Superconductivity in Charge Kondo Systems

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We present a theory for superconductivity and charge Kondo fluctuations, i.e., resonant quantum valence fluctuations by two charge units, for Tl-doped PbTe. We show that Tl is very special as it first supplies a certain amount of charge carriers to the PbTe-valence band and then puts itself into a self-tuned resonant state to yield a new, robust pairing mechanism for these carriers.

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The role of impurities in superconductors is a classic problem in condensed matter physics [1,2]. A reciprocal problem concerns impurities which can cause superconductivity in a host that, on its own, has no intention of superconducting. One version is of course an impurity induced increase in the carrier concentration and density of states at the Fermi level. Much more exotic and interesting is however the prospect of impurities supplying the actual pairing mechanism. Candidates are so called negative-U centers [3], which can, as we will show, induce pairing in a nonsuperconducting host even in a regime of strong quantum, charge Kondo, fluctuations. The latter is crucial to understand superconductivity in $Pb_{1-x}Tl_xTe$ [4], where recent experiments by Matsushita *et al.* [5] found strong evidence for charge Kondo fluctuations close to T_c. It promises a number of new unconventional properties [6] for this very exciting material.

PbTe is a narrow gap IV–VI semiconductor [7] where Tl, for small x, is known to act as an acceptor, adding one hole per atom to the valence band. This is consistent with the valence electron configurations of Pb ($6s^26p^2$) and Tl ($6s^26p^1$). The surprise is that $Pb_{1-x}Tl_xTe$ becomes superconducting with T_c as big as 1.4 K [4], comparable to metallic systems, but for a hole concentration orders of magnitude smaller ($n_0 \simeq 10^{20}$ cm^{-3}). Equally puzzling is that T_c rises with Tl concentration x for x values where n_0 becomes independent of x [8,9].

A special aspect of Tl is that it likes to skip an intermediate valence state in a polarizable host [10,11]. In PbTe, Tl^+, which acts as an acceptor, and Tl^{3+}, where an electron is donated instead, are by several eV more stable than Tl^{2+} [10]. This effect can be described in terms a negative-U Hubbard interaction between holes in the Tl $6s$-shell. If $\delta E = E(Tl^{3+}) - E(Tl^+)$ is the smallest scale of the problem, the two valence states become essentially degenerate. Then, the hybridization of the impurities with valence holes causes a quantum charge dynamics, similar in nature to the Kondo effect of diluted paramagnetic impurities in metals [12,13]. An isospin can be introduced [13] where the "up" and "down" configurations correspond to Tl^{3+} and Tl^+, respectively. $\delta E \neq 0$ plays the role of the magnetic field and the isospin flip corresponds to a coherent motion of an electron pair into or out of the impurity. This motion of pairs suggest a connection between the charge Kondo dynamics, with Kondo temperature T_K, and superconductivity. Numerical simulations [14] indeed demonstrate that negative-U centers increase T_c of a superconducting host if δE is small. For $\delta E = 0$ pairing in a nonsuperconducting host was discussed under the assumptions $T_c \gg T_K$ [15].

Two important open questions arise: (i) Why is it possible to assume almost perfect degeneracy ($\delta E < T_c$) given that Tl is known to act as an acceptor (requiring $E(Tl^{1+}) < E(Tl^{3+})$) even at room temperature? (ii) Are charge Kondo impurities able to cause superconductivity with $T_c \simeq T_K$, as requires by recent experiments [5]? Then the scattering rate of the centers is highly singular and the pseudospin moment is about to be quenched.

