30 years of high Tc:
Superfluid and normal-fluid densities in the cuprate superconductors

David Tanner

University of Florida

April 17, 1986 – just over 30 years!

Z. Phys. B – Condensed Matter 64, 189–193 (1986)

Condensed Matter
Zeitschrift für Physik B

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

J.G. Bednorz and K.A. Müller
IBM Zürich Research Laboratory,

Received April 17, 1986

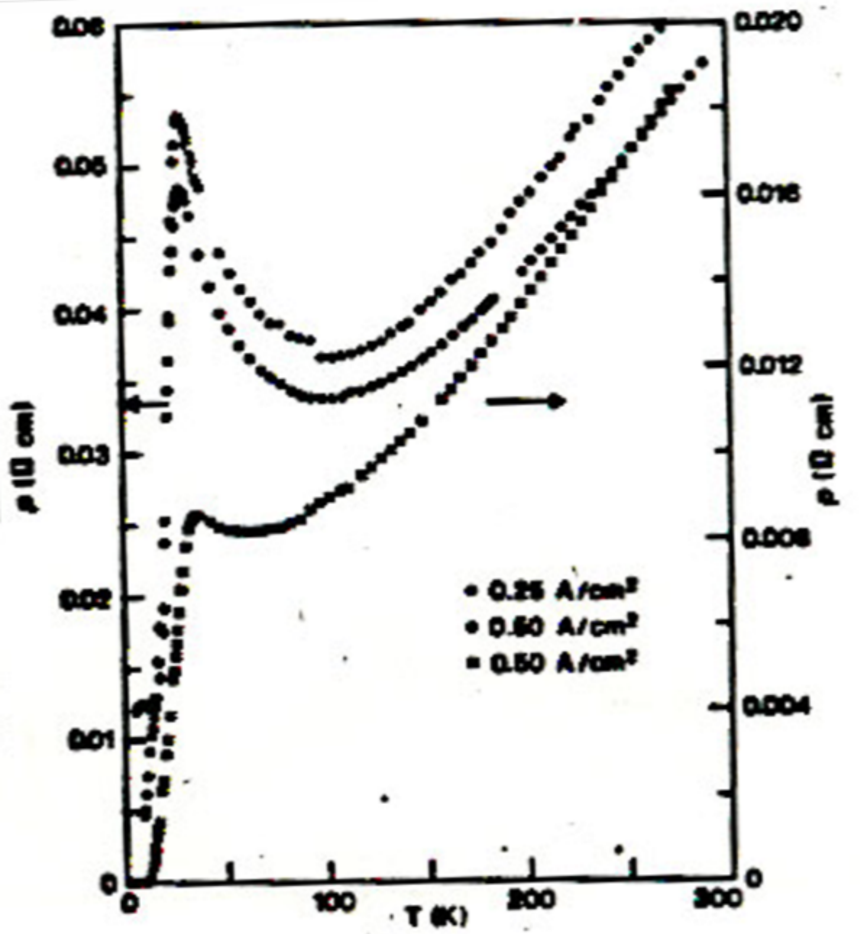


Fig. 1. Temperature dependence of resistivity in $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ –

April 17, 1986 – just over 30 years!

J. Georg Bednorz, left, and K. Alex Müller after learning they had won the Nobel Prize in physics.

2 Get Nobel for Unlocking Superconductor Secret

By JAMES GLEICK

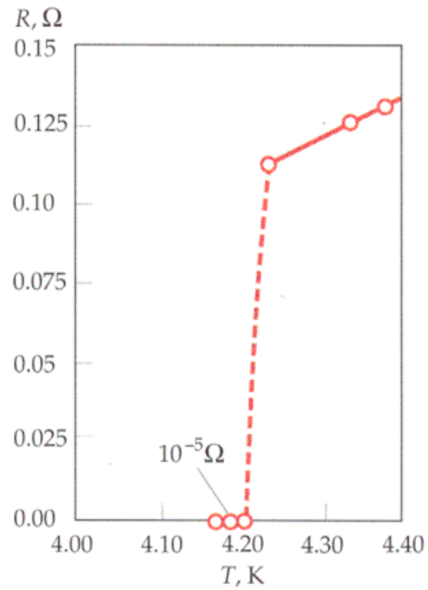
With a swiftness that echoed the rush of discovery over the last few months, the Nobel Prize in Physics was awarded yesterday to two scientists in Switzerland whose breakthrough just last year has touched off a torrent of research in the long-dormant field of superconductivity.

Sciences said in its announcement from Stockholm yesterday. "This set off an avalanche."

Physicists have already surpassed the discovery with new s... become superconducti... higher temperatures, ra... of applications from m... cient generators and p... tiny supercomputers a...

their work on the structure of molecules, including the creation of artificial molecules that mimic the processes of life. [Page 8.]

- 1911: H. K. Onnes, who had figured out how to make liquid helium, used it to cool mercury to 4.2 K and looked at its resistance:

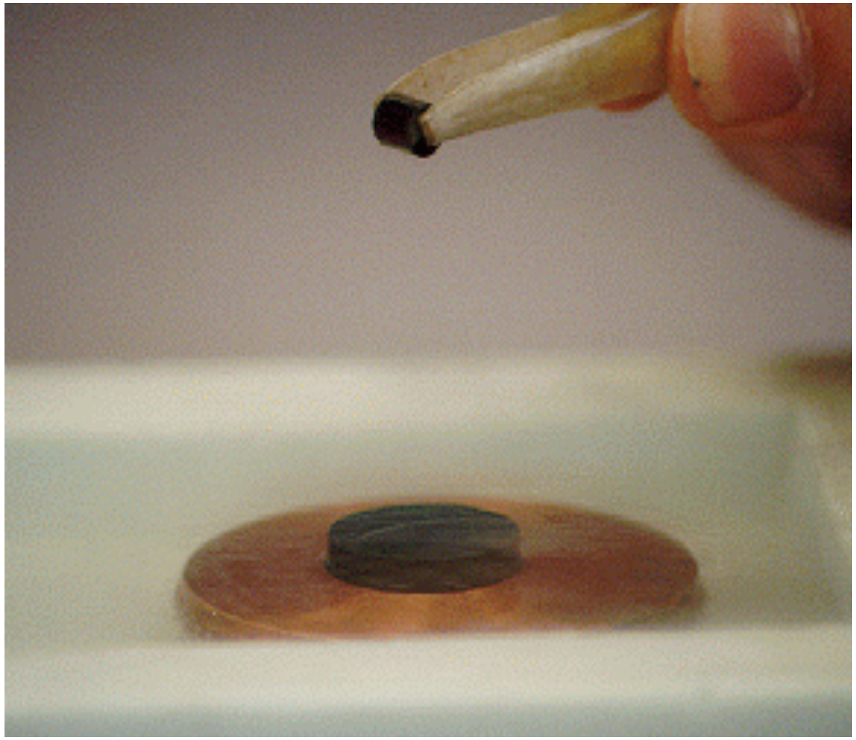


- At low temperatures the resistance of some metals→0, measured to be less than $10^{-16} \cdot \rho_{conductor}$ (i.e., $\rho < 10^{-24}\ \Omega m$)!
  - –Current can flow, even if $E=0$.
  - –Current in superconducting rings can flow for years with no decrease!
- 1933: Meissner effect: Magnetic field is zero inside a superconductor!
- 1957: Bardeen, Cooper, and Schrieffer ("BCS") publish theoretical explanation. Nobel prize in 1972.
  - –Bardeen's *second* Nobel prize (1956 – transistor)
- 1986: Bednorz and Mueller discover HTSC.
  - –No longer a low temperature phenomenon

The Meissner Effect

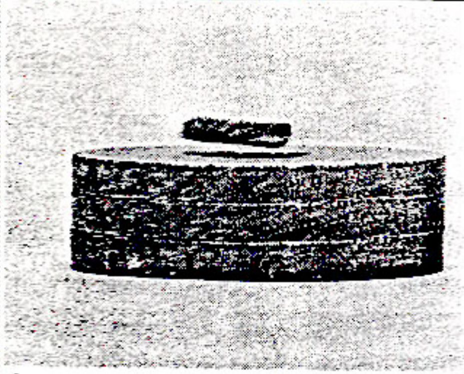
- A diamagnetic property exhibited by superconductors.

- End result is the exclusion of magnetic field from the interior of a superconductor.



本誌編集部の試作品が世界記録にあと一歩!!

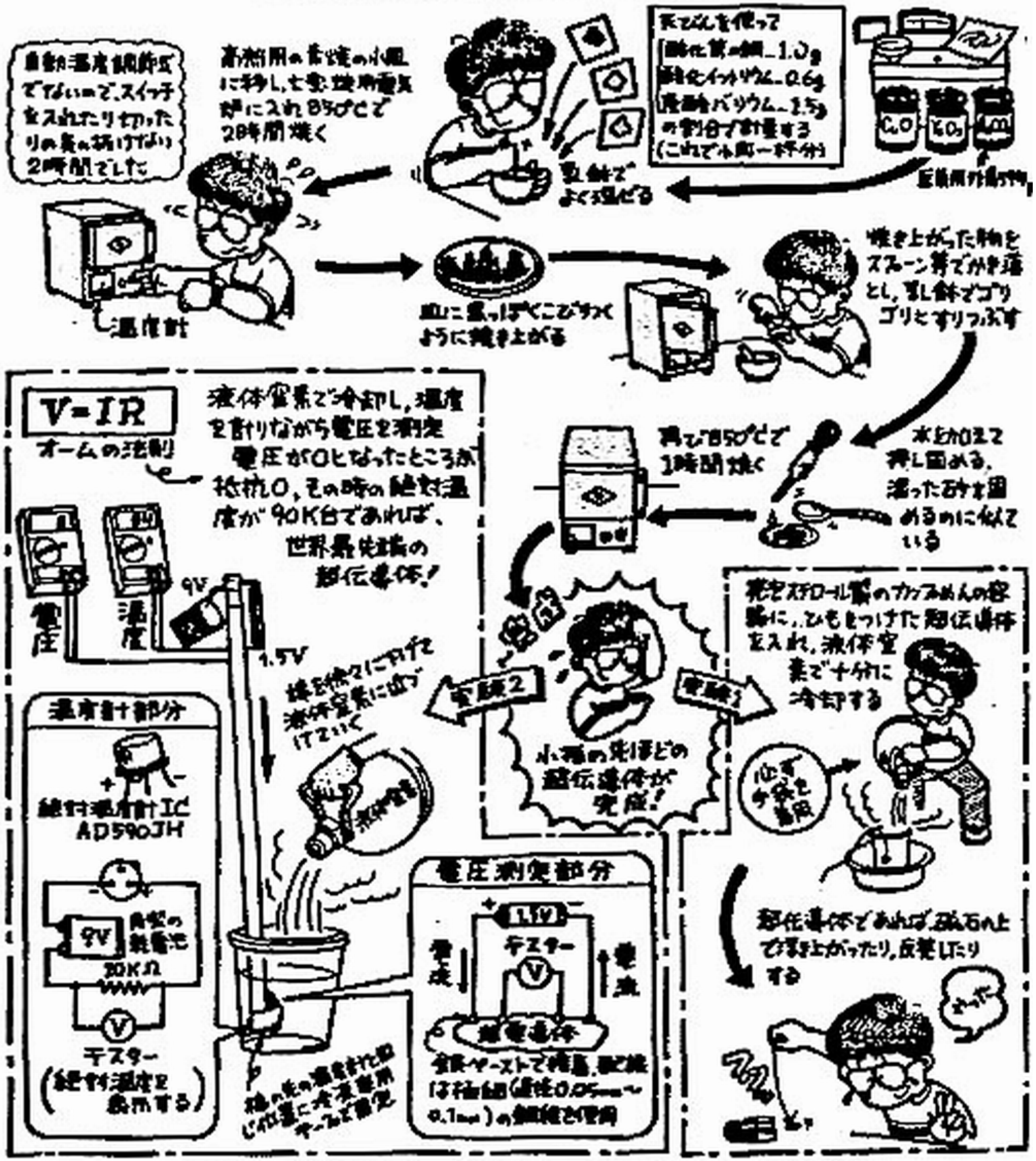
超伝導体



自画自賛ではあるけれども、本誌はあえて言う「世紀の快挙」といいたい。なお、「第二の産業革命が起ころうとしている」と、世界中の科学者を興奮させている超伝導体を本誌編集部が製作、絶対温度七十七度（氷点下一九六度）の液体窒素温度以上で超伝導現象確認に実験に成功したからだ。材料や器具はいずれも市販のもの。総費用は約三万円という超低額予算。以下は、三カ月前ゼロ＝イチからの「ハイテク最先端技術に本誌がいかに挑んだかの記録である。

新英

[illegible]



自動温度調節式でないので、スイッチを入れたり切ったりの気の抜けない2時間でした
高熱用の素焼の小皿に移し、卓上型電気炉に入れ850℃で2時間焼く
天びんを使って
酸化第二銅_1.0g
酸化イットリウム_0.6g
炭酸バリウム_1.5g
の割合で計量する
(これで小皿一杯分)
乳鉢でよく混ぜる
温度計
皿に黒っぽくこびりつくように焼き上がる
焼き上がった物をスプーン等でかき落とし、乳鉢でゴリゴリとすりつぶす
水を加えて押し固める。湿った砂を固めるのに似ている
再び850℃で1時間焼く
V=IR
オームの法則
液体窒素で冷却し、温度を計りながら電圧を測定
電圧が0となったところが抵抗0、その時の絶対温度が90K台であれば、
世界最先端の超伝導体！
電圧
温度
9V
1.5V
棒を徐々に下げて液体窒素に近づけていく
液体窒素
温度計部分
絶対温度計IC AD590JH
9V
角型の乾電池
10KΩ
テスター
(絶対温度を表示する)
電圧測定部分
1.5V
テスター
電流
電流
銀ペーストで接着、配線は極細(直径0.05mm~0.1mm)の銅線を使用
完成
小指の先ほどの超伝導体が完成！
実験2
実験1
発泡スチロール製のカップめんの容器に、ひもをつけた超伝導体を入れ、液体窒素で十分に冷却する
必ず手袋を着用
超伝導体であれば磁石の上で浮き上がったり、反発したりする

に酉独の
分に発表
目されな
火をつけ

昨年十一月、東大工学部の田中
昭二教授のグループがその論文の
結果を確認。十二月には同じ東大
工学部の笛木和雄教授らがバリウ
ムの代わりにストロンチウムを使

って、三十七Kで抵抗が落ち始める
超伝導体を発表するという素早さ
だった。
それからというものは、世界中
の研究者が競ってセラミックスを
焼き始めたといって良
冶で
「超
抵抗
ぎ登
二月
トン
ラン
ムに
驚異
から

きた論文を積み上げると、高さ二
㍍以上になり、
「過去十年分に匹敵する量の論文
が、このわずか二カ月間に書かれ
た」
……

<超伝導体の製造実験費>

	(円)
酸化イットリウム(25g)	4.000
炭酸バリウム(25g)	3.000
酸化第二銅(25g)	2.000
七宝焼用電気炉	25.200
電気炉用小皿(4枚)	400
乳　鉢	780
絶対温度計用IC	1.000
テスター(2台)	9.200
抵　抗(10kΩ)	20
冷凍庫用テープ	270
銀ペースト	4.420
乾電池(1.5V、9V)等	210
液体窒素（5ℓ）	1.000
計	51.500

画期的な超伝導体を発表した。

なにしろ、つい一年前までは、液体窒素温度を超えることすら、「がんの特効薬同様、今世紀中はとても無理だろう」と研究者の間でいわれていた。それが、いとも簡単に実現してしまったのだ。

東北大金属材料研究所の立木昌教授によれば、最近の二カ月余の間に世界中からファクスや航空便で送られて

……

電気炉の火加減をみるという、素朴な手作り作業で製造される。その実験風景は、まさに「現代の錬金術」と呼ぶにふさわしい。

本誌が実験に乗り出したというのも、指導してもらった東大教養学部の氷上助教授の「小学校の理科クラブ並みの実験」という言葉を信じたからである。担当記者は私大文科系の出身、手伝ったアルバイトのM君も、私大商学部三年生。ともに科学的教養が高いとは、お世辞にもいえない。

