Searching for Higher T_cs by observing T_c

RTS Workshop - Loen, Norway

T. H. Geballe

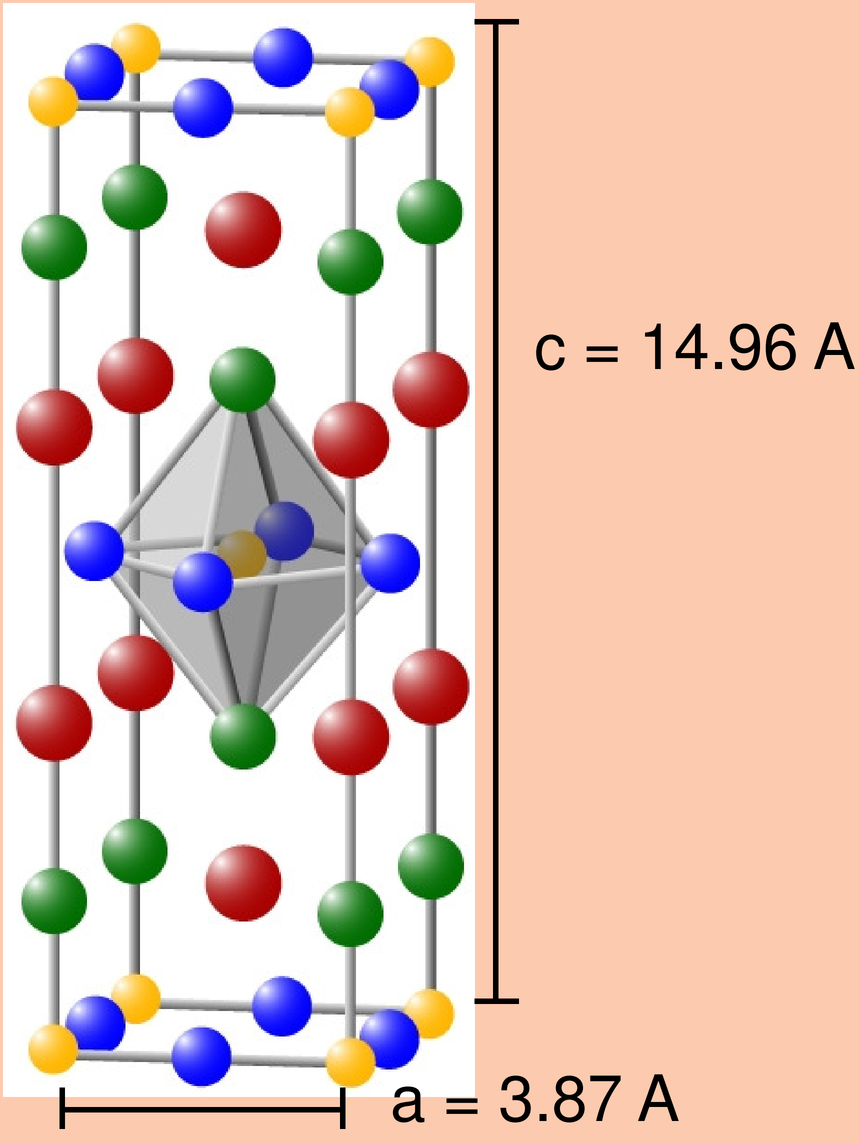
Stanford University, June 17-24 2007

Outline

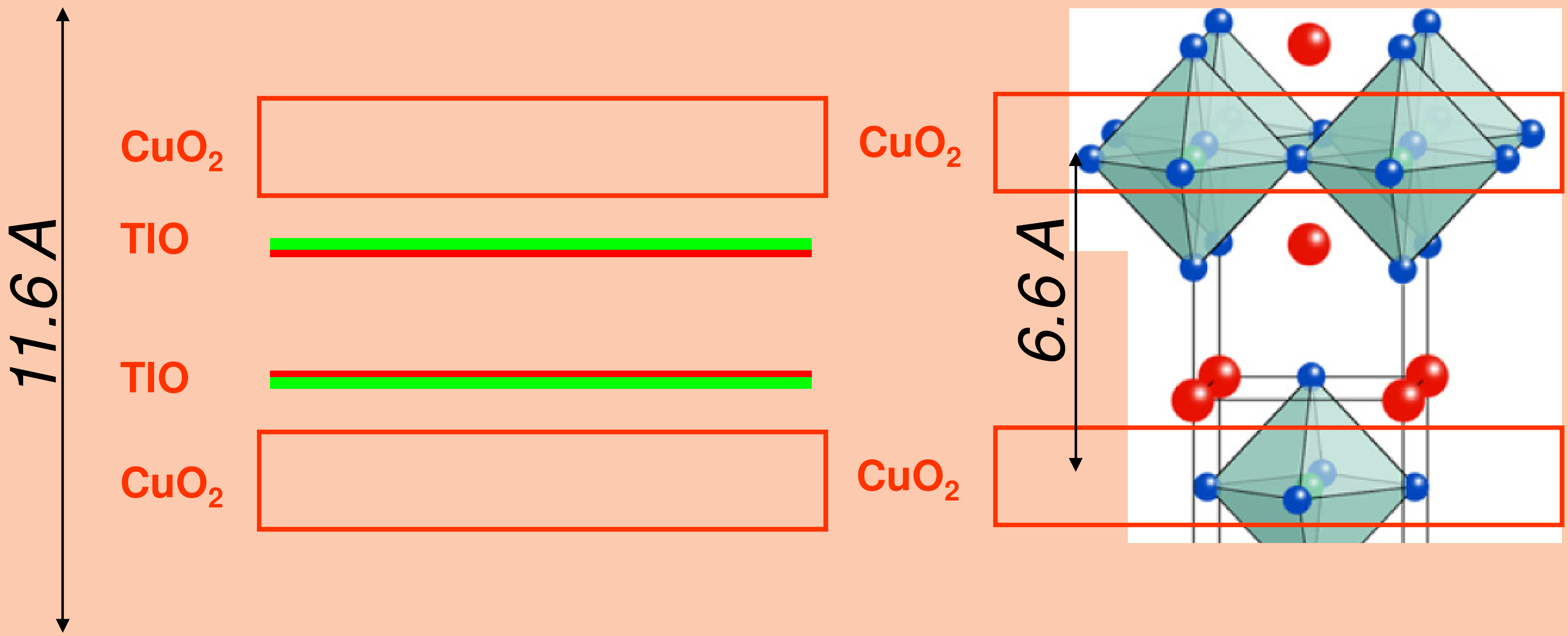
Insights from

- variation of T_c with structure and phase
- variation of T_c with composition
- variation of T_c with external parameters
- follow up on unknown trace signals

Bednorz-Mueller Cuprate



"214" with two TlO layers inserted between



$Tl_2Ba_2CuO_8$
T_c = 95K

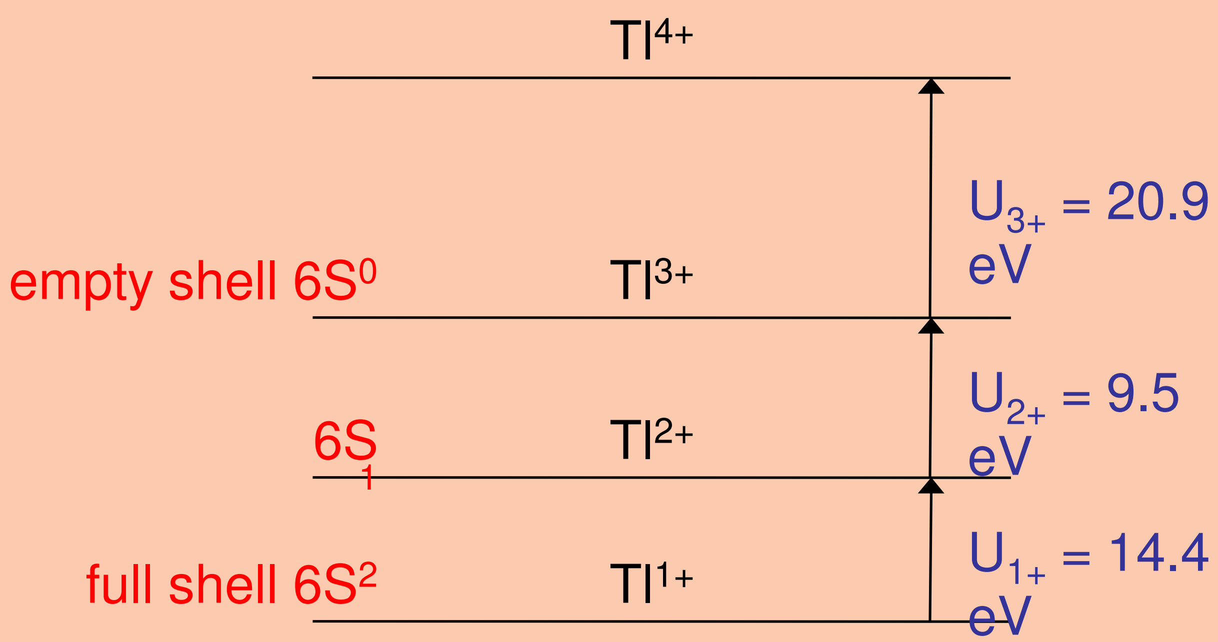
$La_{2-x}Sr_xCuO_4$
T_c= 40K

Tl,Pb,Bi ions

skip $6S^1$ in solid state

- eg: Tl^{1+} & Tl^{3+}; Pb^{2+} & Pb^{4+}; Bi^{3+} & Bi^{5+}
- Skipped valence means negative $U_{eff} = (E_{n+1} – E_n) – (E_n – E_{n-1})$
- Origin: correlation energy and polarization energy

Correlation energy evident in gaseous ion



Tl 4f corelevel in 2223 between +1 and +3

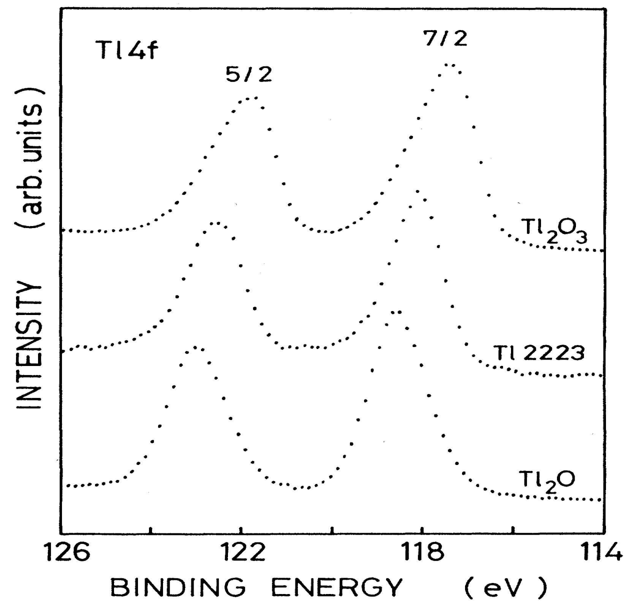
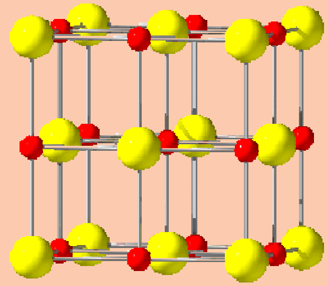


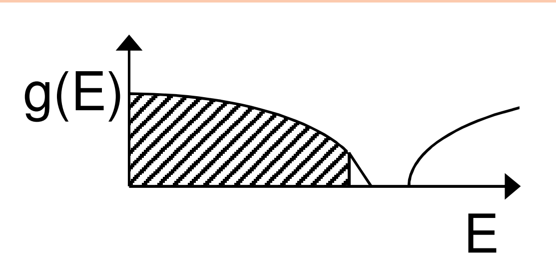
FIG. 2. XPS spectra of the Tl 4*f* core levels in Tl_2O_3, $Tl_2Ba_2Ca_2Cu_3O_{10}$, and Tl_2O. The energy scale of the spectrum for Tl_2O is corrected by using C 1*s* (284.9 eV) obtained in $Tl_2Ba_2Ca_2Cu_3O_{10}$ as a reference in order to cancel out a charge up shift.

