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International Atomic
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Miniworkshop on
New States of Stable and Unstable Quantum Matter
(14 - 25 August 2006)

Charge Kondo Effect in Superconducting Tl-doped PbTe?

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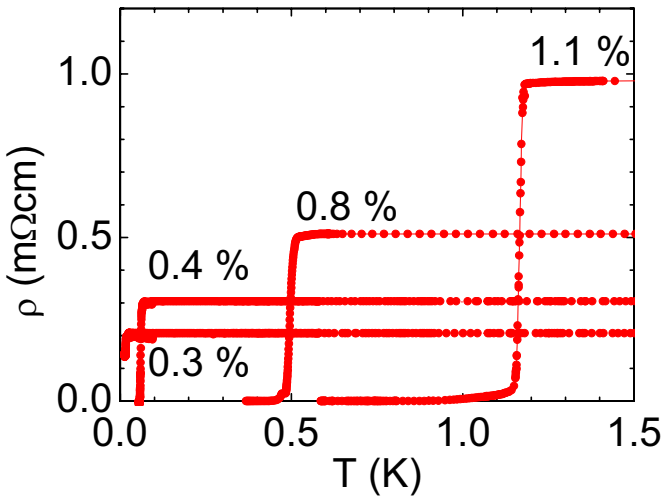

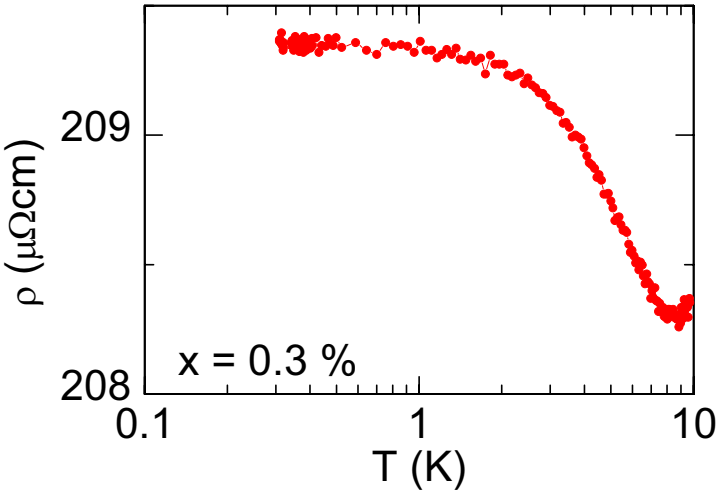

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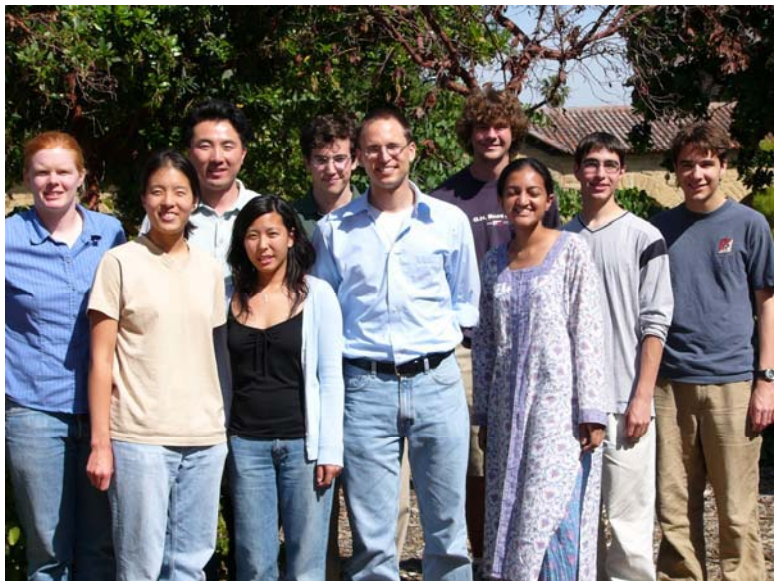
R. Ormeno, P. Baker and C. E. Gough

UCSC:

D. Havice-Hull & F. Bridges

Ames Laboratory:

M. Dzero & J. Schmalian



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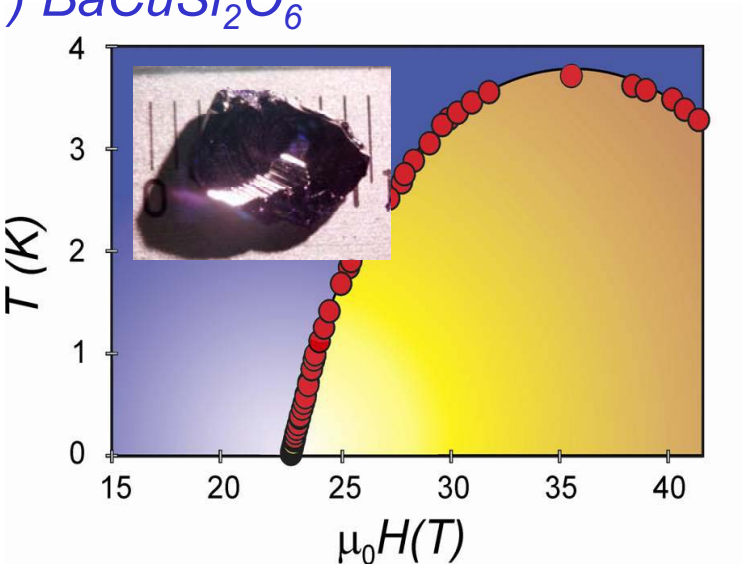
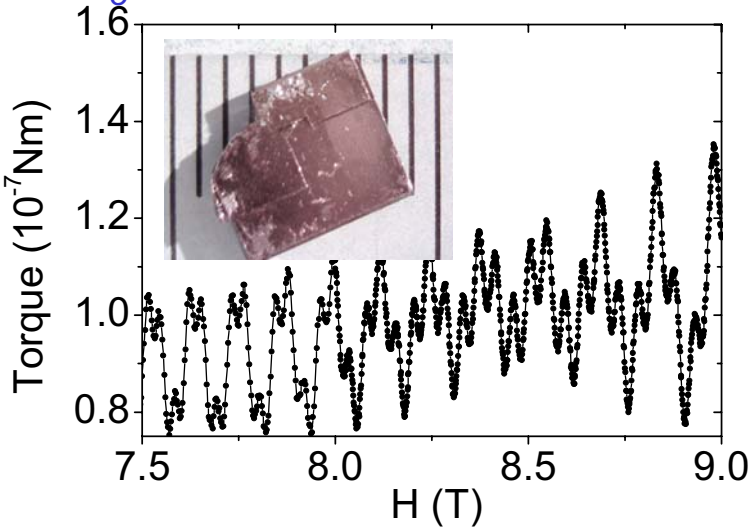
Materials advertisement: some other neat new materials for correlated electron physics

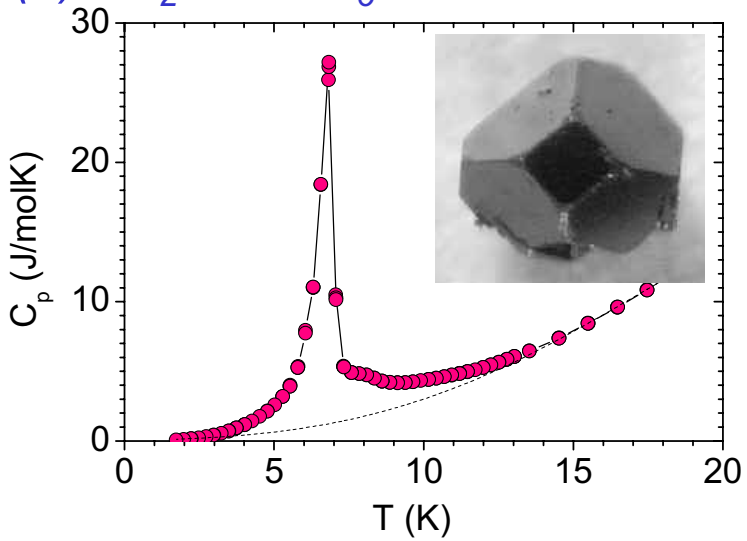
(1) $BaCuSi_2O_6$



(2) RTe_3



(3) Ba_2NaOsO_6



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A. Erickson, J. Kim, Y. Matsushita, N. Ru,
E. Samulon, S. E. Sebastian, K. Y. Shin

Outline

(1) Superconductivity in Tl-doped PbTe

(2) The chemistry of Tl

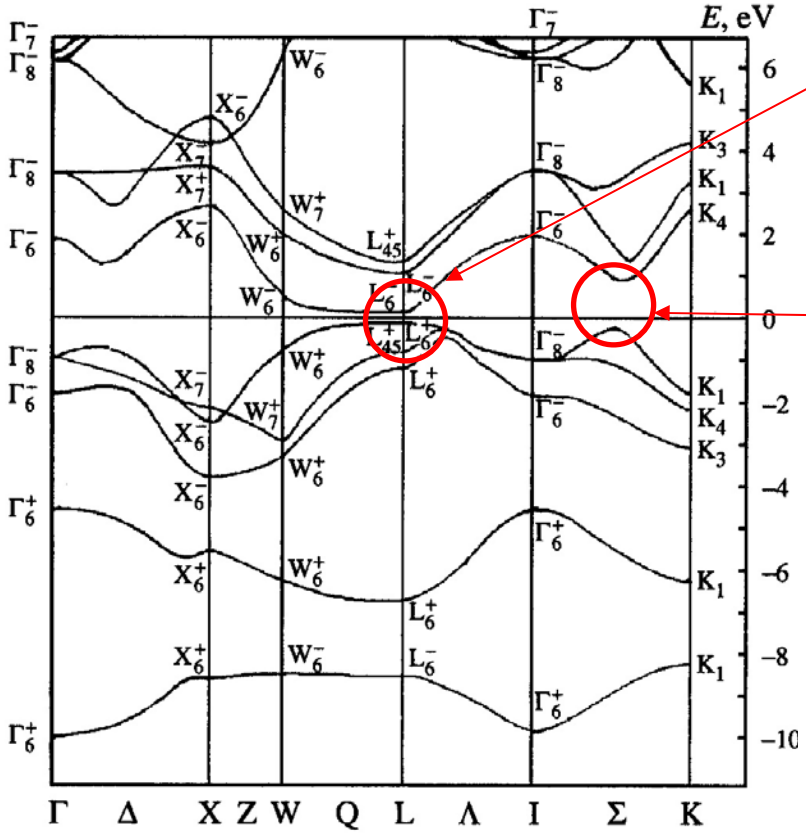
(3) Anomalous normal state properties

(4) The charge Kondo effect

Y. Matsushita et al., PRL **94**, 157002 (2005).
Y. Matsushita et al., cond-mat/0605717 (2006).
M. Dzero & J. Schmalian, PRL **94**, 157003 (2005).

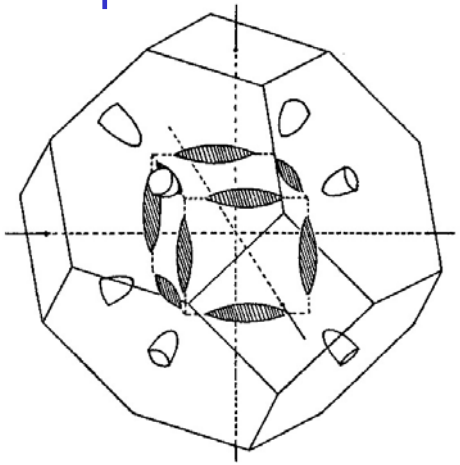
PbTe

- small gap semiconductor
- can be treated rather successfully using ionic models: $Pb^{2+}Te^{2-}$
  (a) rock salt structure; cohesive energy; ionic separation
  (b) pseudopotential calc: 75% of electrons on Te, 25% on Pb
  compared with 80% and 20% for a purely ionic model



L-point:
- $m_\perp = 0.022\ m_0$
- $m_{||} = 0.31\ m_0$

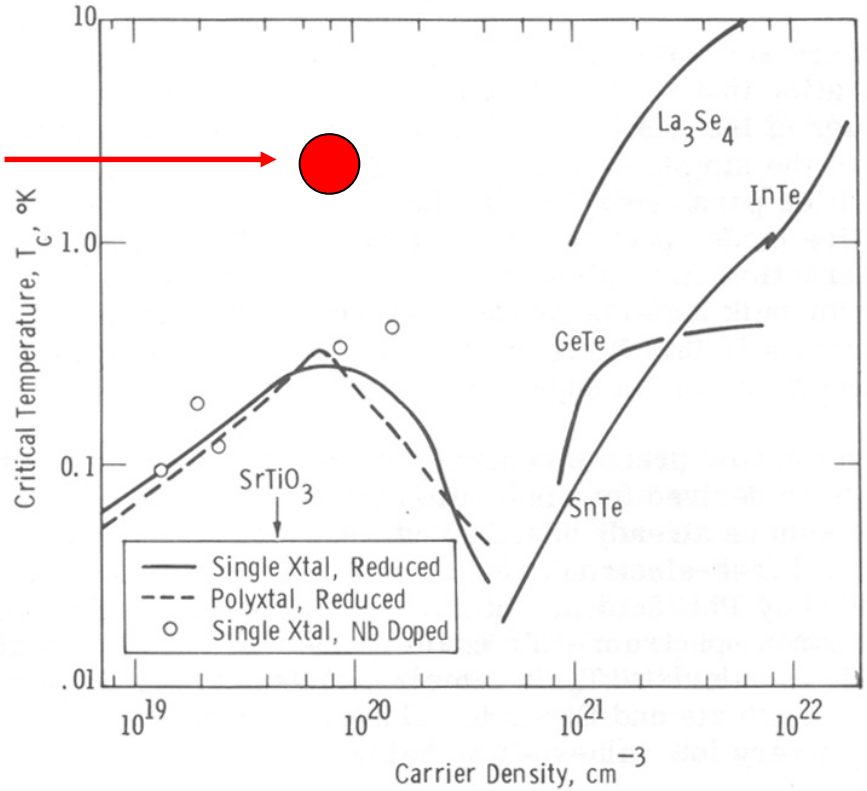
Σ-point:
- 2nd valence band edge
- ~ 170 meV below top of valence band
- $m \sim 0.6\ m_0$
- $\mu_\Sigma \sim \mu_L$



Pseudopotential calculation from “Lead chalcogenides”, ed D. Khokhlov (2002).