とはいえ、氷上助教授も本誌の実験とあまり大差ない方法によって、イットリウムを使ったセラミ

Materials

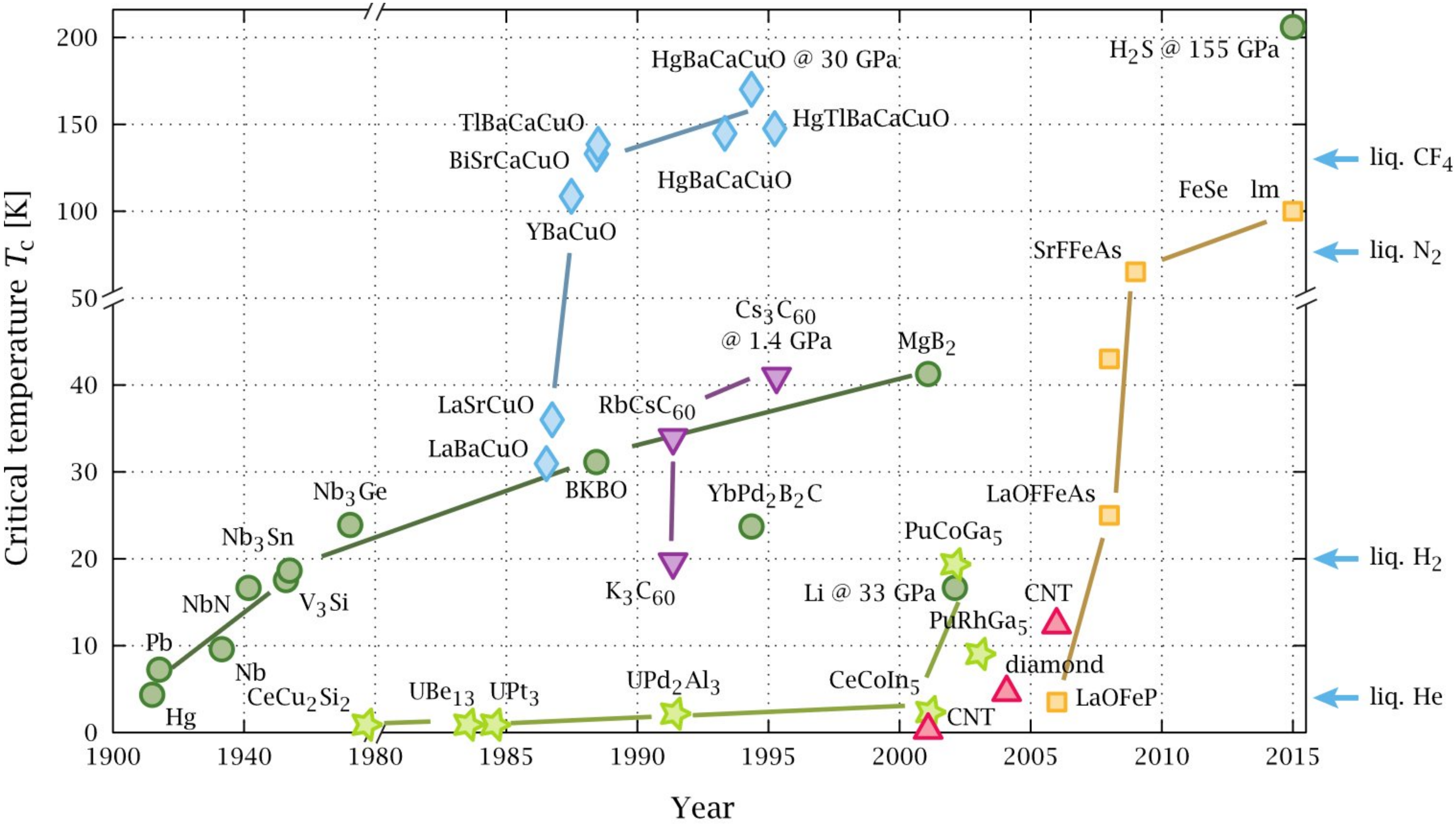
- YBCO == 123: $YBa_2Cu_3O_7$ 94 K
- BSCO == 2212: $Bi_2Sr_2CaCu_2O_8$ 91 K
- LSCO == 214: $La_{2-x}Sr_xCuO_4$ 39 K

Materials

- YBCO == 123: $YBa_2Cu_3O_7$
- BSCO == 2212: $Bi_2Sr_2CaCu_2O_8$
- LSCO == 214: $La_{2-x}Sr_xCuO_4$

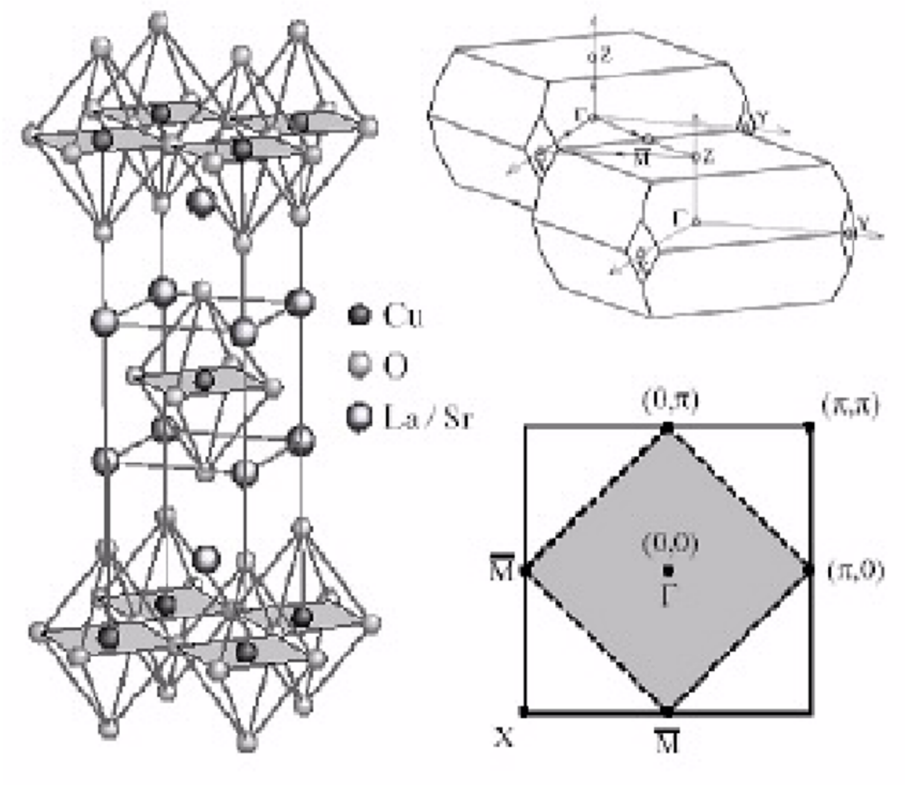
- TBACO up to 110 K
- HgBaCuO up to 134 K (153 K under pressure)

Superconductivity timeline



What sort of materials are the cuprates?

- La_2Cu0_4 is the "parent" material
- Would be half filled band metal



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- La_2Cu0_4 is the "parent" material
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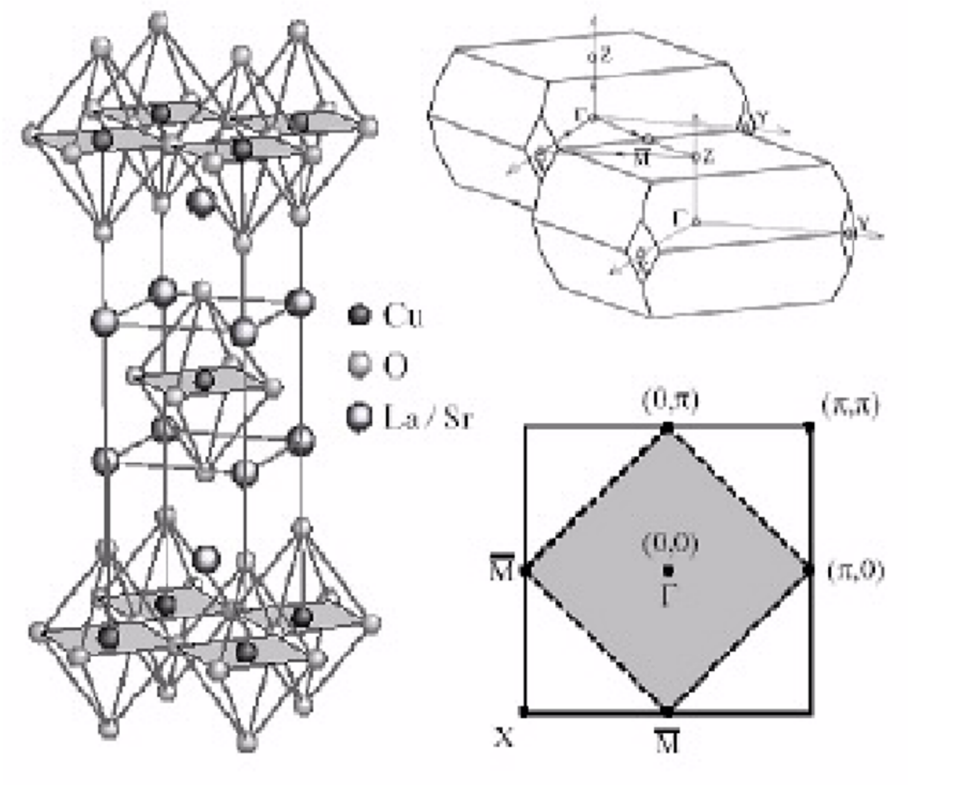
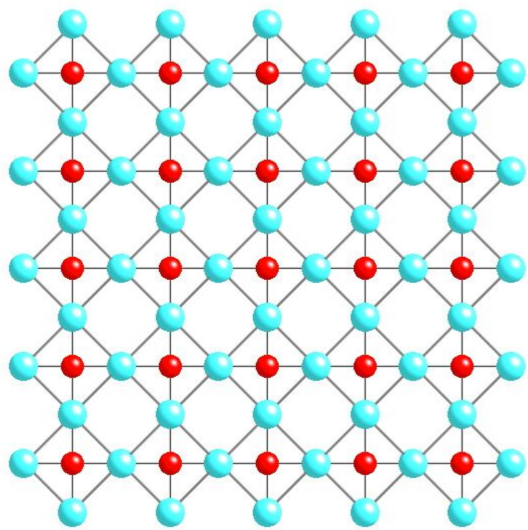
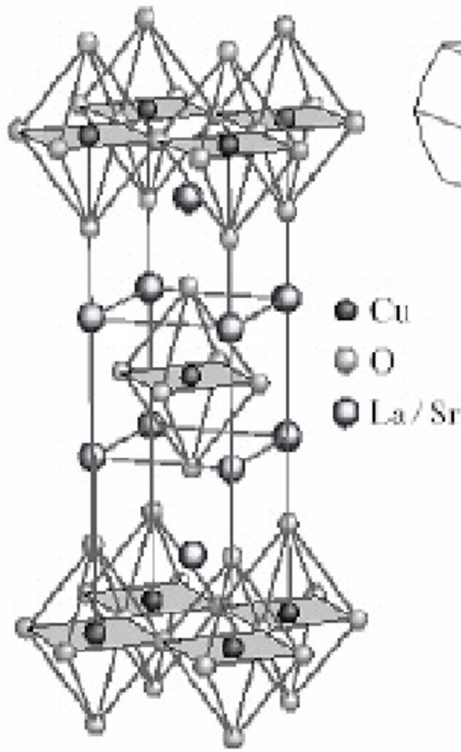
- Layered, with square-planar CuO_2 sheets

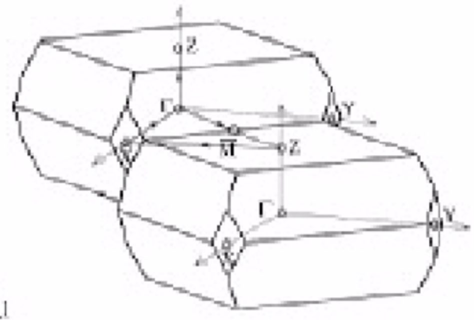


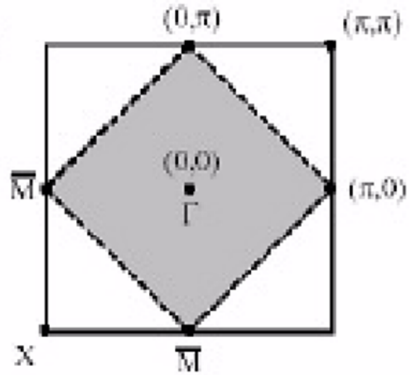


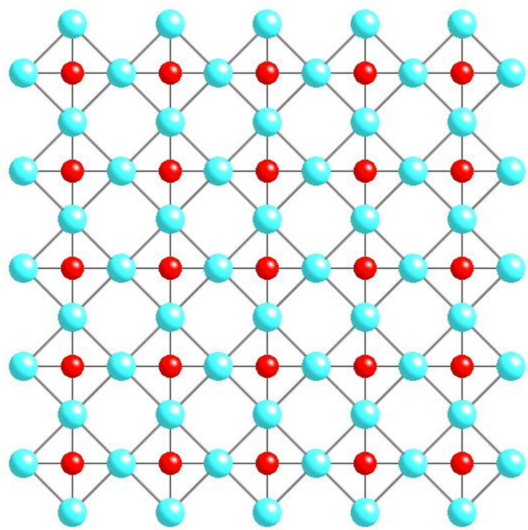
What sort of materials are the cuprates?

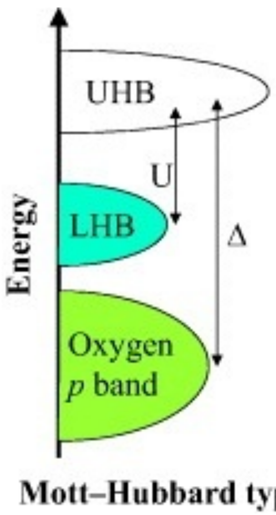
- La_2Cu0_4 is the "parent" material
- Would be half filled band metal
- Layered, with square-planar CuO_2 sheets
- Actually a "charge-transfer" insulator