T. Suzuki, et. al., "Chemical state of Tl in the superconductor $Tl_2Ba_2Ca_2Cu_3O_{10}$ *Physical Review B* **40**, 7 (1989).

Tl-doped PbTe



PbTe:
- small gap semiconductor
- rock salt structure-- $Pb^{2+}Te^{2-}$
- $\varepsilon_\infty \sim 30 - 40$ & $\varepsilon_0 \sim 1000$
- Pb vacancies ~10^{18} - 10^{19} holes/cm^3
  (degenerate semiconductor)



Tl substitution:
- Tl substitutes on Pb^{+2} site

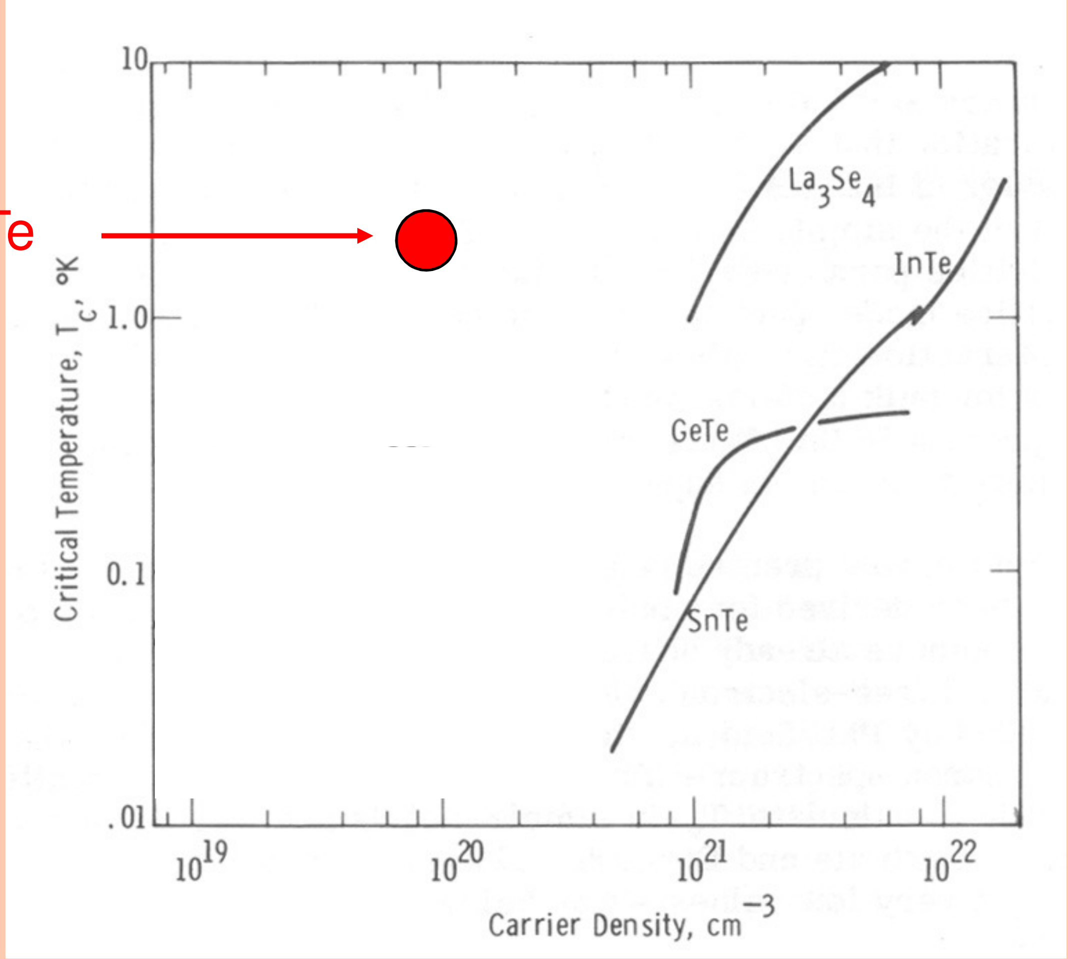
→ expect spontaneous disproportionation to balance charge…

$2Tl^{2+} \rightarrow Tl^{+} + Tl^{3+}$

Superconductivity in PbTe model system

Tl-doped PbTe

J. A. Chernik and S.N. Lykov
Lett. J. Tch Phys **7** (1981) 94



- T_c ~ 1.5 K of PbTe is 2 orders > comparable superconductors (J. K. Hulm NRL Report 6972 (1969)).
- no superconductivity for any other impurities in PbTe…

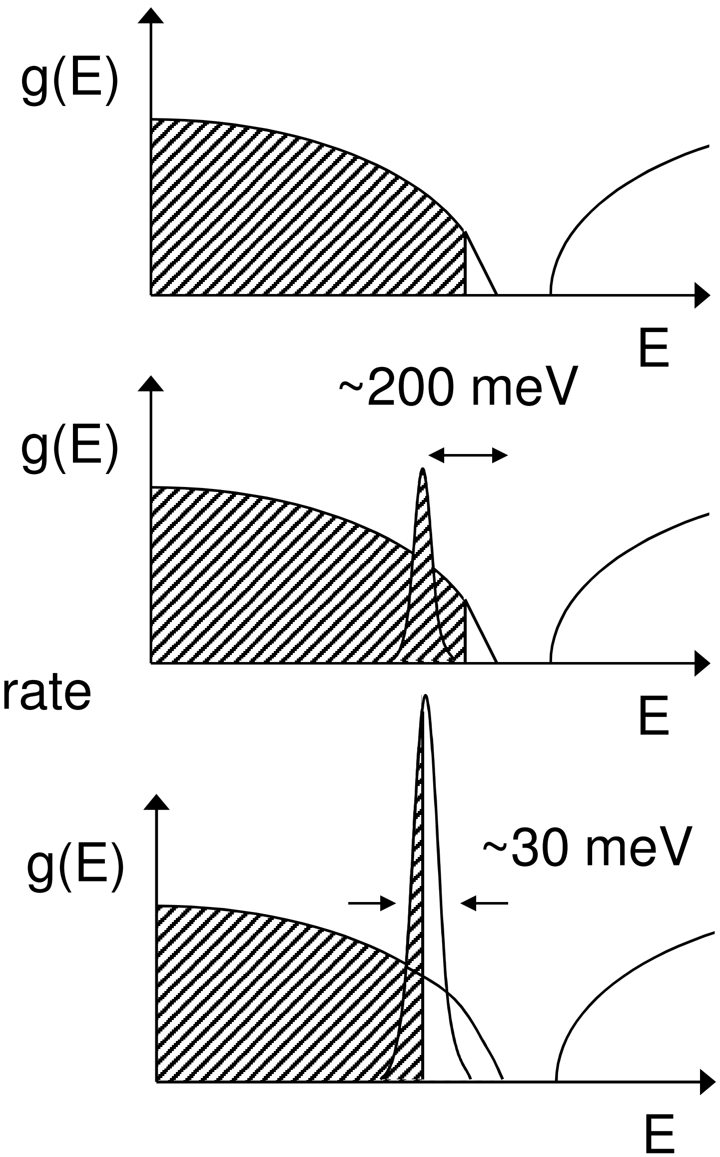
Resonant energy levels

PbTe has Pb vacancies
- E_F ~ 80 meV below top of valence band
- ~10^{19} holes/cm^3

First Tl impurities:
- Below E_F (i.e. Tl^{1+})
- i.e. hole concentration increases

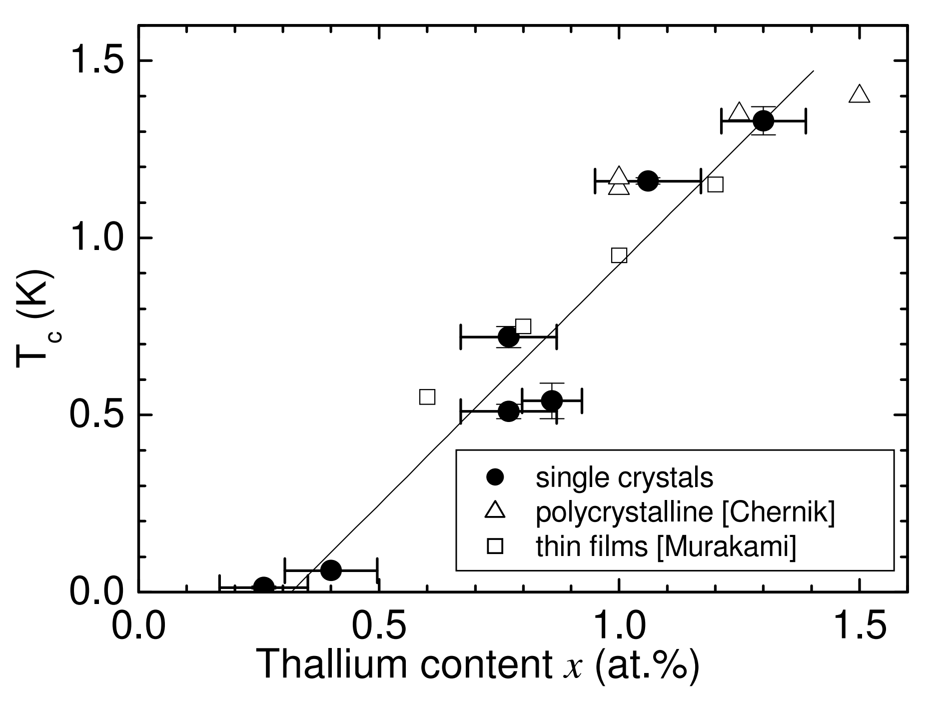
More Tl impurities: 1+ and 3+ become degenerate
- hole conc. increases until E_F reaches v_{bs}
- ~10^{20} holes/cm^3
- Fermi level pinned by two-electron states

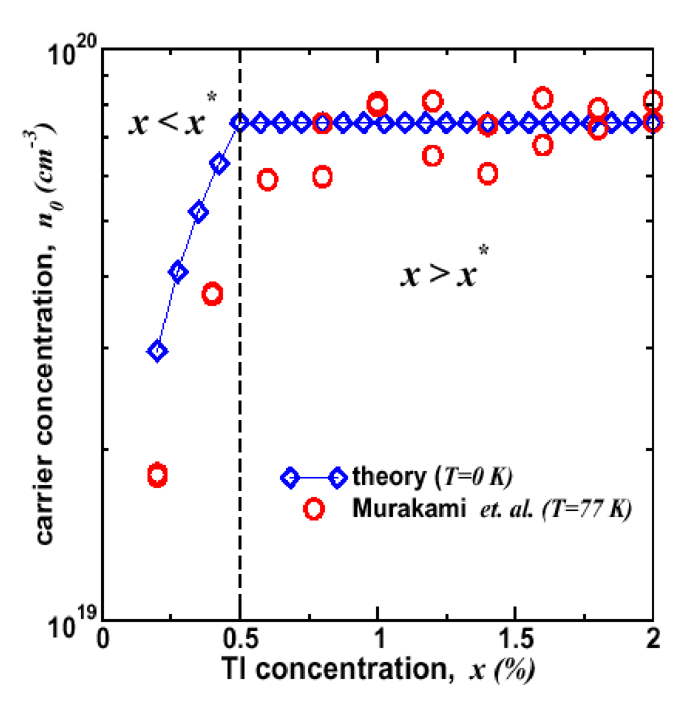
…



Nemov, Phys. USP. **41**, 735 (1998).
Kaidanov, Sov. Phys. USP. **28**, 31 (1985).

