Journal Club 12 Dec 1986

- Superconductivity at 30K is a reality!

- IBM Zurich Research Strikes Again

- Japan Inc. is moving fast once again

but so are we (I hope)

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Possible High T_c Superconductivity in the Ba–La–Cu–O System

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Metallic, oxygen-deficient compounds in the Ba–La–Cu–O system, with the composition $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ have been prepared in polycrystalline form. Samples with $x=1$ and 0.75, $y>0$, annealed below 900 °C under reducing conditions, consist of three phases, one of them a perovskite-like mixed-valent copper compound. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally an abrupt decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 30 K range. It is markedly reduced by high current densities. Thus, it results partially from the percolative nature, bute possibly also from $2D$ superconducting fluctuations of double perovskite layers of one of the phases present.

I. Introduction

"At the extreme forefront of research in superconductivity is the empirical search for new materials" [1]. Transition-metal alloy compounds of A 15 (Nb_3Sn) and B 1 (NbN) structure have so far shown the highest superconducting transition temperatures. Among many A 15 compounds, careful optimization of Nb–Ge thin films near the stoichiometric composition of Nb_3Ge by Gavalev et al. and Testardi et al. a decade ago allowed them to reach the highest $T_c=23.3$ K reported until now [2, 3]. The heavy Fermion systems with low Fermi energy, newly discovered, are not expected to reach very high T_c's [4].

Only a small number of oxides is known to exhibit superconductivity. High-temperature superconductivity in the Li–Ti–O system with onsets as high as 13.7 K was reported by Johnston et al. [5]. Their x-ray analysis revealed the presence of three different crystallographic phases, one of them, with a spinel structure, showing the high T_c [5]. Other oxides like perovskites exhibit superconductivity despite their small carrier concentrations, n. In Nb-doped $SrTiO_3$, with $n=2\times10^{20}$ cm^{-3}, the plasma edge is below the highest optical phonon, which is therefore unshielded [6]. This large electron-phonon coupling allows a T_c of 0.7 K [7] with Cooper pairing. The occurrence of high electron-phonon coupling in another metallic oxide, also a perovskite, became evident with the discovery of superconductivity in the mixed-valent compound $BaPb_{1-x}Bi_xO_3$ by Sleight et al., also a decade ago [8]. The highest T_c in homogeneous oxygen-deficient mixed crystals is 13 K with a comparatively low concentration of carries $n=2\text{-}4\times10^{21}$ cm^{-3} [9]. Flat electronic bands and a strong breathing mode with a phonon feature near 100 cm^{-1}, whose intensity is proportional to T_c, exist [10]. This last example indicates that within the BCS mechanism, one may find still higher T_c's in perovskite-type or related metallic oxides, if the electron-phonon interactions and the carrier densities at the Fermi level can be enhanced further.

Strong electron-phonon interactions in oxides can occur owing to polaron formation as well as in mixed-valent systems. A superconductivity (metallic) to bipolaronic (insulator) transition phase diagram was proposed theoretically by Chakraverty [11]. A mechanism for polaron formation is the Jahn-Teller effect, as studied by Höck et al. [12]. Isolated Fe^{4+}, Ni^{3+} and Cu^{2+} in octahedral oxygen environment

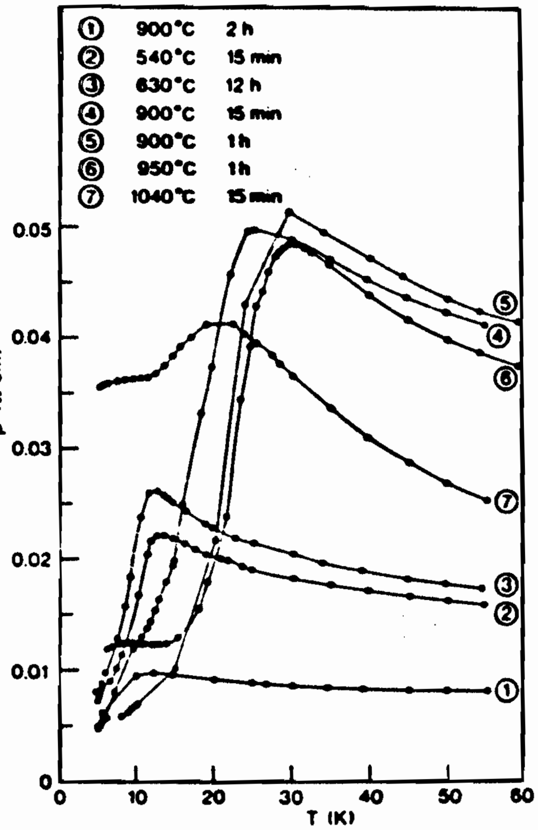

Fig. 2. Low-temperature resistivity of samples with $x(\mathrm{Ba})=1.0$, annealed at O_2 partial pressure of 0.2 bar (curve ①) and 0.2×10^{-4} bar (curves ② to ⑦)

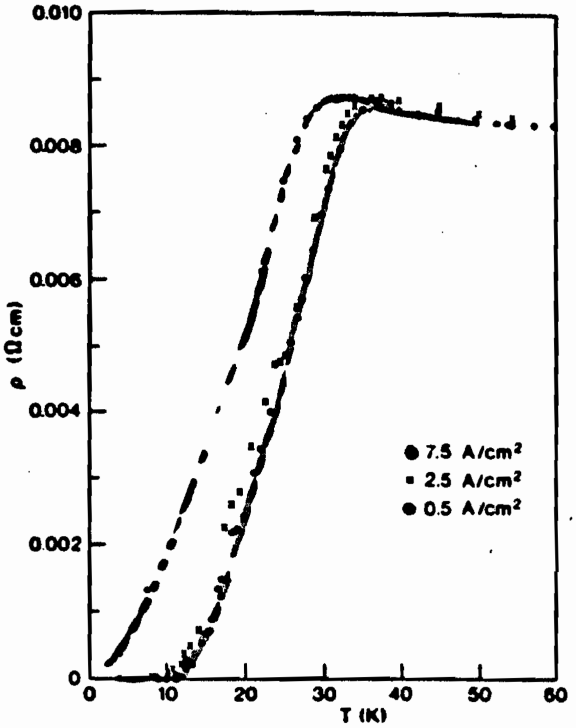

Fig. 3. Low-temperature resistivity of a sample with $x(\mathrm{Ba})=0.75$, recorded for different current densities

towards the 30 K region. Curves ④ and ⑤, recorded for samples treated at 900 °C, show the occurrence of a shoulder at still lower temperature, more pronounced in curve ⑥. At annealing temperatures of 1,040 °C, the highly conducting phase has almost vanished. As mentioned in the Introduction, the mixed-valent state of copper is of importance for electron-phonon coupling. Therefore, the concentration of electrons was varied by the Ba/La ratio. A typical curve for a sample with a lower Ba concentration of 0.75 is shown in Fig. 1 (right scale). Its resistivity decreases by at least three orders of magnitude, giving evidence for the bulk being superconducting below 13 K with an onset around 35 K, as shown in Fig. 3, on an expanded temperature scale. The latter figure also shows the influence of the current density, typical for granular compounds.

