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 to superconduct. 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 non-superconducting host even in a regime of strong quantum, charge Kondo, fluctuations. The latter is crucial to understand superconductivity in Pb$_{1-x}$Tl$_x$Te[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 acceptor, adding one hole per atom to the valence band. This is consistent with the valence electron configurations of Pb (6$s^2$6$p^2$) and Tl (6$s^2$6$p^1$). The surprise is that Pb$_{1-x}$Tl$_x$Te becomes superconducting with $T_c$ as big as 1.4K[6], comparable to metallic systems, but for a hole concentration orders of magnitude smaller ($n_0 \simeq 10^{20}\text{cm}^{-3}$). Equally puzzling is that $T_c$ rises with Tl concentration, $x$, for $x$-values where $n_0$ becomes independent of $x[6, 7]$.

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$6$s-shell. If $\delta E = E(Tl^{1+}) - E(Tl^{3+})$ 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[8,13]. 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 $\delta E$ is small. For $\delta E = 0$ pairing in a non-superconducting 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 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 pseudo-spin moment is about to be quenched.

In this paper we answer both questions. We show that beyond a characteristic Tl-concentration Pb$_{1-x}$Tl$_x$Te 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$_x$Te. In addition we predict a re-entrance 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,

$$H_{\text{imp}} = (\varepsilon_0 - \mu) \sum_{\sigma} n_{s,\sigma} + U n_{s^+} n_{s^-}$$

where $n_{s,\sigma} = s_{i\sigma}^T s_{i\sigma}$ is the occupation for a spin $\sigma$ hole in the Ti 6$s$-shell, i.e. $\delta E = 2(\varepsilon_0 - \mu) + U$. $\mu$ is the chemical potential of the system and $U < 0$. The valence band is characterized by $H_{\text{band}} = \sum_{k,\sigma} (\varepsilon_k - \mu) \hat{c}_{k\sigma}^\dagger \hat{c}_{k\sigma}$. 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 case of an acceptor, Ti$^3+$, and $n_0 < 0$ (corresponding to electrons in the conduction band) for the donor, Ti$^1+$. This enables us to determine $\mu$ and thus $\delta E$ as function of Ti concentration. We first assume that the chemical potential, $\mu$, is below the value $\mu^* = \varepsilon_0 + \frac{1}{2} U$, where $\delta E = 0$. Then $\delta E > 0$ and Ti$^1+$ is more stable. There are no holes in the Ti 6$s$ levels. All holes are in the valence band: $n_0 = x$, as seen in experiment for small $x$.

Increasing the Ti concentration increases $\mu$ until it reaches $\mu^*$ for some $x^*$. If we further add Ti-impurities and if they continued acting as acceptors, the chemical potential would rise above $\mu^*$. However, then $\delta E < 0$ and Ti$^1+$ become more stable acting as donor, in contradiction to our assumption. Thus, instead of increasing $\mu$, additional impurities will equally split into Ti$^1+$ and Ti$^3+$ valence states such that no new charge carriers are added to the valence band and $\mu$ remains equal to $\mu^*$. Ti$^1+$ and Ti$^3+$ are degenerate and coexist with concentration $\frac{x+x^*}{2}$ and $\frac{x-x^*}{2}$, respectively. No fine tuning is needed to reach a state with perfect degeneracy, except for the fact that $\mu^*$ is reachable. This phenomenon is related, but not identical, to the pinning of the Fermi level in amorphous semiconductors, discussed in Ref. 8.

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 $x^* \approx 0.55\%$ (see Fig. 1). Using the bandwidth structure of PbTe [10], this yields $\mu^* \approx 175 \pm 20$meV and $\mu^* n_0 \approx 0.07$ with density of states at the Fermi level, $n_0$. This value for $\mu^*$ agrees very well with the tunneling data of Ref. 8, who finds $\mu^* \approx 200$meV.

Next we include an additional hybridization of the impurity with the band electrons, $V \sum_{i\sigma} \left( s_{i\sigma}^\dagger c_{i\sigma} + c_{i\sigma}^\dagger s_{i\sigma} \right)$, causing transitions between the degenerate valence states. For large $|U|/V$, the problem can be simplified by projecting out states with $n_{i\sigma} = 1$, i.e. the close relation to the spin Kondo problem becomes evident if one introduces the Nambu spinor $\left( c_{i\spin}^\dagger, c_{i\spin} \right)$ as well as the isospin $t_i = \frac{1}{2} \delta_{\spin}^\dagger \tau \delta_{\spin}$ and similarly $\delta_{\spin}^\dagger$ and $\delta_{\spin}$. Here $\tau$ is the vector of the Pauli matrices. For $\delta E = 0$ follows