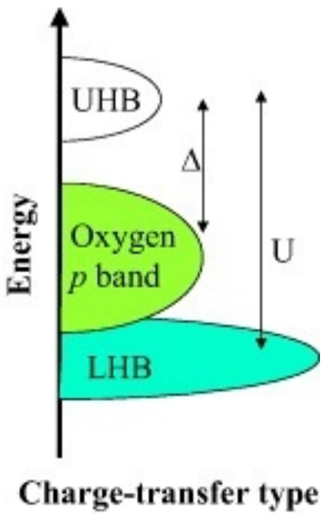








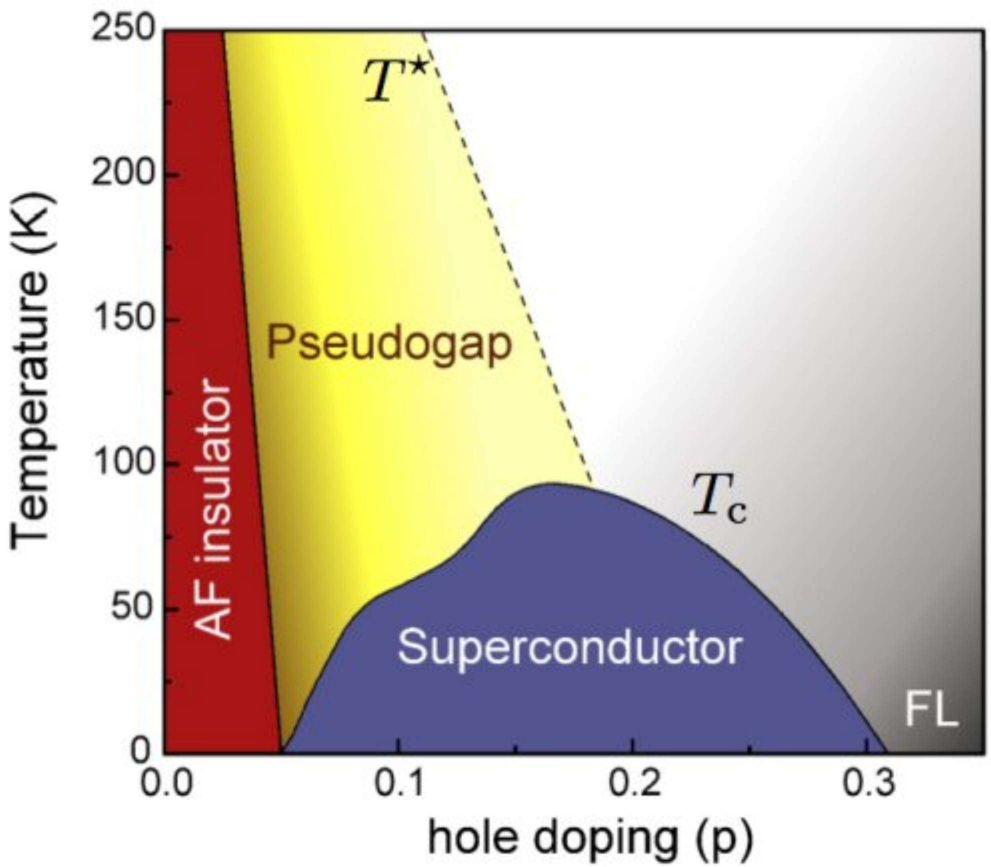




Phase diagram

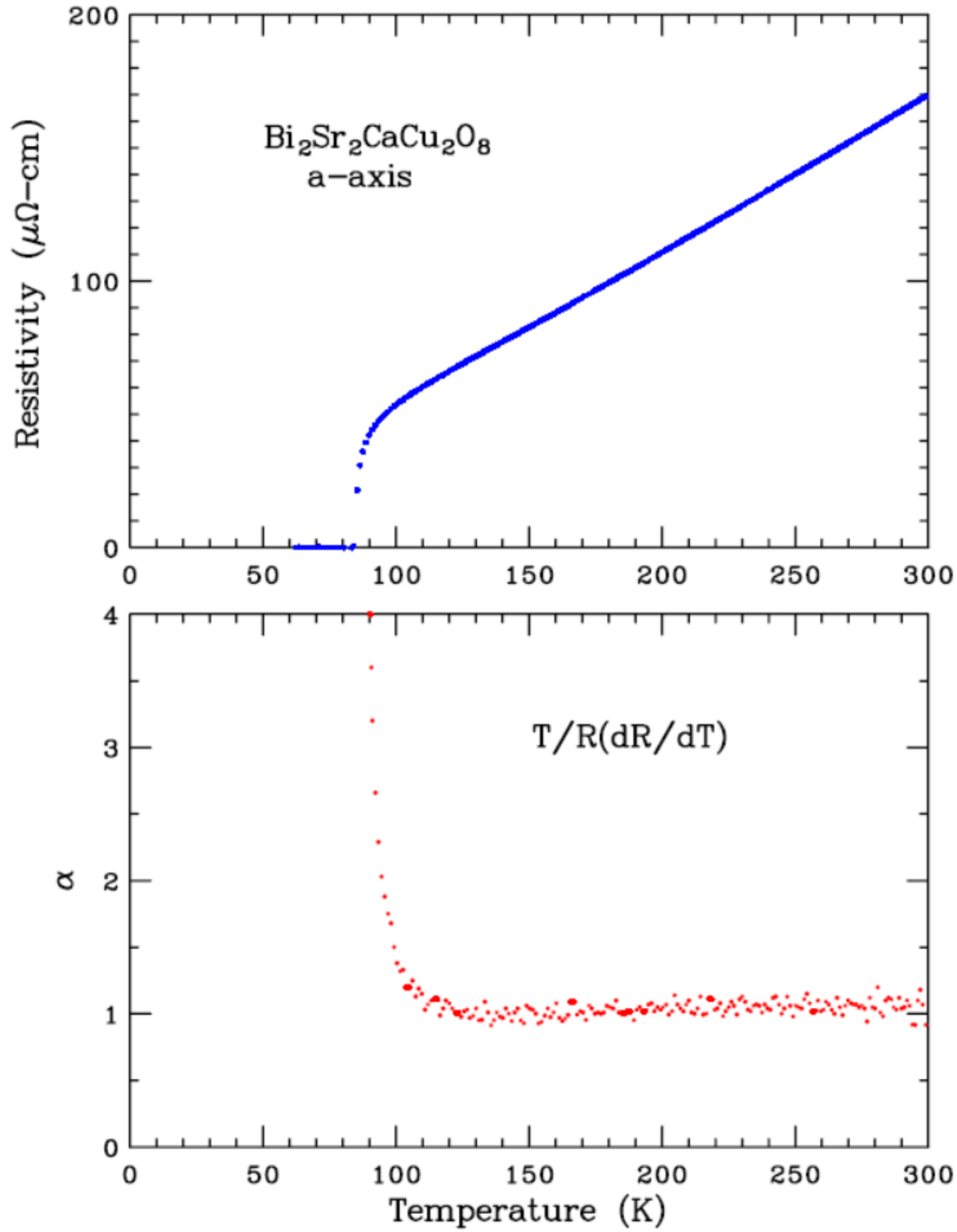
- Charge carriers are holes
- Adding holes (above ~5% produces superconductivity
- "Optimal doping"
  - ➔ max Tc
  - ➔ linear resistivity

"strange metal"



Charge transport

- Cuprates: "metallic" dc resistance
- $\rho = A + BT^{\alpha}$
  $\alpha \approx 1;\ A \sim 0.$
- $\alpha = (T/\rho) \cdot (d\rho/dT)$



Starting points

1. Start with a charge transfer insulator
   - CT gap: 1.5 eV
2. Doping -> holes -> low-energy spectral weight
3. It's a superconductor
   - Condensate => Has a $\delta(\omega)$ contribution to $\sigma_1(\omega)$

$$\sigma_1(\omega) = A\delta(\omega) = \frac{\pi \rho_s e^2}{m_e}\delta(\omega)$$

with ρ_s the superfluid density

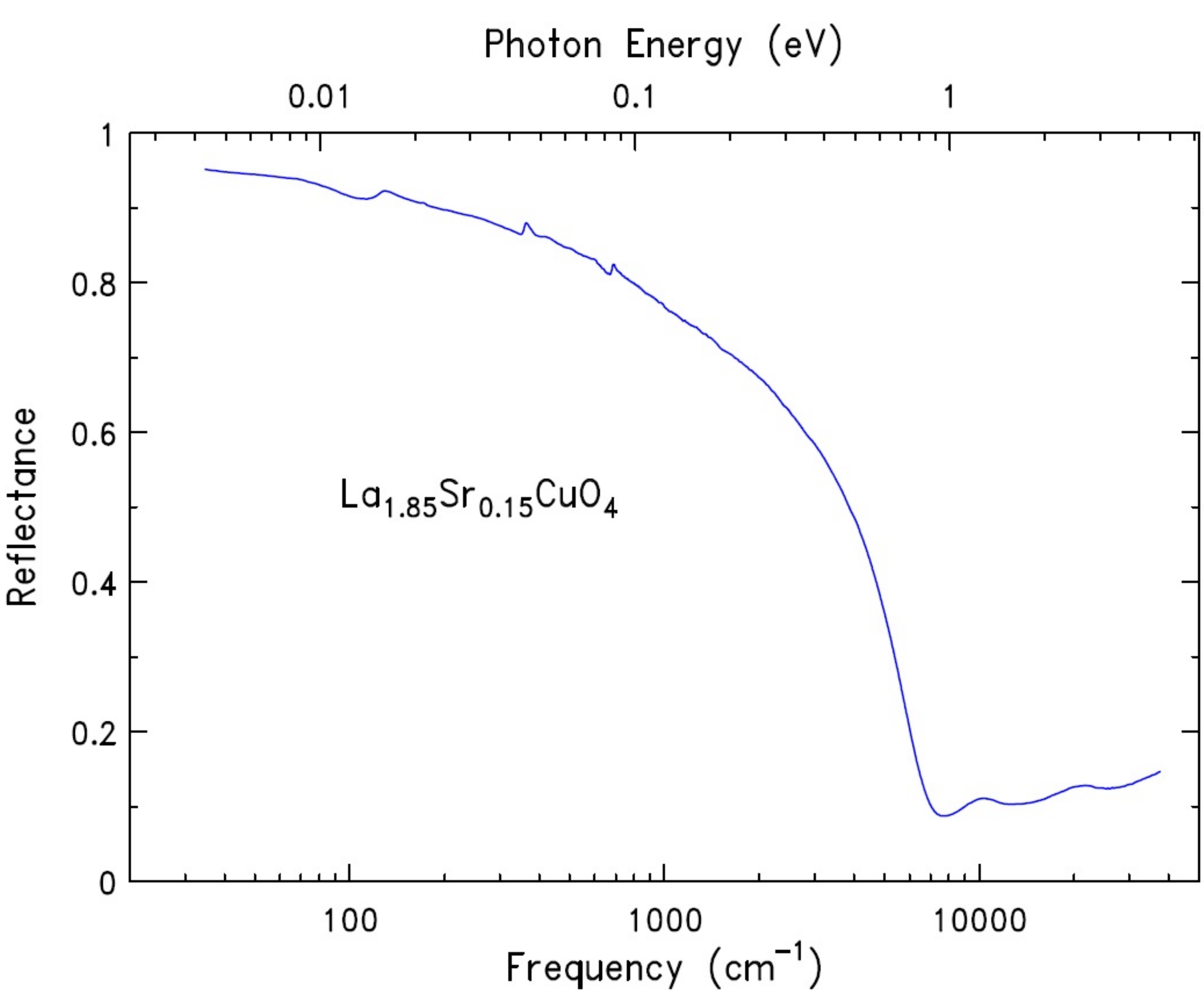
- London screening (Meissner effect) a consequence of the $\delta(\omega)$ in $\sigma_1(\omega)$

Superfluid density

- Superfluid density, $\rho_s(T)$: fundamental macroscopic quantity of a superconductor.
- Superconducting condensate signaled by spectral weight transfer to $\omega = 0$ delta function.
- Superfluid density, $\rho_s \leftrightarrow$ Strength of the delta function. (Obtained from sum rule [FGT].)
- Superfluid density, $\rho_s \leftrightarrow$ Optical penetration depth. ($\rho_s \sim 1/\lambda_L^2$)

Recall that essentially every conduction electron participates in the $T = 0$ superfluid of a clean metallic superconductor. ($\lambda_L <-> c/\omega_p$)

300 K reflectance of LaSrCuO



Kramers-Kronig of reflectance

- Relates real and imaginary parts of response functions

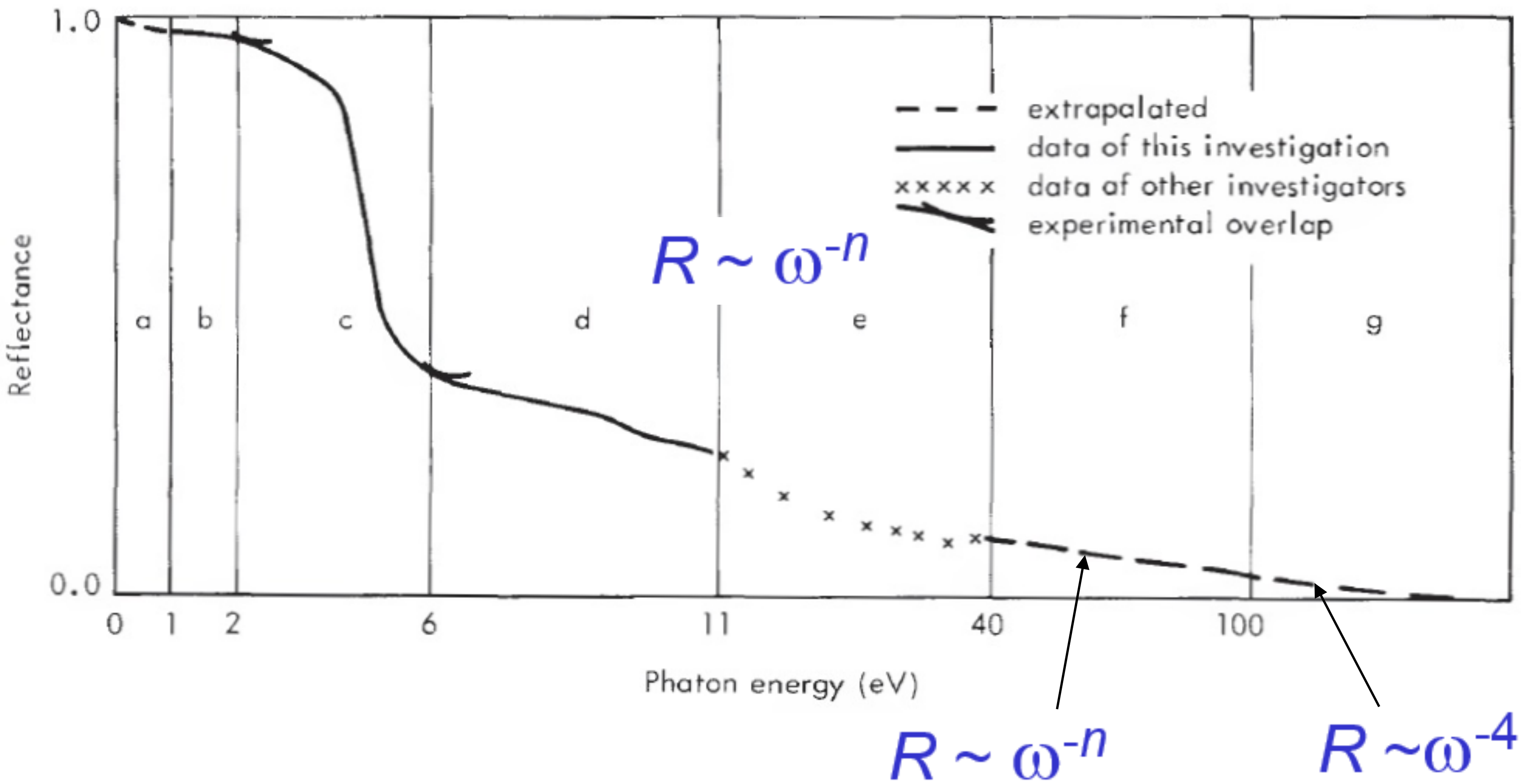
$$r = \rho\, e^{i\phi} = \frac{1 - N}{1 + N} \qquad \ln r = \ln \rho + i\phi.$$

$$\phi(\omega) = -\frac{\omega}{\pi}\mathcal{P}\int_0^\infty d\omega' \, \frac{\ln[\mathscr{R}(\omega')/\mathscr{R}(\omega)]}{\omega'^2 - \omega^2}$$

- Typical data: 30-40,000 cm-1 (4 meV-5 3V)
- Integral: zero to infinity
- ∴ extrapolations are needed, above and below measured data
- High end gives the most problems