III. Discussion

The resistivity behaviour of our samples, Fig. 1, is qualitatively very similar to the one reported in the Li–Ti–O system, and in superconducting $BaPb_{1-x}Bi_xO_3$ polycrystalline thin films [5, 18]. Upon cooling from room temperature, the latter exhibit a nearly linear metallic decrease of $\rho(T)$, then a logarithmic type of increase, before undergoing the transition to superconductivity. One could, of course, speculate that in our samples a metal-to-metal structural phase transition occurs in one of the phases. The shift in the drop in $\rho(T)$ with increasing current density (Fig. 3), however, would be hard to explain with such an assumption, while it supports our interpretation that we observe the onset of superconductivity of percolative nature, as discussed below. In $BaPb_{1-x}Bi_xO_3$, the onset of superconductivity has been taken at the resistivity peak [18]. This assumption appears to be valid in percolative systems, i.e., in the thin films [18] consisting of polycrystals with grain boundaries, or when different crystalline phases with interpenetrating grains are present, as found in the Li–Ti–O [5] or in our Ba–La–Cu–O system. The onset can also be due to fluctuations in the superconducting wave functions. We assume one of the Ba–La–Cu–O phases exhibits this behaviour. Therefore, under the above premises, the peak in $\rho(T)$ at 35 K, observed for an $x(\mathrm{Ba})=0.75$ (Fig. 1), has

Europhysics Lett (Feb 87)

best regards
K. Alex M.

Susceptibility Measurements Support High T_c Superconductivity in the Ba-La-Cu-O System.

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(received)

PACS. 74.70.-b
PACS. 74.10.+v
PACS. 74.70.Nr

Abstract. — The susceptibility of ceramic samples in the metallic Ba-La-Cu-O system has been measured as a function of temperature. This system had earlier shown characteristic sharp drops in resistivity at low temperatures. It has been found that the susceptibility for small magnetic fields of less than 0.1 Tesla becomes diamagnetic at somewhat lower temperatures than the resistivity drop. The highest-temperature diamagnetic shift occurs at 33 ± 2 K, and may be related to shielding currents at the onset of percolative superconductivity. The diamagnetic susceptibility can be suppressed with external fields of 1 to 5 Tesla.