In this Letter, we answer both questions. We show that beyond a characteristic Tl concentration $Pb_{1-x}Tl_xTe$ tunes itself, without adjustment of parameters, into a resonant state with $\delta E = 0$. We further present a theory for the superconducting transition temperature of dilute negative-U, charge Kondo impurities to address the behavior in the intermediate regime $T_c \simeq T_K$, where the superconducting and charge Kondo dynamics fluctuate on the same time scale. We argue that our theory can explain the concentration dependence and magnitude of n_0 and T_c for $Pb_{1-x}Tl_xTe$. In addition we predict a reentrance normal state behavior at low temperature and impurity concentration as a unique fingerprint of the charge Kondo mechanism for superconductivity, determine the electromagnetic response close to the transition and show that a low concentration of negative-U centers will *always* increase weak coupling host superconductivity. All this demonstrates the rich and highly nontrivial behavior of this very special class of impurities.

An isolated valence skipper can be described in terms of a negative-U Hubbard model,

$$H_{\rm imp} = (\varepsilon_0 - \mu)\sum_\sigma n_{s,\sigma} + U n_{s\uparrow} n_{s\downarrow} \qquad (1)$$

where $n_{s,\sigma} = s^\dagger_\sigma s_\sigma$ is the occupation for a spin σ hole in the Tl $6s$-shell, i.e., $\delta E = 2(\varepsilon_0 - \mu) + U$. μ is the chemi-

cal potential of the system and $U < 0$. The valence band is characterized by $H_{\text{band}} = \sum_{\mathbf{k},\sigma}(\varepsilon_{\mathbf{k}} - \mu)c^{\dagger}_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}$. The concentration of holes in the valence band, donated via Tl-doping, is $n_0 = x(1 - n_s)$ with $n_s = \sum_{\sigma}\langle n_{s,\sigma}\rangle$, i.e., $n_0 > 0$ in the case of an acceptor, Tl^{+}, and $n_0 < 0$ (corresponding to electrons in the conduction band) for the donor, Tl^{3+}. This enables us to determine μ and thus δE as a function of Tl concentration. We first assume that the chemical potential μ is below the value $\mu^* = \varepsilon_0 + \frac{1}{2}U$, where $\delta E = 0$. Then $\delta E > 0$ and Tl^{+} is more stable. There are no holes in the Tl $6s$ levels. All holes are in the valence band: $n_0 = x$, as seen in experiments for small x [8,9]. Increasing the Tl concentration increases μ until it reaches μ^* for some x^*. If we further add Tl impurities and if they continued acting as acceptors, the chemical potential would rise above μ^*. However, then $\delta E < 0$ and Tl^{3+} become more stable acting as donor, in contradiction to our assumption. Thus, instead of increasing μ, additional impurities will equally split into Tl^{+} and Tl^{3+} valence states such that no new charge carriers are added to the valence band and μ remains equal to μ^*. Tl^{+} and Tl^{3+} are degenerate and coexist with concentration $(x + x^*)/2$ and $(x - x^*)/2$, respectively. No fine tuning is needed to reach a state with perfect degeneracy, except for the fact that μ^* is reachable. This phenomenon is related, but not identical, to the pinning of the Fermi level in amorphous semiconductors, discussed in Ref. [3]. In Fig. 1 we show experimental results of Ref. [8] for $n_0(x)$, in good agreement with this scenario. The comparison with experiment gives an estimate of $x^* \simeq 0.5\%$ (see Fig. 1). Using the band structure of PbTe [16] this yields $\mu^* \simeq 175 \pm 20$ meV and $\mu^*\rho_0 \simeq 0.07$ with density of states at the Fermi level, ρ_0. This value for μ^* agrees very well with the tunneling data of Ref. [8], which finds $\mu^* \approx 200$ meV.