Critical Tl concentration



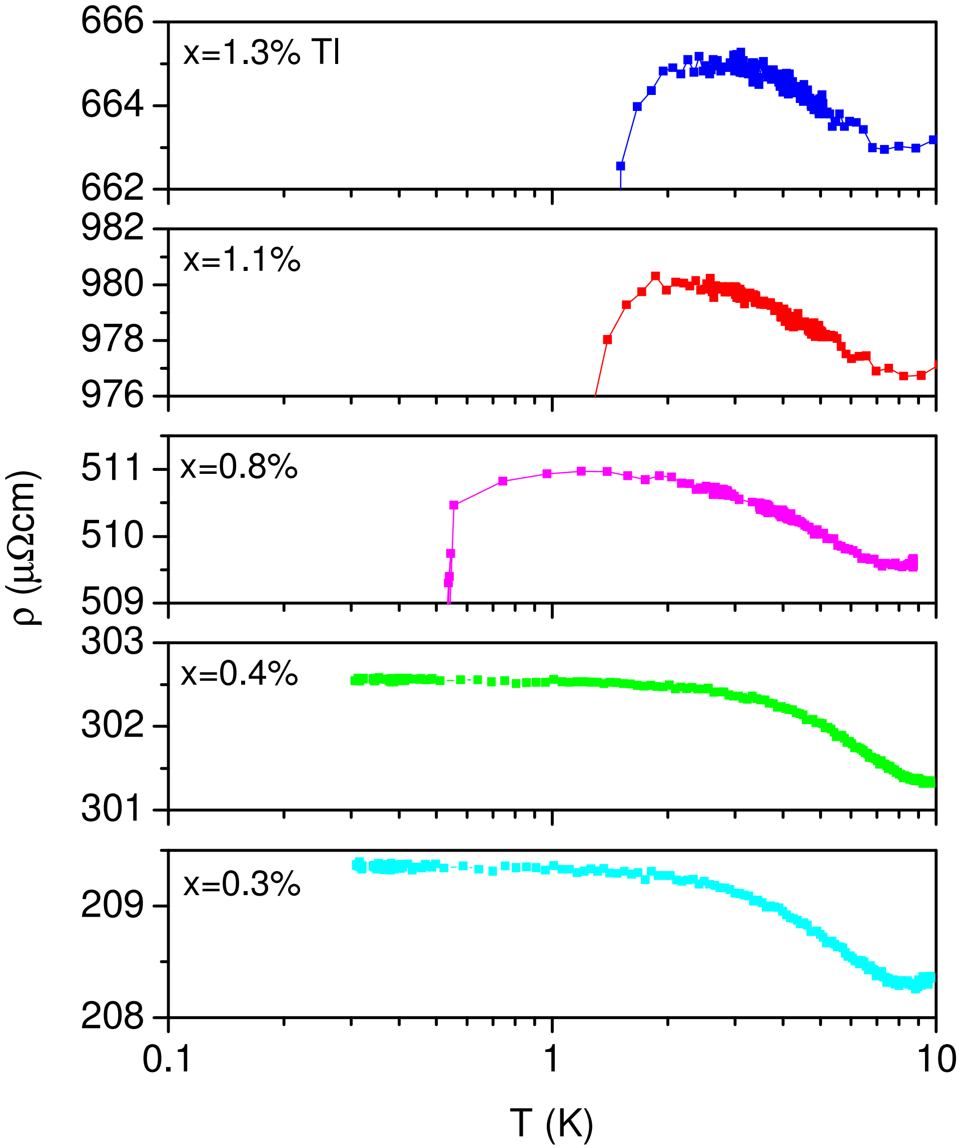


Dzero & Schmalian
PRL **94**, 157003 (2005).

- Critical concentration of impurities x_c for onset of superconductivity
- For $x< x_c$ Hall indicates 1 carrier/Tl
- For $x> x_c$ T_c increases linearly, while Hall number flattens

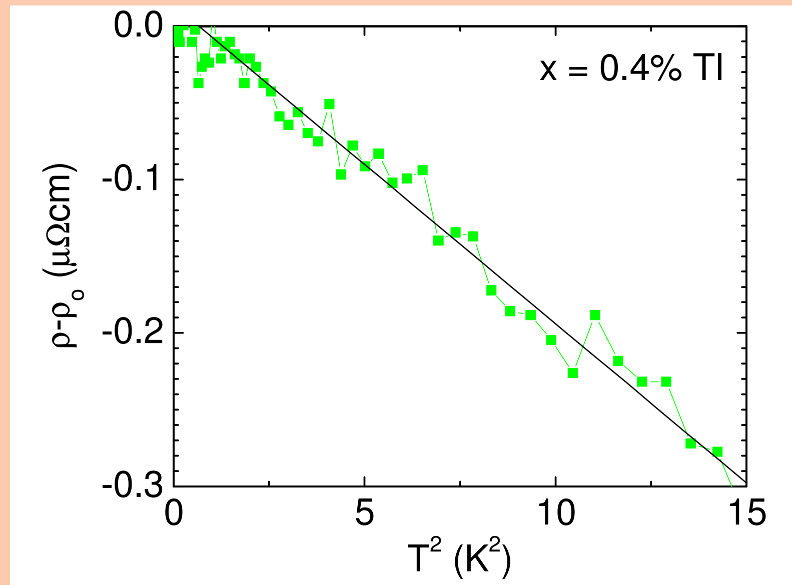
How does Tl play in the superconductivity of Tl-doped PbTe?

Low-T anomaly in resistivity



- size of anomaly scales with x
- log upturn over restricted range?
- T^2 at low T…

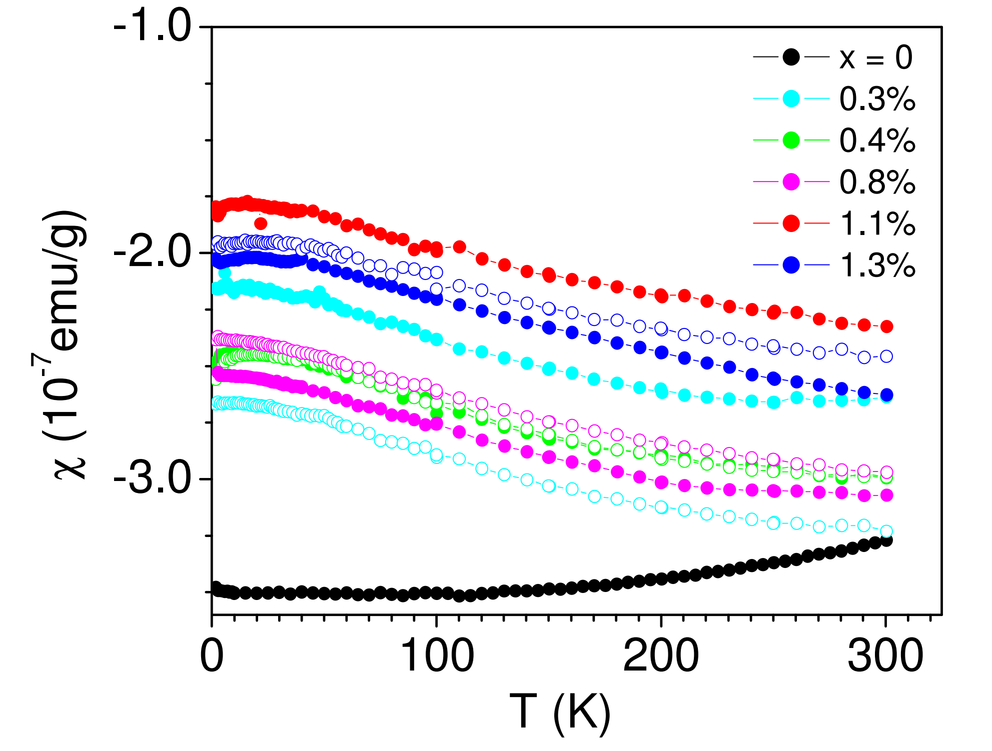
$$\rho(T) \propto \left[1-(T/T_K)^2\right]$$



- estimate T_K ~ 6 K from fits

Y.Matsushita, I. R. Fisher, et al PRL **94** 157002 (2005)
M. Dzero and J. Schmalian, PRL **94** 157003 (2005)

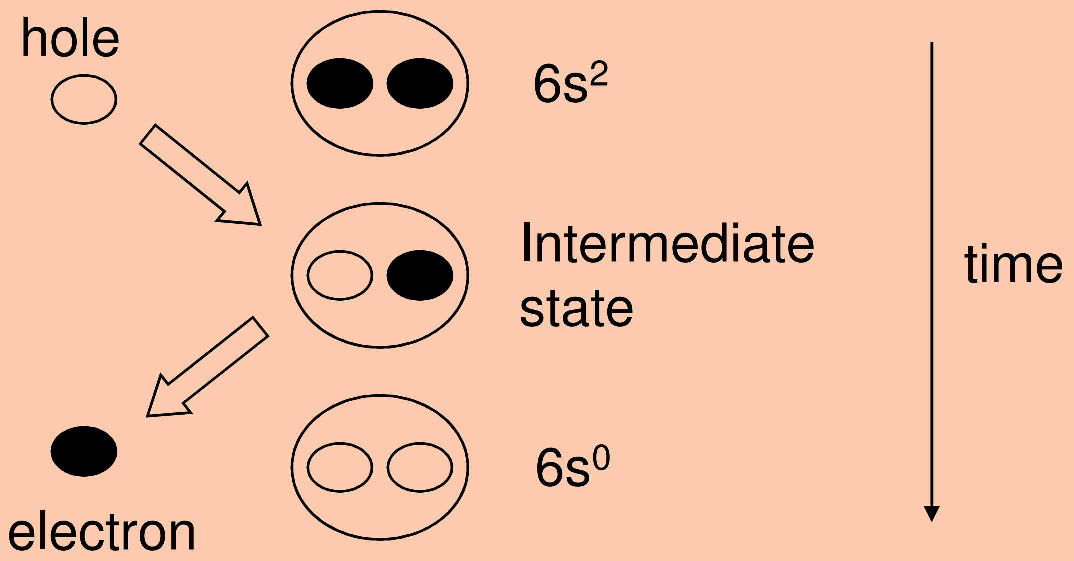
Susceptibility



- diamagnetic (low DOS)
- less diamagnetic for larger Tl concentrations
- no “Curie tail”
- → no magnetic impurities to ~ 5 – 10 ppm level

Charge-Kondo effect

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



- will contribute log term to resistivity & unitary scattering
- dynamic screening of the negative-U impurity below characteristic T_k

T_c and resistance minimum

Tl-doped PbTe:

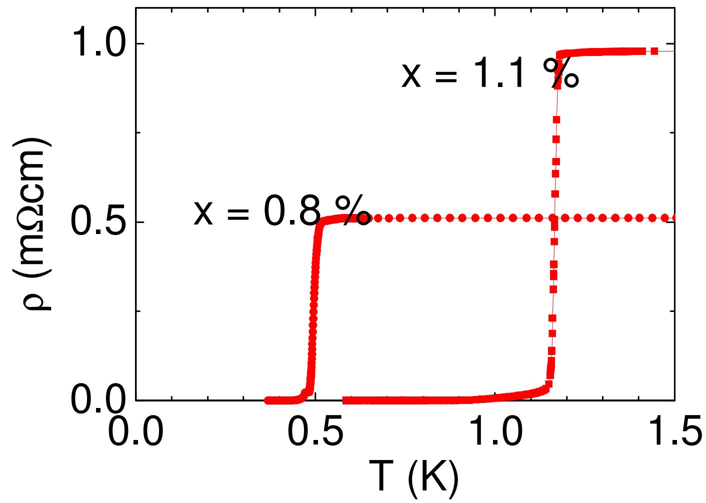
- superconducts with T_c ~ 1.5 K
- only impurity that causes superconductivity
- due to Tl acting as negative-U centers?