October 10, 1986

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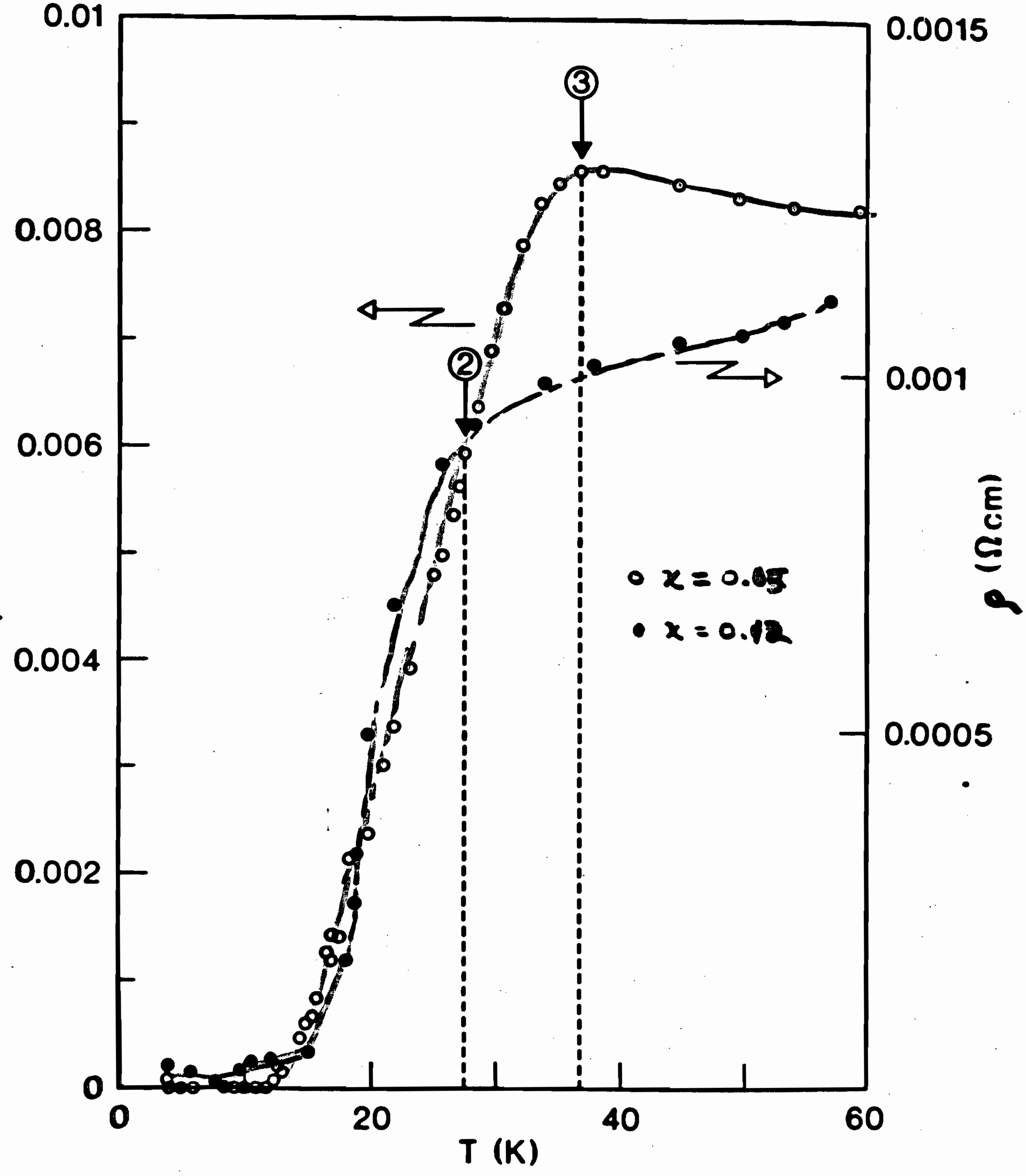
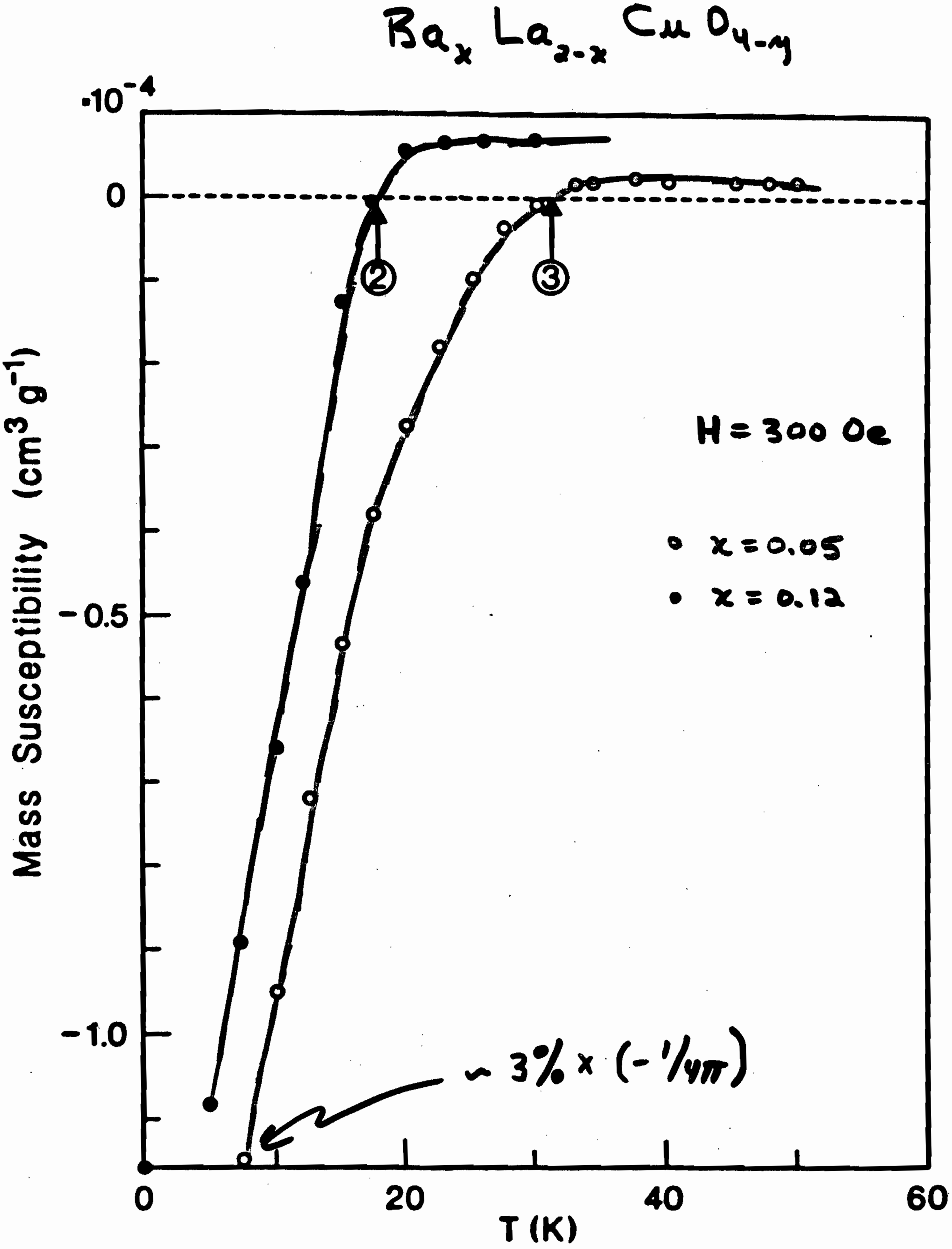
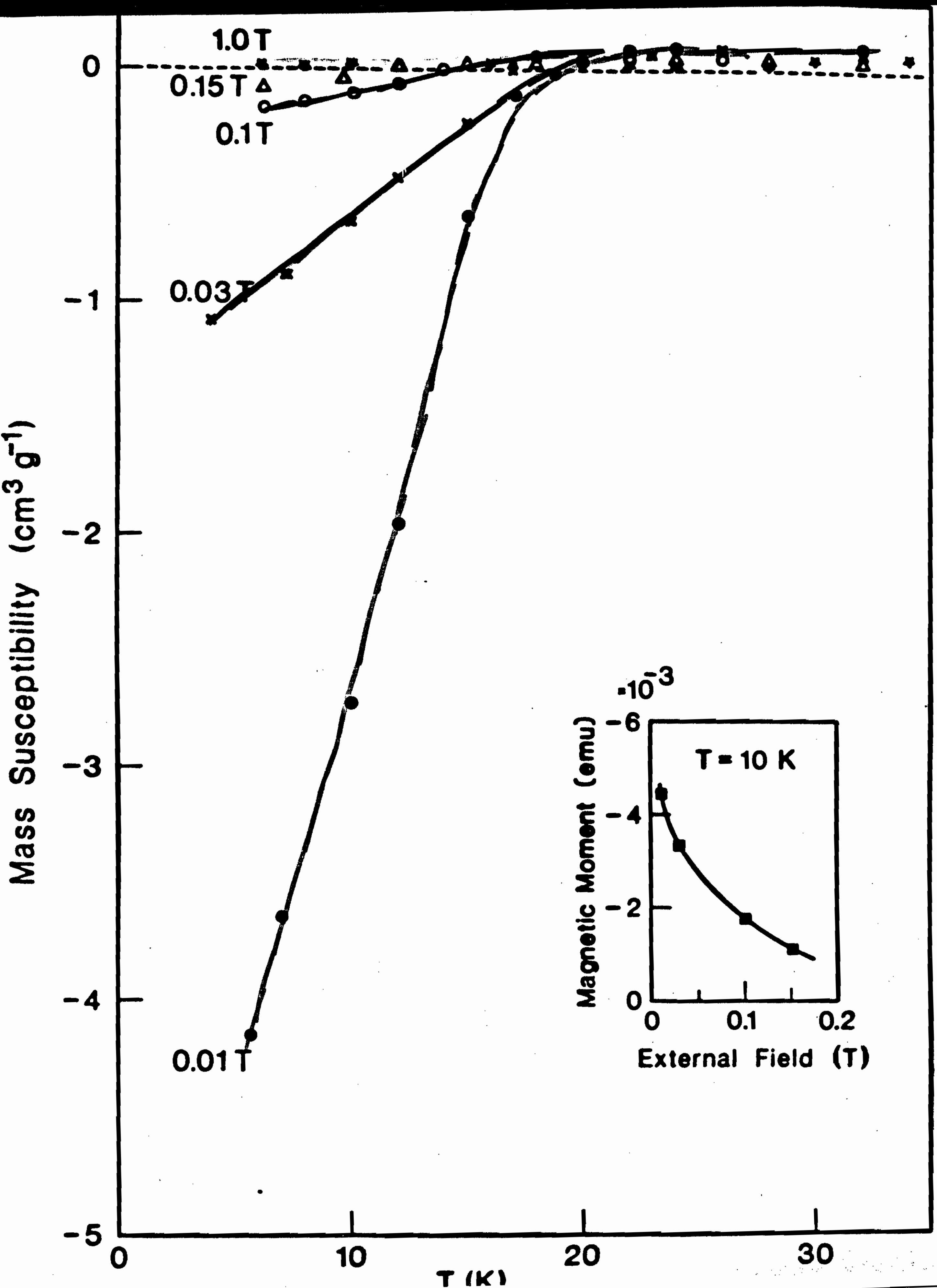
$Ba_x La_{2-x} Cu O_{4-y}$