Superconductivity in PbTe

Tl-doped PbTe

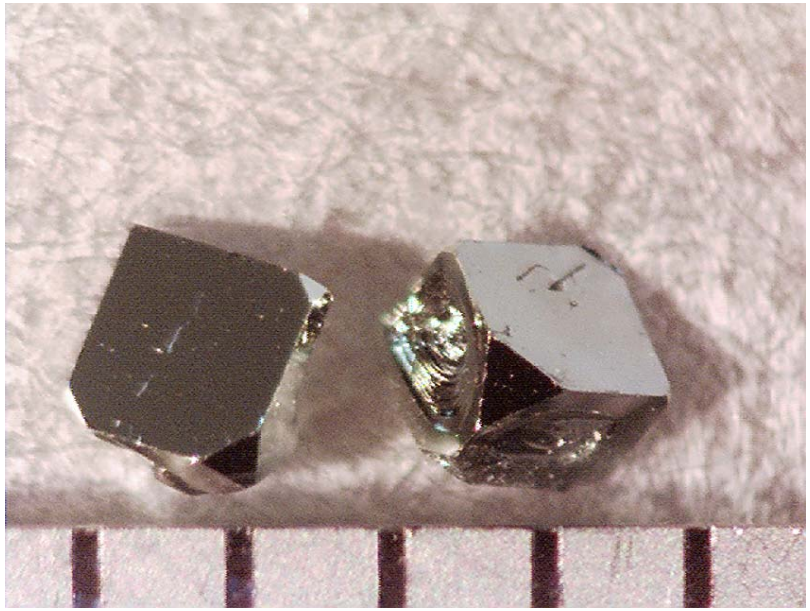


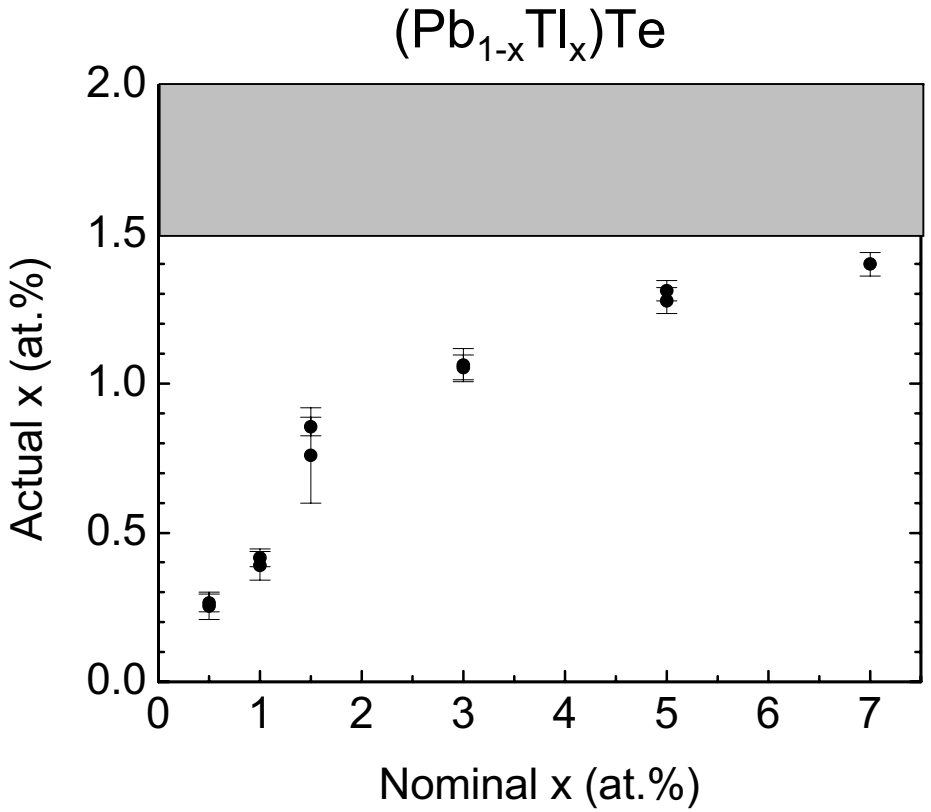
- anticipate T_c of PbTe < 0.01 K for carrier concentrations ~ 10^{20} cm^{-3}
- 1981: Tl -doped PbTe found to superconduct, T_c ~ 1.5 K
- no superconductivity for any other impurities in PbTe…

J. K. Hulm Spring Superconducting Symposia NRL Report 6972 (1969).
I. A. Chernik & S. N. Lykov, Sov. Phys. Solid State **23**, 817 (1981).
S.A. Nemov & Y. I. Ravic, Phys. Usp. **41**, 735 (1998).

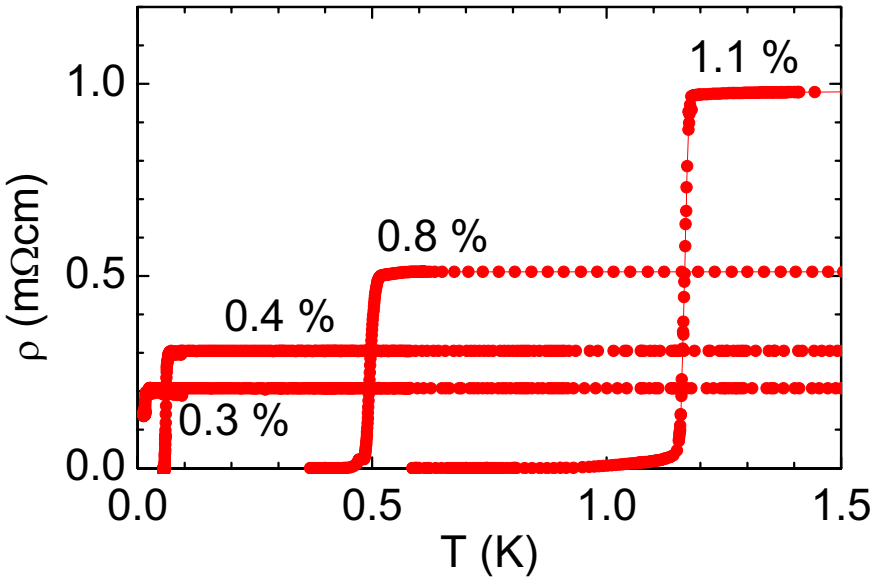
$(Pb_{1-x}Tl_x)Te$ crystal growth

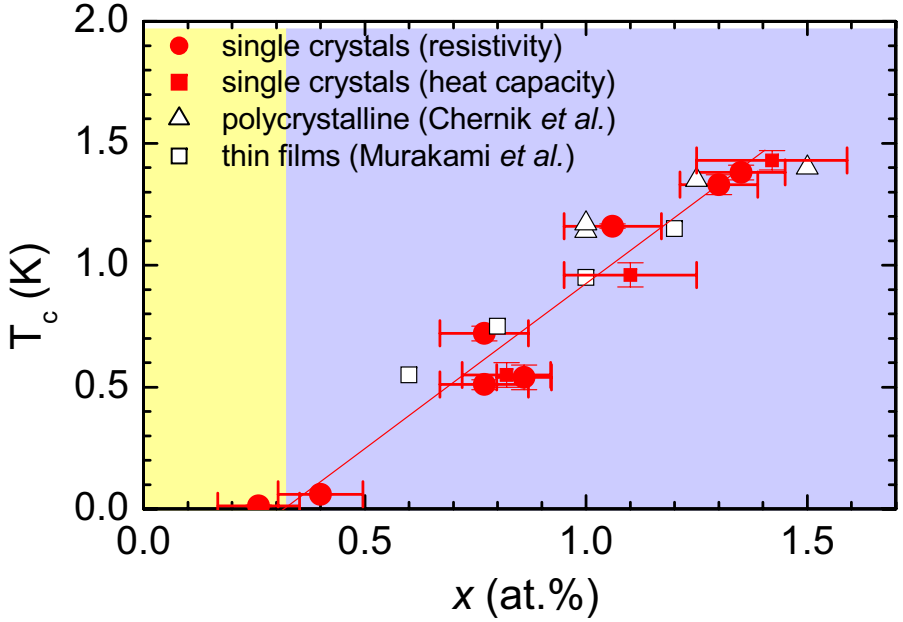
- Single crystals via unseeded physical vapor transport
- Tl content measured via EPMA
- Solubility limit ~ 1.5 % Tl
- EXAFS – no clustering





Superconductivity in $(Pb_{1-x}Tl_x)Te$

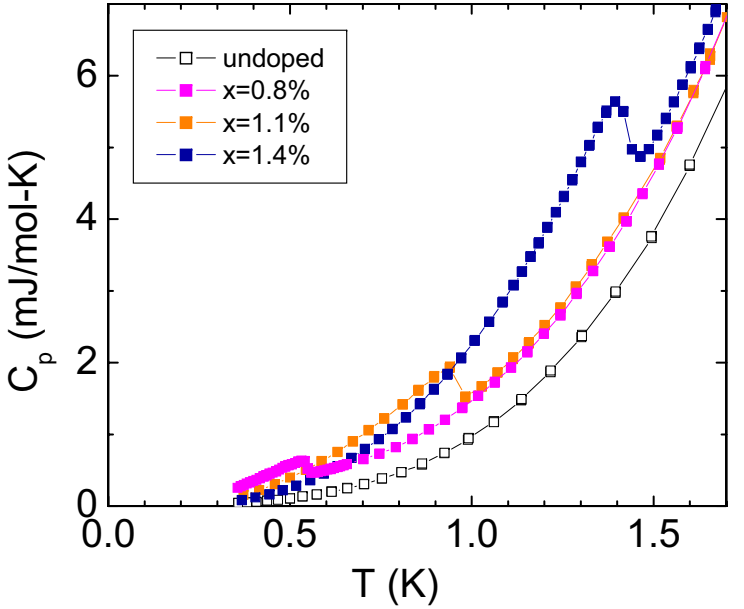


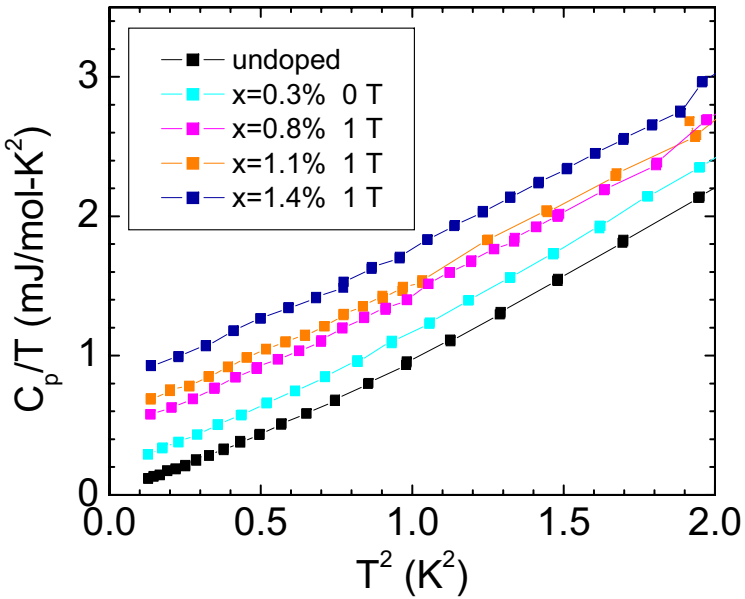


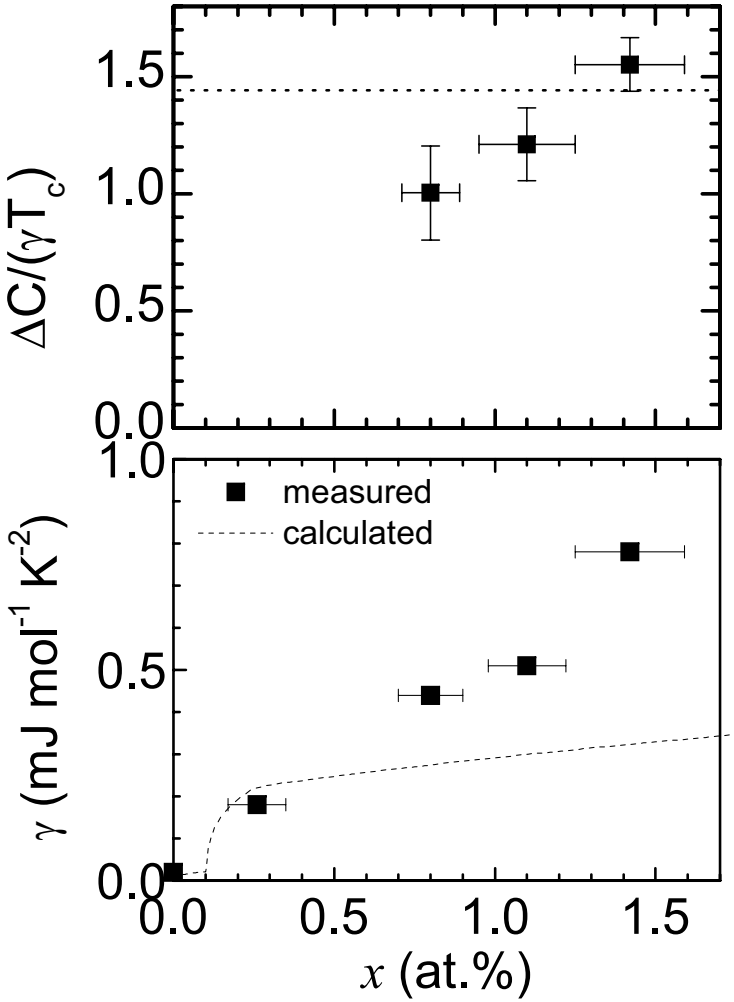
- T_c(max) ~ 1.5 K
- requires a critical concentration
- x_c ~ 0.3%

Y. Matsushita et al., PRL **94**, 157002 (2005).
I. A. Chernik & S. N. Lykov, Sov. Phys. Solid State **23**, 817 (1981).
H. Murakami et al., Physica C **269**, 83 (1996).

Heat capacity

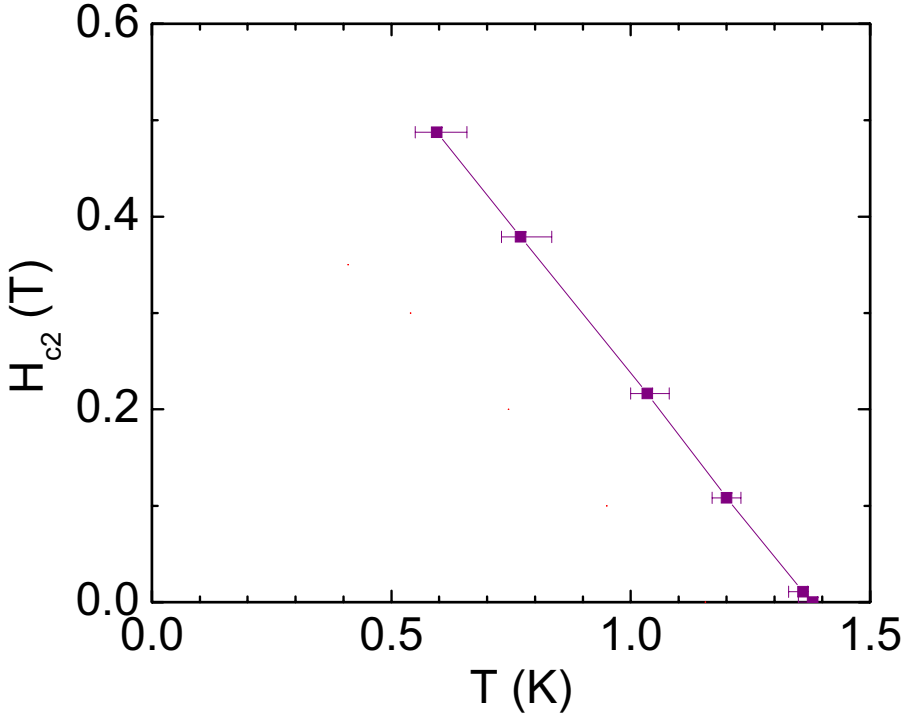




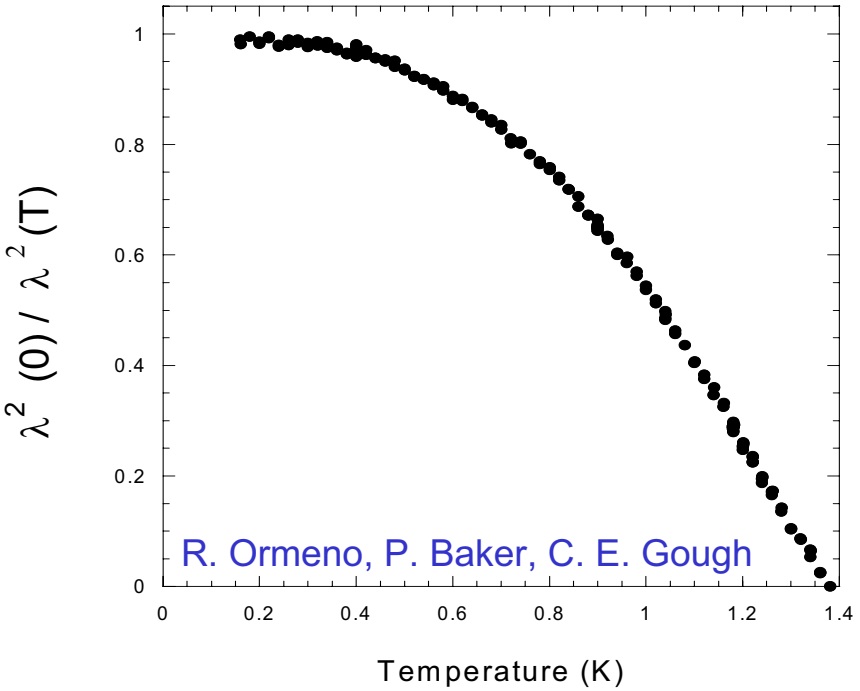


- bulk effect
- $\Delta C/\gamma T_c$ close to BCS value
- additional contribution to γ