$$H_{\text{int}} = J \sum_i t_i \cdot t_i,$$

where $J = \frac{4U}{\pi^2}$. The isospins $t_i$ and $t_i$ obey the usual spin commutation relation. Ordering in the $x$-$y$ plane in isospin space is related to superconductivity ($T_{i+} = s_{i\spin}^\dagger s_{i\spin}$), whereas ordering in the $z$-direction corresponds to charge ordering ($T_{i-} = \frac{1}{2} (\sum_\spin n_{i\spin} - 1)$). 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 $T_K \approx D e^{-\frac{2\mu^*}{\pi}}$, forming unitary scattering centers at $T \ll T_K$ ($D$ is the valence band width of order $\mu^*$). The analog to the spin Kondo problem is however not perfect. The valence band part of the Hamiltonian, $H_{\text{band}} = \sum_{k,\spin} (\varepsilon_k - \mu) \hat{c}_{k\spin}^\dagger \hat{c}_{k\spin}$, is not isospin rotation invariant. This causes an anisotropy of the analog of the RKKY interaction between isospins mediated by either particle-particle excitations, $I^+ (R) = IE_{\text{Kondo}} R^{-3}$ or particle-hole excitations, $I^+ (R) = I^-(R) \cos(2k_F R)$, 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 $T_c$ 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 $T_{\text{c, mf}} \approx xJ^2\rho_F \log \left( D / (xJ^2 \rho_F) \right)$ [12]. 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 $T \approx T_K$. A partial summation of the divergent perturbation series which is quantitatively correct even for $T \approx T_K$ and only fails to recover the low $T$ Fermi liquid behavior, was proposed in Ref. [19]. The approach is based on a non-linear integral equation for the $t$-matrix for non spin flip scattering which determines the one particle Green’s function:

\[
G(p, p'; \omega_n) = G_0(p; \omega_n) \delta(p - p') + x_r J G_0(p; \omega_n) t(\omega_n) G_0(p'; \omega_n),
\]

where $G_0(p; \omega_n) = 1/(i\omega_n - \varepsilon_k + \mu)$ is the bare valence hole Green’s function. $x_r = x - x^*$ is the concentration of the degenerate impurities. Müller-Hartmann and Zittartz [20] solved the non-linear 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 [21]. In what follows we use and generalize this approach to investigate superconductivity in the charge Kondo problem. This scattering matrix generalizes this approach to investigate superconductivity.

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. [20]. In the superconducting state an anomalous scattering matrix, $t_\Delta(\omega)$, occurs. Superconductivity and charge Kondo dynamics are much closer 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, $\Delta$:

\[
t_\Delta(\omega_n) = t_{\Delta, loc}(\omega_n) + t_{\Delta, prox}(\omega_n)
\]

with contribution $t_{\Delta, loc}(\omega_n) = -\Delta \left( \frac{\Delta(\omega_n)}{\omega_n} - \frac{2}{\omega_n} \frac{\delta(\omega_n)}{\omega_n} \right)$ determined solely by the local Kondo dynamics and a nonlocal, ”proximity” contribution $t_{\Delta, prox}(\omega_n) = \frac{1}{(T^+)(1 - 2\pi T J t(\omega_n))}$ which is proportional to $(T^+)$, 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. $t(\omega_n)$ is the normal state $t$-matrix of Ref. [20] and $X_n = \rho F J (\psi(\frac{2}{3} n) - \psi(\frac{1}{3} n) - \log(\frac{T_0}{T}))$ with digamma function $\psi(x)$. Performing the usual disorder average [2] we finally obtain a linearized gap equation

\[
\Delta = -V_0 T \sum_{\omega_n} \frac{\Delta(\omega_n)}{\omega_n + \varepsilon_p},
\]

where $\bar{i}\omega_n = i\omega_n + x_r \rho F J t(i\omega_n)$ and $\bar{\Delta}(\bar{\omega}_n) = \Delta \left( 1 + x_r \rho F J \frac{\Delta(\bar{\omega}_n)}{i\omega_n} \right) + x_r \rho F J \Delta(\bar{\omega}_n)$. $(T^+)$ 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 $(T^+) = \frac{-1}{2\pi T_0} \chi(T_c) \Delta$ 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 $t_\Delta$-contributions which are proportional to $V_0^{-1}$ contribute to $\Delta(\bar{\omega}_n)$. At high temperatures, $T_c \gg T_K$, one easily finds that only $t_{\Delta, prox}$ 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 $t_{\Delta, prox}$ stops being the sole, dominant pairing source. The pairing interaction becomes strongly frequency dependent. $t_{loc}(\omega)$ and $t_{\Delta, prox}(\omega)$ become comparable to each other as well as to the pair breaking scattering rate $\tau^{-1}$ which is directly related to the existence of a finite width, $\sim T_K$, of the Kondo resonance. Just like in case of spin Kondo systems, pair breaking effects are largest for $T_c \approx T_K$. However unlike for the magnetic counter parts, the pairing interaction itself strongly depends on $T_c/T_K$ and increases with concentration.