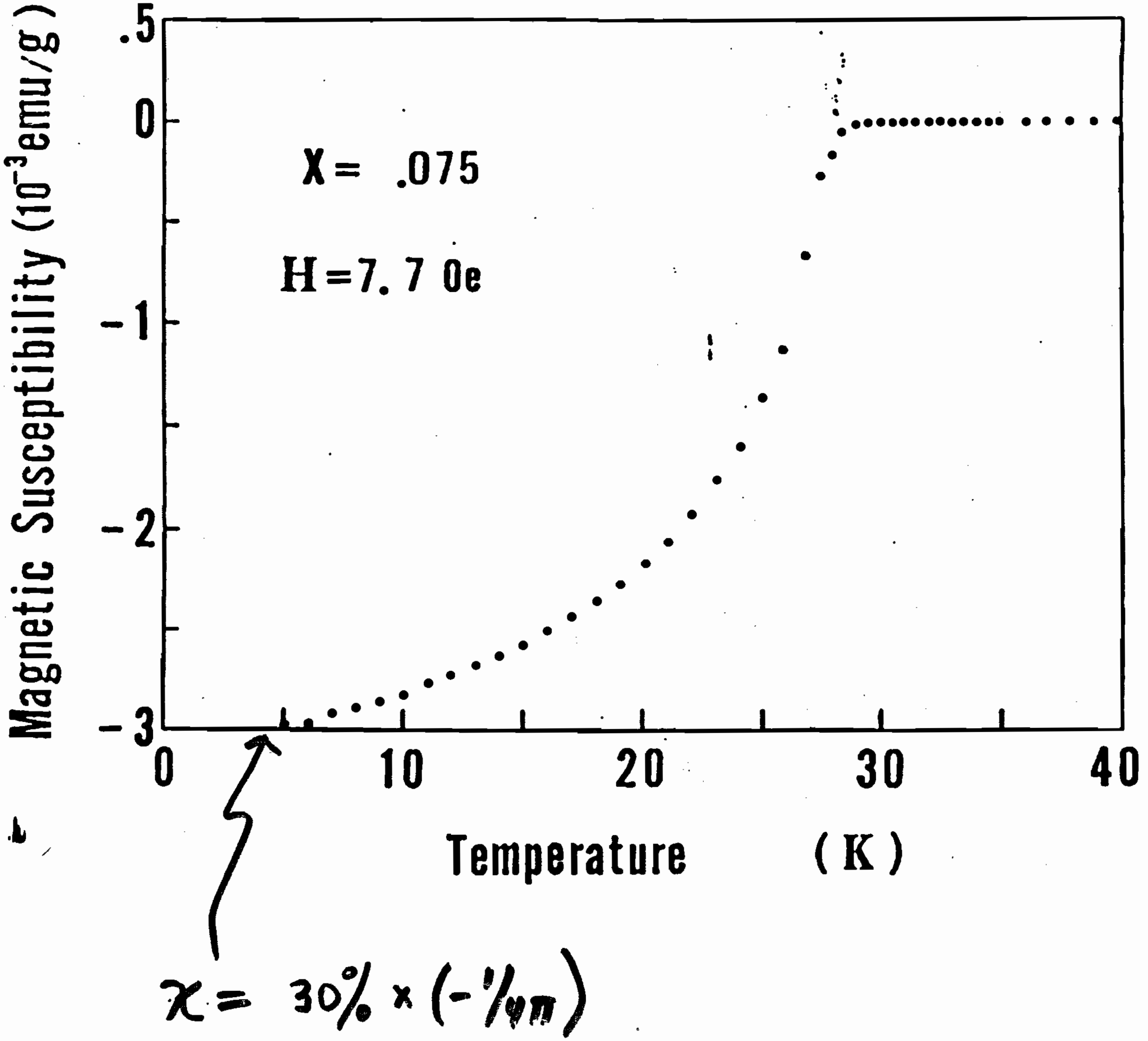



$Ba_x La_{2-x} Cu O_{4-y}$
$\cdot 10^{-4}$
0
−0.5
−1.0
Mass Susceptibility ($cm^3 g^{-1}$)
0
20
40
60
T (K)
H = 300 Oe
○ x = 0.05
● x = 0.12
②
③
~ 3% × (−1/4π)