Superconducting length scales: x = 1.4%



- Microwave penetration depth, 10 GHz



$$\left.\begin{array}{l}\xi(0)\approx 240\text{Å}\\ l\approx 20\,\text{Å}\end{array}\right\}$$ Dirty limit: $\xi(0)\approx\sqrt{l\xi_0}$

$$\xi_0 \approx 3000\text{Å} = 0.18\frac{\hbar v_F}{k_B T_c}$$

$$v_F \approx 3\times 10^5\, ms^{-1}$$

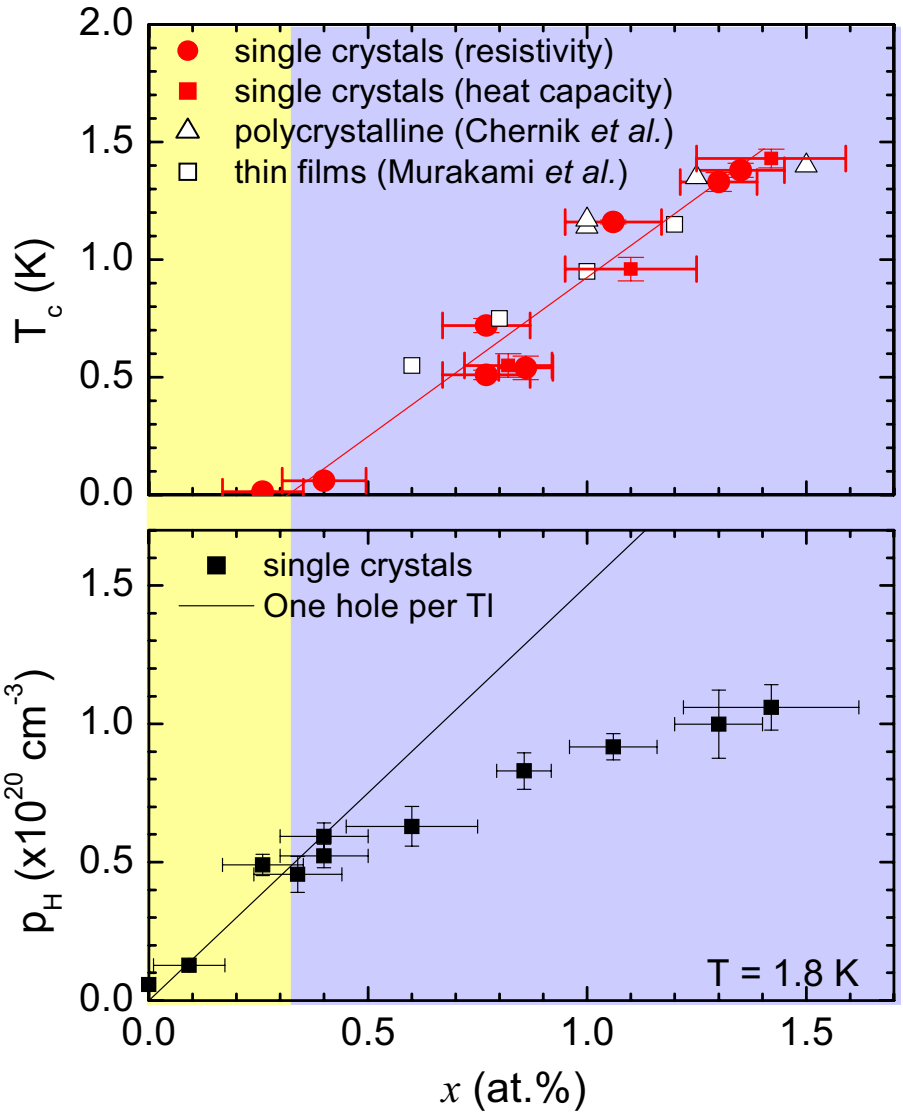
$$\frac{1}{\lambda_L^2}=\frac{\mu_0 n_L e^2}{m_L}+\frac{\mu_0 n_\Sigma e^2}{m_\Sigma}\Rightarrow \lambda_L \approx 1500\ \text{Å}$$

$$\lambda_{eff}\approx\lambda_L\sqrt{\frac{\xi_0}{l}}\approx 2\,\mu m$$

$$\kappa=\lambda_{eff}/\xi(0)\approx 80$$

- type II BCS superconductor in the dirty limit

Critical Tl concentration



Hall Coefficient:

- line calculated using 2-band model with appropriate FS anisotropy
- $\mu_L \sim \mu_\Sigma \rightarrow p_H = 1/R_H e \sim p$

- $x < x_c$: one hole per Tl
- $x > x_c$: Hall number varies much less rapidly & Tl impurities appear to be self-compensating.

Question:

- what is so special about Tl impurities in PbTe?
- will make the case this behavior is intimately linked to presence of a mixed Tl valence…

Y. Matsushita et al., PRL **94**, 157002 (2005).
I. A. Chernik & S. N. Lykov, Sov. Phys. Solid State **23**, 817 (1981).
H. Murakami et al.. Phvsica C **269**. 83 (1996).

Outline

(1) Superconductivity in Tl-doped PbTe

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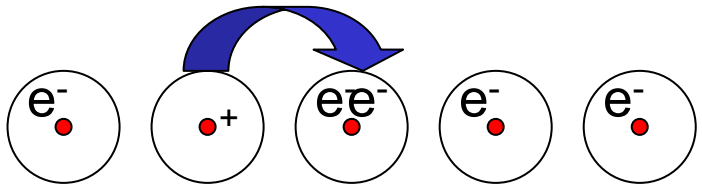
Tl is a valence skipping element

In solids, Tl is found to have a formal valence of:

- 1+ : Tl_2Te
- 3+ : Tl_2O_3
- or a mixture of both: $TlBr_2 \equiv Tl^{I}Tl^{III}Br_4$

- i.e. single occupancy of 6*s* orbital not favored
- formally equivalent to a negative effective *U*

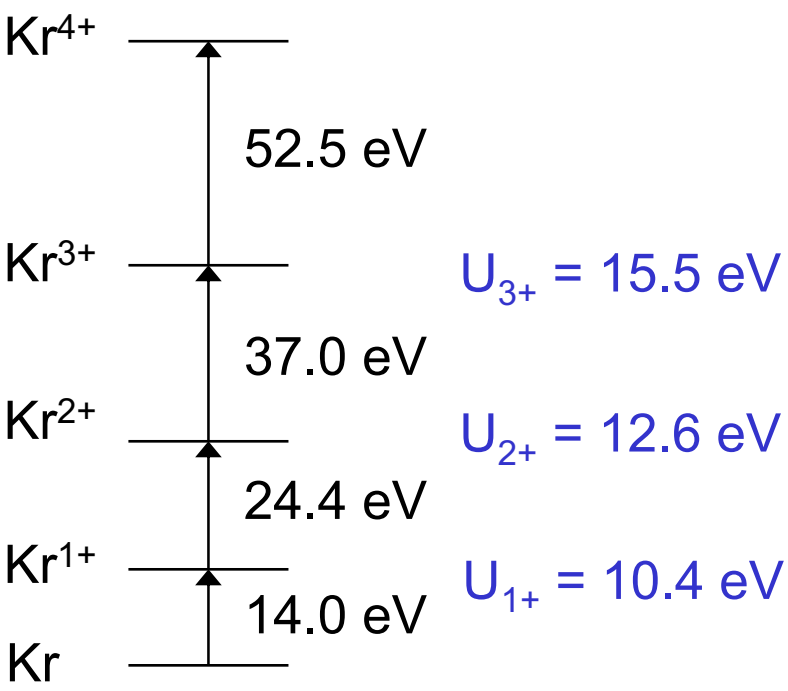


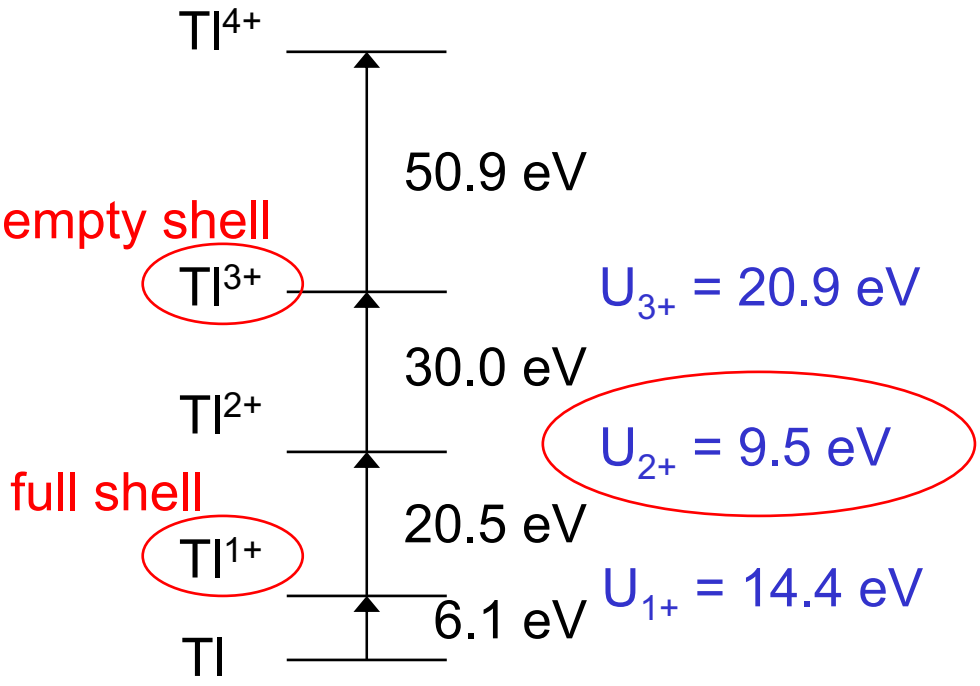
- *U* = ionization energy - electron affinity
- usually, *U* > 0 due to on site Coulomb repulsion
- negative-*U*: another effect overcomes Coulomb repulsion
- origin: stability of filled shells & lattice polarization

Valence skipping elements as negative-*U* centers

C. Varma (PRL **61**, 2713 (1988)):

- useful to characterize the valence states of elements in terms of the difference of successive ionization energies
- effective intra-atomic repulsion energy for the nth valence state
- $U_{eff} = (E_{n+1} - E_n) - (E_n - E_{n-1})$



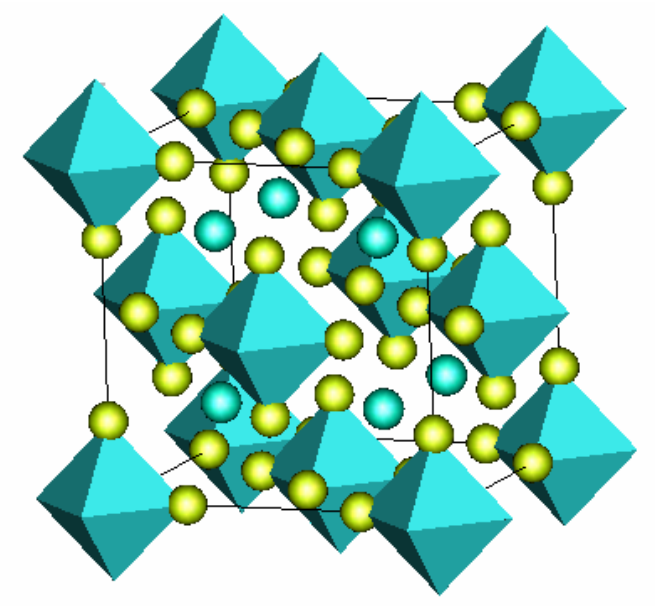


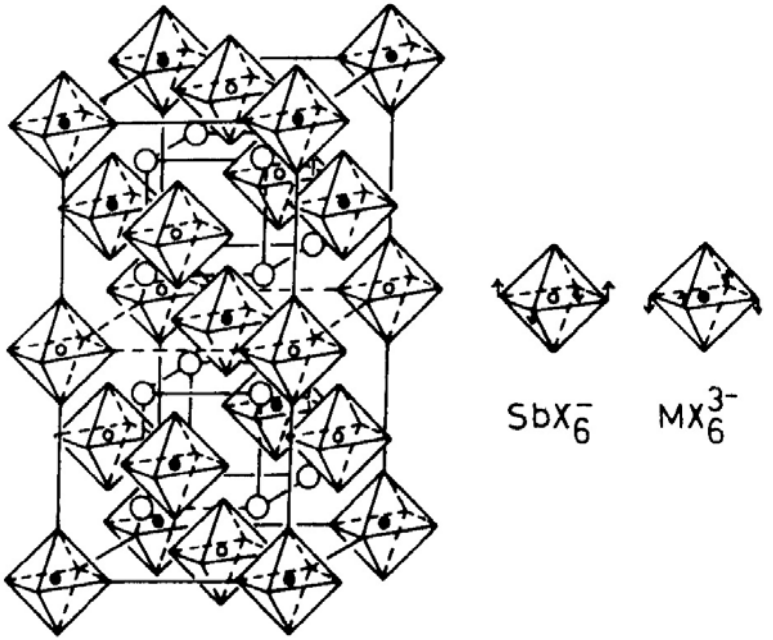
- polarization further reduces U_{eff}
- for valence skipping elements, $U_{eff} < 0$

Example: mixed Sb valence in Cs_2SbCl_6

$Cs_2Sn(IV)Cl_6$:
- semiconductor
- FCC structure

$Cs_2Sb(III)_{0.5}Sb(V)_{0.5}Cl_6$:
- two different Sb sites
- superlattice, doubles unit cell



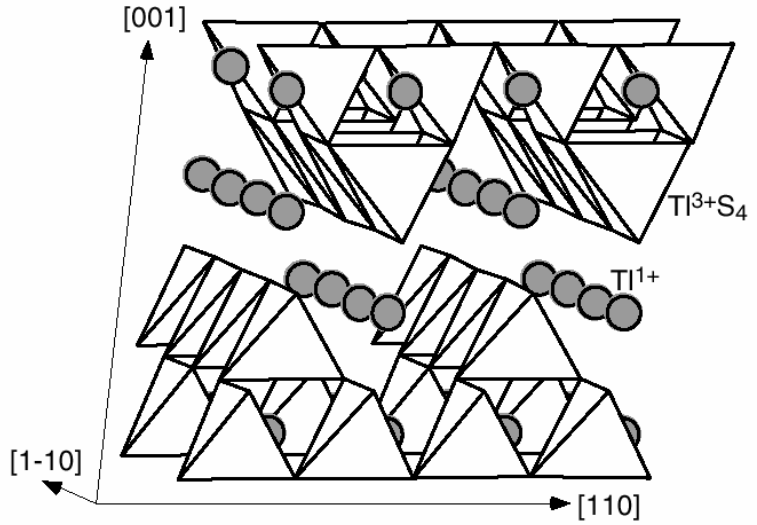


M. Robin & P. Day, *Mixed valence chemistry – a survey & classification*, pp247 in Adv. in Inorg. Chem. & Radiochem. (1967).
Prassides et al, Inorg. Chem. **24**, 545 (1985).