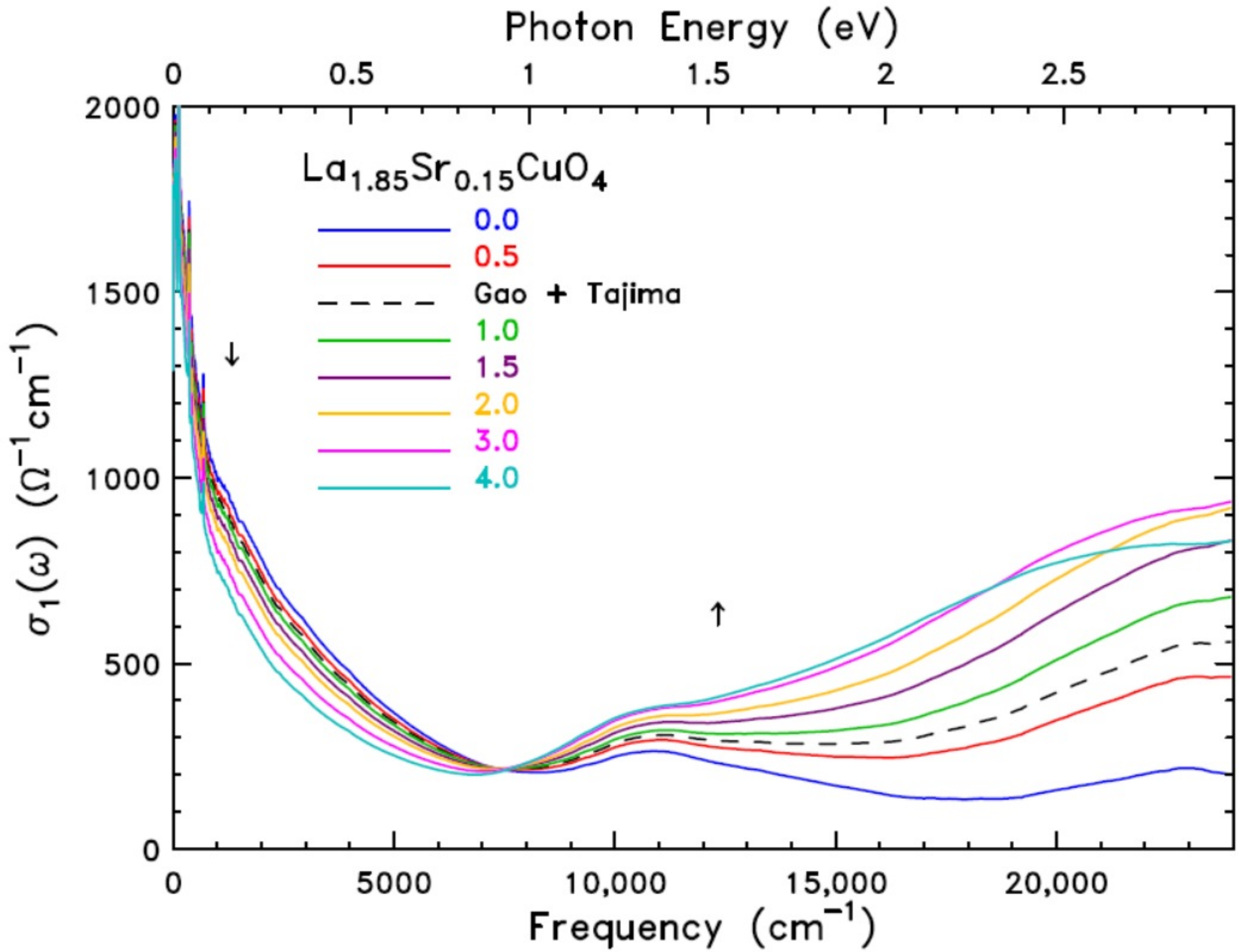
Kramers-Kronig analysis of reflectance: Wooten (1972)

$$\phi(\omega) = -\frac{\omega}{\pi}\mathcal{P}\int_0^\infty d\omega' \, \frac{\ln[\mathscr{R}(\omega')/\mathscr{R}(\omega)]}{\omega'^2 - \omega^2}$$



- *How does it do?*

KK with power law



X-ray optics

- Atomic scattering factors* f
- The dielectric function is

$$\epsilon = 1 - \sum_j \frac{4\pi n_j e^2}{m\omega^2}(f_1^j - i f_2^j)$$

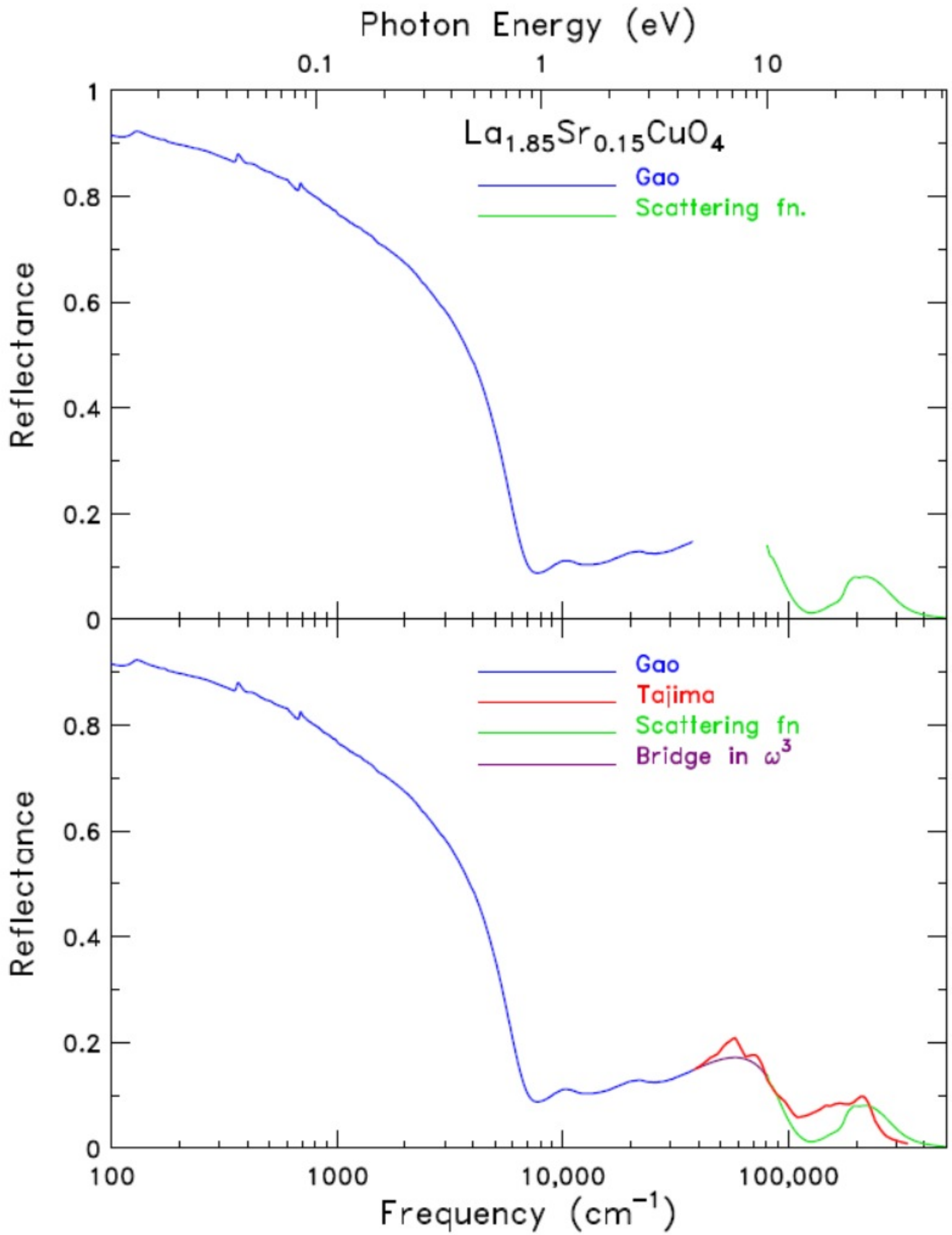
- Sum: atoms j at number density n_j and with complex scattering factor f_j
- Limiting high-frequency behavior:

$$f_1^j \to Z^j \quad f_2 \to 0 \qquad \epsilon \to 1 - \sum_j 4\pi n_j Z^j e^2 / m\omega^2$$

- Reflectance calculated as usual

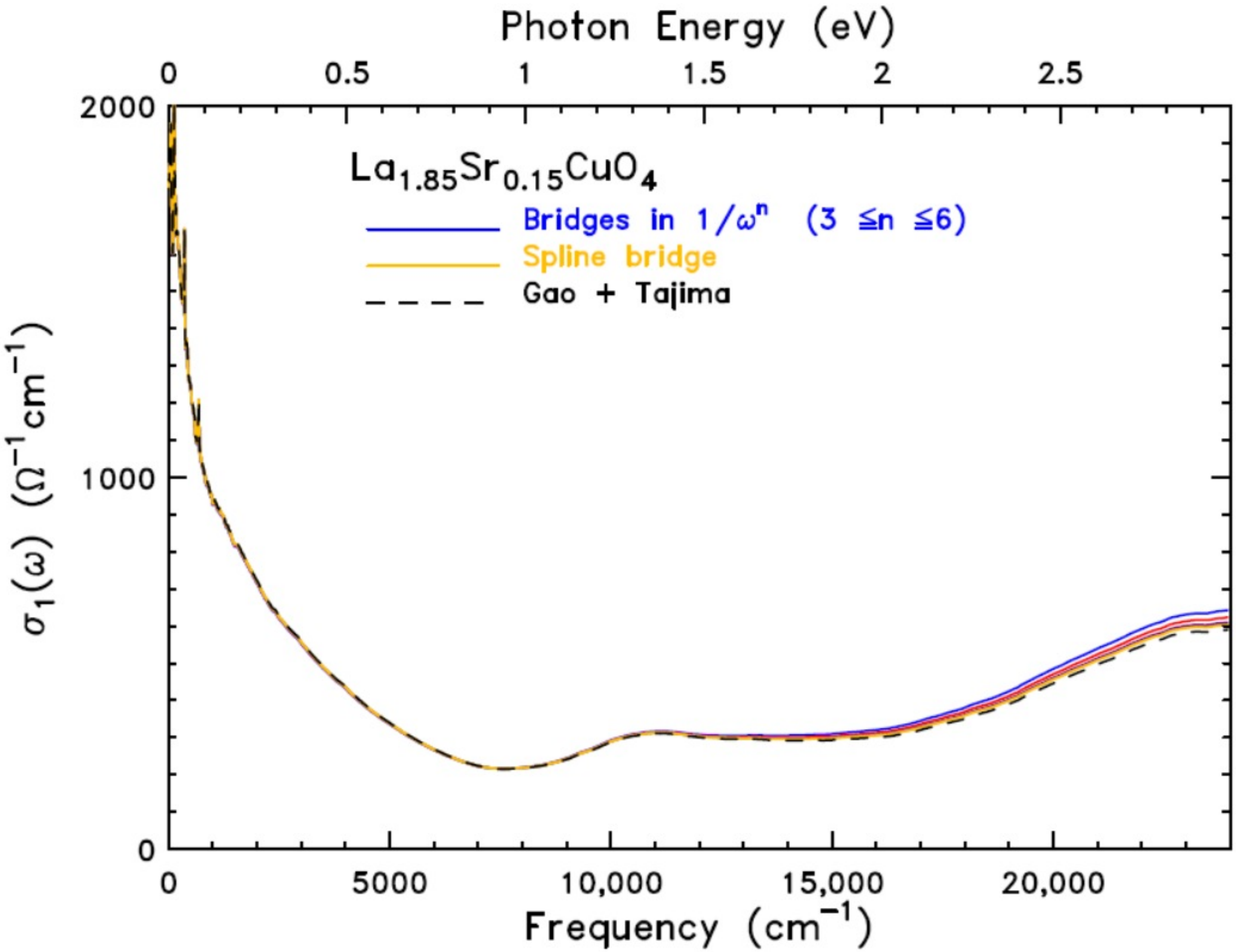
*See: http://henke.lbl.gov/optical_constants/

LSCO: some vuv data do exist



- *How does it do?*

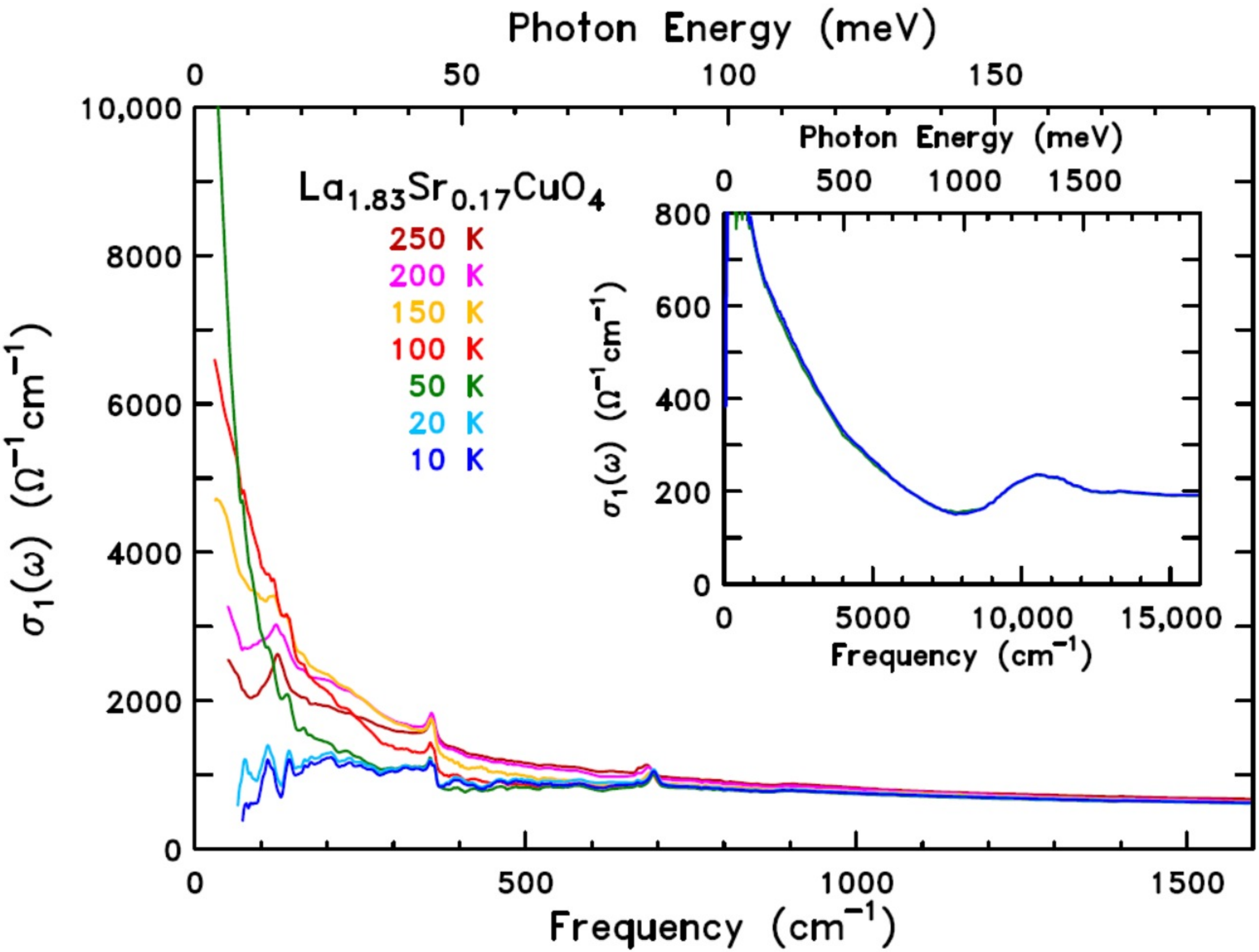
IR and CT band independent of bridge
Smll variations above 16,000 cm^{-1} (2 eV)