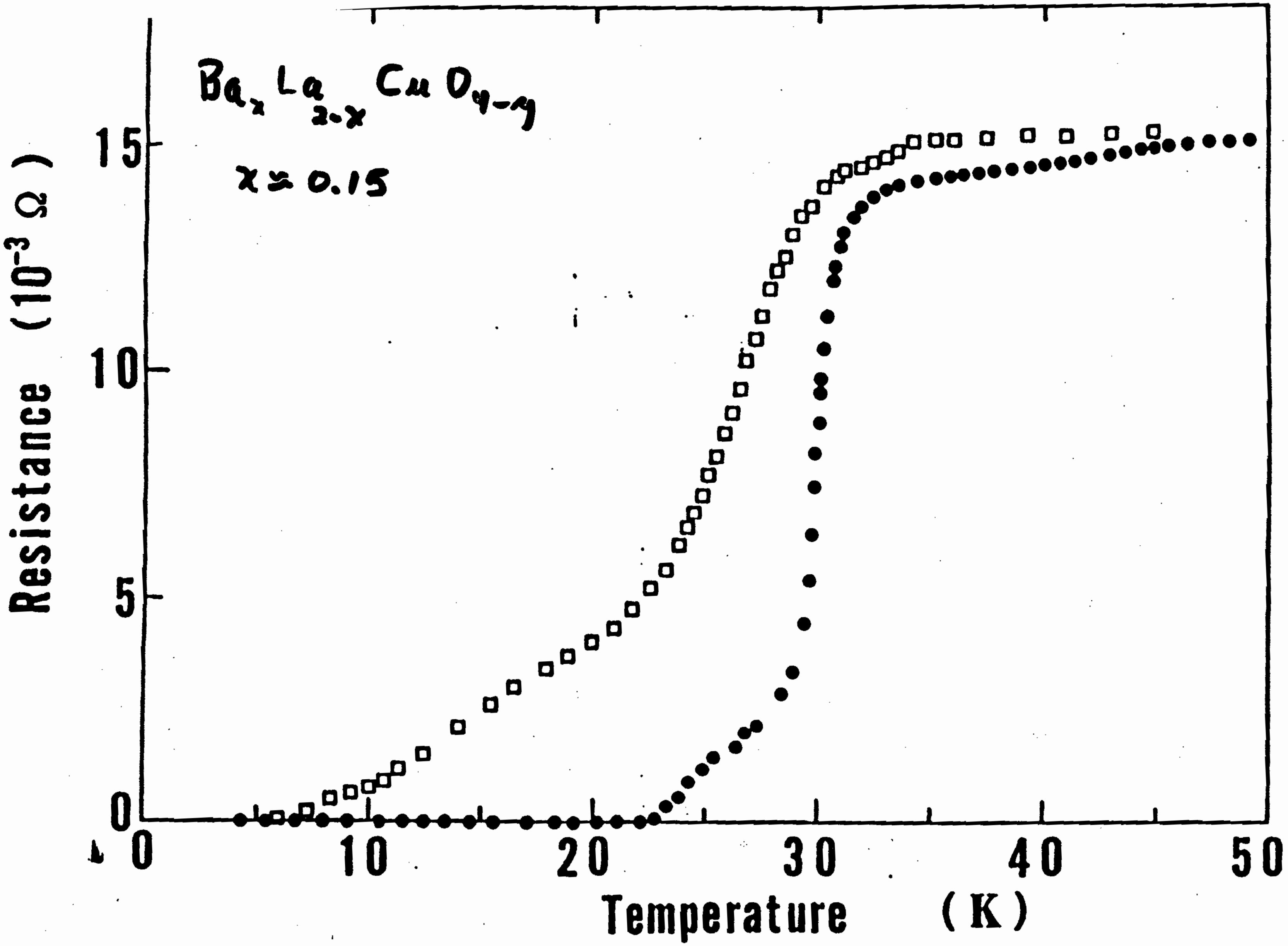


1.0 T
0.15 T
0.1 T
0.03 T
0.01 T
0
-1
-2
-3
-4
-5
Mass Susceptibility (cm^3 g^{-1})
0
10
20
30
T (K)
$\times 10^{-3}$
-6
-4
-2
0
Magnetic Moment (emu)
T = 10 K
0
0.1
0.2
External Field (T)

Takagi et al (JJAP Lett.) $(Ba_x La_{1-x})_2 Cu O_{4-y}$



$\chi = 30\% \times (-1/4\pi)$



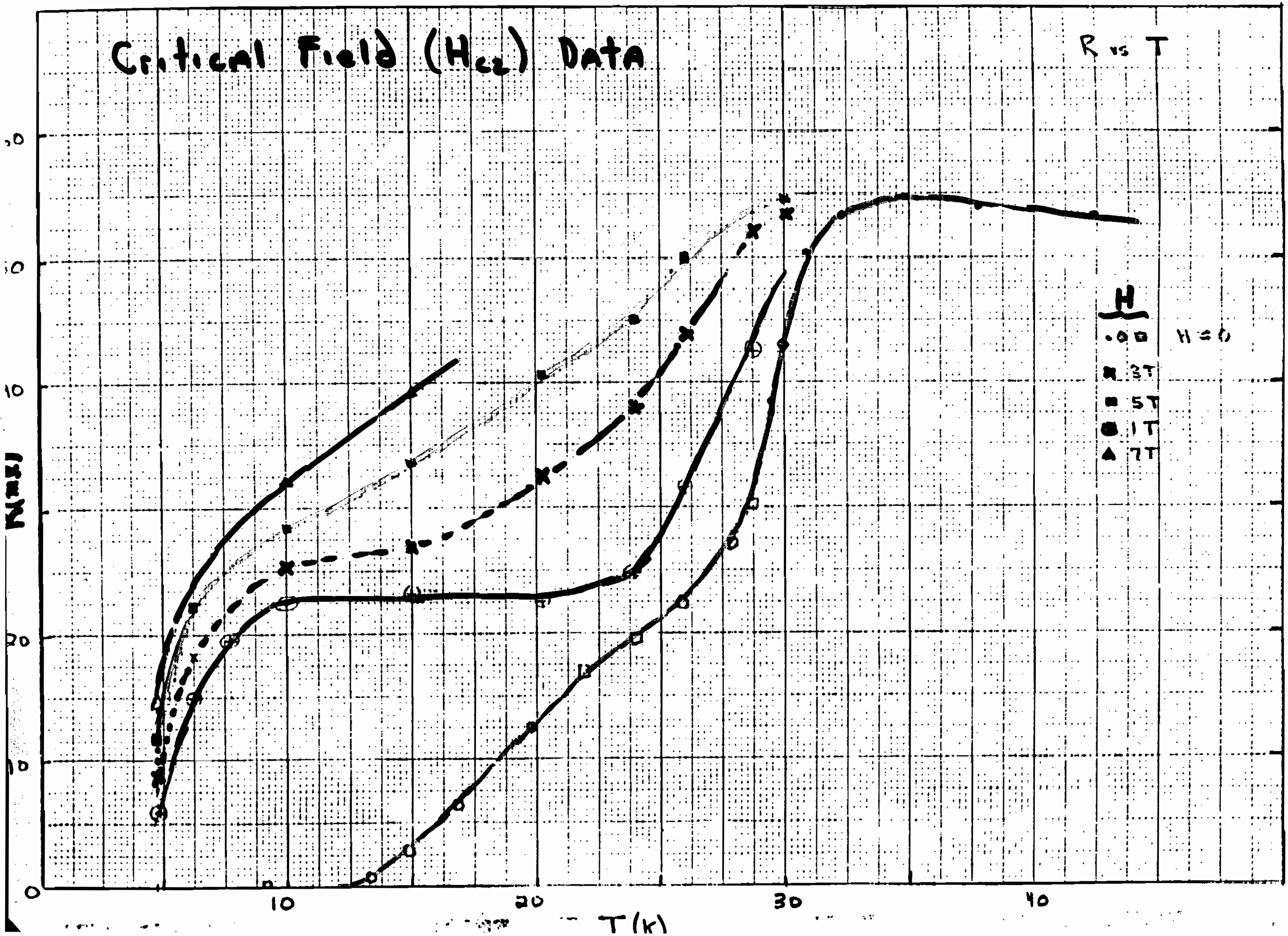
Takagi et al (JJAPLett)