Examples of Tl mixed valence compounds

TlS:

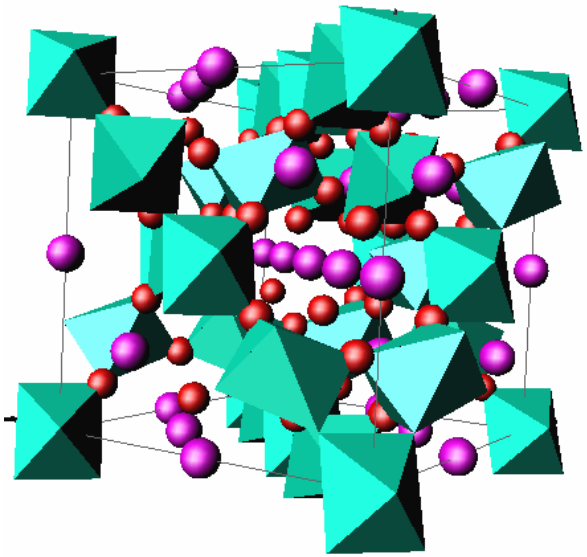
- monoclinic form: layered structure
- 2 distinct crystallographic sites
- $Tl(I)Tl(III)S_2$
- semiconductor



Panich & Kashida,
J. Phys.: Cond. Mat. **16**, 3071 (2004).

$Tl_2Nb_2O_{6+x}$:

- x=0, all Tl^{1+}
- additional O up to x = 0.64
- $Tl(I)_{1-x}Tl(III)_xNb(V)_2O_{6+x}$
- randomly positioned, static mixed valence
- semiconductor



Mizoguchi et al.,
Bull. Chem. Soc. Jap. **69**, 111 (1996).

Tl substitution in PbTe

Tl -substitution:

- substitutes on Pb site
- solubility limit ~ 1.5 %
- no clustering (EXAFS)

Crude argument:

- Tl^{2+} is "neutral" impurity state to preserve Te^{2-} valence
- but Tl^{2+} is characterized by $U_{eff} < 0$
- → expect spontaneous disproportionation to balance charge…

$$2Tl^{2+} \rightarrow Tl^{+} + Tl^{3+}$$
$$6s^{1} \quad 6s^{2} \quad 6s^{0}$$

More careful argument:

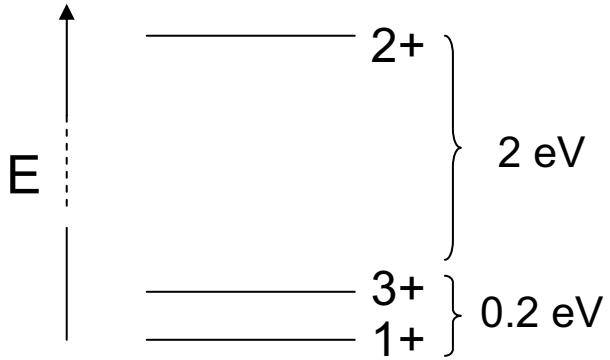
- calculate relative energy of Tl^{+} and Tl^{3+} impurities in PbTe lattice
- find that Tl^{+} has a lower energy → Tl impurities should act as *acceptors*
- but the difference is very small indeed
- small changes in the chemical potential affect this difference & can in principle lead to a mixed Tl valence…

K. Weiser PRB **23**, 2741 (1981).

Model Hamiltonian for Tl impurities in PbTe

$$H_{imp} = E_0 + (\varepsilon_0 - \mu)\sum_{\sigma} n_{s,\sigma} + U n_{s\uparrow} n_{s\downarrow}$$

- $E(Tl^{+}) = E_0$
- $E(Tl^{2+}) = E_0 + \varepsilon_0 - \mu$
- $E(Tl^{3+}) = E_0 + 2(\varepsilon_0 - \mu) + U$



Condition for degenerate valence states:

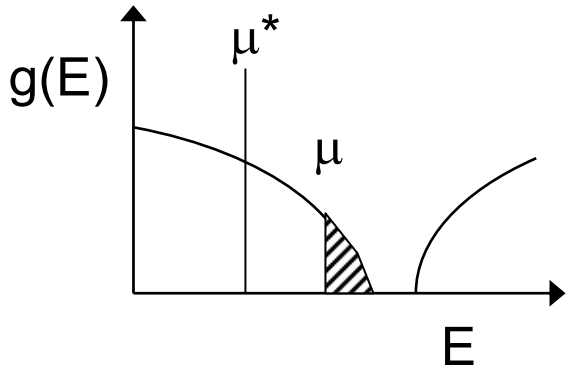
- $\delta E = E(Tl^{3+}) - E(Tl^{1+}) = 2(\varepsilon_0 - \mu) + U = 0$
- $\mu^* = \varepsilon_0 + \frac{1}{2}U$

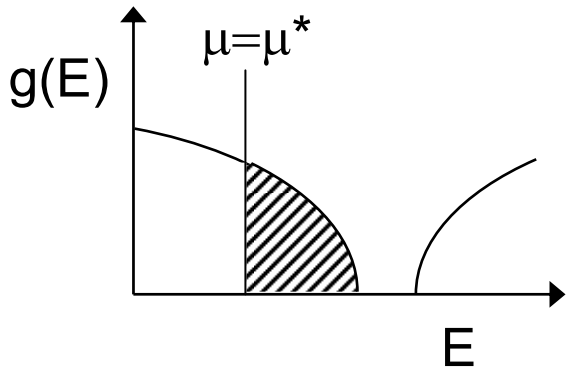
Initial doping conditions:

- $E(Tl^{+}) < E(Tl^{3+})$; $\mu < \mu^*$
- each Tl impurity donates 1 hole, increasing μ

Condition $\mu = \mu^*$:

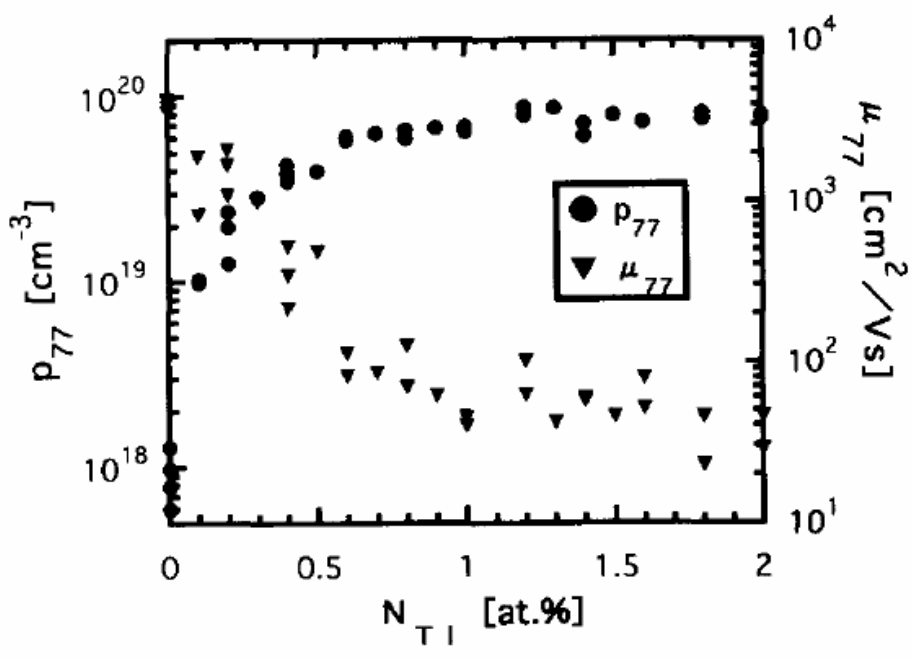
- μ *cannot* increase beyond this value
- ($\mu > \mu^*$ would imply Tl^{3+} stable, i.e. all donors)
- i.e. chemical potential pinned and $\delta E = 0$ exactly

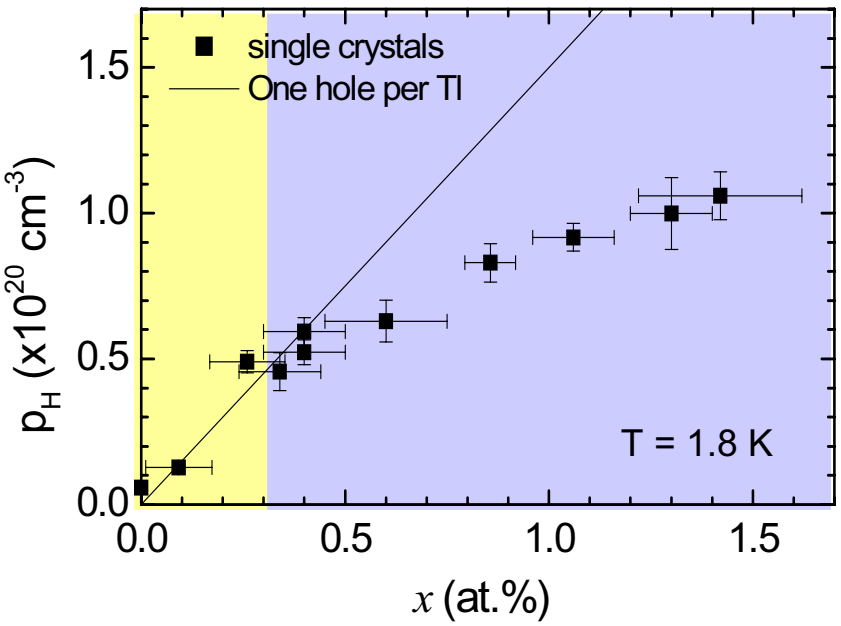




M. Dzero & J. Schmalian, PRL **94**, 157003 (2005).

Evidence for mixed Tl valence in $(Pb_{1-x}Tl_x)Te$: Hall effect





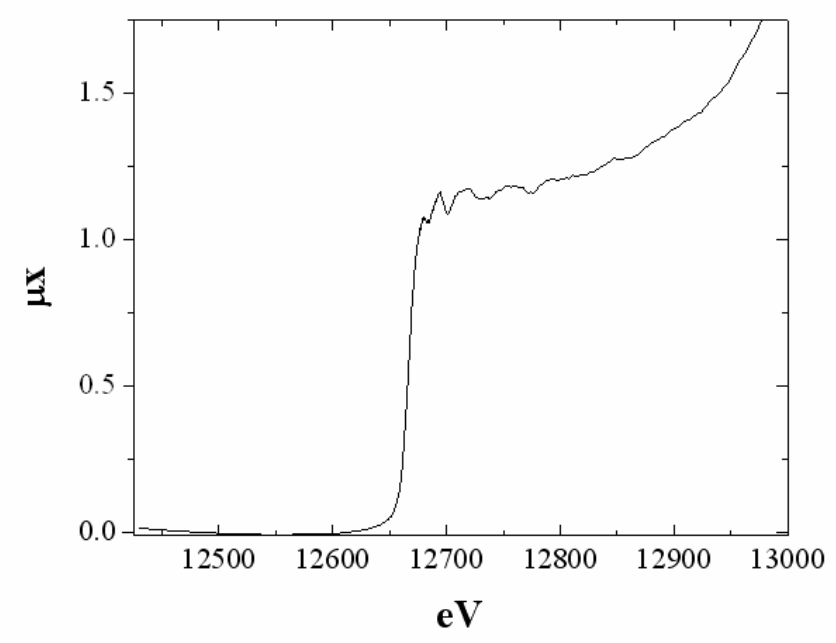
Estimates of μ^* and x_c:

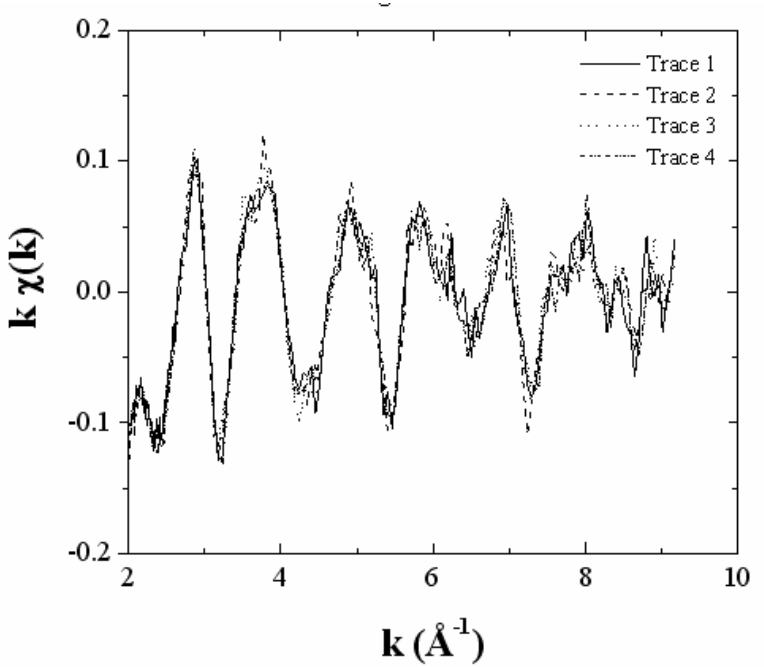
- x_c ~ 0.3 %
- μ^* ~ 180 meV
- comparable to δE

Murakami *et al*., Physica C **269**, 83 (1996).
Matsushita *et al*., cond-mat/0605717 (2006).

Evidence for mixed Tl valence in $(Pb_{1-x}Tl_x)Te$: x-ray absorption

- F. Bridges (UCSC)
- Tl L3 absorption edge at 3.1 K for x = 1.0 %





- no discernable chemical shift
- EXAFS best fit by *two* Tl-Te distances: difference ~ 0.15 Å
- however, Pb edge restricts range in k-space of oscillations
- suggestive of 2 Tl valences, but not conclusive

- what extra evidence does the normal state offer?