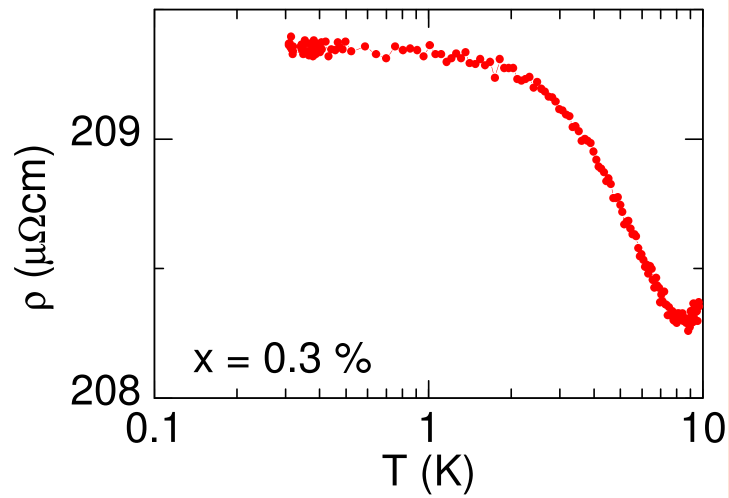
Anomalous transport properties:

- upturn in resistivity, saturates at low-T
- unlikely localization or magnetic Kondo

Charge Kondo effect?

- Strong case for neg U superconductivity being *electronic* rather than polaronic





Model of superconductivity in Tl-doped PbTe

(1) Dynamical mixed valence:

- charge Kondo scattering depends upon quantum valence fluctuations

- valence fluctuations can lead to superconductivity (i.e. an electronic pairing mechanism)

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 - not seen for T > 20 mK)

2 requirements for neg U centers to be sc pairing centers

1) Degeneracy (within kT) between paired and unpaired configurations

2) overlap with band states or with each other

Charge reservoir layers

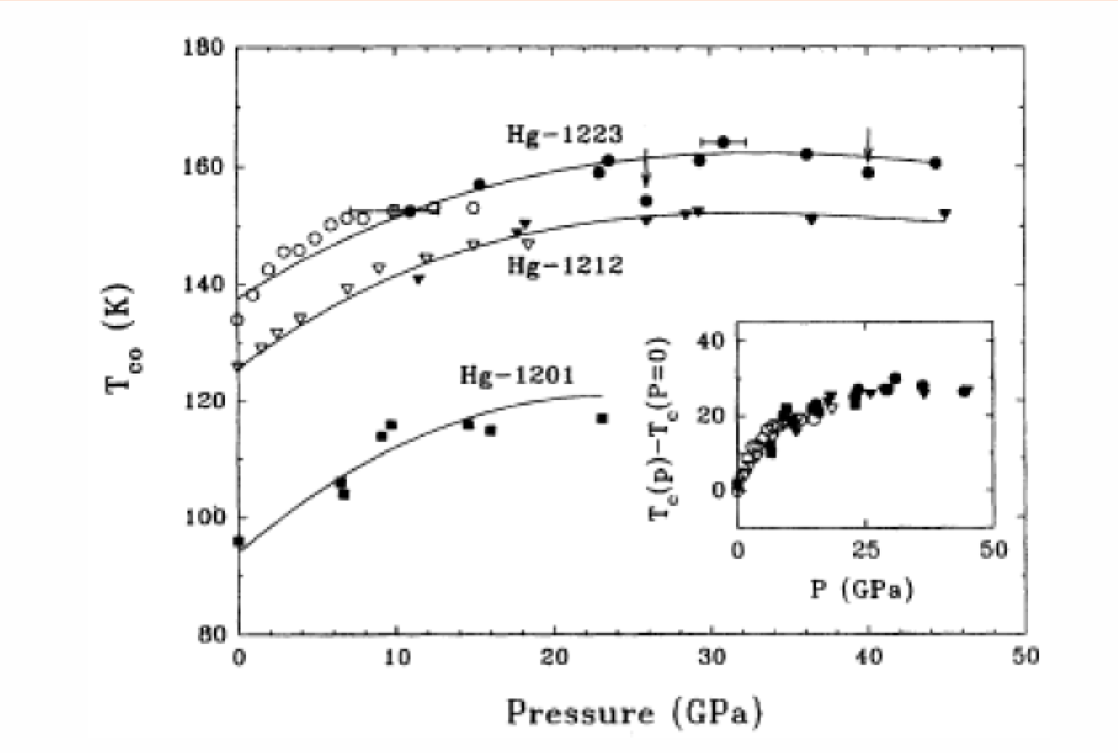
- Hg-O
  - $HgBa_2CuO_{4+\delta}$ (Hg1201)
  - $HgBa_2CaCu_2O_{6+\delta}$(Hg1212)
  - Hg(12(n-1)n)

- Tl-O,
  - Tl(12(n-1)n), Tl_2O_2

- Bi-O

- All are neg U ions, potential pairing centers
- All are very high T_c
- Degeneracy is assured if CRL layers can vary doping

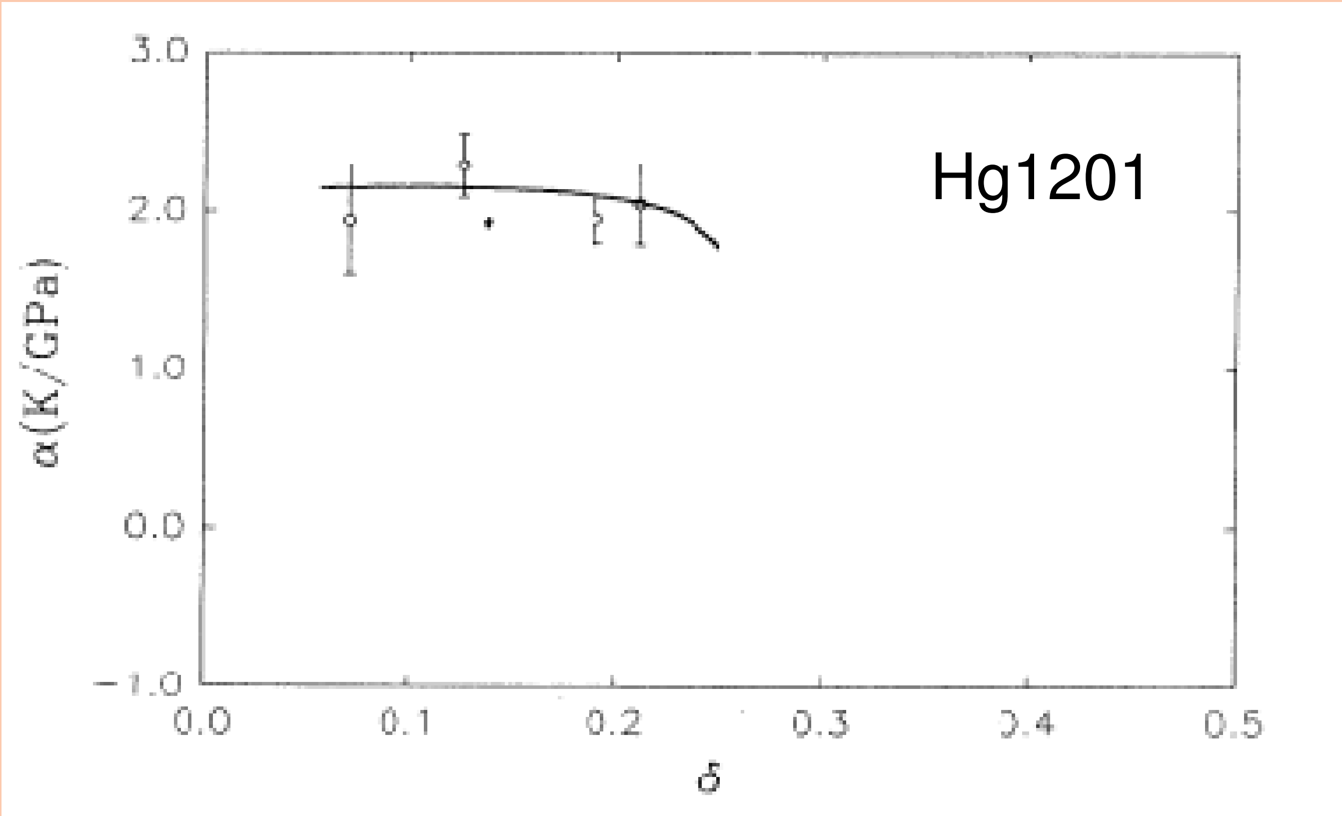
Hg cuprates



T_c as a function of P and number of layers for *optimally*-doped.

C. W. Chu et al.

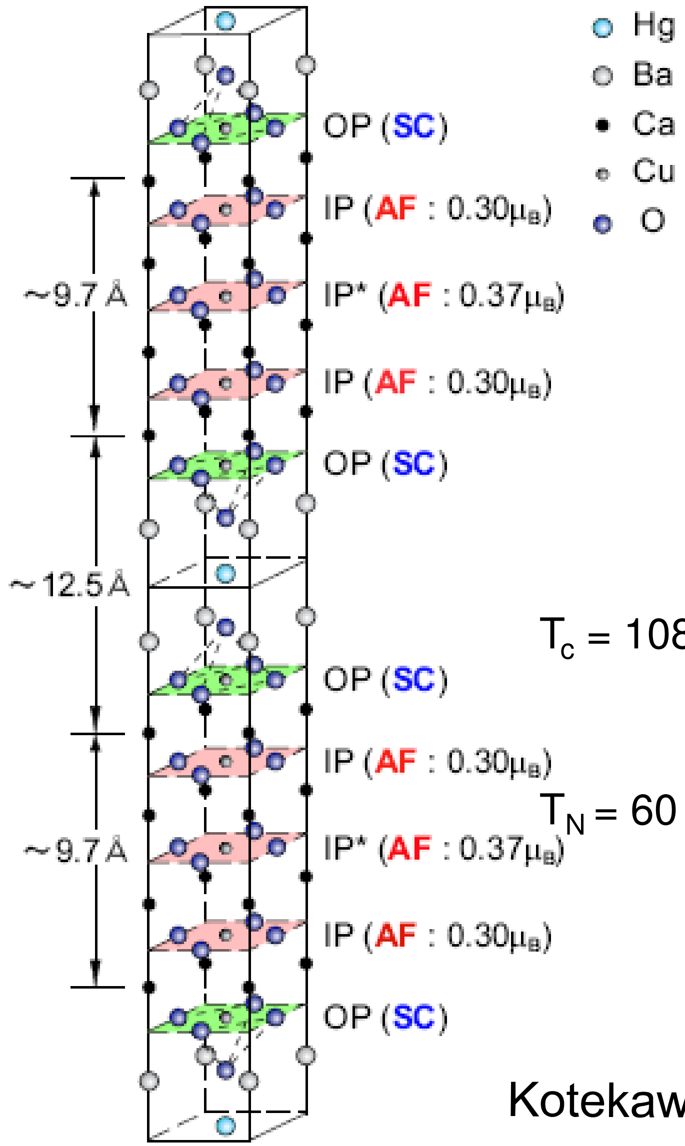
Hg cuprates



dT_c/dP as a function of doping from *underdoped* region to *optimally doped* . Behavior is inconsistent with charge transfer; is consistent with pairing centers in HgO layers