NO. 340-20 DIETZGEN GRAPH PAPER
20 X 20 PER INCH

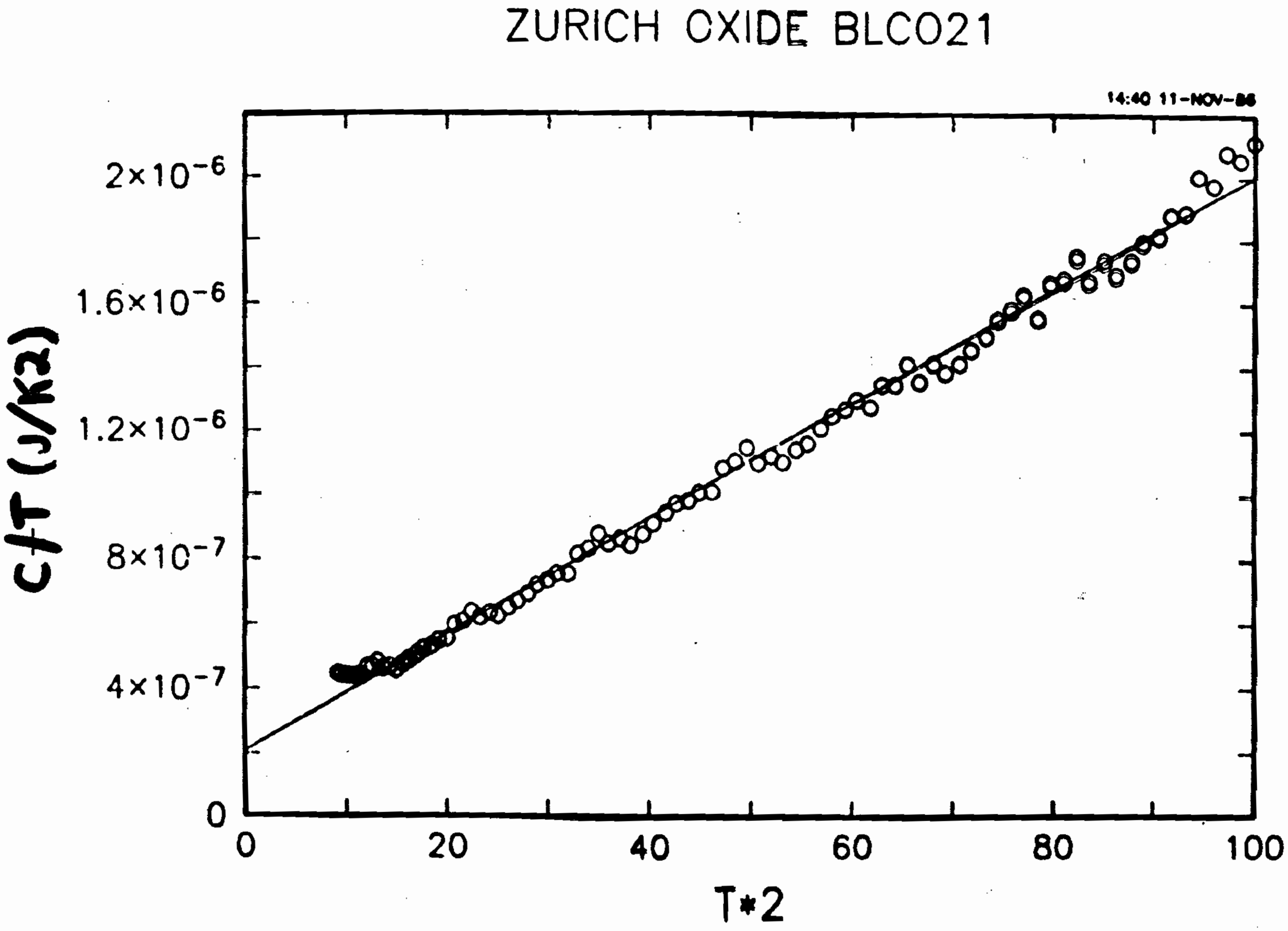
R. Greene – Torressen, et al

BaLaCuO 21II

12/8/86



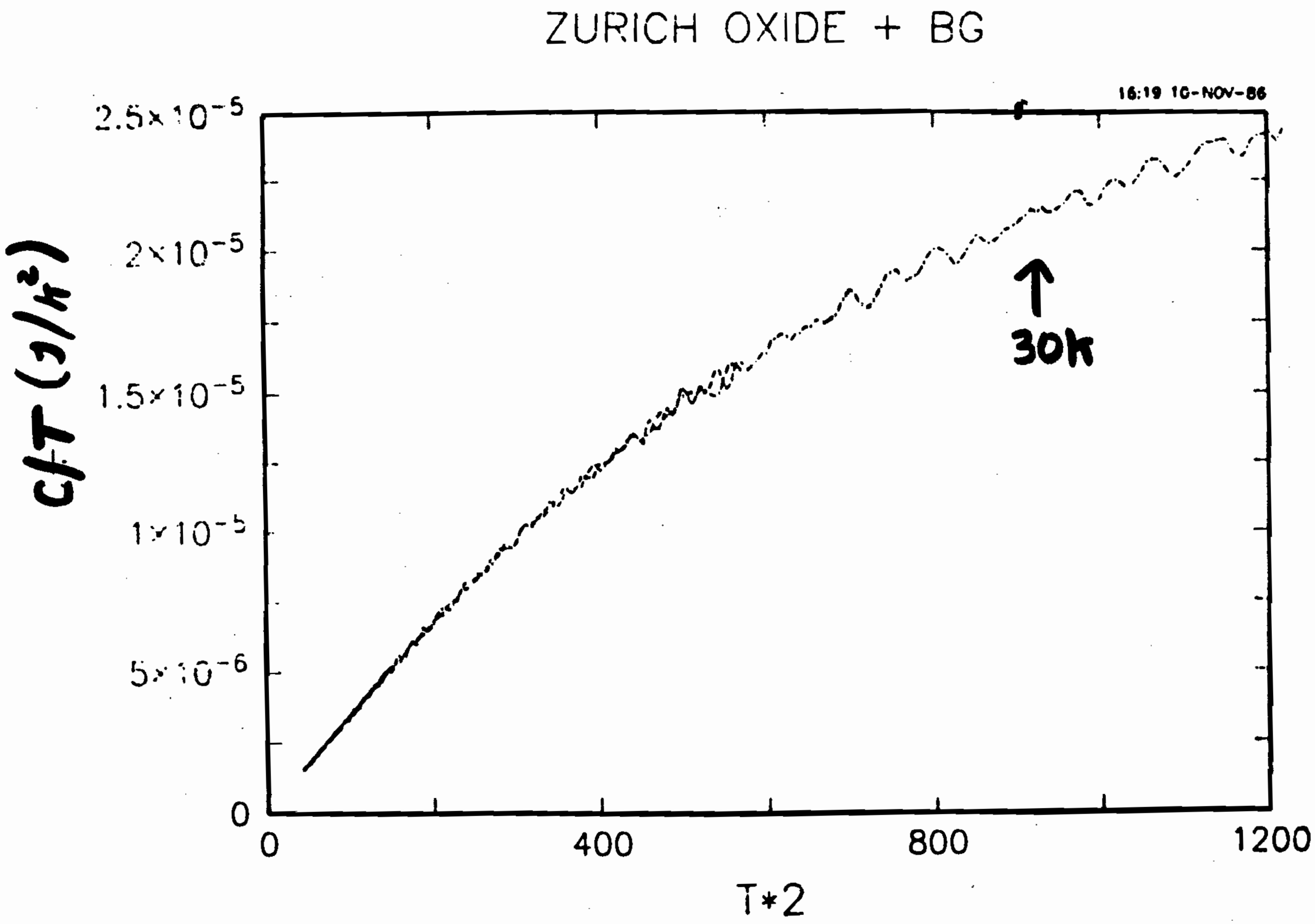
Greene – Torressen – von Molnar – Muller – Bedworz



$C = \gamma T + \beta T^3$

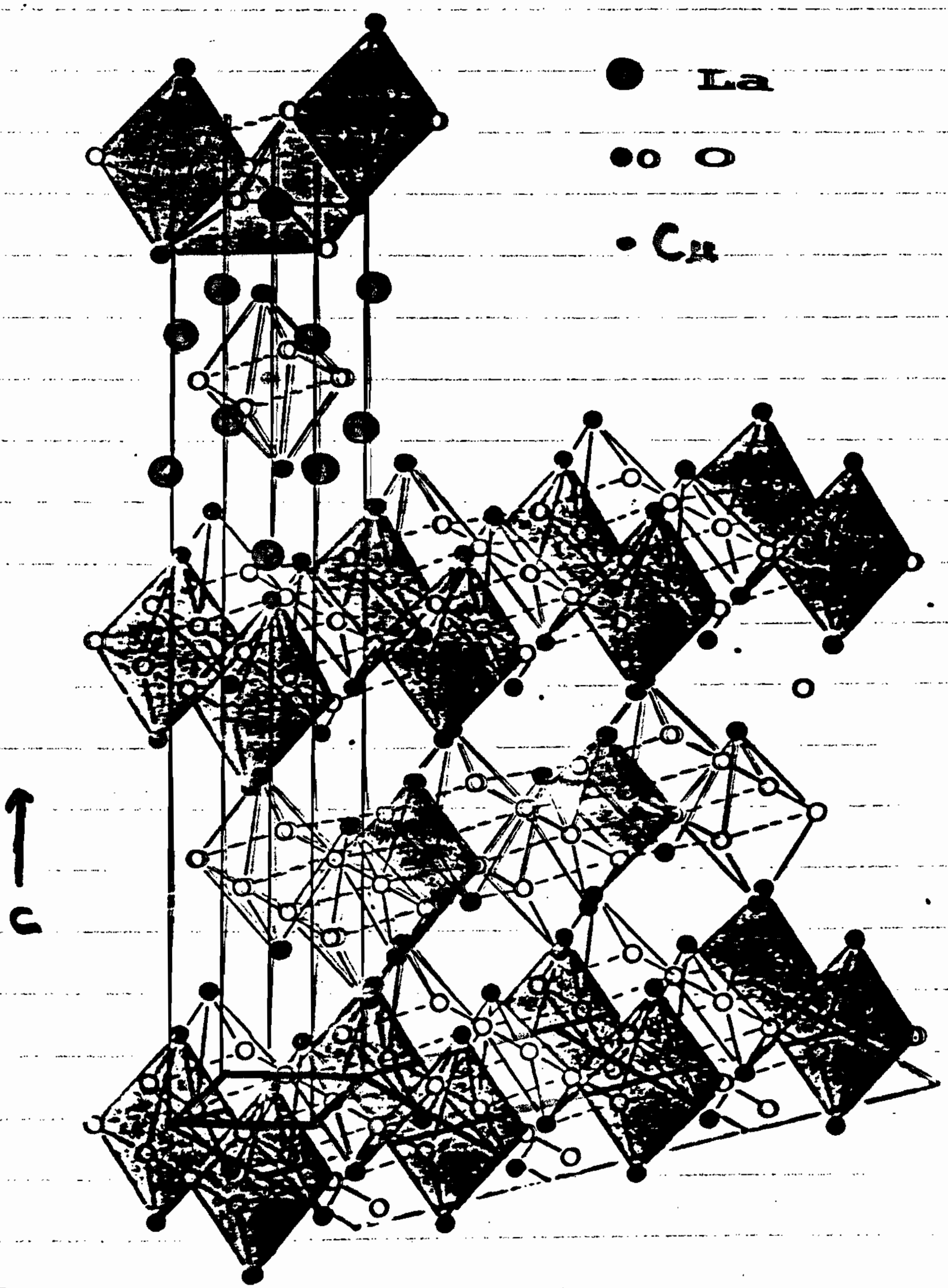
$\gamma = 2.08 \times 10^{-7} (J/K^2) = 5.9 \text{ mj/mole-K}^2$

$\beta = 1.80 \times 10^{-8} (J/K^4)$



$\Delta C \simeq 1.4 \gamma T_c \Rightarrow \left.\frac{\Delta C}{C}\right|_{30K} \simeq 4\%$

Bednorz - Müller



a = 3.8 Å
c = 13.2 Å

La_2CuO_4 Orthorhombic distorted K_2NiF_4 structure

$Ba_xLa_{2-x}CuO_4$ body centered tetragonal

[K_2NiF_4 structure type] $\frac{\text{2 molecules}}{\text{unit cell}}$

Why high T_c?