Outline

(1) Superconductivity in Tl-doped PbTe

(2) The chemistry of Tl

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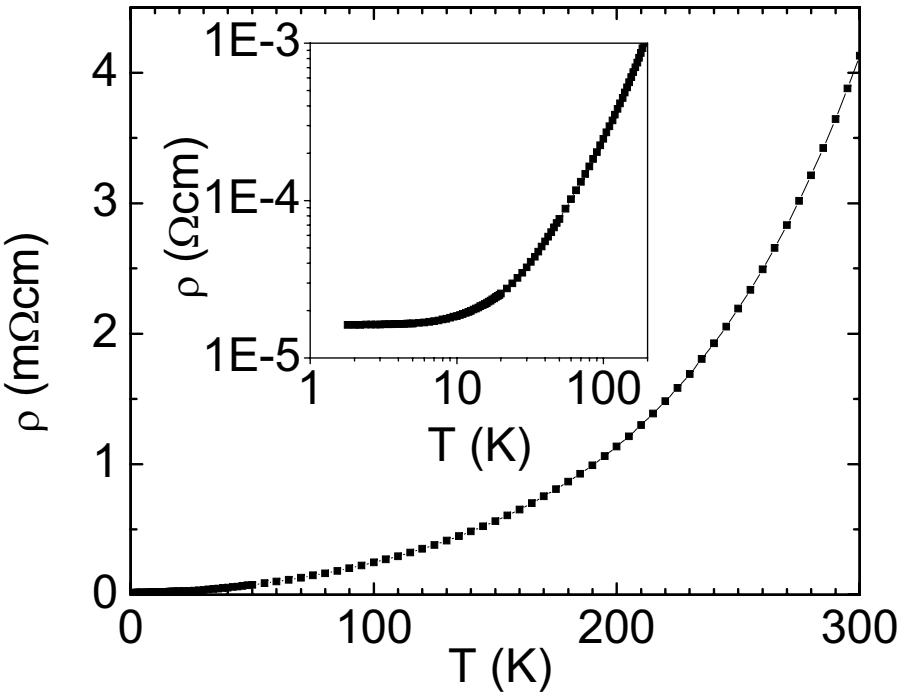
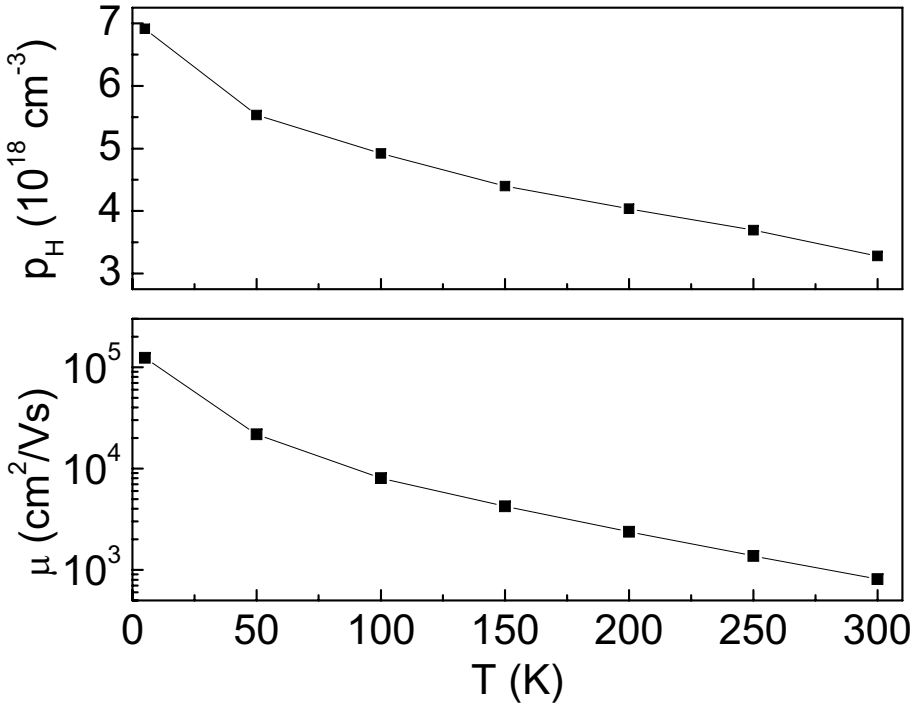
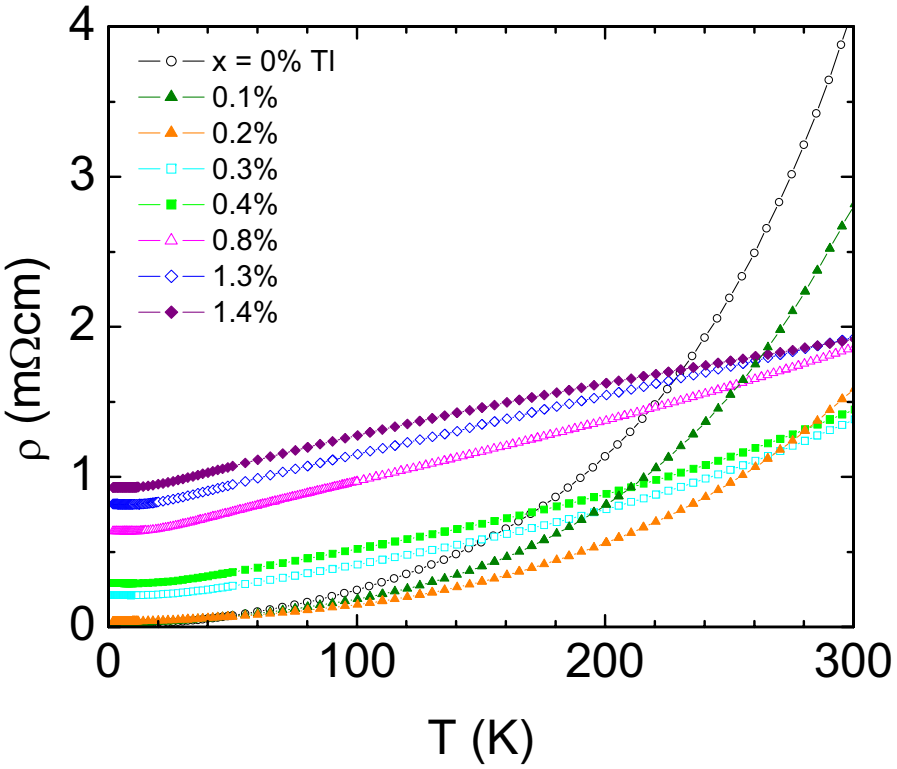
Undoped PbTe

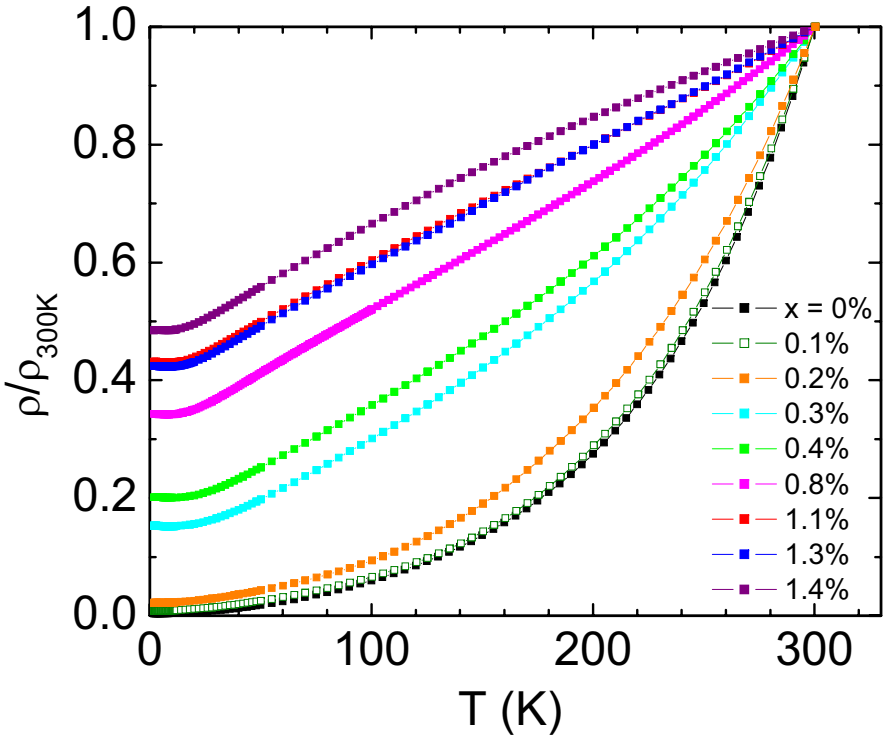
- Pb vacancies contribute a hole concentration ~ 7 × 10^{18} cm^{-3}
- E_F ~ 100 meV below top of valence band
- degenerate semiconductor, metallic resistivity
- mobility ~ 10^5 cm^2/Vs
- mean free path, l ~ 3 μm



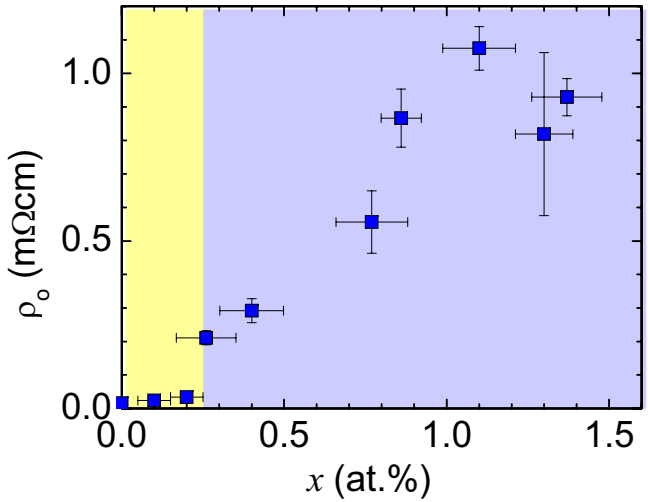


Evolution of normal state resistivity

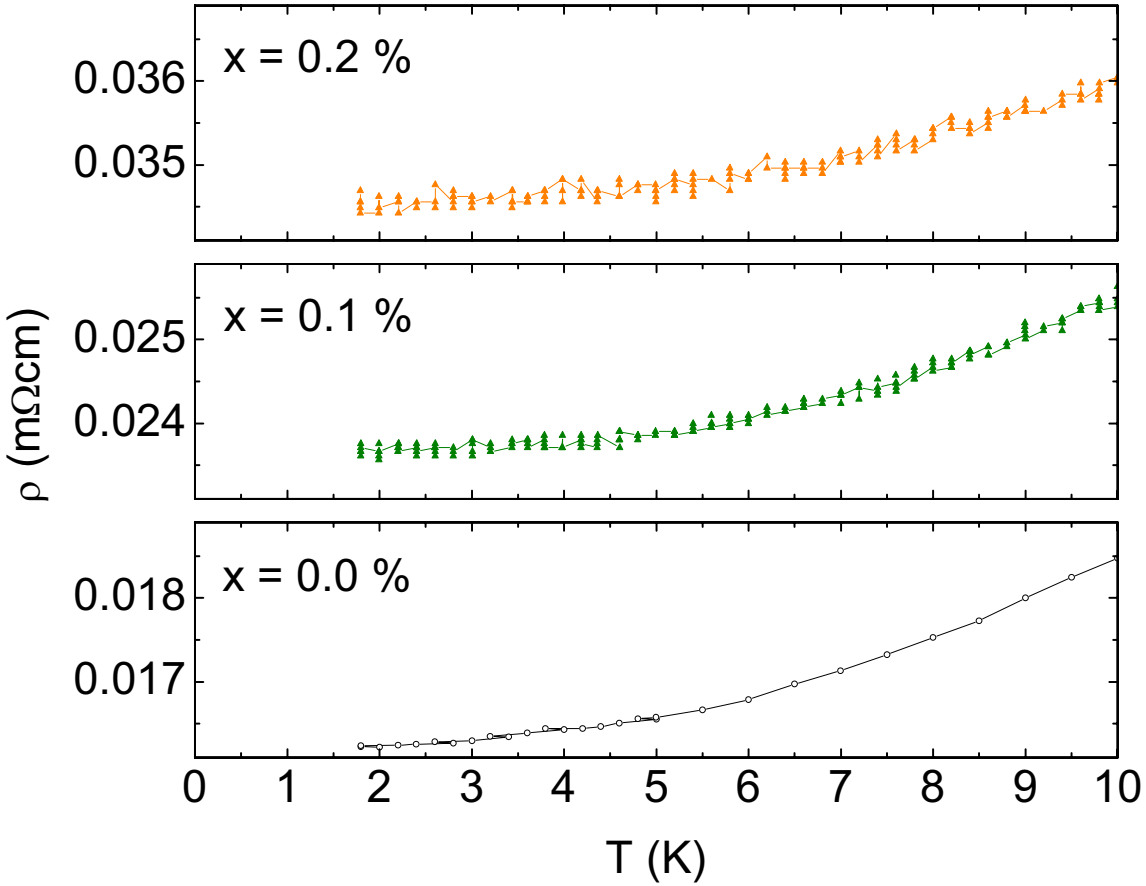




- Tl strongly affects the scattering
- substantial increase in ρ_0 at critical concentration $x_c \sim 0.3\%$
- T-dependence of resistivity evolves towards a more linear behavior

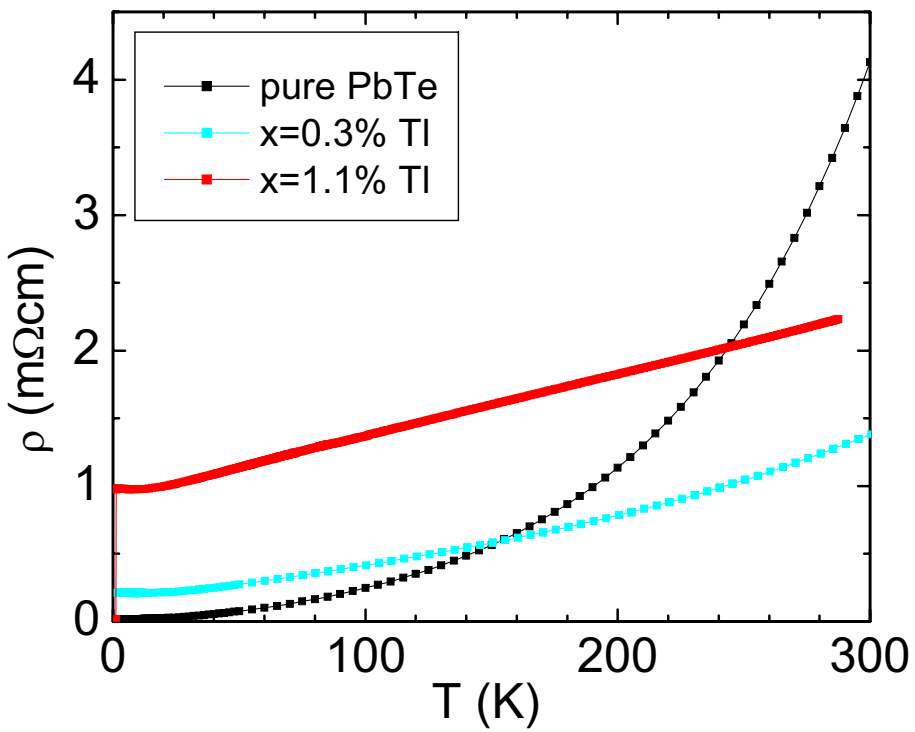


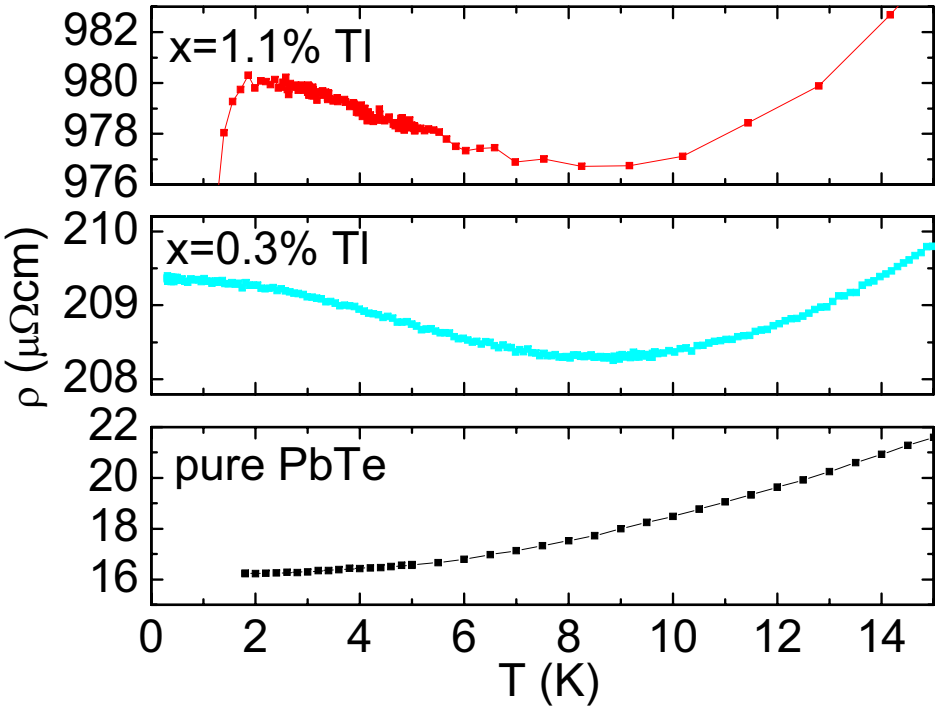
Low T resistivity: non-superconducting samples (x < 0.3 %)