Y. Cao et al., PRB 52, 6854 (1995)

Hg-1245 Optimally-doped

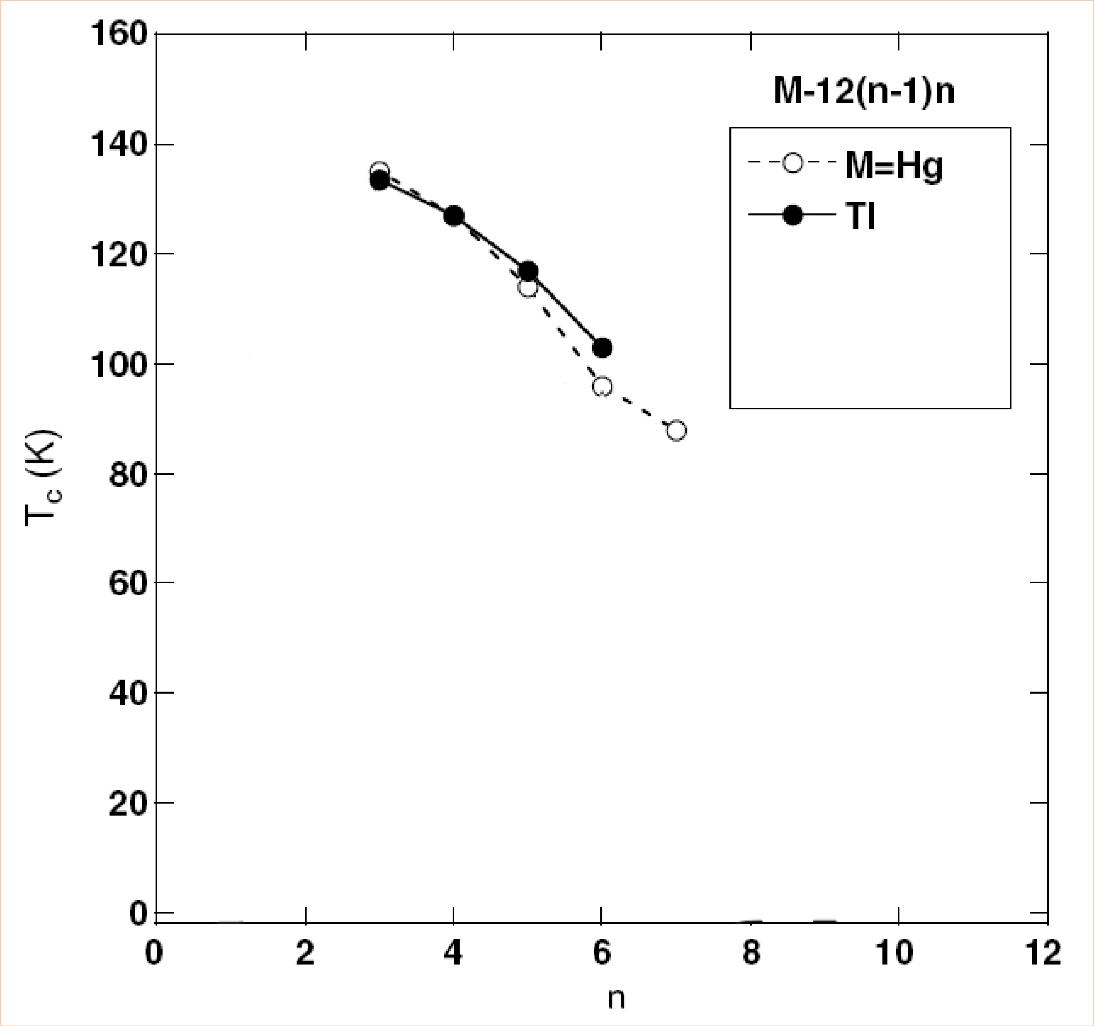


T_c = 108 K

T_N = 60 K

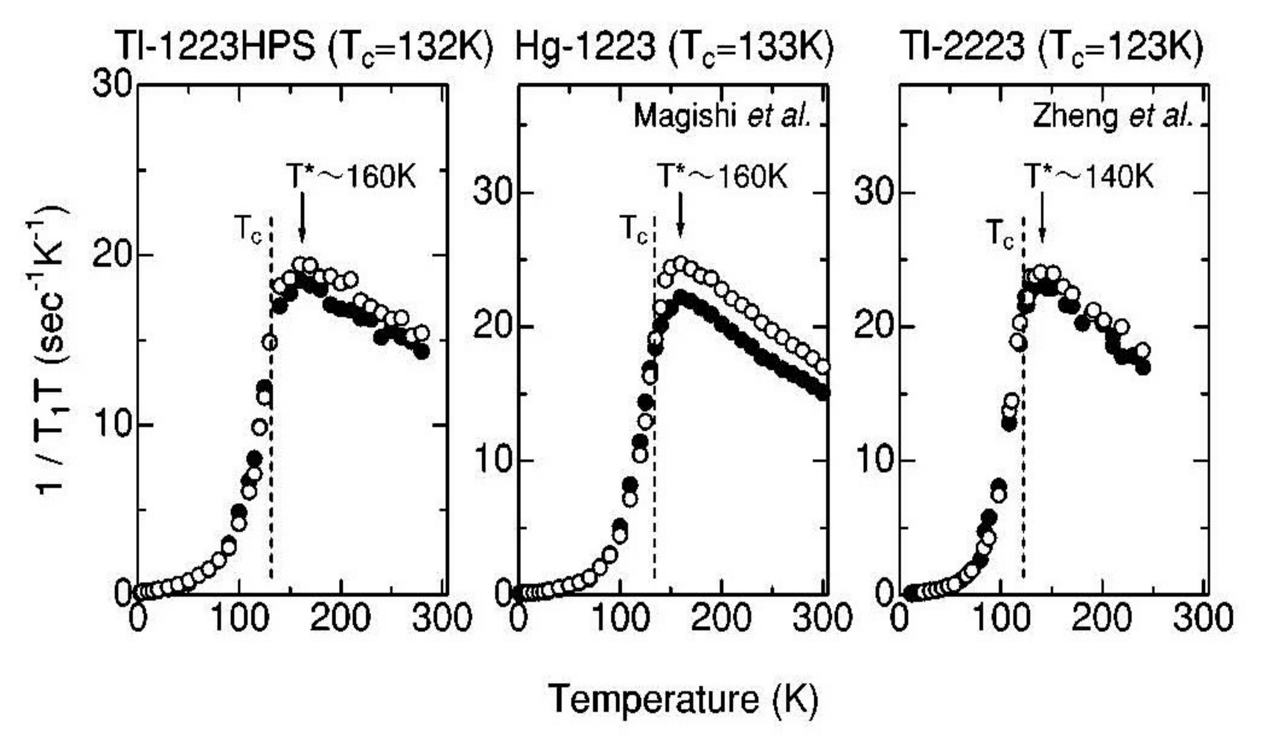
Kotekawa *et al.*

T_c vs n= 3 to 7 for Hg and Tl
T_c is remarkably the same



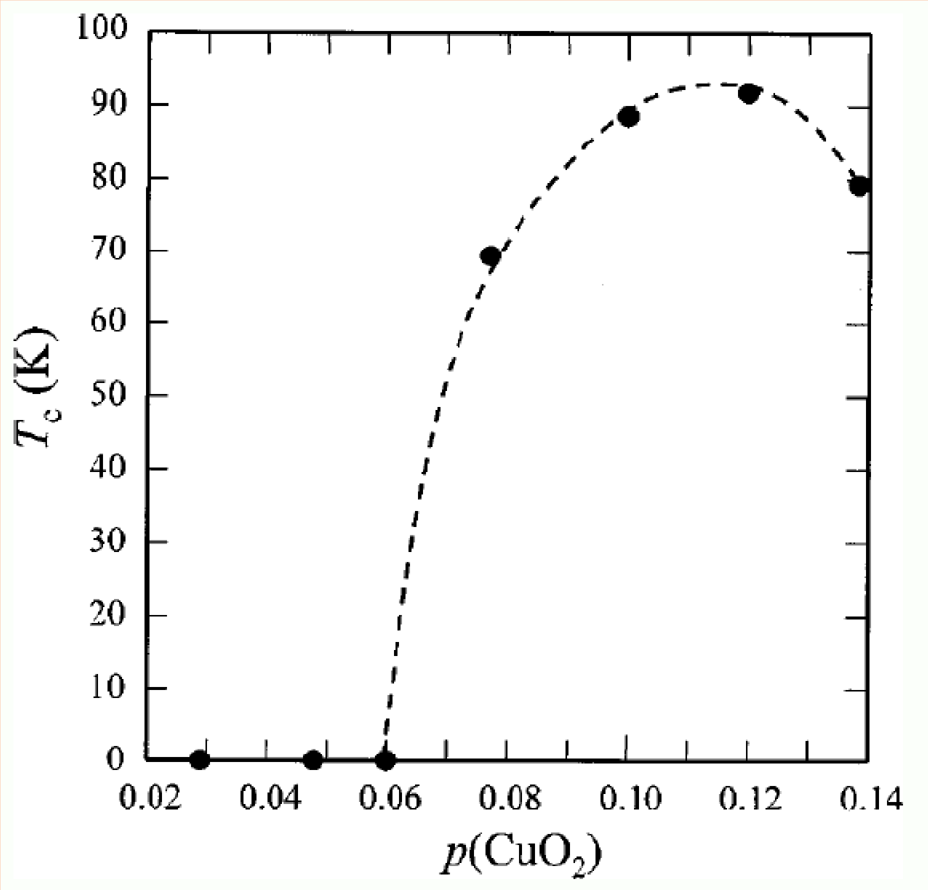
A.Iyo *et al.*, Physica C, Superconductivity 445-448 (2006) 17

Nuclear relaxation of Cu



H. Kotegawa et al., Physical Review B **65** 184504 (2002)

Bi2212



T_{max} for p ~.12 (doubly checked by XANES and titration) on both Cu and Bi layers

M. Karppinen *et al.*, PRB **67** (2003) 134522.

$T_{c\ (max)}$ vs doping

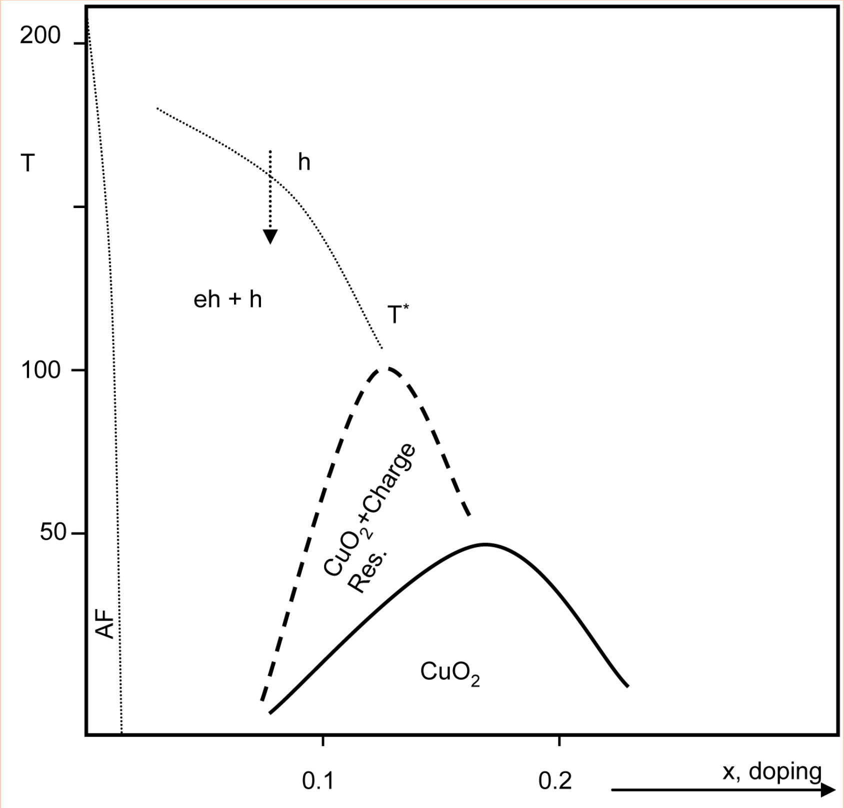
- No reason for $T_{c(max)}$ to be a universal function of the doping of (CuO_2).
- Coupling between layers can be stiffened by resonant pair tunneling across neg-U pairing ions or clusters of them in BiO layers.