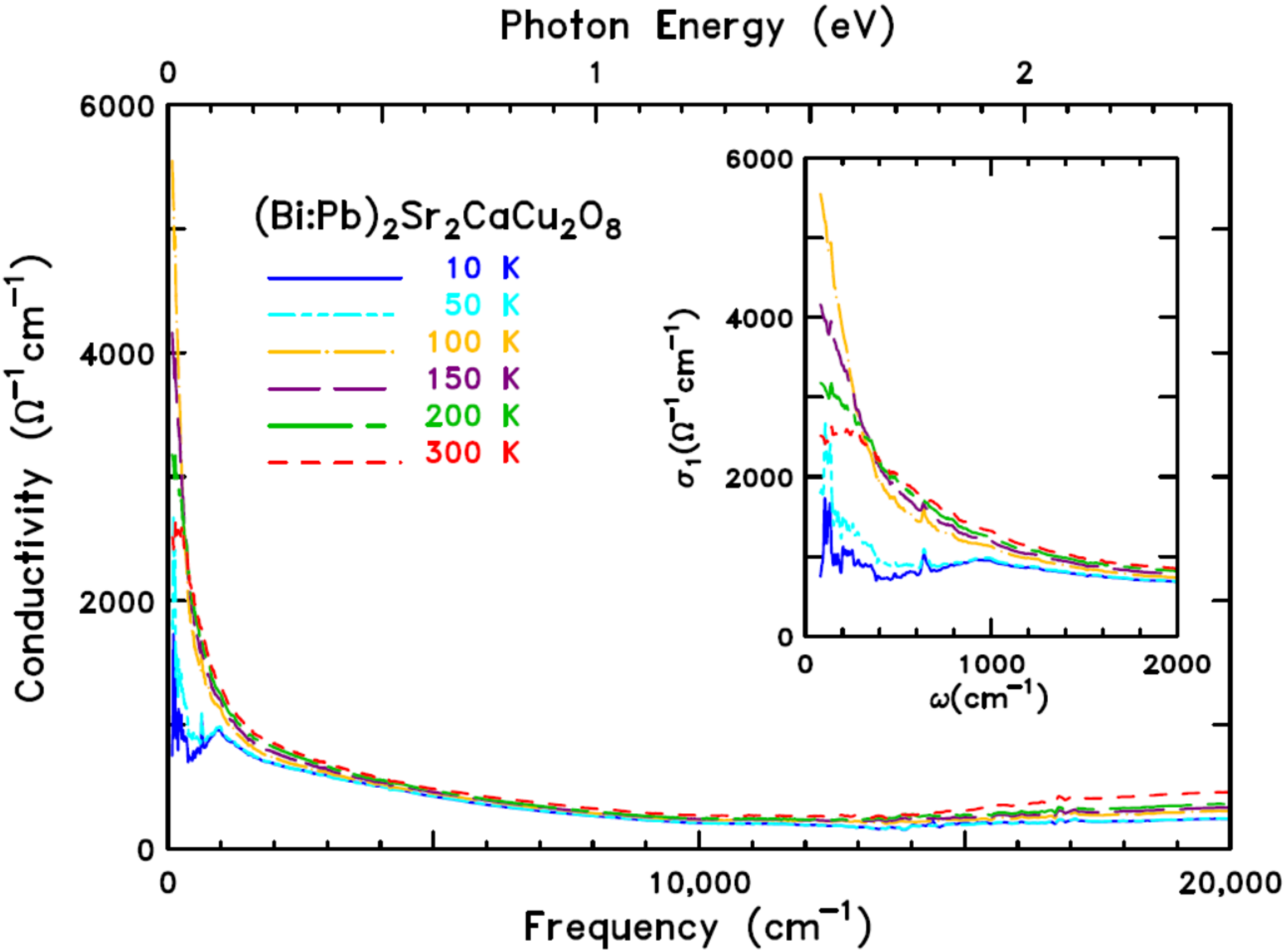
- So far so good.

http://www.phys.ufl.edu/~tanner/ZIPS/datan.zip

$La_{2-x}Sr_xCuO_4$ *ab*-plane optical conductivity

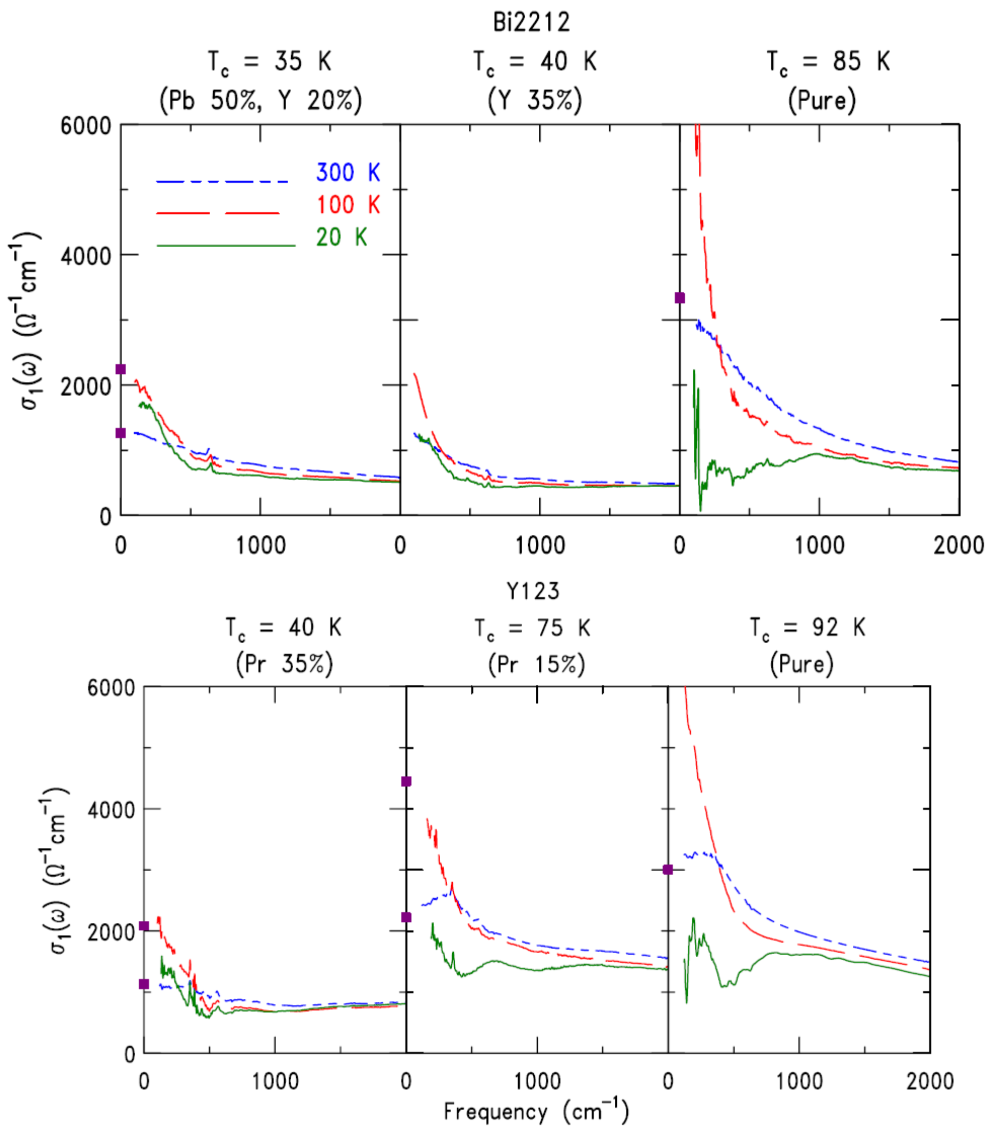


Bisco 2212 *ab*-plane optical conductivity



A set of underdoped crystals

- Area under curves decreases as doping is reduced
- Area smaller below T_c



Partial sum rule

- Low-energy carrier density and superfluid density:

  Partial sum rule

$$\rho_{eff}(\omega) \equiv N_{eff}(\omega)\frac{m}{m^*} = \frac{2mV_{Cu}}{\pi e^2}\int_0^{\omega} \sigma_1(\omega')d\omega'$$

- e (m) free-electron charge (mass), m^* the effective mass, and V_{Cu} the volume allocated to each CuO_2 unit and associated atoms. (V_{cell} / Z^*N_{Cu})

Goal: Compare ρ_{eff} with ρ_s for a variety of samples

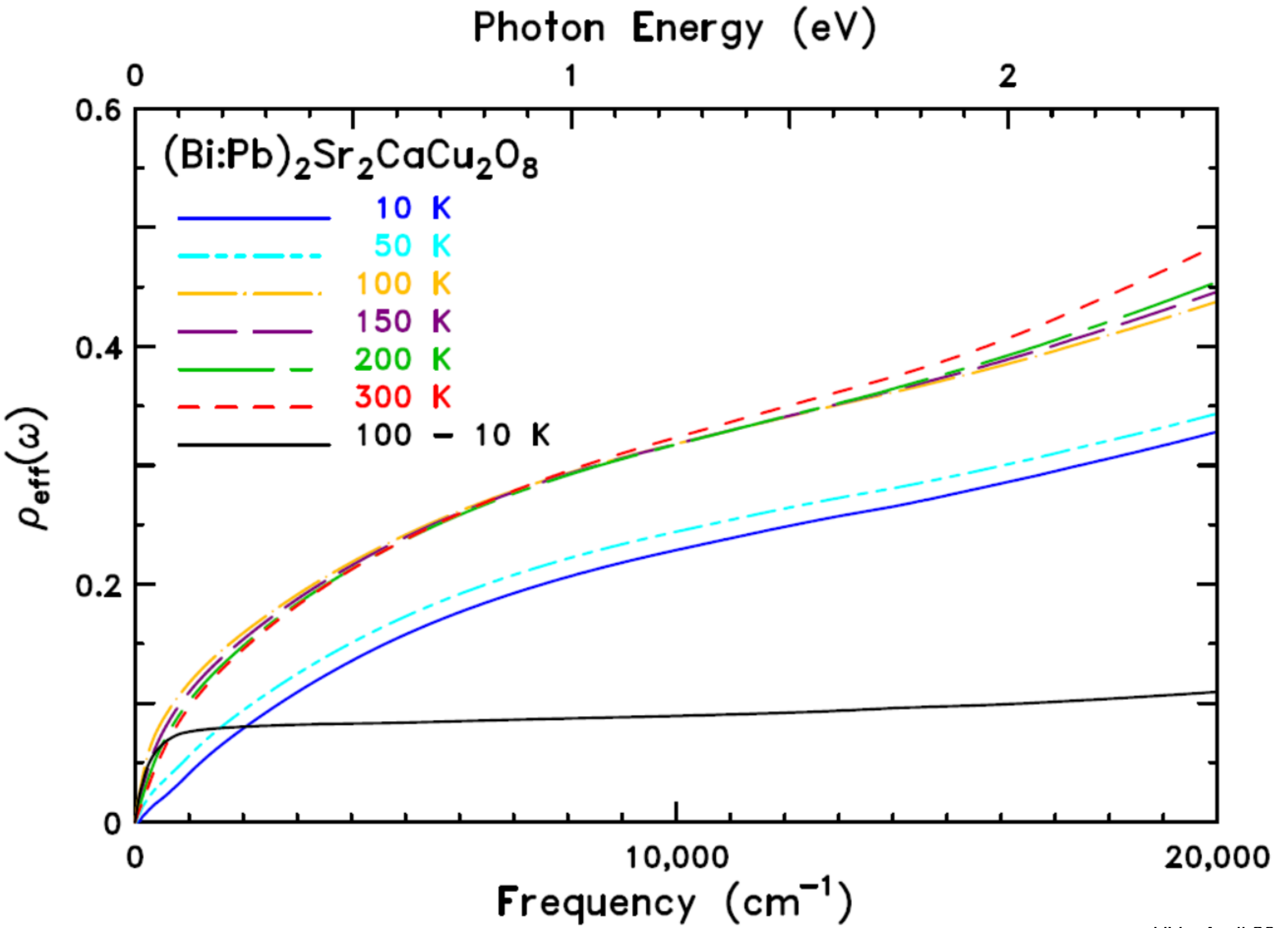
Two things:

$$\rho_{eff}(\omega) = \frac{2mV_{\text{Cu}}}{\pi e^2}\int_0^{\omega} \sigma_{1n}(\omega')d\omega'$$

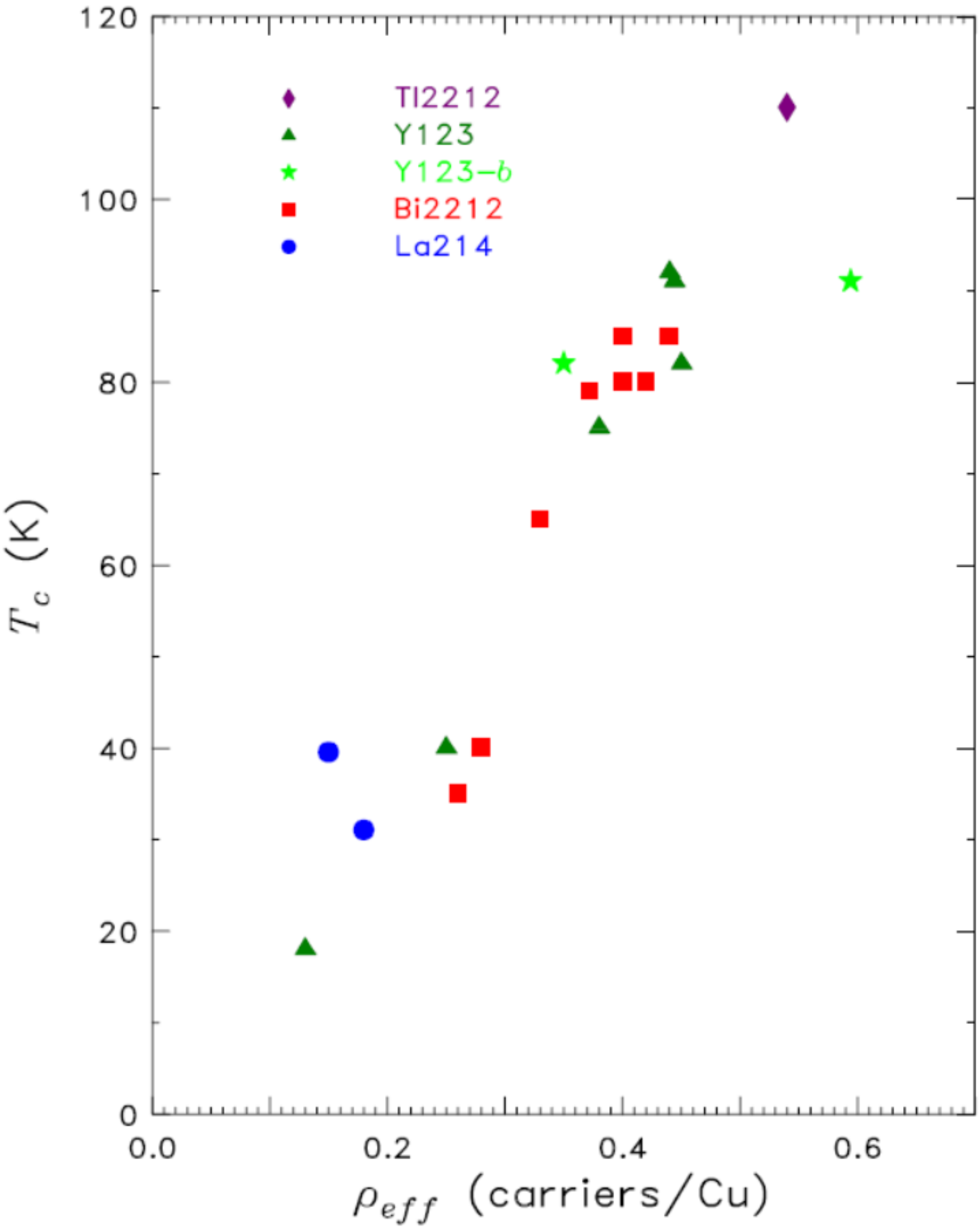
And

$$\rho_s(\omega) = \frac{2mV_{\text{Cu}}}{\pi e^2}\int_0^{\omega} [\sigma_{1n}(\omega') - \sigma_{1s}(\omega')]d\omega'$$