- Approach a T-independent residual resistance as expected
- Tl content confirmed by EPMA and x-ray absorption

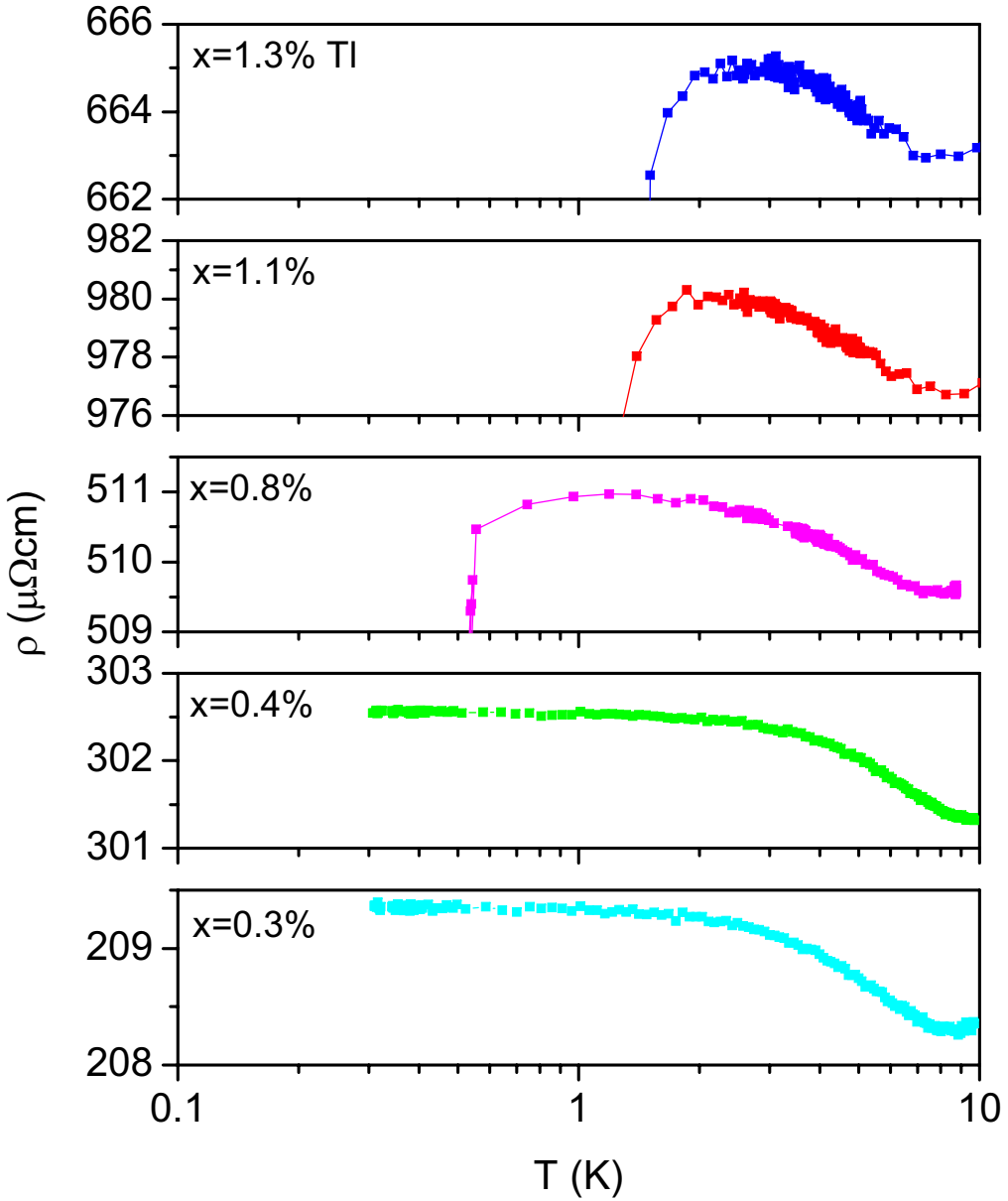
Low T resistivity: superconducting samples





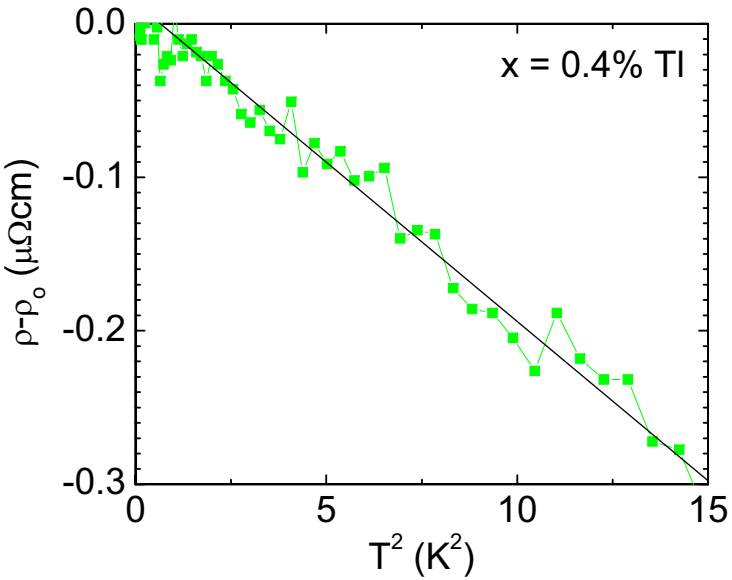
- anomalous upturn below 10 K for superconducting samples
- appears to saturate at low T
- larger effect for larger Tl content, but cut off by T_c

Low T resistivity: superconducting samples



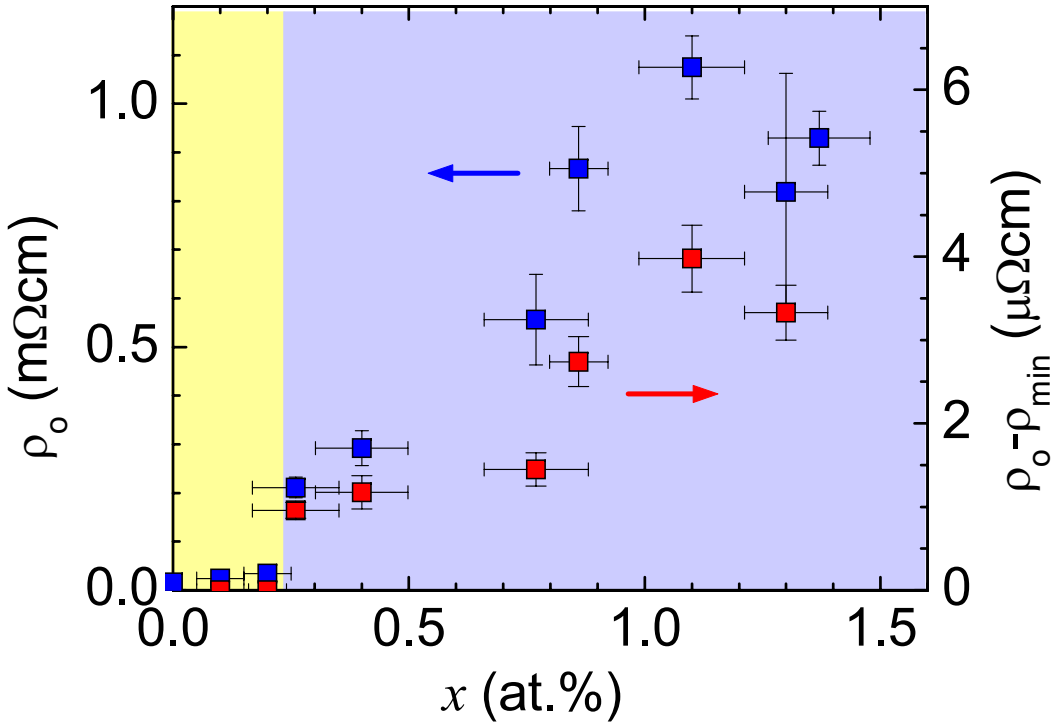
- reminiscent of Kondo effect…
- log upturn over restricted range?
- T^2 at low T for x = 0.3 & 0.4 %

$$\rho(T) \propto \left[1 - (T/T_K)^2\right]$$



- estimate T_K ~ 6 K from fits

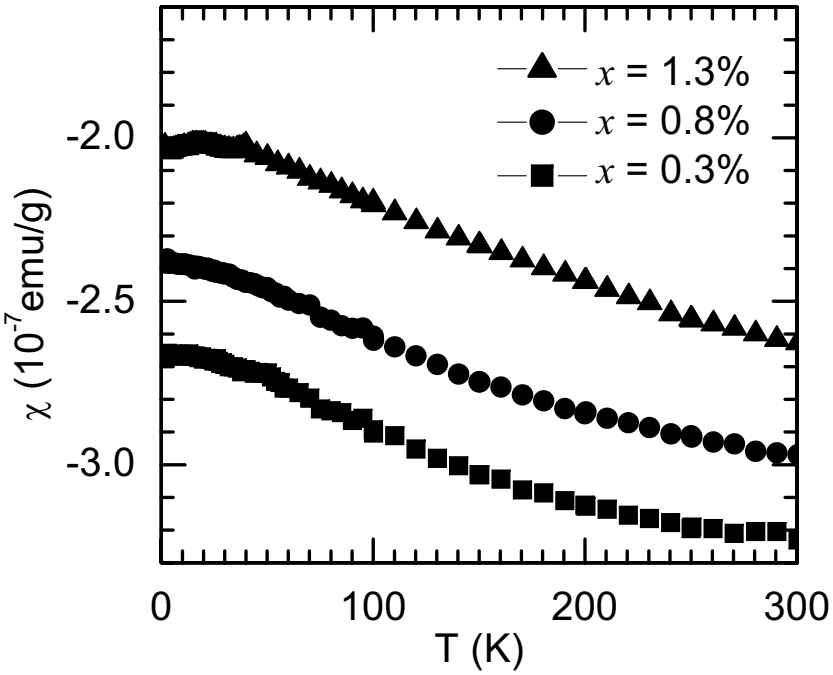
Scaling of low-T anomaly



- size of upturn scales approximately linearly with Tl content for x > 0.3%
- reproduced for different Tl sources (elemental Tl and Tl_2Te)

Magnetic impurities?

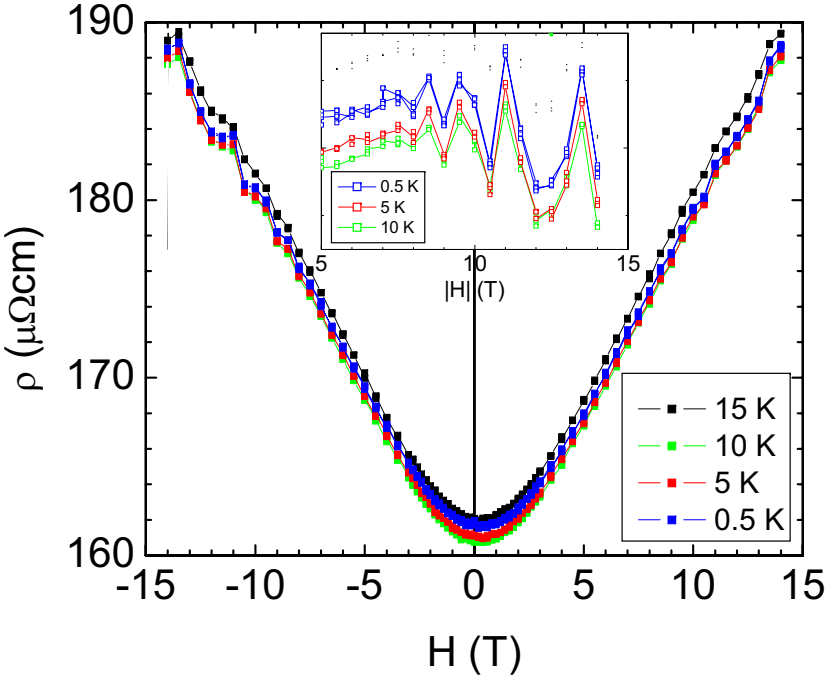
- no magnetic impurities detected (to 5ppm level)
- resistivity upturn scales with Tl concentration, but results repeated for different Tl sources
- no resistivity upturn for x < 0.3% (Tl content confirmed via XAS and EPMA)

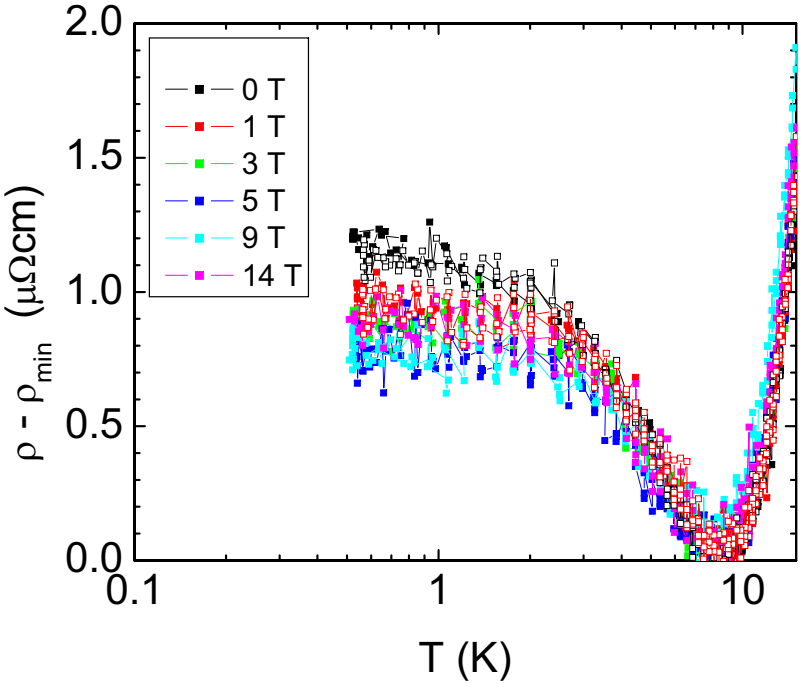


- i.e. resistivity upturn not associated with paramagnetic impurities (either from the Tl or from extrinsic impurities)

Weak localization?

x = 0.3%:





- linear MR & quantum oscillations → $\omega_c\tau > 1$
- l ~ 210 Å; $k_F l$ ~ 5 - 8

} resistance upturn not due to weak localization

- resistance upturn only weakly suppressed by large applied fields
- identical relative suppression for larger Tl-concentrations

Structural phase transition?