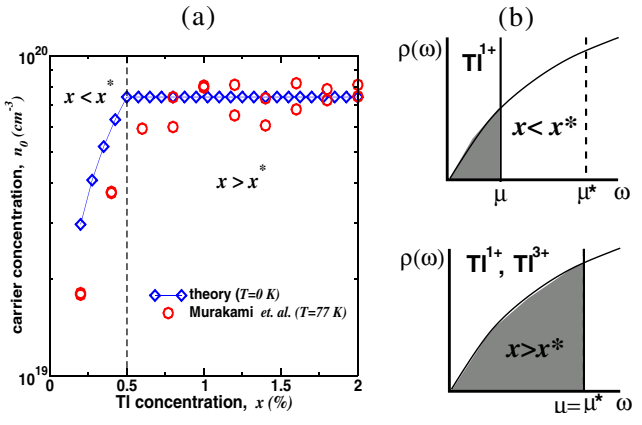

FIG. 1 (color online). (a) Valence band hole concentration as a function of Tl content in $Pb_{1-x}Tl_xTe$ in comparison with experiments [8]; (b) valence band density of states for $x < x^*$ (upper panel) and $x > x^*$ (lower panel). A pinning of the chemical potential at $\mu = \mu^*$ for $x > x^*$ gives rise to a degeneracy between the Tl^{1+} and Tl^{3+} states and to $n_0(x) = \text{const}$.

Next we include an additional hybridization of the impurity with the band electrons, $V\sum_{i\sigma}(s^{\dagger}_{i\sigma}c_{i\sigma} + c^{\dagger}_{i\sigma}s_{i\sigma})$, causing transitions between the degenerate valence states. For large $|U|/V$, the problem can be simplified by projecting out states with $n_{is\sigma} = 1$ [17]. The close relation to the spin Kondo problem becomes evident if one introduces the Nambu spinor [13] $\hat{c}_i = (c_{i\downarrow}, c^{\dagger}_{i\uparrow})$ as well as the isospin $\mathbf{t}_i = \frac{1}{2}\hat{c}^{\dagger}_i\tau\hat{c}_i$ and similarly $\hat{s}_i$ and $\mathbf{T}_i = \frac{1}{2}\hat{s}^{\dagger}_i\tau\hat{s}_i$. Here τ is the vector of the Pauli matrices. For $\delta E = 0$ follows

$$H_{\text{int}} = J\sum_i \mathbf{T}_i \cdot \mathbf{t}_i, \tag{2}$$

where $J = 8V^2/|U|$. The isospins $\mathbf{T}_i$ and $\mathbf{t}_i$ obey the usual spin commutation relation. Ordering in the $x - y$ plane in isospin space is related to superconductivity ($T^{+}_i = s^{\dagger}_{i\downarrow}s^{\dagger}_{i\uparrow}$), whereas ordering in the z-direction corresponds to charge ordering ($T^{z}_i = \frac{1}{2}(\sum_{\sigma} n_{is\sigma} - 1)$). The model undergoes a Kondo effect where the low temperature bound state is a resonance of a pair of charges tunneling between the impurity and the conduction electron states at a rate $T_K \simeq De^{-(1/\rho_F J)}$, forming unitary scattering centers at $T \ll T_K$ (D is the valence hole band width of order μ^*). The analogy to the spin Kondo problem is however not perfect. The valence band part of the Hamiltonian, $H_{\text{band}} = \sum_{\mathbf{k},\sigma}(\varepsilon_{\mathbf{k}} - \mu)\hat{c}^{\dagger}_{\mathbf{k}}\tau_z\hat{c}_{\mathbf{k}}$, is not isospin rotation invariant. This causes an anisotropy of the analog of the RKKY interaction between isospins mediated by either particle-particle excitations, $I^{+-}(R) = (J^2\rho_F/8\pi)R^{-3}$ or particle-hole excitations, $I^{zz}(R) = I^{+-}(R)\cos(2k_F R)$, respectively. The in-plane coupling in isospin space, I^{+-}, is the Josephson or proximity coupling between distinct impurities, whereas I^{zz} determines charge ordering. The absence of Friedel oscillations in the particle-particle channel causes the different behavior of I^{+-} and I^{zz}.