as $\omega \rightarrow \omega_{CT}$

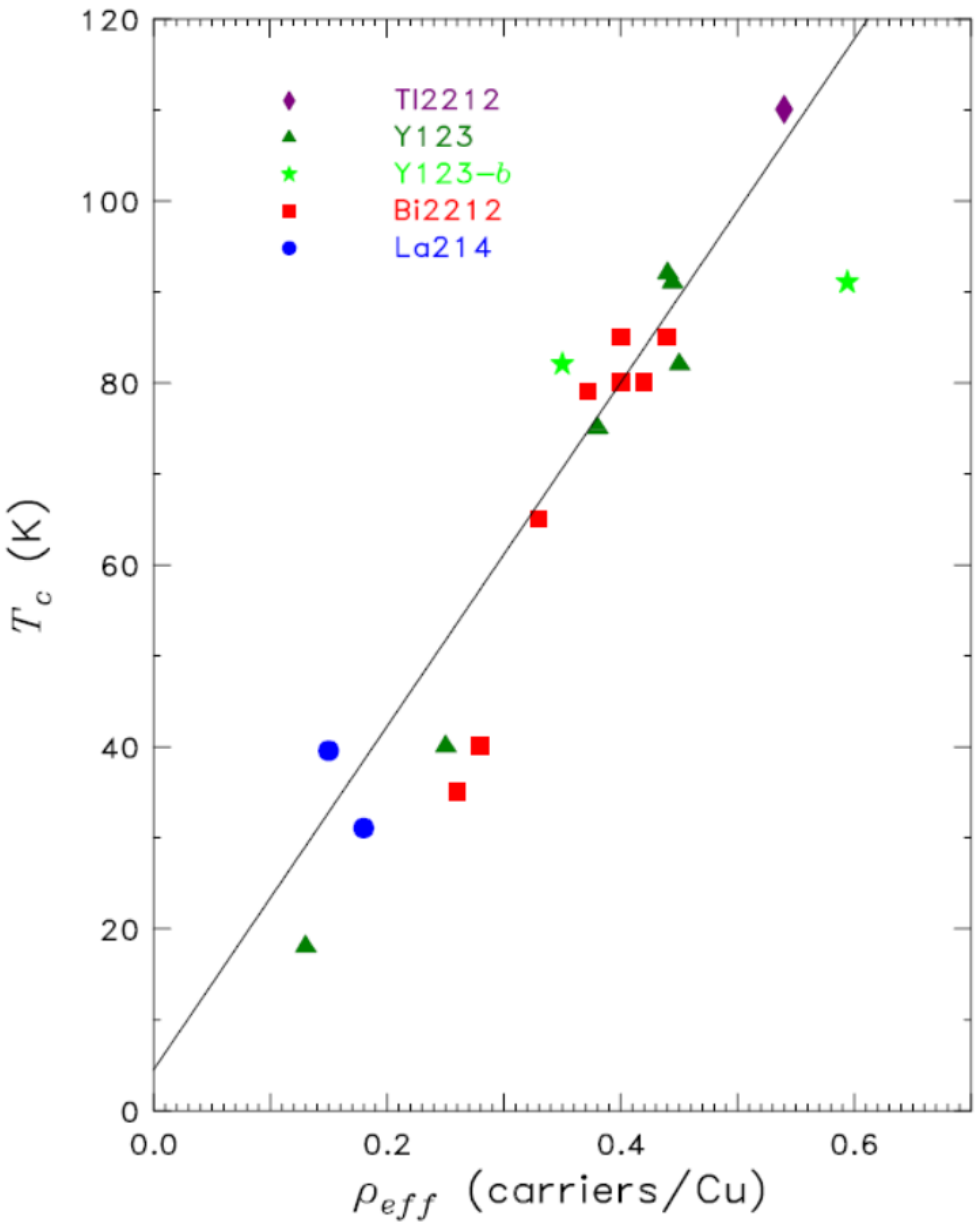


ρ_{eff}

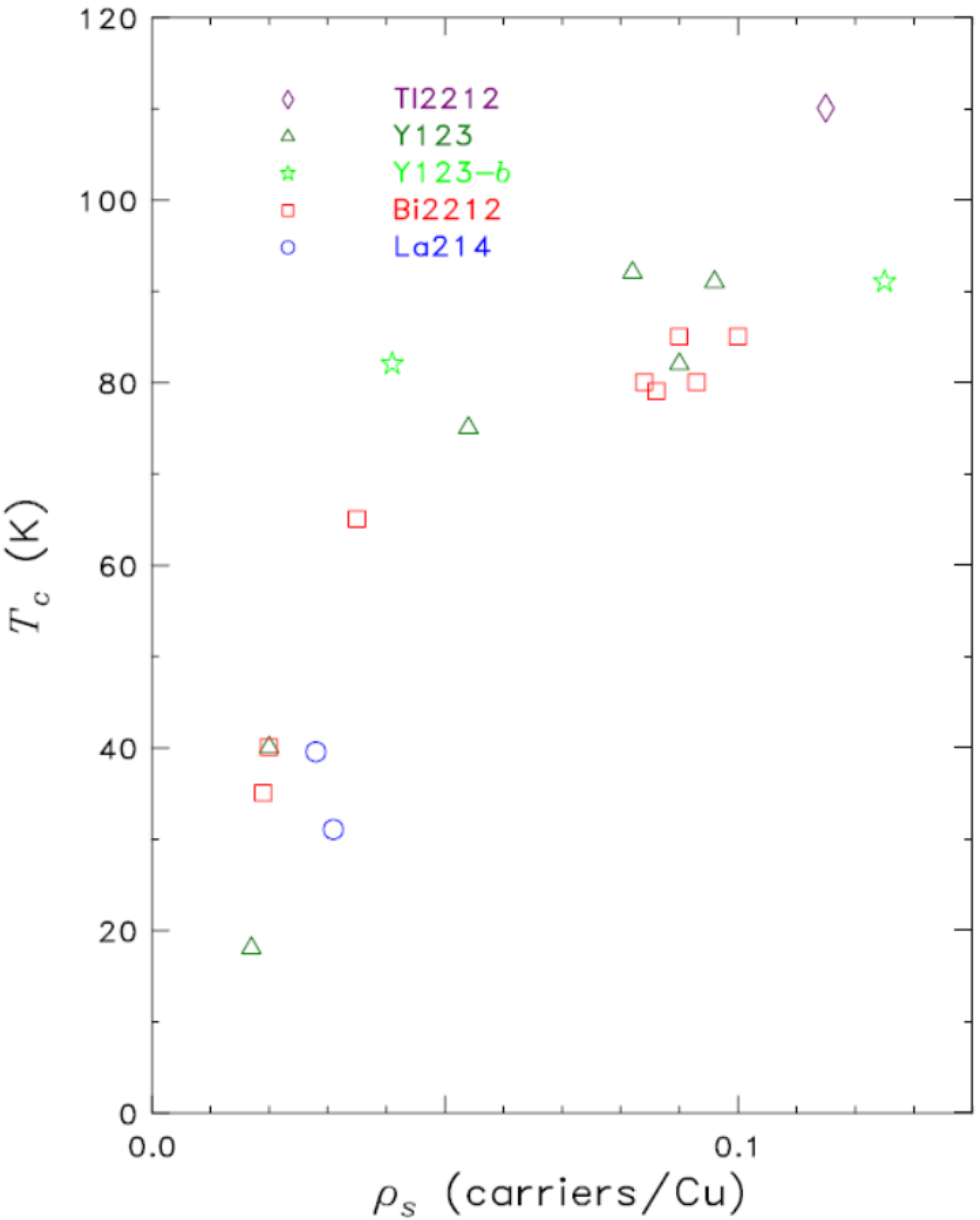


Tl2212
Y123
Y123-b
Bi2212
La214
120
100
80
60
40
20
0
0.0
0.2
0.4
0.6
T_c (K)
ρ_{eff} (carriers/Cu)

is linear in T_c

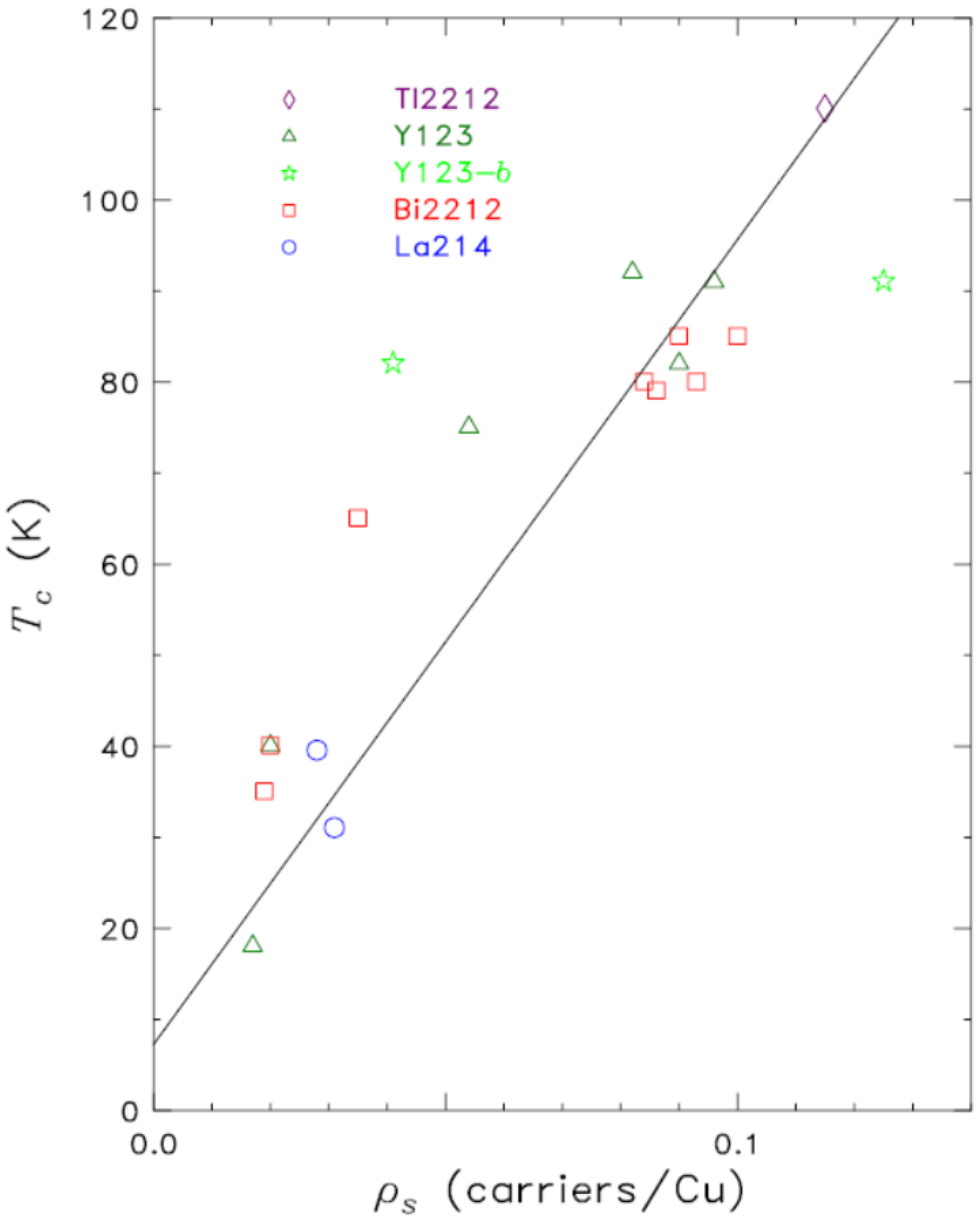


ρ_s

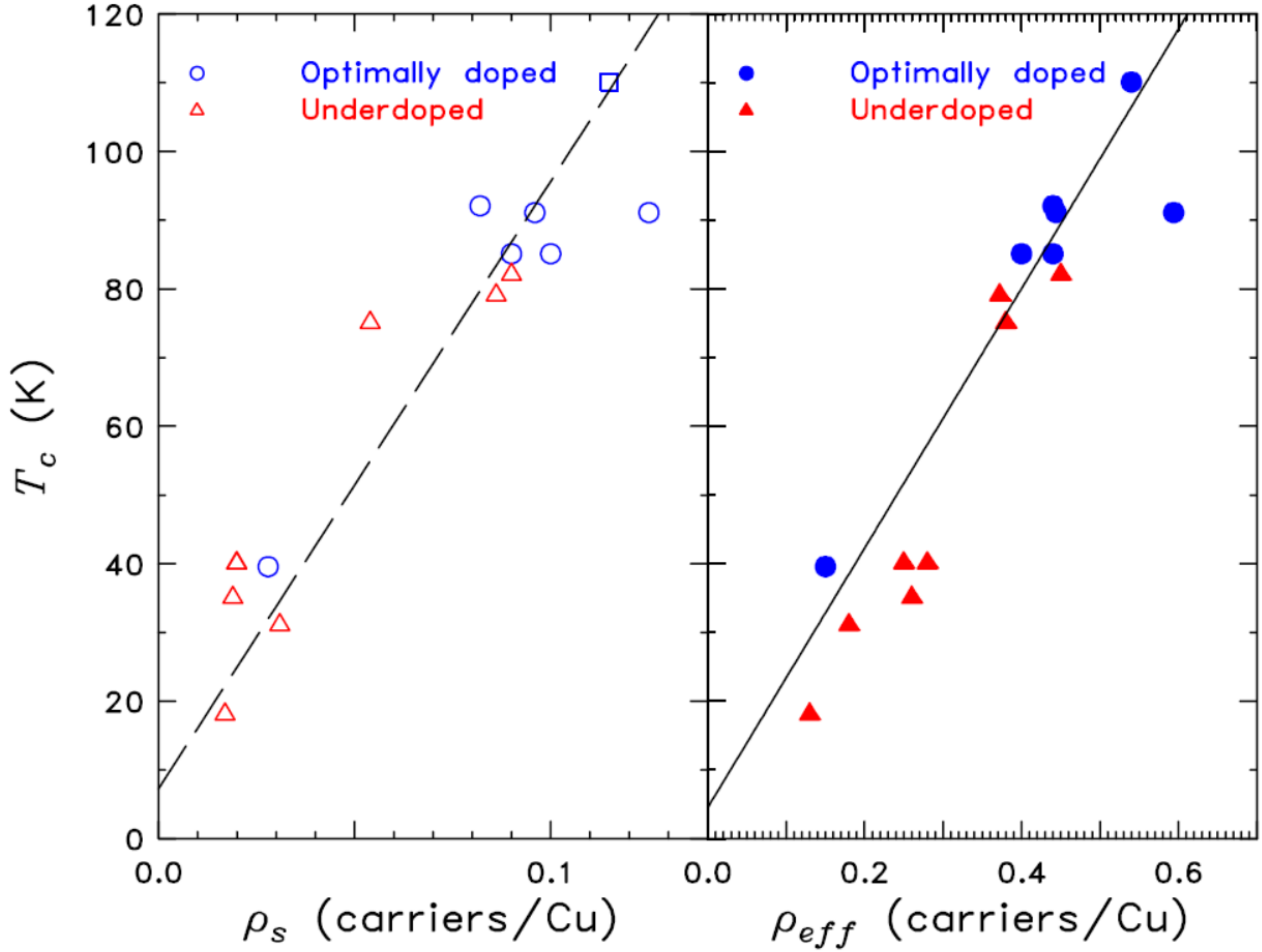


120
100
80
60
40
20
0
0.0
0.1
T_c (K)
ρ_s (carriers/Cu)
Tl2212
Y123
Y123-b
Bi2212
La214

is linear in T_c



Different ρ scales (1:5)



Superfluid density is small part of total

- ρ_s increases with T_c. (Uemura plot)
- ρ_{eff} increases with T_c. (doping)
- $\rho_s/\rho_{eff} \approx 0.2$
- In one component picture, the midinfrared absorption is a Holstein sideband, giving

$$\rho_s = \frac{\rho_{eff}}{1+\lambda}$$

- (λ = mass enhancement factor)

$\Rightarrow \lambda = 4$!