V. Oganeysan *et al*., PRB 65 (2002) 1725041

Phase diagram

$T_{c(max)}$ shift to lower concentration from .16 (214) to .12 (BSSCO) can be understood by increase in coupling between layers (i.e., stiffness).

J. Emery and S.A. Kivelson, Nature **374** (1995) 434.



Other pairing centers?

Oxygen vacancies as an example

Oxygen vacancies

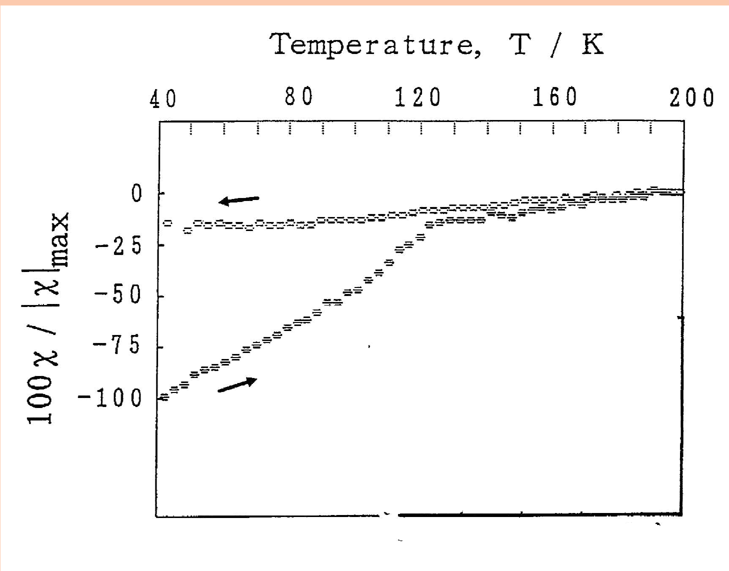
- Oxygen vacancies can be either F centers (localized 2-electron states), or
- Delocalized, donating 2 electrons to the cb
- Candidates for pairing centers if localized and delocalized states are degenerate

- Oxygen vacancies can be produced by annealing in vac, N_2 etc and by PLD in low p(O) ~ 10^{-6} torr produces oxygen vacancies

eg. Wolter Siemons *et al.* PRL **98** 196802 (2007).

Infinite Layer Structures

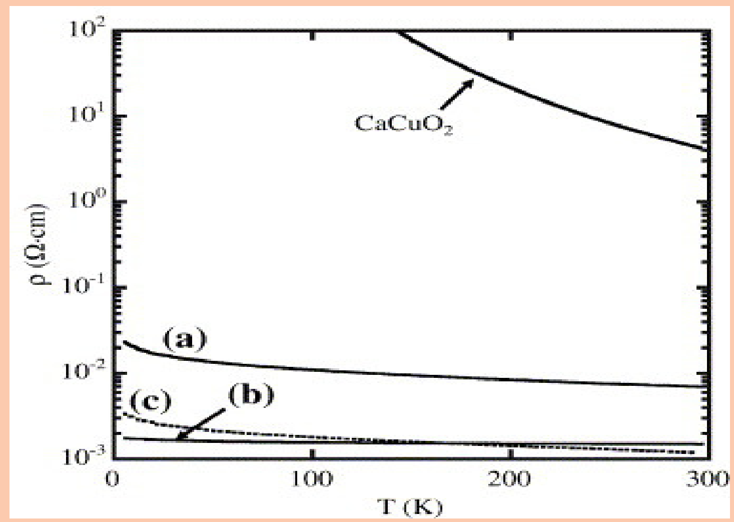
With O vacancies



Magnetic susceptibility curve (●: Zero-field cooling. ○: Field cooling. $Ca_{0.2}Sr_{0.8}CuO_2$ formed under the substrate temperature of 480°C and NO_2 pressure of $5x10^{-6}$ mbar.

X. Li et al., Jpn.J. Appl. Phys. **31** (1992)

Without O vacancies

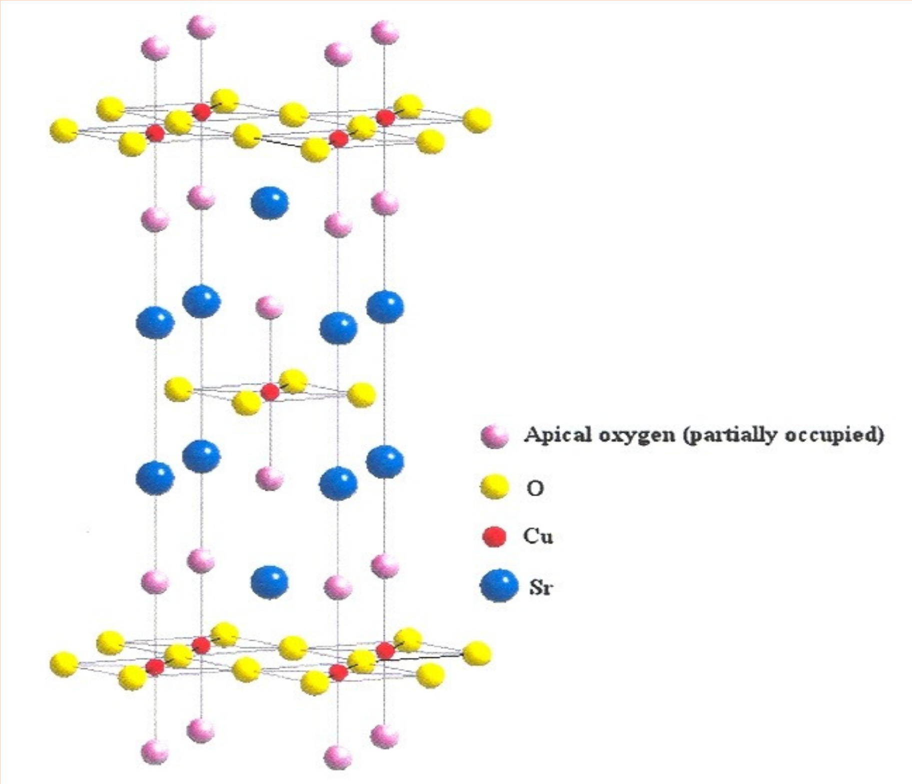


Resistivity vs. temperature plots for different hole doping schemes. (a) $Ca_{0.3}Sr_{0.7}CuO_2$. (b) $(Ca_{0.3}Sr_{0.7})_{0.9}$ (c) $Ca_{0.93}Na_{0.07}CuO_2$ deposited with ozone.

S. Oh and J.N. Eckstein,

Thin Solid Films **483** (2005).

$Sr_2CuO_{3+\delta}$



Schematic structure of $Sr_2CuO_{3+\delta}$, [formula also Sr2$CuO_{4-(1-\delta)}$]

Q.Q Liu *et al.*, Physical Review B **74** (2006).

DC magnetic susceptibility

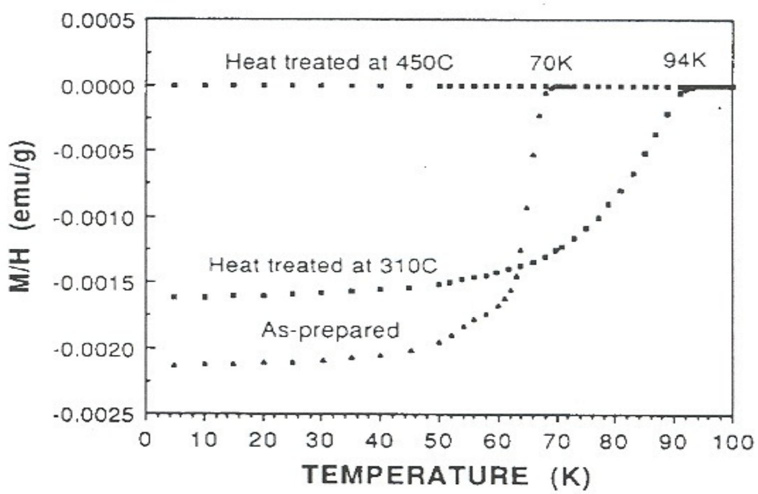
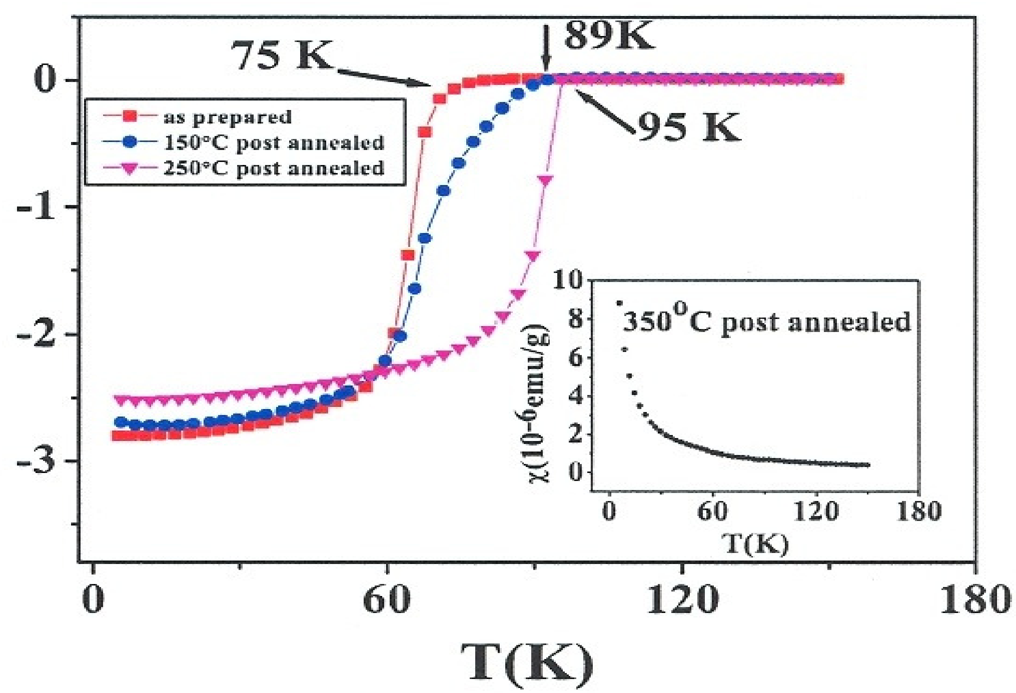


Fig. 1. Diamagnetic susceptibility as a function of temperature for as-prepared $Sr_2CuO_{3+\delta}$, and after different heat treatments.