Ge doped PbTe:

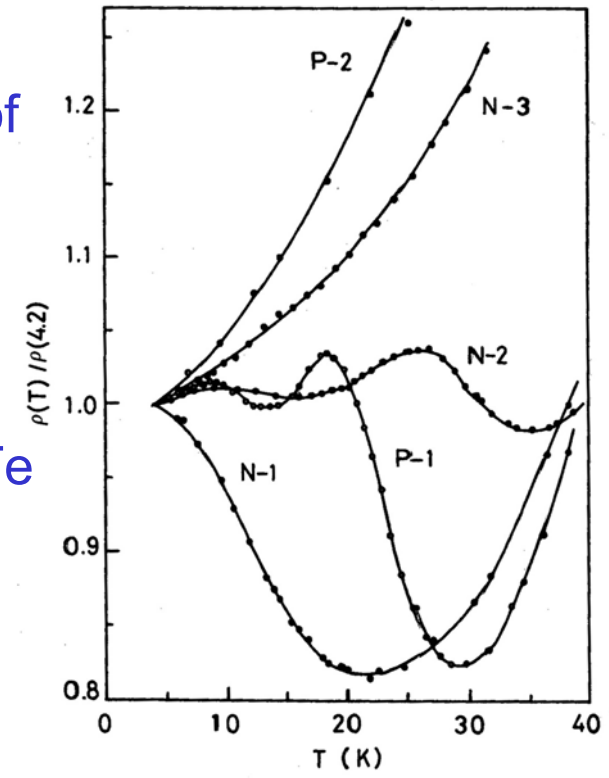
- ferroelectric for x > 0.5 %
- various features in the electrical transport
- could a soft mode play a role in unusual properties of Tl-doped PbTe?

(1) no structural phase transition in Tl-doped PbTe:

- i.e. resistivity anomaly not associated with onset of ferroelectricity
- nor for In or Ga doped PbTe

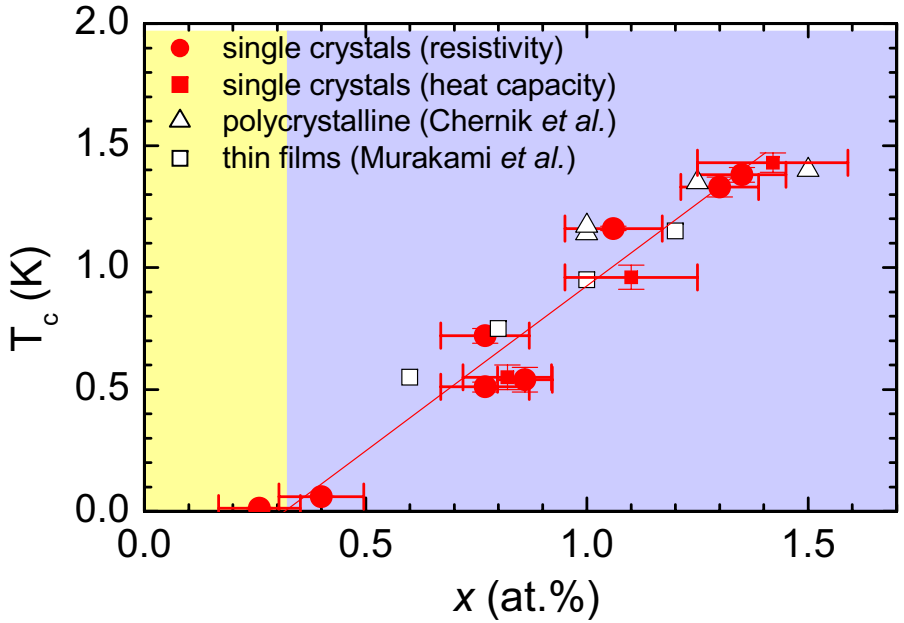
(2) Ge doped PbTe does not superconduct:

- small amounts of Ge *suppress* T_c in Tl-doped PbTe
- i.e. high T_c unlikely due to soft mode



Takano et al., J. Phys. Soc. Japan **53**, 4309 (1984).

Summary of observations



$x < x_c$:
- non-superconducting
- perfectly normal metal

$x > x_c$:
- superconducting
- Tl impurities are self-compensating
- something strongly affecting scattering
- Kondo-esque T-dependence below 10 K
- not magnetic impurities; not weak localization
- not a structural phase transition

Question: could the resistivity upturn be associated with degenerate valence states of the Tl impurities – a charge Kondo effect?

Outline

(1) Superconductivity in Tl-doped PbTe

(2) The chemistry of Tl

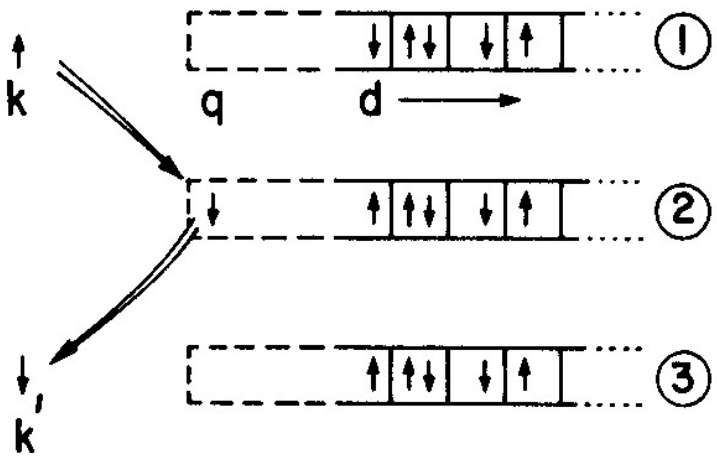
(3) Anomalous normal state properties

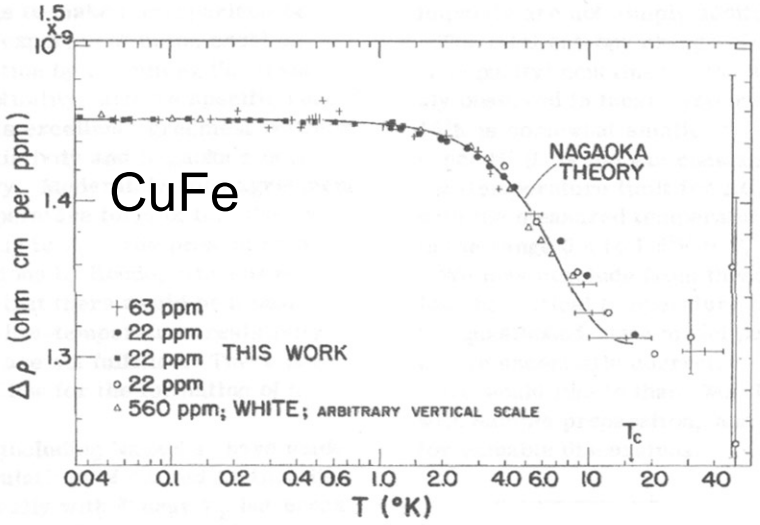
(4) The charge Kondo effect

The Kondo effect

Magnetic impurities in a non-magnetic host:

- virtual bound state
- degenerate “up” or “down” states for one spin
- second order spin-flip processes contribute to log term in resistivity
- at low T, $\rho \sim [1-(T/T_K)^2]$





A. J. Heeger, in Solid State Physics vol 23 (1969)

- other degenerate two-level systems can also lead to Kondo-like behavior
- including degenerate valence states…

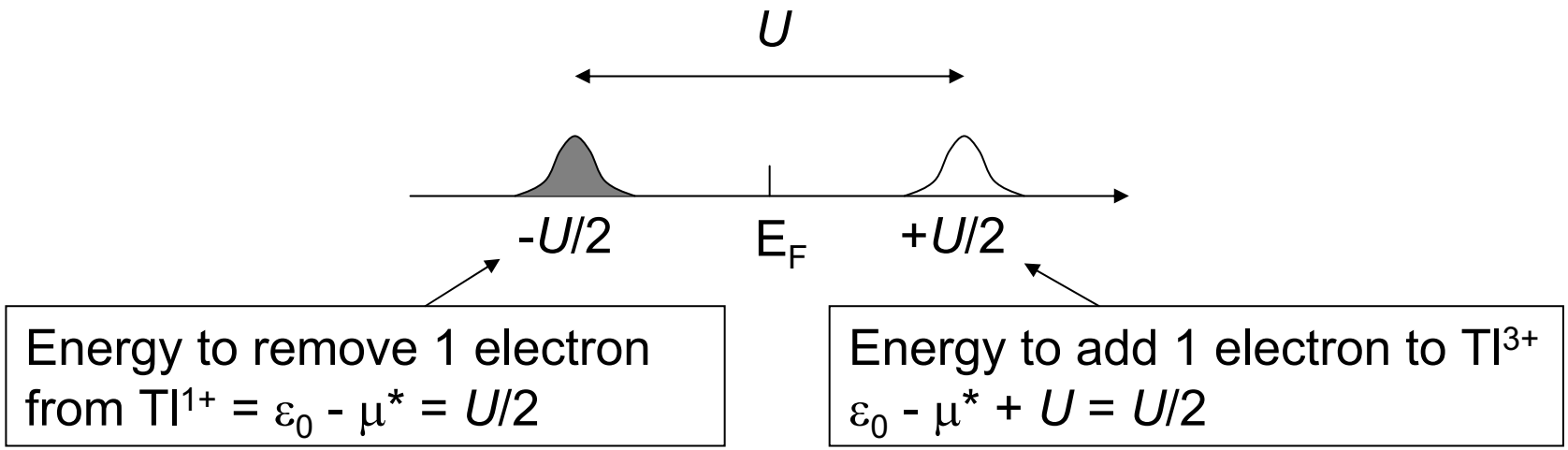
“Heavy Fermion Behavior in a Negative-U Anderson Model” Taraphder & Coleman, PRL **66**, 2814 (1991).

Charge Kondo effect from degenerate valence states

Negative-*U* impurities:

- $E(Tl^{+}) = E_0$
- $E(Tl^{2+}) = E_0 + \varepsilon_0 - \mu$
- $E(Tl^{3+}) = E_0 + 2(\varepsilon_0 - \mu) + U$

Consider the case $\mu = \mu^* = \varepsilon_0 + \frac{1}{2}U$…



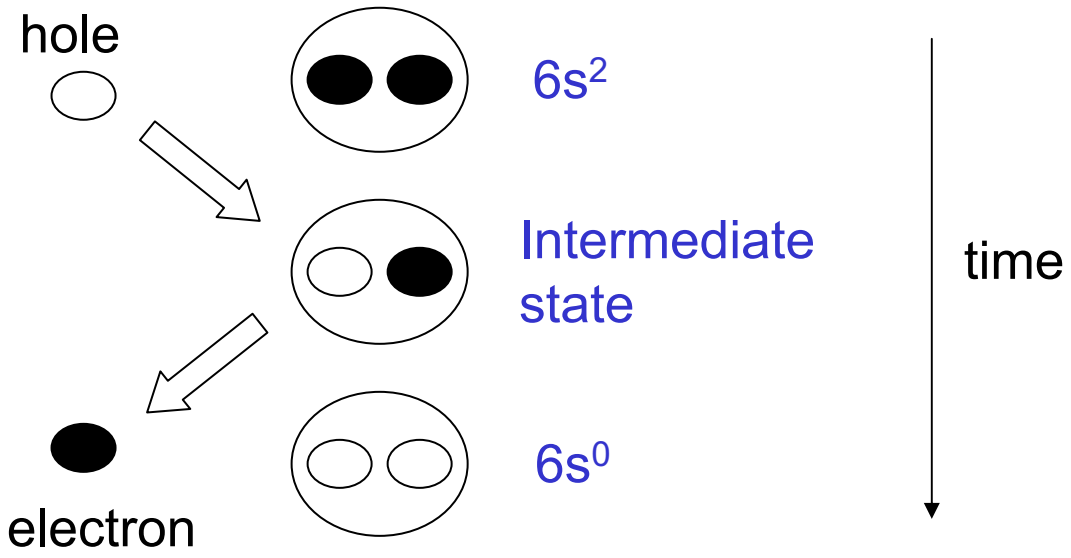
- same spectrum as for +ve *U*, but different underlying interactions
- hybridization with valence band → Kondo effect
- pseudo-spin = pair occupancy; δE plays role of magnetic field

"Heavy Fermion Behavior in a Negative-U Anderson Model" Taraphder & Coleman, PRL **66**, 2814 (1991).
"Superconductivity in charge Kondo systems" Dzero and Schmalian, PRL **94**, 157003 (2005).

Pseudo-spin-flip in charge-Kondo effect

Dilute negative-U impurities:

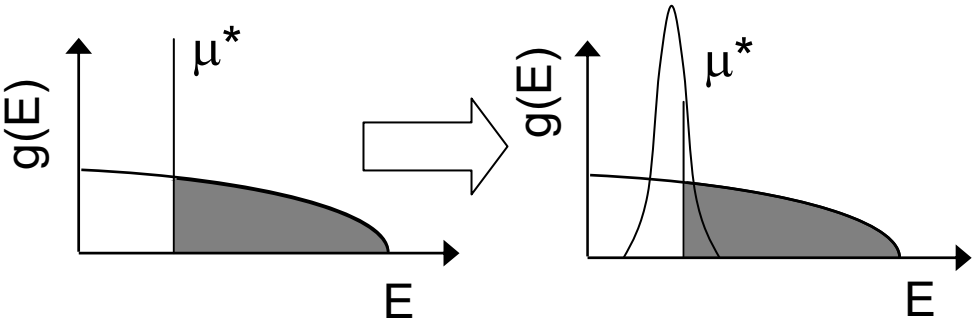
- pseudo-spins correspond to $6s^0$ and $6s^2$
- second order "spin flip" processes swap 0 ↔ 2 electrons

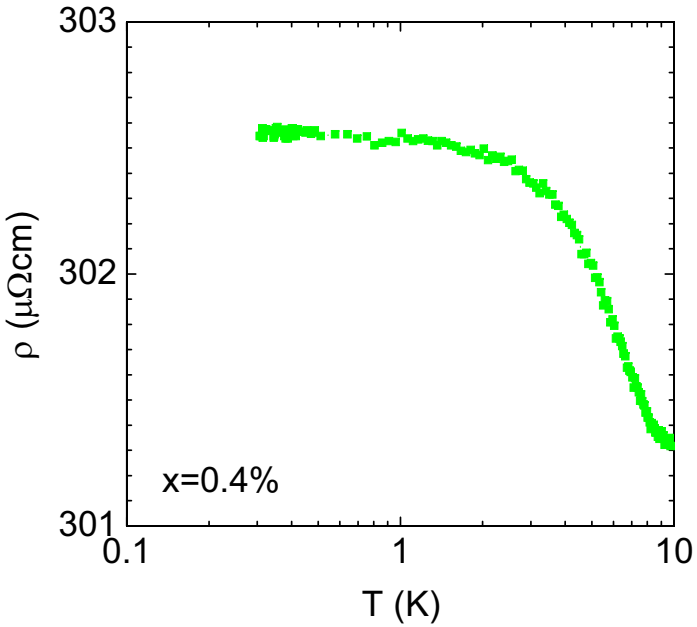


- in absence of orbital degeneracy, single channel effect
- will contribute log term to resistivity & unitary scattering
- a unique property of the negative-*U* model
- does this account for observed behavior of Tl-doped PbTe, with T_K ~ 6 K?