As a check, use the relation of σ_2 to n_s

- Start with Kramers-Kronig for sigma1 – epsilon1

$$\epsilon_1(\omega) = 1 + 8\mathcal{P}\int_0^\infty d\omega' \, \frac{A\delta(\omega')}{\omega'^2 - \omega^2}.$$

- Do the integral

$$\epsilon_1(\omega) = 1 - \frac{4A}{\omega^2},$$

- Convert to $\sigma_2 = \omega(1\text{-}\varepsilon_1)/4\pi$

$$\sigma_2(\omega) = \frac{A}{\pi\omega}$$

- As before

$$A = \omega_{ps}^2/4 = \pi n_s e^2/m$$

Compare two quantities:

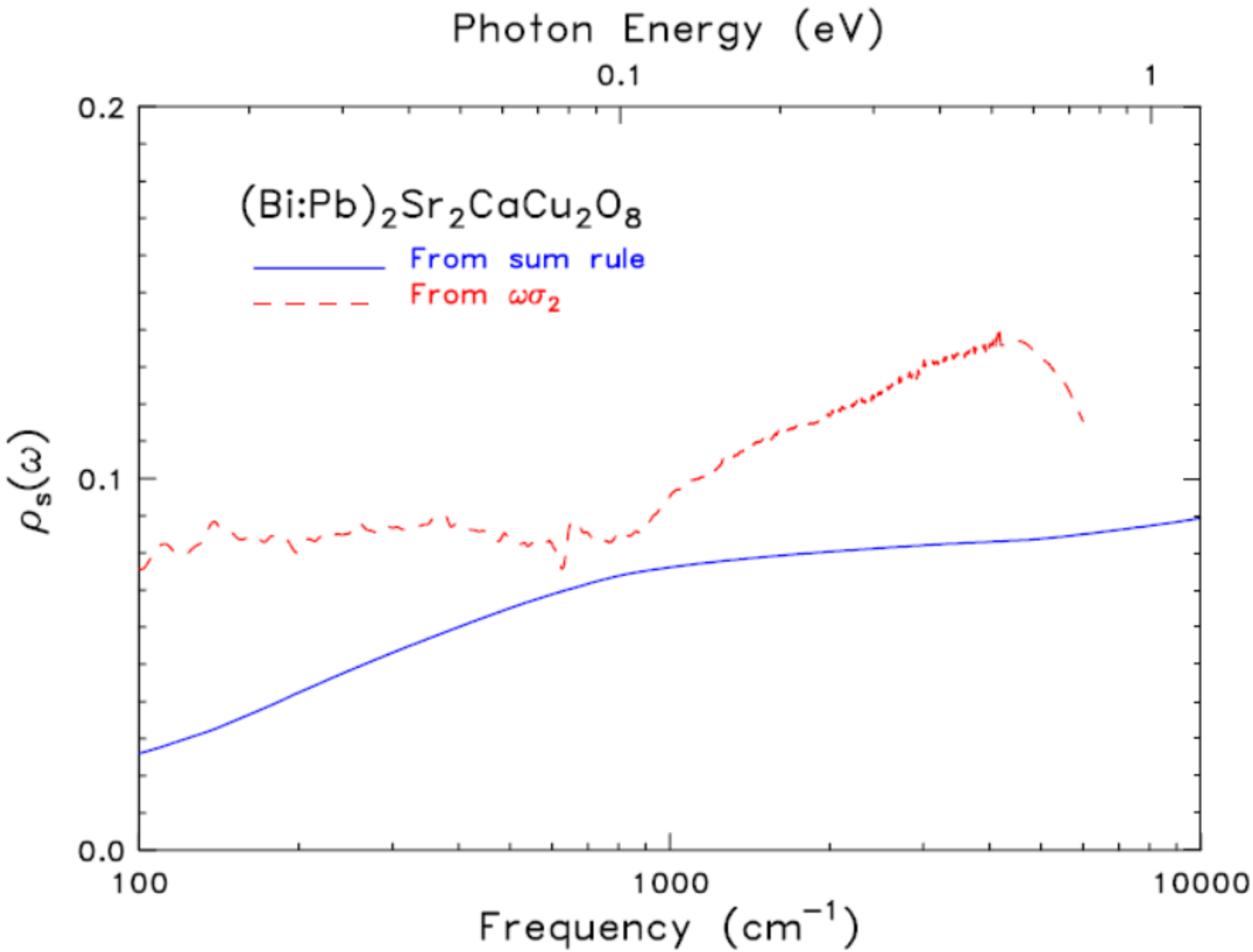
$$\rho_s(\omega) = \frac{2mV_{\mathrm{Cu}}}{\pi e^2}\int_0^{\omega}[\sigma_{1n}(\omega') - \sigma_{1s}(\omega')]d\omega' \quad \text{(Sum Rule)}$$

- which should saturate at high frequencies, and

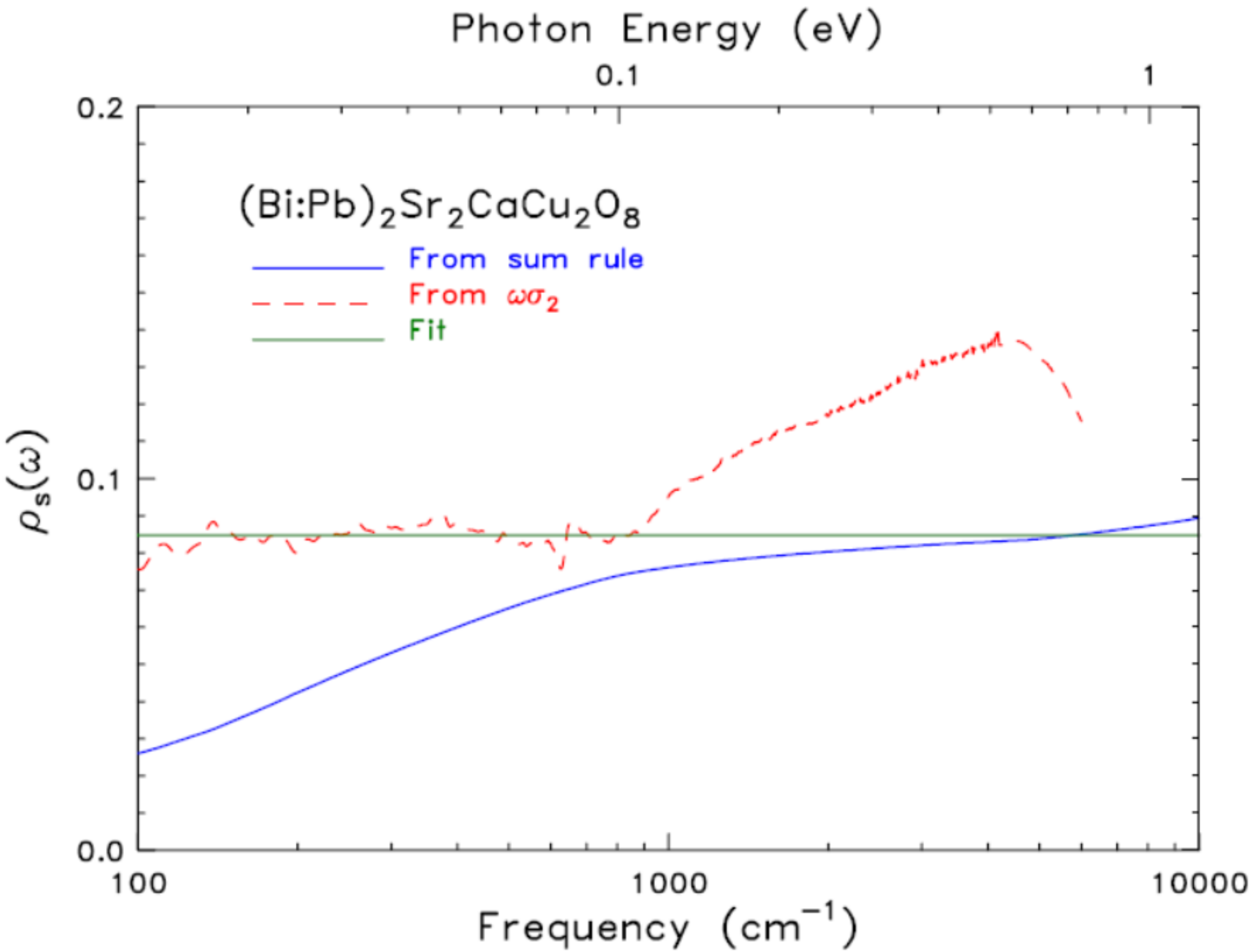
$$\rho_s(\omega) = \frac{mV_{\mathrm{Cu}}}{e^2}\omega\sigma_{2s}(\omega) \quad \text{(London)}$$

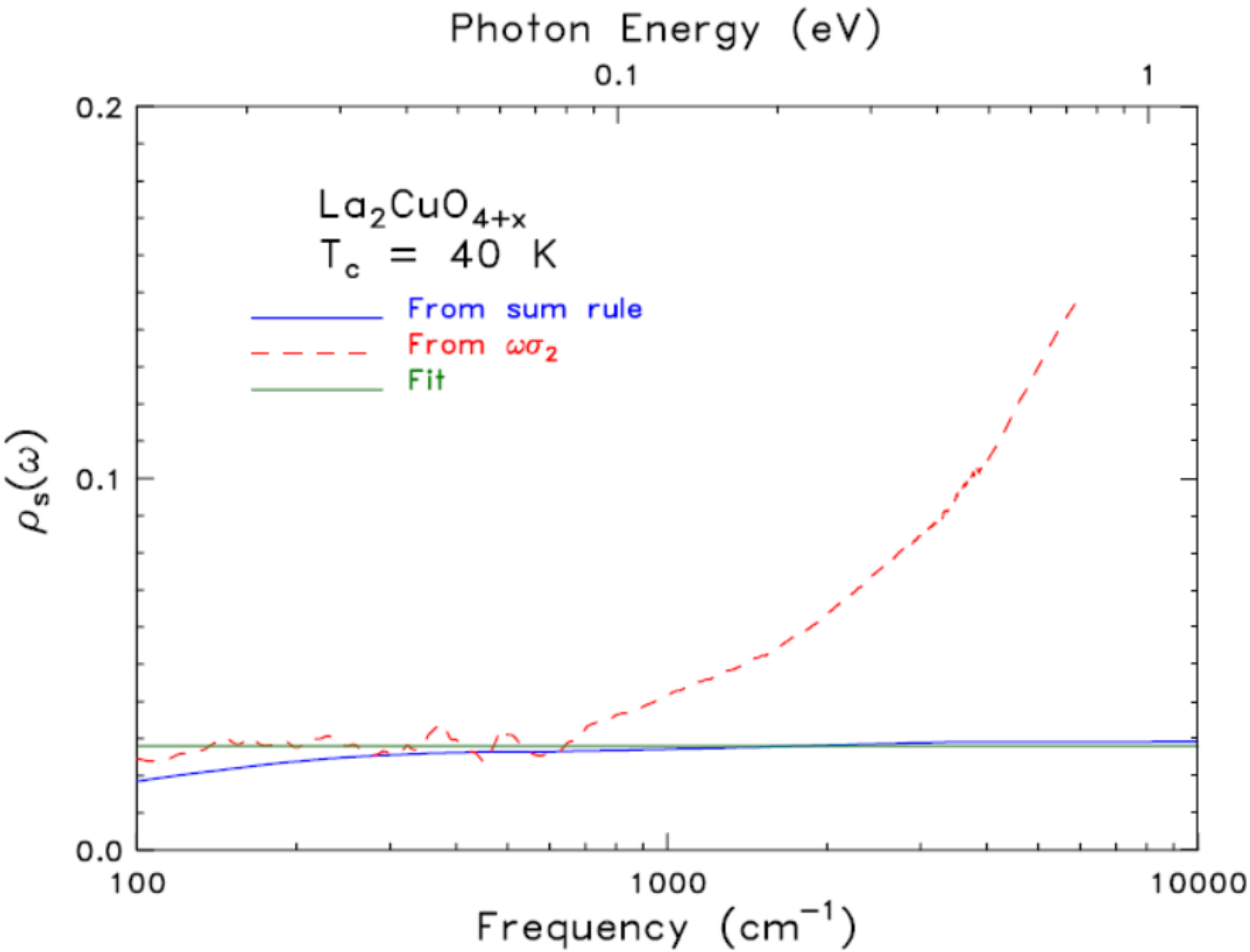
- which should be constant at low frequencies.

- And, which should represent the "true" weight of the delta function.



Photon Energy (eV)
0.1
1
0.2
0.1
0.0
$(Bi:Pb)_2Sr_2CaCu_2O_8$
From sum rule
From $\omega\sigma_2$
$\rho_s(\omega)$
100
1000
10000
Frequency (cm^{-1})


Photon Energy (eV)
0.1
1
0.2
0.1
0.0
$(Bi:Pb)_2Sr_2CaCu_2O_8$
From sum rule
From $\omega\sigma_2$
Fit
$\rho_s(\omega)$
100
1000
10000
Frequency (cm^{-1})



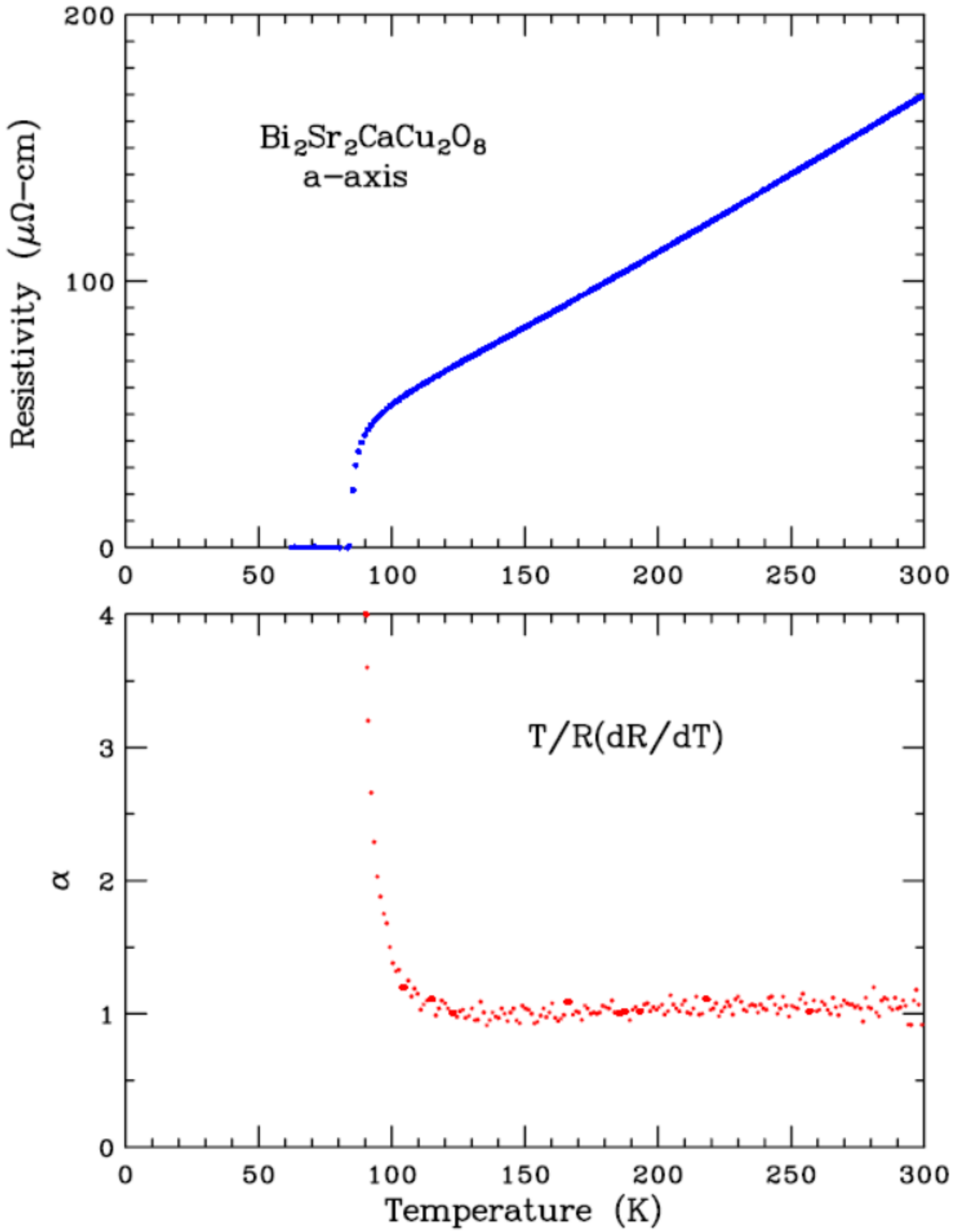
Photon Energy (eV)
0.1
1
0.2
0.1
0.0
La_2CuO_{4+x}
T_c = 40 K
From sum rule
From $\omega\sigma_2$
Fit
$\rho_s(\omega)$
100
1000
10000
Frequency (cm^{-1})