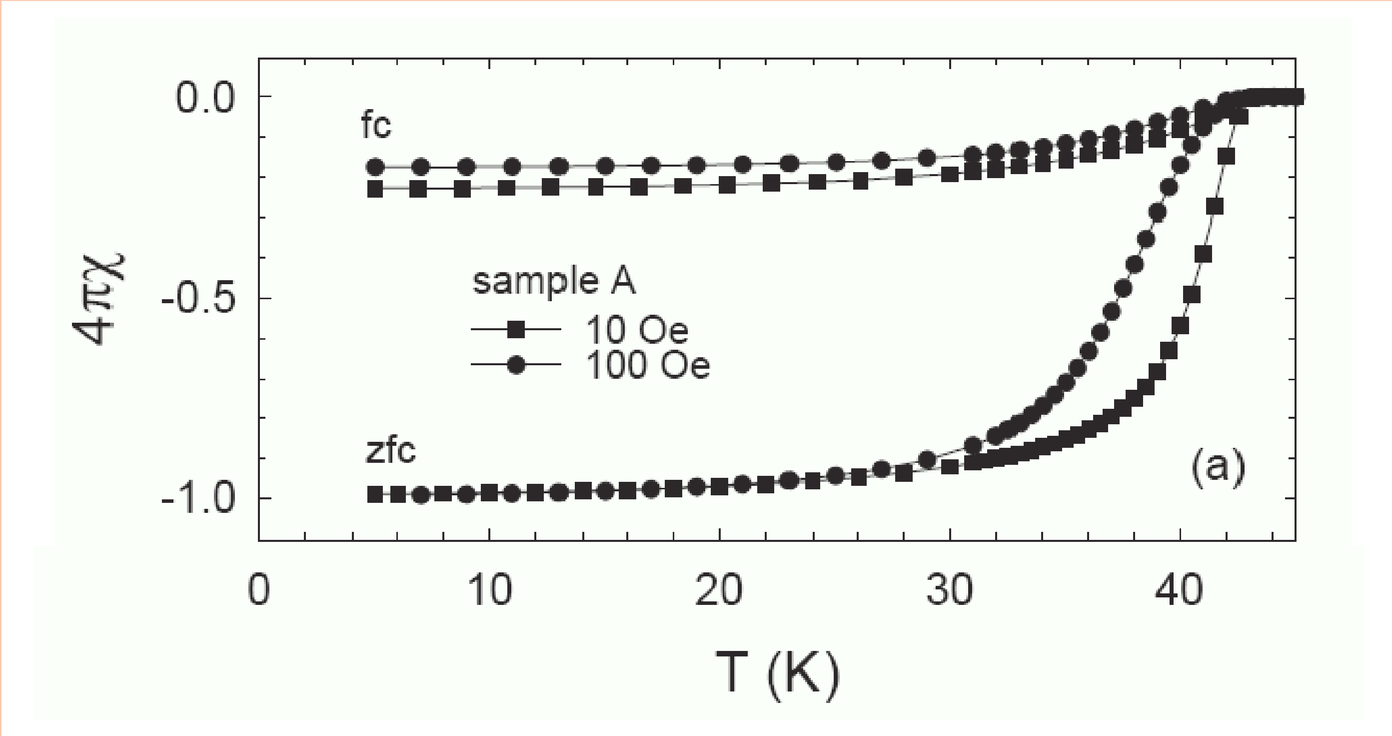
P.D. Han *et al.*, “High-pressure synthesis of the $Sr_2CuO_{3+\delta}$ superconductor Observation of an increase in T_c from 70K to 94K with heat treatment”
Physica C **228**, 129 (1994).

Temperature dependence of the dc magnetic susceptibility in the field-cooling mode for as-prepared $Sr_2CuO_{3+0.4}$,and those after annealing at various temperatures in the N_2 atmosphere.
Q.Q. Liu *et al.*, Physical Review B **74** (2006).

Remarkable resemblance (not noted by Liu *et al.*)

Infinite-layer $Sr_{0.9}La_{0.1}CuO_2$

Typical difference between field cooled and zero field cooled



C.U. Jung *et al.*, arXiv:cond-mat 0010304 (2000).

Identity of Superconducting Phase

- Liu *et al*. have argued that sc is due to 15% minority phase, ~ vacancies on apical O sites
- Liu *et al*. dismissal of Han sample “very small volume fraction and oxychloride contamination ”
- Comparison [magnitude of T_{cs} and Meissner signals are the same, majority phase has same lattice constants; both decompose above 350 - 400 ^{o}C post anneal.]
- Han *et al*. argue majority phase is sc phase. Careful TEM, EELS and simulation (Y.Y. Wang et al and H. Zhang et al Physica C **255** (1995) 247-265) determine vacancies are on CuO_2 layers!!?
- An OPEN question

$Sr_2CuO_{4-\delta}$ ($Sr_2CuO_{3+\delta}$)

Possible reasons for enhancement up to 95K-

- Impurities (oxidants) introduced in synthesis
- Periodic ordering of vacancies on apical O sites resulting in reduced Coulomb disorder (Liu et al)
- 30% of oxygen sites are vacant- neg-U pairing (THG)
- C axis reduced ~ 0.7 A w.r. $(LaSr)_2CuO_4$

$SrTiO_3$ superconductivity
A Brief History

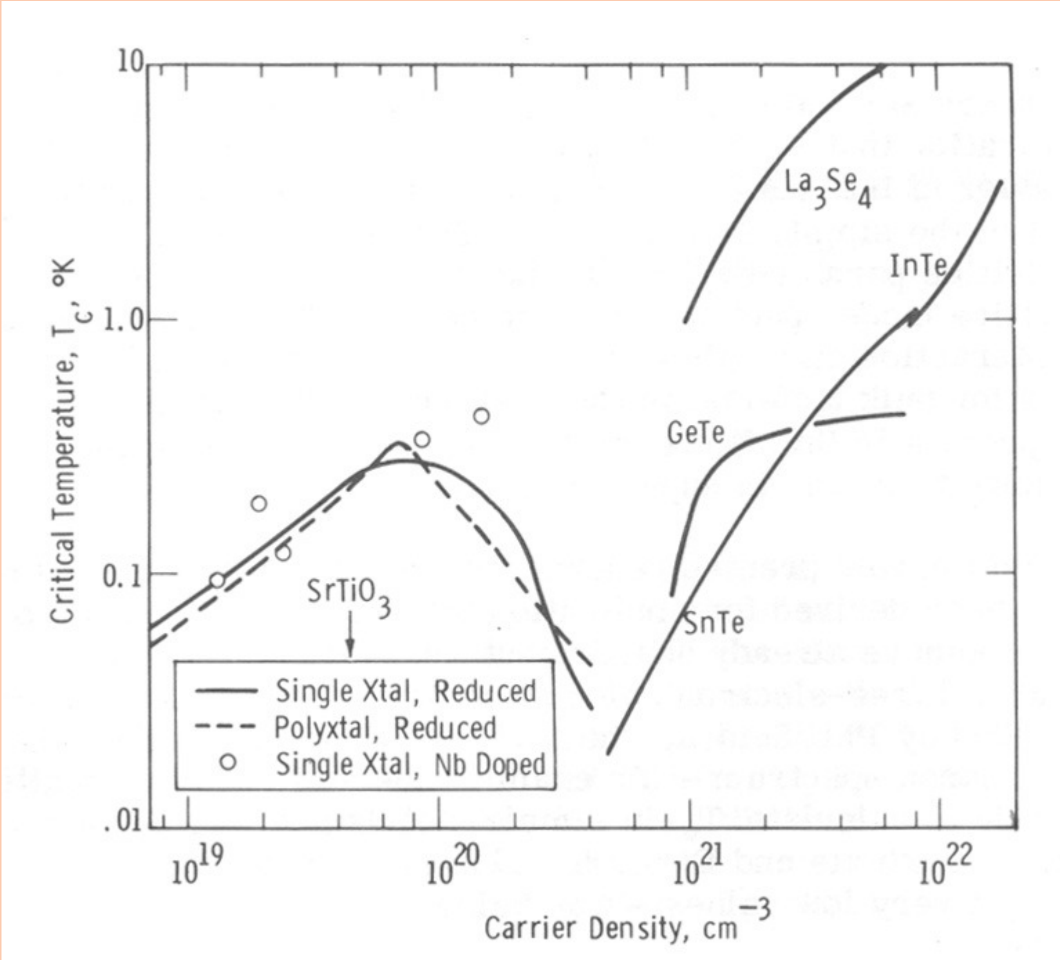
Theory

- M.L. Cohen - multi-valley phonon pairing (1964)[1,2]
- Appel - soft phonon pairing (1969)[3]
- Mattheiss (1972)[4] warped 2-band single minimum
- Jarlborg - low-q, large lambda (2000)[5]
- Micnas *et al*. - bipolaron (1990)[6]

Experiments

- Schooley, Koonce, Cohen- discovery in (1964)[7]
- J.K. Hulm *et al*. 1966 -T_c>>other low density superconductors
- N. E. Phillips *et al*. (1969) T^2 component in heat capacity?
- K. Meyer (thesis, Stanford 1993, unpublished)

T_c vs. carrier concentration

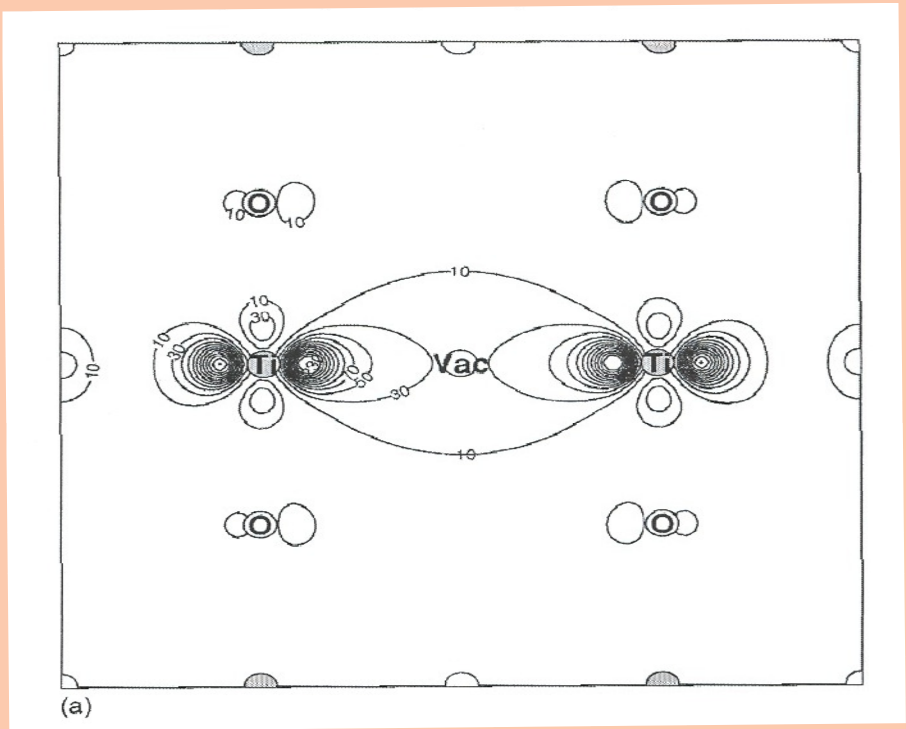


J. K. Hulm
Spring Superconducting Symposia
NRL Report 6972 (1969).

$SrTiO_3$ References

1. V.L. Gurevich, A.I. Larkin and Yu A. Firsov, Solid State **4,** 131 (1962).
2. M.L. Cohen, Phys. Rev. **134,** A511 (1964).
3. J. Appel, Superconductivity 26-29 (1969).
4. L.F. Mattheiss, Phys. Rev. B **6,** 4740 (1972).
5. T. Jarlborg, Phys. Rev B **61**, 15 (2000)
6. R. Micnas, J. Ranninger and S. Robaszkiewicz, Rev. Mod. Phys. **62**, 113 (1990)
7. J.F. Schooley, W.R. Hosler, and M.L. Cohen, Phys. Rev. Letters **12**, 474 (1964), C.S.Koonce et al Phys. Rev. B **163** 380 (1967)
8. J.K. Hulm, C.K. Jones, and R. Mazelsky, Superconductivity Proc. International Conf on Science of Superconductivity [Frank Chilton ed, North Holland(1969).]
9. N.E. Phillips, B.B Triplett, R.D. Clear and H.E. Simon, *ibid* Superconductivity (1969).

