ground state, obscured only at the crossover between these two behaviors close to $y_c \sim 1\%$. Variation in the Tl content from batch to batch (Table I), and possibly even from sample to sample, presumably leads to the slight nonmonatonicity observed in Fig. 1.

In the case of lithium[16] and sodium[17,18] counterdopants, a correlation between elevated density of states, chemical potential pinning, and superconductivity has also been observed. The authors of those studies attributed this correlation to formation of a narrow Tl impurity band, in contrast to the charge-Kondo picture developed in Refs. 1 and 14. The additional correlation of Kondo-type scattering with superconductivity and chemical potential pinning noted in the present work provides further evidence for the applicability of a charge-Kondo picture for Tl impurities in PbTe. Direct probes of the Tl valence in these counterdoped samples would be of great interest. Based on previous results for $Pb_{1-x}Tl_xTe$, it is anticipated that a mixed valence state will be found in $Pb_{0.99-y}Tl_{0.01}In_yTe$ for $y \leq 0.8\%$, whereas only a single Tl valence (corresponding to Tl^{+}) will be found for $y \geq 1.4\%$.

The mixed doping investigated here has benefits and detractions. On the positive side, counterdoping for a fixed (high) Tl concentration means that the Tl concentration is considerably higher in $Pb_{0.99-y}Tl_{0.01}In_yTe$ than in $Pb_{1-x}Tl_xTe$ at the onset/offset of Fermi-level pinning. In principle, this means that one could compare in a quantitative fashion the concentration of Kondo impurities (which we have previously argued to be less than the actual number of Tl impurities due to disorder effects[1,6]) in the two concentration regimes, the correlation of which with T_c would be of considerable interest. In practice, however, the degree to which it is possible to keep a fixed Tl concentration while the In concentration is varied is limited, especially for these low impurity levels. The inherent variation that this induces, both between crystals from different batches, and to some extent even within a single crystal, imposes rather severe limitations on the extent to which a meaningful quantitative analysis is possible.

V. CONCLUSIONS

In summary, we have found a clear correlation between chemical potential pinning, superconductivity, and the presence of Kondo-type resistance upturn in $Pb_{0.99-y}Tl_{0.01}In_yTe$. A similar correlation has previously been observed for the simpler system $Pb_{1-x}Tl_xTe$.[1] The current work clarifies that the anomalous low-temperature behavior in this material is a function of the Fermi level, which we have shown can be controlled independent of the Tl concentration. This provides a distinction between spurious effects, such as those introduced by magnetic impurities, and effects resulting from the intrinsic mixed-valent state that has been found in Tl-doped PbTe.[10] These observations provide additional support for the hypothesis that superconductivity in $Pb_{1-x}Tl_xTe$ arises from a negative-U mechanism associated with mixed valency of the Tl impurities, which also induces a charge-Kondo effect.[14]

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