Using this pseudospin analogy one can easily conclude that superconductivity is possible if T_c turns out to be large compared to T_K and quantum fluctuations of $\mathbf{T}_i$ can be neglected. The pseudospin moment is unscreened, corresponding to preformed pairs. The interaction I^{+-} between these pairs in the isospin x-y plane is unfrustrated, supporting superconducting rather than charge ordering for randomly placed impurities. A mean field calculation in this regime gives $T_{c,\text{mf}} \simeq xJ^2\rho_F \log(D/(xJ^2\rho_F))$ [15]. The origin of superconductivity is then similar to Josephson coupling between small superconducting grains located at the impurity sites.

For T_c comparable to T_K the behavior is considerably more subtle. The time it takes to create a Cooper pair in the host equals the time for a valence change causing the pairing, i.e., the moments which are supposed to order are being quenched and a description in terms of preformed pairs is inapplicable. In addition, Kondo flip scattering is expected to be pair breaking.

Theoretically, the Kondo effect manifests itself in the appearance of the logarithmic divergence of the perturbation theory in J for $T \simeq T_K$. A partial summation of the divergent perturbation series which is quantitatively correct even for $T \simeq T_K$ and only fails to recover the low T Fermi liquid behavior, was proposed in Ref. [18]. The approach is based on a nonlinear integral equation for the t matrix for non spin flip scattering which determines the one particle Green's function:

$$\mathcal{G}(\mathbf{p}, \mathbf{p}'; \omega_n) = \mathcal{G}_0(\mathbf{p}; \omega_n)\delta(\mathbf{p} - \mathbf{p}') + x_r J \mathcal{G}_0(\mathbf{p}; \omega_n) t(\omega_n) \mathcal{G}_0(\mathbf{p}'; \omega_n), \quad (3)$$

where $\mathcal{G}_0(\mathbf{p}; \omega_n) = 1/(i\omega_n - \varepsilon_{\mathbf{k}} + \mu)$ is the bare valence hole Green's function. $x_r = x - x^*$ is the concentration of the degenerate impurities. Müller-Hartmann and Zittartz [19] solved the nonlinear integral equation for $t(\omega)$ exactly. The approach was applied to study spin Kondo impurities in a superconducting host. A rich behavior for $T_c(x)$ was obtained which was shown to agree well with experiments [20]. In what follows we use and generalize this approach to investigate superconductivity in the charge Kondo problem. This scattering matrix approach is unique as it allows us to investigate the subtle crossover close to T_K and, as we will see, naturally includes effects related to the coupling between impurities, $I^{\pm}(R)$, effects which are very hard to include in other, more modern approaches to the Kondo problem [21].

In the normal state $t(\omega)$ of the charge and spin Kondo problems turn out to be identical and we can simply use the results of Ref. [19]. In the superconducting state an anomalous scattering matrix, $t_\Delta(\omega)$, occurs. Superconductivity and charge Kondo dynamics are much more closely intertwined than in the magnetic problem and determining $t_\Delta(\omega)$ becomes a considerably more complex task. However, for the linearized gap equation which determines T_c, $t_\Delta(\omega)$ is small and progress can be made analytically. We obtain for small superconducting gap, Δ

$$t_\Delta(\omega_n) = t_{\Delta,\mathrm{loc}}(\omega_n) + t_{\Delta,\mathrm{prox}}(\omega_n) \quad (4)$$

with contribution $t_{\Delta,\mathrm{loc}}(\omega_n) = -\frac{\Delta}{3}[t(\omega_n)/i\omega_n - (\frac{2}{V_0})(dt(\omega_n)/di\omega_n)]$ determined solely by the local Kondo dynamics and a nonlocal, "proximity" contribution $t_{\Delta,\mathrm{prox}}(\omega_n) = -[\langle T^+\rangle(1 - 2\pi i \rho_F J t(\omega_n))/2X_n]$ which is proportional to $\langle T^+\rangle$, reflecting the broken symmetry at the impurity in the superconducting state. We allow for a finite attractive BCS-interaction, $V_0 < 0$, of the host. $t(i\omega_n)$ is the normal state t matrix of Ref. [19] and $X_n = \rho_F J(\psi(\frac{1}{2} + n) - \psi(\frac{1}{2}) - \log(T_K/T))$ with the digamma function $\psi(x)$. Performing the usual disorder average [2] we finally obtain a linearized gap equation