Very strong coupling limit of SC?

- similar to other oxide SC?

$BaPb_{1-x}Bi_xO_3$ $T_c = 12K$

$x = 0.25$

$Li_{1+x}Ti_{2-x}O_4$ $T_c \approx 13K$

$x = 0.05$

M_xWO_3 M = Alkaline or Alkaline Earth

$x < 0.3$ $T_c \leq 5K$

$SrTiO_{3-y}$ $T_c < 1K$

General features of oxide SC's

- M-I transition as x is varied
- poor conductors in metallic state
- low carrier concentration
- low $N(\epsilon_F)$ $\Rightarrow$ strong e-p interaction in $BaPbBiO_3$ ~~and $LiTi_2O_4$~~ case~~s~~
- Mixed valence or valence fluctuation seems to be important

$Ti^{3+} - Ti^{5+}$

$Bi^{3+} - Bi^{5+}$

Look at BLCO – Cu valence?

$La_2CuO_4 \Rightarrow Cu^{2+} \quad d^9$

$Ba_x^{2+} La_{2-x}^{3+} CuO_4 \Rightarrow Cu^{2+}, Cu^{3+}$

electron ~~goes~~ ~~to~~ conc. changes in the conduction band!

but oxygen deficiency

$Ba_x^{2+} La_{2-x}^{3+} CuO_{4-y} \Rightarrow Cu^{2+}$ only

These materials are not SC but are metallic

$BaPb_{1-x}Bi_xO_3$

SC for $x \lesssim 0.3$ ~~but not $x = 0$~~

Semicond $x \gtrsim 0.3$

Ortho — Tet — Ortho perovskite type

↑ ↑ structure changes

0 0.1 0.35 as x ↗

x →

$x = 0.25$ $n \approx 2.5 \times 10^{21}\ \text{cm}^{-3}$, $N(\epsilon_F)$ low

$T_c \approx 12K$

$\rho \approx 500\ \mu\Omega\ \text{cm}$ $d\rho/dT$ neg

⇒ l small

$\lambda \approx 1-2$ ⇒ strong coupling SC

⇙ sp like conduction band

but $\frac{2\Delta}{kT_c} \approx 3.5$ weak coupling value

(Pb 4.3)

Type II SC

Theoretical Models

Origin of SC in $BaPb_{1-x}Bi_xO_3$ still not understood (12 years after discovery of high T_c)

Band Structure calc. $\Rightarrow$

- wide conduction band from O-2p Pb-6s hybridization (16eV)
- little change in Fermi Surface as x increases thru O-T-O phase transitions
- simple FE like BS for $x \lesssim 0.3$
- charge disproportionation between inequivalent Bi sites small

$\Rightarrow$ weak coupling not strong coupling SC

So BS calc can apparently not explain

- Why T_c so high
- Why ρ of metallic state so high
- Why $T_c \to 0$ and semiconducting state appears for $x \gtrsim 0.3$

Must go beyond single particle theories

$$T_c \simeq \langle\omega\rangle \exp\left(\frac{1+\lambda}{\lambda-\mu^*}\right)$$

Models for SC

$$\lambda_{exp} \simeq 1-2 \qquad \lambda = N(0)\,\frac{\langle I^2\rangle}{M\langle\omega\rangle^2}$$

low energy phonon modes have been seen in tunneling exps

So T_c may be explained by conventional strong coupling (Eliashberg) theory

What if $\lambda >> 1$? No good theory here. Midgal approx breaks down.

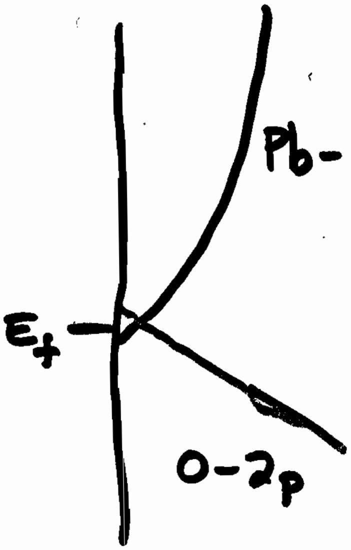
$\langle \omega \rangle$ not $<< \epsilon_F$

- Local Instability Model — Rice & Sneddon

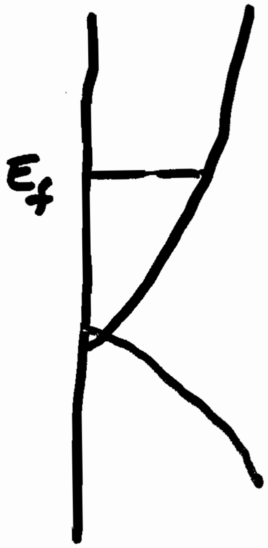
  not clear how this applies in wide band system

- Coupling of polarons or bipolarons — Alexandrov & Ranninger
  - Very diff. predictions than BCS but λ has to be very large ↘ like He^4 superfluid
  - get narrow polaronic band $\langle \omega \rangle \sim \epsilon_F \sim W$ if $\lambda \gtrsim 1$

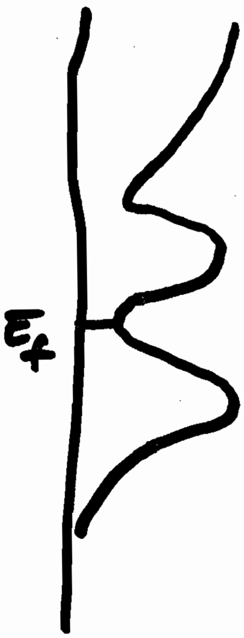
* Need new or better ideas here



$x = 0$



$x = 0.15$



$x = 0.3$

FE like

Local
Instability
Model
Bi^{3+} – Bi^{5+} sites

Band picture will be similar in La_2CuO_4 materials (Art Williams)

expect Cu d_{z^2} or $d_{x^2-y^2}$ will hybridize with O 2p to form partially filled conduction band.

So — lots to do to understand
New Zurich SC's

and perhaps raise T_c even more

Exps in progress

Specific heat, critical field, Hall &
Thermopower, ρ, $\rho(T)$ under pressure
Structure as $f(T)$

← may have been done already

Collaborating with Muller-Bednorz at present

Will try to make films for tunneling (Park, Tsuei) & to evaluate new materials

* — Need more homogeneous polycrystals or single crystals — Scott, Holtzberg interested

Band Structure — Art Williams

Journal Club 12 Dec 1986
At Yorktown

Seminar given after MRS meeting
Has my unpublished critical field data and
specific heat data (basis of MM Abstract that
I submitted)

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