Oxygen Vacancy in cubic $SrTiO_{3-x}$



Ti ---vacancy---Ti

1. W. Luo *et al.*, Phys. Rev B **70,** 214109 (2004).
2. D. Ricci *et al.*, Phys. Rev. B **68**, 224105 (2003).

Periodic LCU study of F Centers in cubic and tetragonal $SrTiO_3$

Calculation shows:

(i) Defect-produced perturbation in the tetragonal phase structure is stronger than in cubic lattice

(ii) F center wave function is localized cubic phase and is much less localized in the tetragonal

A. Stashans, *et al.*, "Periodic LUC study of F centers in cubic and tetragonal $SrTiO_3$," *Materials Letters* **50**, 145 (2001).

Tungsten Bronzes A_xWO_3

- 3D stiochiometric perovskites for x = 1/3, $T_c < 2K$.
- T_c rises up to 6 K in metastable regions, x < 1/3
- $T_c = 90K$ sc signal single crystal Na_xWO_3 (annealed in N_2) ESR and tunneling support but do not prove - Reich, S.; Leitus, G.; Tssaba, Y.; Levi, Y.; Sharoni, A.; Millo, O., Journal of Superconductivity (2000); A. Shengalaya, K.A. Muller, S. Reich and Y. Tsabba, Eur. J. Phys. B; Reich, S.; Leitus, G.; Tssaba, Y.; Levi, Y.; Sharoni, A.; Millo, O. Journal of Superconductivity, 13(5) (2000) 855-861
- No further confirming results - a careful study of oxygen annealing is called for

Interface superconductivity?

- Granular deposited Al/AlO interfaces
- Sulfur /graphite heat treated interphases

Kopelevich *et al.*, J. Low. Temp. Phys. 119 (2000) 69.

- Trace signals in pulse-annealed Cu/single crystal CuO interfaces,

Osipov *et al.*, JETP **93** (2001) 1082.

- in multiphase cuprates, and numerous other reports all of which may not be spurious.

Granular Metal Superconductivity

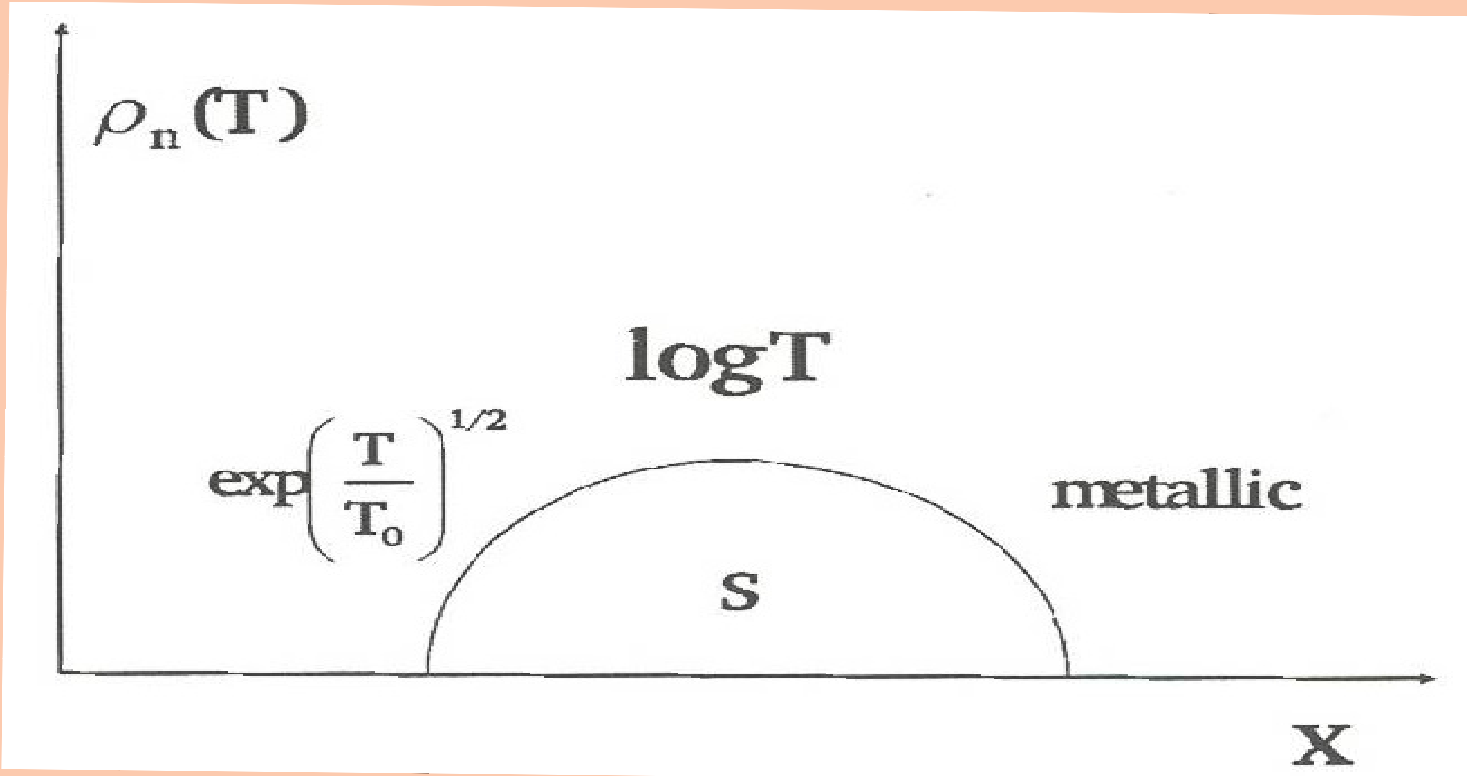
1. History dates back to the beginning of the 20th century (B. Abeles -- Applied Solid State Science Vol 6; Advances in Materials and Device Research, R. Wolfe Ed, Academic Press, pp 1-109, 1976)
2. Recent update (G. Deutscher -- New Superconductors From Granular to High T_c, World Scientific 2006)

Vapor phase growth granular Al

(films deposited in the presence of oxygen)

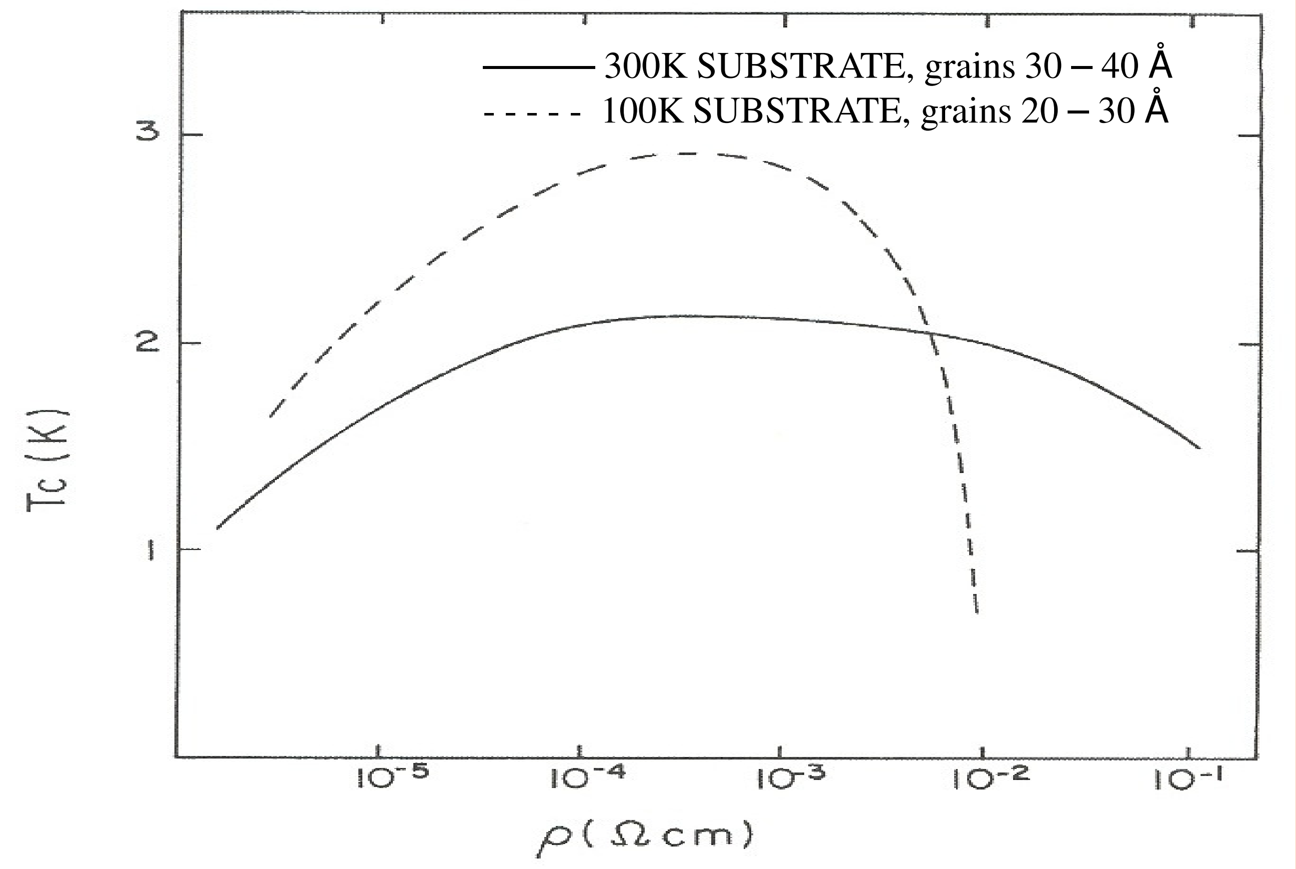
1. Nucleation and growth of Al nanoparticles
2. Expulsion of amorphous Al_2O_3 to periphery
3. Al_2O_3 encapsulates Al; growth stops
4. Experimental control of size and distribution
5. Al/Al_2O_3 ratio determines transport

Three regions of temperature dependent resistance in normal state as function of Al fraction



Temperature dependences of the normal state resistivity from below Mott transition to metallic (adapted from Deutscher p72).

Unexplained enhancement of T_c



Critical temperature of granular Al deposited at room temperature (continuous line) and liquid nitrogen temperature (broken line) (Deutscher, p 73). [Note-T_c ~ 3T_c bulk]

Superconductivity and ferromagnetism in graphite-S

- Kopelevich and coworkers since 1999 report trace fm and sc signals at high T. Heat treated fine graphite particles in sulfur- no new phases, pristine lattice constants.
  Kopelevich et al. J. Low. Temp. Phys. 119 (2000) 69.
- True sc signals (T_c= 9K) measured in 3 year old sample

  Moehlecke, Ho and Maple, Phil. Mag. B 82 (2002) 1335.

References

- Some discussion and many references are given in recent publications.
  - Vol 19, J. of Superconductivity and Novel Magnetism, the special edition dedicated to V. L. Ginsburg, edited by I. Bozovic (2006)
  - The chapter by Geballe and Koster in “Treatise on Superconductivity”, (Springer 2007) initiated by Bob Schrieffer and edited by James Brooks

Conclusion

- There are good avenues and reasons for searching.
- Better understanding of the role of oxygen vacancies in cuprates (can they account for identical behavior in Tl and Hg multilayers? T max in chain 123?) and in many cases where annealing in reduced O is necessary
- Find new negative U pairing centers (and maybe other pairing mechanisms)- adjust chemical potential
- Investigate metastable interfaces
- Investigate unidentified trace signals ("USO's"- Chu classification) using new scanning probe techniques
- Be prepared (Pasteur) and be LUCKY!

Thank you!!, THG