$$\Delta = -V_0 T \sum_{\omega_n, \mathbf{p}} \frac{\tilde{\Delta}(\tilde{\omega}_n)}{\tilde{\omega}_n^2 + \varepsilon_{\mathbf{p}}^2}, \quad (5)$$

where $i\tilde{\omega}_n = i\omega_n + x_r \rho_F J t(i\tilde{\omega}_n)$ and $\tilde{\Delta}(\tilde{\omega}_n) = \Delta[1 + x_r \rho_F J(t(\tilde{\omega}_n)/i|\omega_n|)] + x_r \rho_F J t_\Delta(\tilde{\omega}_n)$. $\langle T^+\rangle$ is determined by the ability to polarize a static pairing state at the impurity site, just like in the proximity effect in superconductors or the RKKY interaction in the magnetic case. Close to T_c, we find $\langle T^+\rangle = -(J/2V_0)\chi(T_c)\Delta$ with local susceptibility of the Kondo problem, $\chi(T) \propto (T + T_K)^{-1}$.

We first consider the limit $V_0 = 0$, i.e., the host material is not superconducting on its own, like PbTe. Only the t_Δ contributions that are proportional to V_0^{-1} contribute to $\tilde{\Delta}(\tilde{\omega}_n)$. At high temperatures, $T_c \gg T_K$, one easily finds that only $t_{\Delta,\mathrm{prox}}$ contributes to T_c and we recover the mean field result of Ref. [22]. The behavior changes as T approaches T_K. Now $\chi(T) \sim T_K^{-1}$ and $t_{\Delta,\mathrm{prox}}$ stops being the sole, dominant pairing source. The pairing interaction becomes strongly frequency dependent. $t_{\mathrm{loc}}(\omega)$ and $t_{\Delta,\mathrm{prox}}(\omega)$ become comparable to each other as well as to the pair breaking scattering rate τ^{-1}, which is directly related to the existence of a finite width $\sim T_K$ of the Kondo resonance. Just like in the case of spin Kondo systems, pair breaking effects are largest for $T_c \simeq T_K$. However unlike for the magnetic counterparts, the pairing interaction itself strongly depends on T_c/T_K and increases with concentration.

Our results for the concentration dependence of T_c are shown in Fig. 2. Charge Kondo impurities do indeed cause a superconducting state with $T_c \simeq T_K$. At higher concentration we find T_c rises almost linearly with x whereas a rich behavior occurs in the low temperature limit. The competition between pair breaking and pairing interaction causes a reentrance normal state behavior which might serve as a unique fingerprint for a charge Kondo origin of superconductivity. Because of the uncertainty of the $\rho_F J$ value for Tl-doped PbTe it is unclear whether this effect is observable in this material. In Fig. 2 we compare our

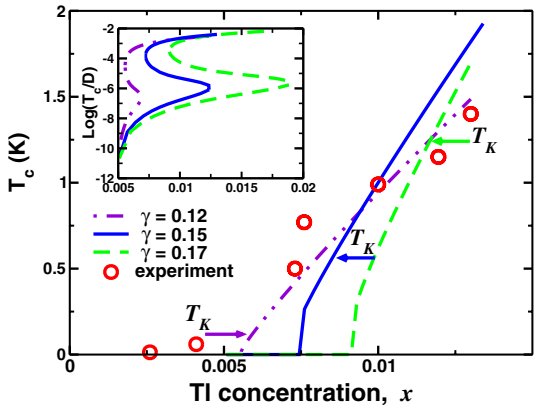

FIG. 2 (color online). T_c as a function of concentration for various values of the dimensionless exchange coupling constant $\gamma = \rho_F J$. Experimental points [5] are plotted for comparison. Inset shows low-T part of concentration dependence of T_c where reentrance behavior appears.