**FIG. 2:** $T_c$ as a function of concentration for various values of the dimensionless exchange coupling constant $\gamma = \rho F J$. Experimental points [2] are plotted for comparison. Inset shows low-$T$ part of concentration dependence of $T_c$ where re-entrance behavior appears.

Our results for the concentration dependence of $T_c$ are shown in Fig. 2. Charge Kondo impurities do indeed cause a superconducting state with $T_c \approx T_K$. 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. Due to 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 results for several values of $\rho F J$, chosen such that $T_K \approx T_c$, with experiment [2]. To obtain
$T_c \simeq 1\text{K}$ we used $D = \mu^*/4.5$ and $\rho_F D \simeq 0.08$. Given the above listed values for $\rho_F/\mu^*$ and $\mu^*$, 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 $\simeq 30\text{mK}$, 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 for a charge Kondo impurity which reduces the stability of the superconducting state with respect to phase fluctuations. From $\alpha = \pi T \sum \Delta^2 (\tilde{\omega}_n)/\tilde{\omega}_n^3$ close to $T_c$, where $\rho_s \propto \Delta^2$.

In Fig. 3 we show our results for the dimensionless ratio $\alpha = \pi T \sum \Delta^2 (\tilde{\omega}_n)/\tilde{\omega}_n^3$ as function of $T_K/T_c$. $\alpha$ has a local minimum for $T_c \simeq T_K$, caused by the strong scattering rate of a charge Kondo impurity which reduces $\rho_s$. From $\alpha$ 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 $T_c < T_K$ the phase stiffness becomes rapidly small. In Ref. [22] charge Kondo superconductivity was analyzed for $T_c < T_K$ with the result that $T_c \simeq T_K \exp (-\lambda_{\text{eff}}^{-1})$ and $\lambda_{\text{eff}} \sim \frac{\pi T}{\rho_F D}$.

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, that $T_c$ increases. Independent on $J$, $x$ is pair stabilization due to negative $U$ centers 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 Ti-doped PbTe. We showed that Ti 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 [3, 8, 9] for Pb$_{1-x}$ Ti$_x$Te, strongly suggesting a charge Kondo origin for superconductivity in this material.

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[1] P. W. Anderson, J. Phys. Chem. Solids 11, 26 (1959).
[2] A. A. Abrikosov and L. P. Gor’kov, Sov. Phys. JETP 12, 1243 (1961).
[3] P. W. Anderson, Phys. Rev. Lett. 34, 953 (1975).
[4] I. A. Chernik and S. N. Lykov, Sov. Phys. Solid State 23, 817 (1981).
[5] Y. Matsushita, H. Bluhm, T. H. Geballe, and I R. Fisher, preprint [cond-mat/0409174].
[6] V. Oganesyan, S. Kivelson, T. Geballe, B. Moyses, Phys. Rev. B 65, 172504 (2002).
[7] R. Dornhaus, G. Nimtz, and B. Schicht, in Narrow Gap Semiconductors, Springer Tracts in Modern Physics 98, ed. G. Höhler (Springer-Verlag, New York, 1983).
[8] H. Murakami, W. Hattori, Y. Mizomata, and R. Aoki, Physica C 273, 41 (1996).
[9] S. A. Nemov, Y. I. Ravich, Phys. Usp. 41, 735 (1998).
[10] K. Weiser, Phys. Rev. B 23, 2741 (1981).
[11] C. M. Varma Phys. Rev. Lett. 61, 2713 (1988).
[12] A. C. Hewson, The Kondo Problem to Heavy Fermions, (Cambridge Univ. Press, 1993).
[13] A. Taraphder, P. Coleman, Phys. Rev. Lett. 66, 2814 (1991).
[14] H.-B. Schüttler, M. Jarrell, and D. J. Scalapino, Phys. Rev. B 39, 6501 (1989).
[15] A. G. Mal’shukov, D. M. Newns, J. Phys. C 77, 41 (1989).
[16] Following Refs. [8, 9] we include the bands around the $L$ and $\Sigma$-points of the Brillouine zone.
[17] J. R. Schrieffer, P. A. Wolff, Phys. Rev. 149, 491 (1966).
[18] P. Coleman, Phys. Rev. B 29, 3035 (1984); N. Read and D. M. Newns, J. Phys. C 16, 3273 (1983).
[19] Y. Nagaoka, Phys. Rev. 138, A112 (1965); H. Suhl, Phys. Rev. 138, A515 (1965); D. R. Hamann, Phys. Rev. 158, 570 (1967).
[20] E. Müller-Hartmann and J. Zittartz, Z. Phys. 232, 11 (1970); ibid Phys. Rev. Lett. 26, 428 (1971).
[21] M. B. Maple, Appl. Phys. 9, 179 (1976).
[22] A. G. Mal’shukov, JETP Lett. 48, 430 (1988).