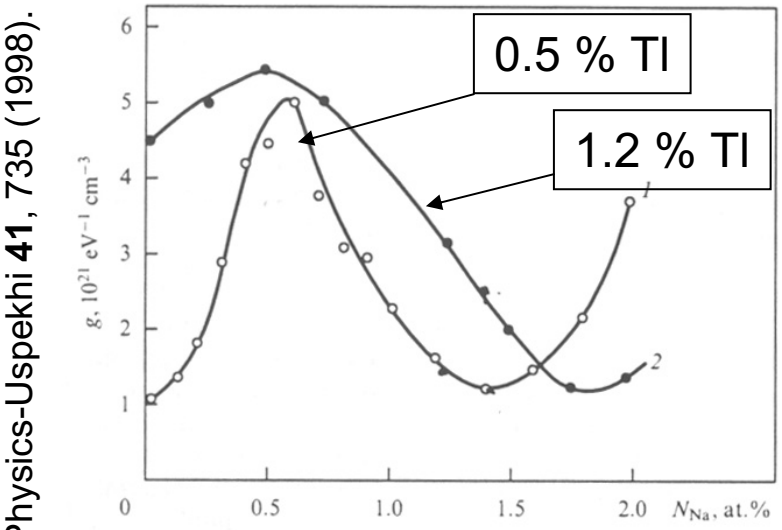
Concentration of degenerate Tl impurities & unitary scattering

Different Tl environments:





Na counter-doping:



Nemov, Physics-Uspekhi **41**, 735 (1998).

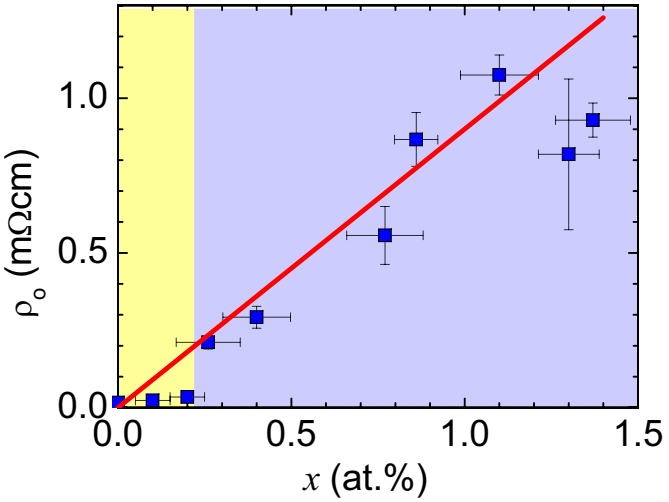
$$\rho_{imp} = \frac{2m}{ne^2\pi\hbar g(E_F)} c_{imp}$$

- $\Gamma \sim 30$ meV for $x = 0.5$ %
- ~ 1% of Tl impurities degenerate

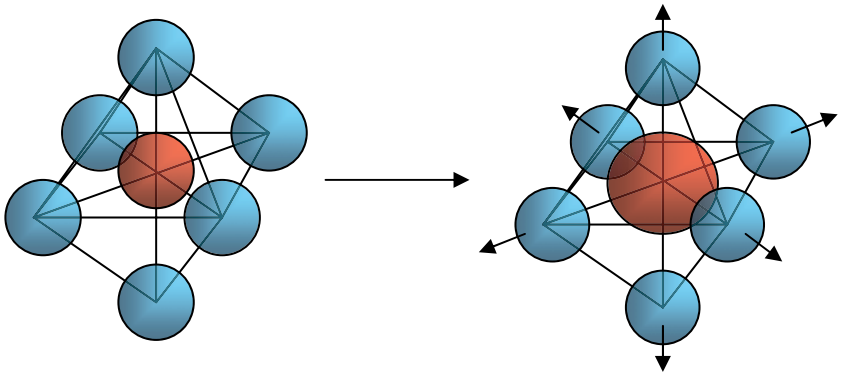
- $c_{imp} \sim 10^{17} - 10^{18}$ cm^{-3}
- $x = 0.4\% \equiv 6\times10^{19}$ cm^{-3}
- $c_{imp} \sim 0.2 - 2\%$ of Tl impurities
- consistent with γ enhancement

Comment on some alternative scenarios

Alternative scenario #1:
- all Tl impurities fluctuating?
- note: ρ_0 close to unitary scattering limit (red line)
- reduces size of resistivity upturn at low T?



Alternative scenario #2:
- mixed valence, but no valence fluctuations?
- ionic motion provides negative-U, stifles valence fluctuation



Coulomb cost: $U_C = \dfrac{U}{\varepsilon_0}$

Energy gain: $\Delta E \sim F_0 x - \frac{1}{2} k x^2$

Alternative scenario #3:
- Tl impurity band? (i.e. 3rd band with low mobility)
- what scattering mechanism causes the resistivity upturn?

Consequences for superconductivity in Tl-doped PbTe

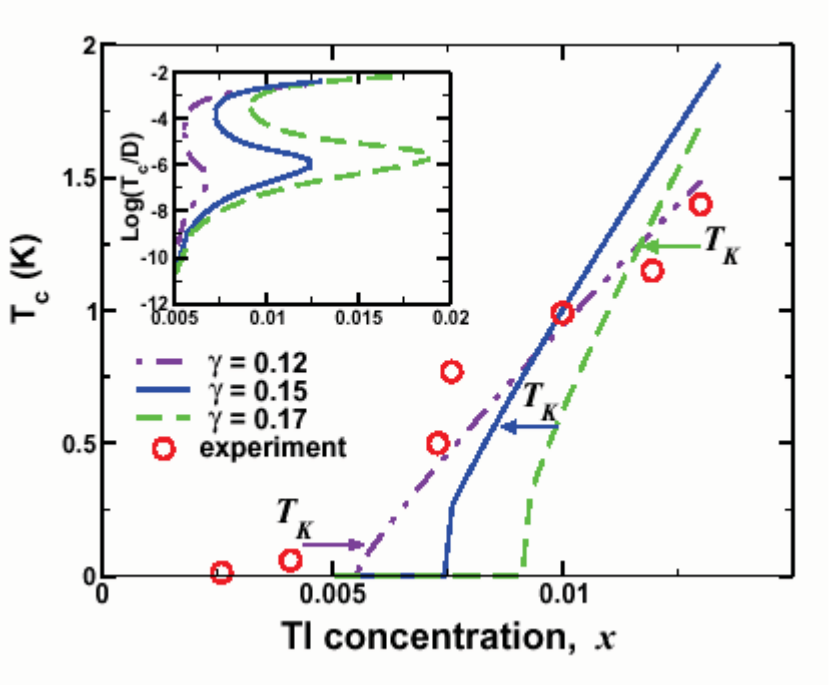
(1) Dynamical mixed valence:

- if this effect derives from a charge Kondo effect, this directly attests to quantum valence fluctuations in Tl-doped PbTe
- it has been shown theoretically that such valence fluctuations can lead to superconductivity (i.e. an alternative pairing mechanism)
- corresponds to in-plane order in iso-spin space, mediated by RKKY

Schuttler, Jarrel & Scalapino, PRB **39**, 6501 (1989).

(2) Interaction of T_c and T_K:

- Dzero and Schmalian, PRL **94**, 157003.
- predict re-entrant behavior at very low T due to pair-breaking effects
- unclear whether effect observable for Tl-doped PbTe (certainly < 20 mK)



Why PbTe?

(1) μ^*:
- value of μ^* is achievable
- likely due to charge balance requirements of substituting Tl in $Pb^{2+}Te^{2-}$

(2) large high-frequency dielectric constant:
- ε_∞ ~ 30 - 40
- enables rapid, adiabatic tunneling of electrons

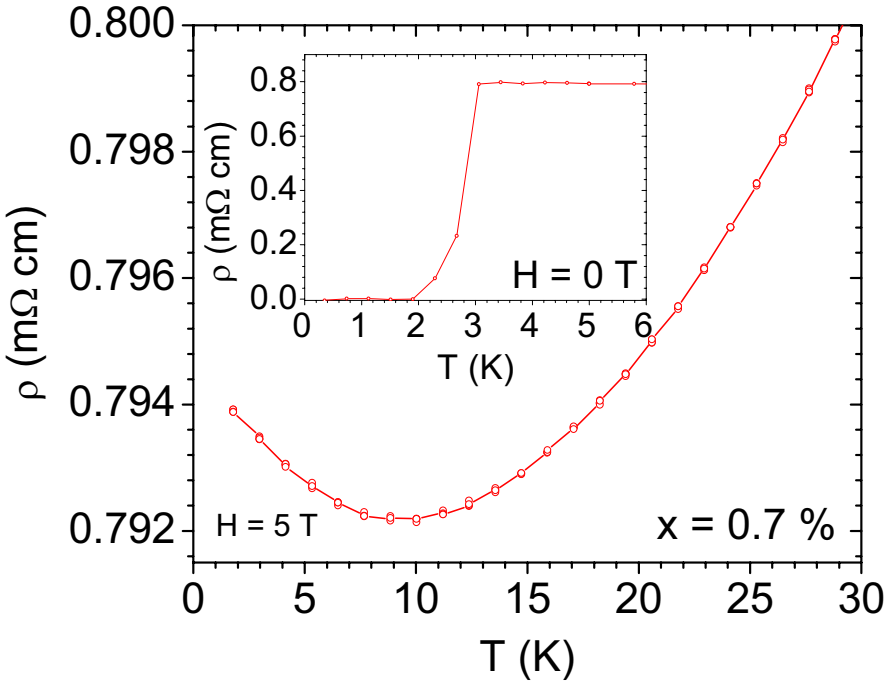
(3) Tl ions "fit":
- average ionic radius of Tl^+ and Tl^{3+} equals that of Pb^{2+}
- i.e. average radius of fluctuating ion fits in lattice

(4) ionicity of host:
- very low carrier concentration; very localized charge distribution
- Tl impurities are not hybridized away to nothing
- i.e. meaningful to have a 6s virtual bound state

Outlook – related materials

In-doped SnTe:

- indium increases T_c of SnTe
- resistivity anomaly at low T
- appears to be a generic effect…



Summary

Tl-doped PbTe:

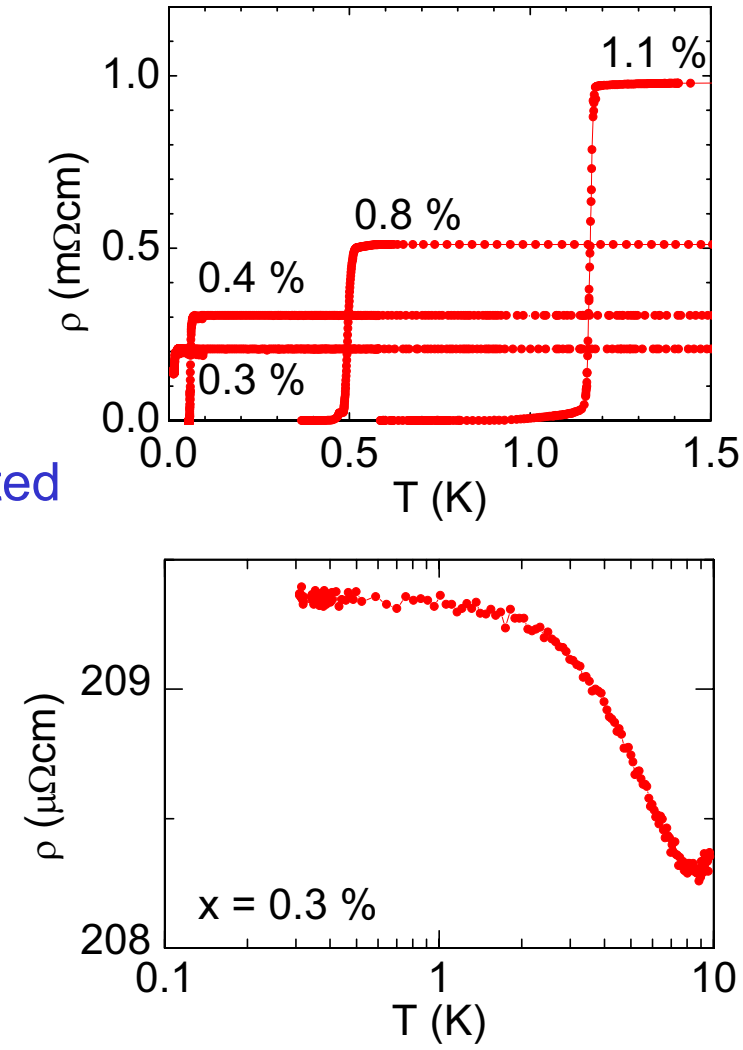
- superconducts with T_c ~ 1.5 K
- only impurity that causes superconductivity

Anomalous transport properties:

- upturn in resistivity associated with s/c
- does not appear to originate from magnetic impurities or localization effects
- first evidence for charge Kondo effect associated with degenerate valence states?

Consequences:

- supports notion of an alternative pairing mechanism for Tl-doped PbTe
- might account for anomalously high T_c value



Y. Matsushita et al., PRL **94**, 157002 (2005).

Y. Matsushita et al., cond-mat/0605717 (2006).

Mean free path estimates

x	**0.3%**	**0.4%**	**0.8%**	**1.4%**
E_F (meV)	180	182	188	192
k_F (Å^{-1}) *	0.023 – 0.039	0.025 – 0.039	0.03 – 0.04	0.034 – 0.04
***l* (Å)**	209	130	50	20
$k_F l$ *	5 – 8	3 – 5	~ 2	~ 1

* values for the *L* and Σ bands

Superconducting parameters

	$x = 1.1$ at.%	$x = 1.4$ at.%
T_c	1.16 ± 0.01 K	1.38 ± 0.03 K
$H_{c2}(0)$	0.39 ± 0.04 T	0.60 ± 0.07 T
l	32 ± 8 Å	19 ± 5 Å
$\xi(0)$	290 ± 15 Å	240 ± 14 Å
ξ_0	2600 ± 700 Å	3000 ± 850 Å
v_F	$2.2 \pm 0.6 \times 10^5$ m/s	$3.0 \pm 0.8 \times 10^5$ m/s
λ_L	1600 ± 80 Å	1500 ± 120 Å
λ_{eff}	1.4 ± 0.4 μm	1.9 ± 0.5 μm
κ	48 ± 12	79 ± 20
H_c	57 ± 14 Oe	54 ± 13 Oe
H_{c1}	3 ± 0.8 Oe	2 ± 0.5 Oe

Y. Matsushita et al., cond-mat/0605717 (2006).