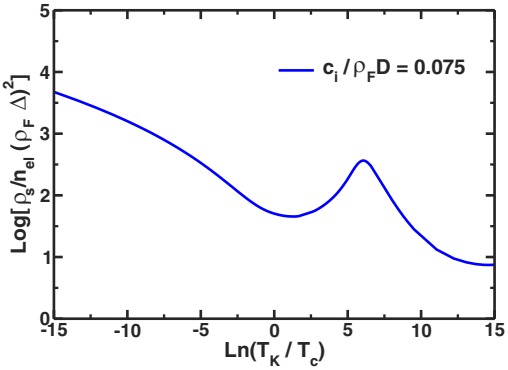

FIG. 3 (color online). Normalized superfluid density as a function of T_K/T_c shown on a log scale.

results for several values of $\rho_F J$, chosen such that $T_K \simeq T_c$, with experiment [5]. To obtain $T_c \simeq 1$ K we used $D = \mu^*/4.5$ and $\rho_F D \simeq 0.08$. Given the above listed values for $\rho_F \mu^*$ and μ^*, these are perfectly reasonable parameters, chiefly demonstrating that T_c of several Kelvin is possible within the charge Kondo theory for $x \approx 1\%$. These numbers further allow us to estimate the temperature ≈ 30 mK, below which the normal state reappears.

Unlike ordinary superconductivity, pairing in charge Kondo systems is caused by dilute impurities which are coupled by host carriers with low concentration and the stability of the superconducting state with respect to fluctuations becomes an important issue. In order to quantify this we determine the superfluid density $\rho_s/n_0 = \pi T \sum_{\omega_n} \tilde{\Delta}^2(\tilde{\omega}_n)/\tilde{\omega}_n^3$ close to T_c, where $\rho_s \propto \Delta^2$. In Fig. 3 we show our results for the dimensionless ratio $\alpha \equiv (\rho_s/n_0)(\rho_F \Delta)^{-2}$ as a function of T_K/T_c. α has a local minimum for $T_c \simeq T_K$, caused by the strong scattering rate of a charge Kondo impurity which reduce ρ_s. From α we can estimate the temperature, where phase fluctuations affect the transition significantly and find that for $T_c \simeq T_K$ superconductivity is robust, whereas for $T_c \ll T_K$ the phase stiffness becomes rapidly small. In Ref. [22] charge Kondo superconductivity was analyzed for $T_c \ll T_K$ with the result that $T_c \simeq T_K \exp(-\lambda_{\text{eff}}^{-1})$ and $\lambda_{\text{eff}} \sim x/\rho_F T_K$. Our result strongly suggest that this state is unstable against phase fluctuations.

Within our theory we can also discuss the impact of charge Kondo impurities in a system which is superconducting for $x = 0$. We find, in agreement with the quantum Monte Carlo simulations [14], that T_c increases. Independent of J, x pair stabilization due to negative U centers is always more efficient than pair breaking.

In summary we have developed a theory for superconductivity in charge Kondo systems valid in the crossover region where $T \simeq T_K$ which can explain the comparatively large transition temperature in Tl-doped PbTe. We showed that Tl is a very special impurity as it first supplies a certain amount of charge carriers to the PbTe-valence band and then puts itself into a self-tuned resonant state to supply a new mechanism for superconductivity of these carriers. The subtle interplay of pair formation and pair breaking by the same impurities can cause a rich behavior including an enhancement of the host transition temperature by impurities, a reentrance normal state transition and large phase fluctuations of weakly coupled local pairs for $T_c \ll T_K$. Our results agree in order of magnitude and generic concentration dependence of T_c and n_0 with the experiments [5,8,9] for $Pb_{1-x}Tl_xTe$, strongly suggesting a charge Kondo origin for superconductivity in this material.

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