Superfluid weight comes from low energies

Material	From $\omega\sigma_2$	From sum rule	ratio
$(Bi{:}Pb)_2Sr_2CaCu_2O_8$	0.085	0.080	0.95
$La_2CuO_{4+\delta}$	0.028	0.028	1.01
$Bi_2Sr_2CaCu_2O_8$ (a-axis)	0.101	0.100	0.99
$Bi_2Sr_2CaCu_2O_8$ (b-axis)	0.088	0.083	0.95
I-doped $Bi_2Sr_2CaCu_2O_8$	0.098	0.095	0.97
$Bi_2Sr_2CaCu_2O_8$ (transmittance)	0.120	0.122	1.02
$YBa_2Cu_3O_{7-\delta}$ a-axis	0.085	0.083	0.98
$YBa_2Cu_3O_{7-\delta}$ film	0.062	0.061	0.99
$Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$	0.057	0.052	0.92
$Tl_2Ba_2CaCu_2O_8$	0.112	0.109	0.97

Charge transport

- Cuprates: "metallic" dc resistance
- $\rho = A + BT^{\alpha}$
  $\alpha \approx 1$; $A \sim 0$.
- $\alpha = (T/\rho) \cdot (d\rho/dT)$



Charge transport

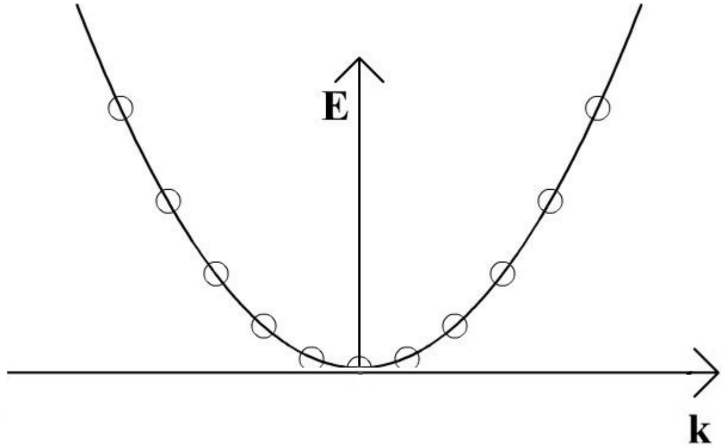
- ρ ~ 150–300 $\mu\Omega$-cm at 300 K
- Natural to think of a Drude model
- Inadequate once midinfrared absorption kicks in
- Restricts your view to frequencies below about 8 THz (250 cm^{-1}; 30 meV):

- Then, *ab*-plane conductivity is described well by a Drude model.
- The idea of simple free carriers was discarded out long ago.
- Should it be reconsidered in light of experiments showing Fermi Surface reconstruction?

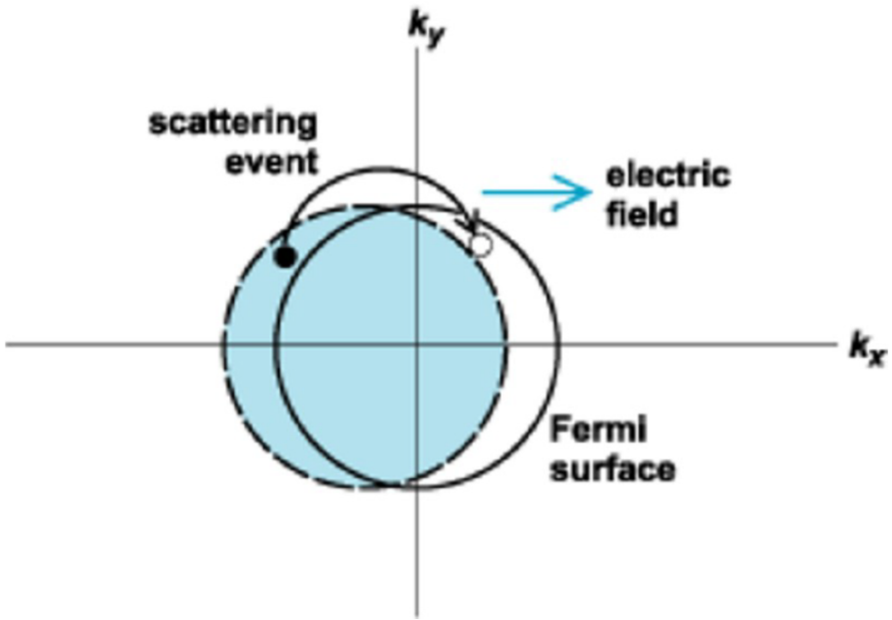
Fermi surface

- Energy dispersion

$$\mathcal{E} = \frac{\hbar^2 k^2}{2m}$$

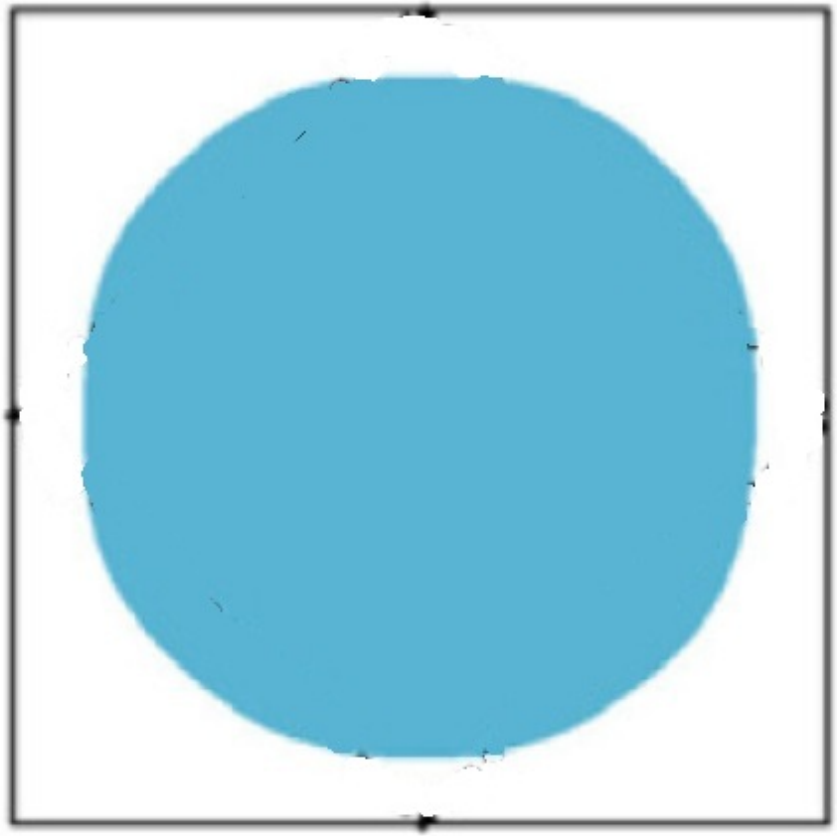


- Max → Fermi energy
- Fermi surface is a circle in 2D
- Displaced when current flows



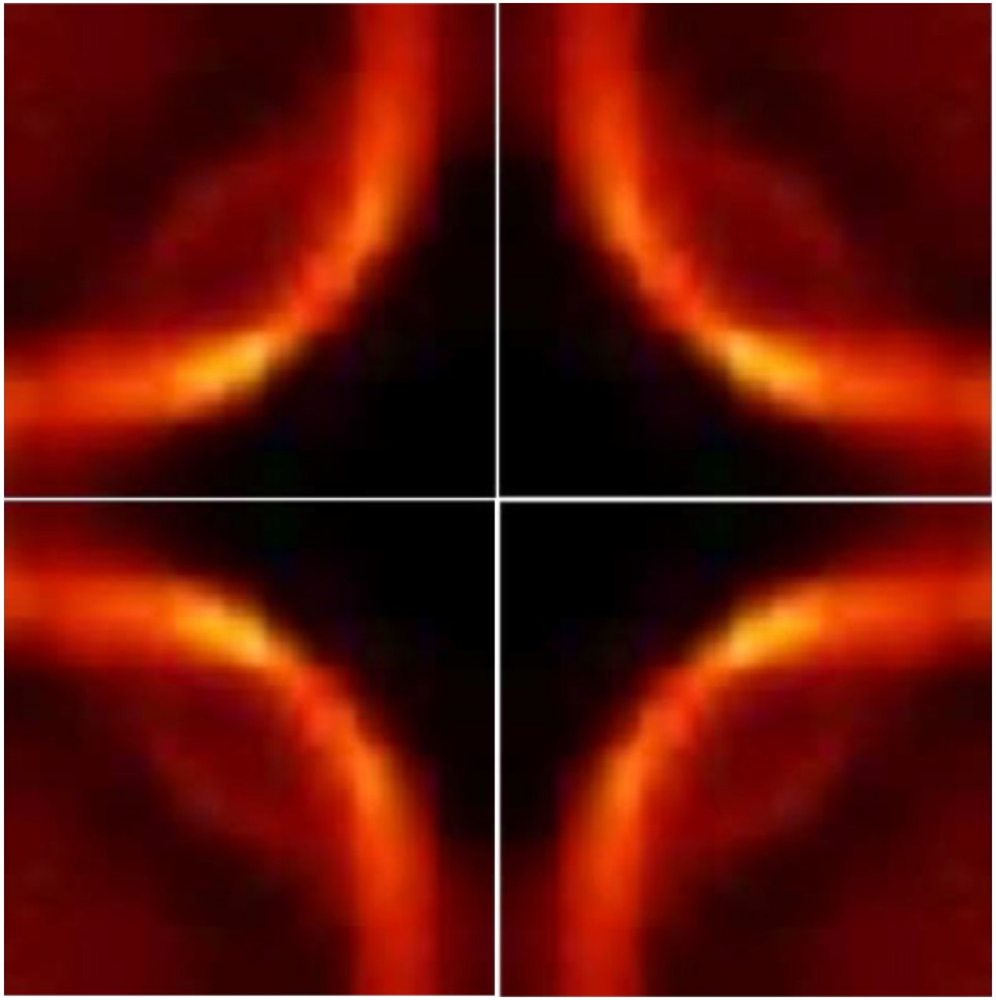
Fermi surface reconstruction

- This is what I thought the Fermi surface looked like



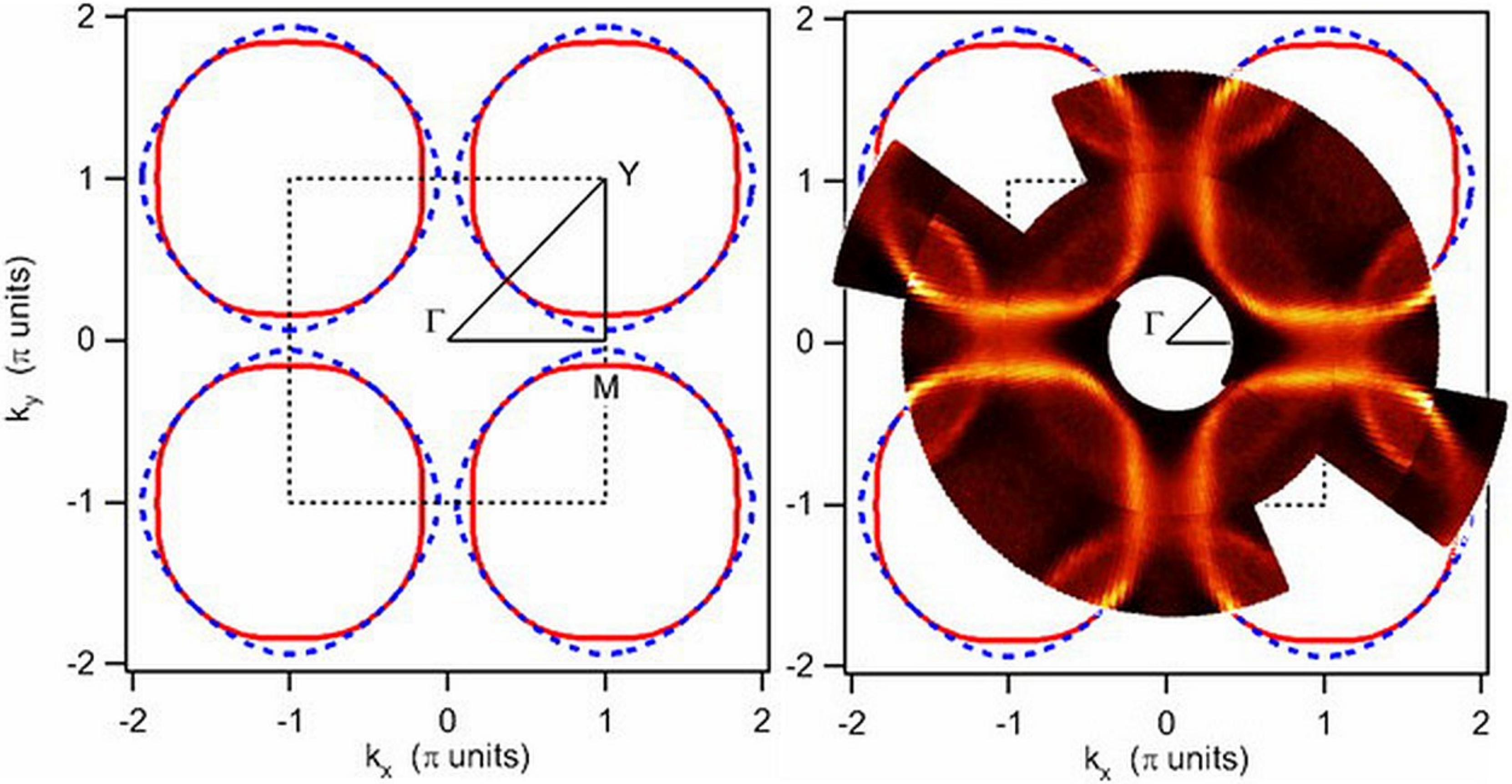
Fermi surface reconstruction

- Or maybe this (ARPES results for BiSrCaCuO)



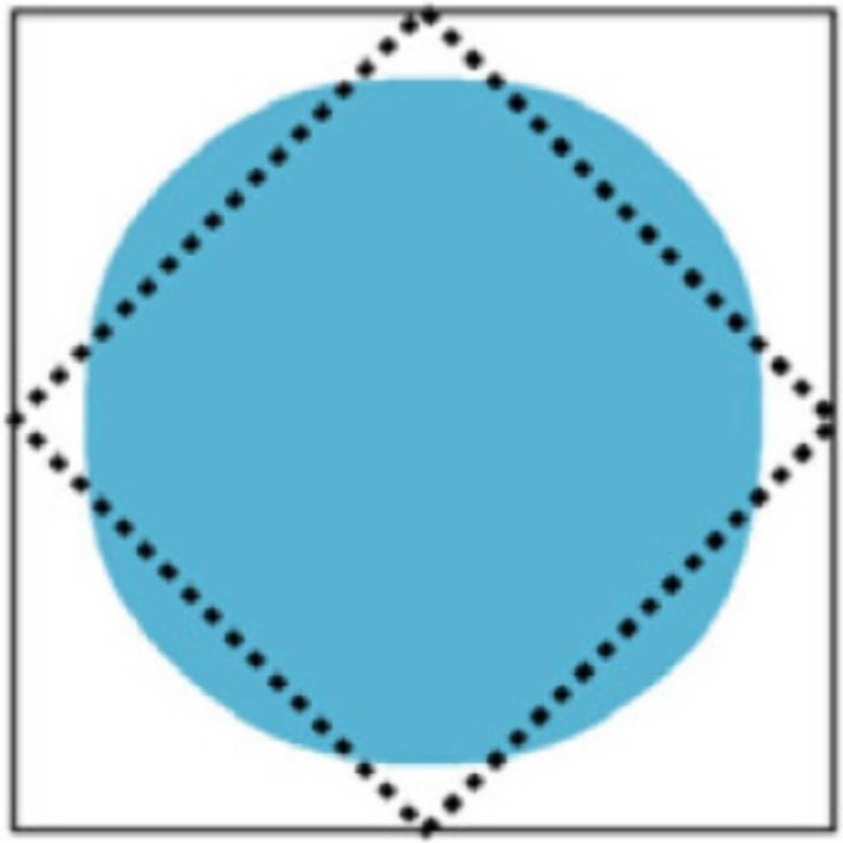
Fermi surface reconstruction

- Or maybe this (ARPES results for BiSrCaCuO)



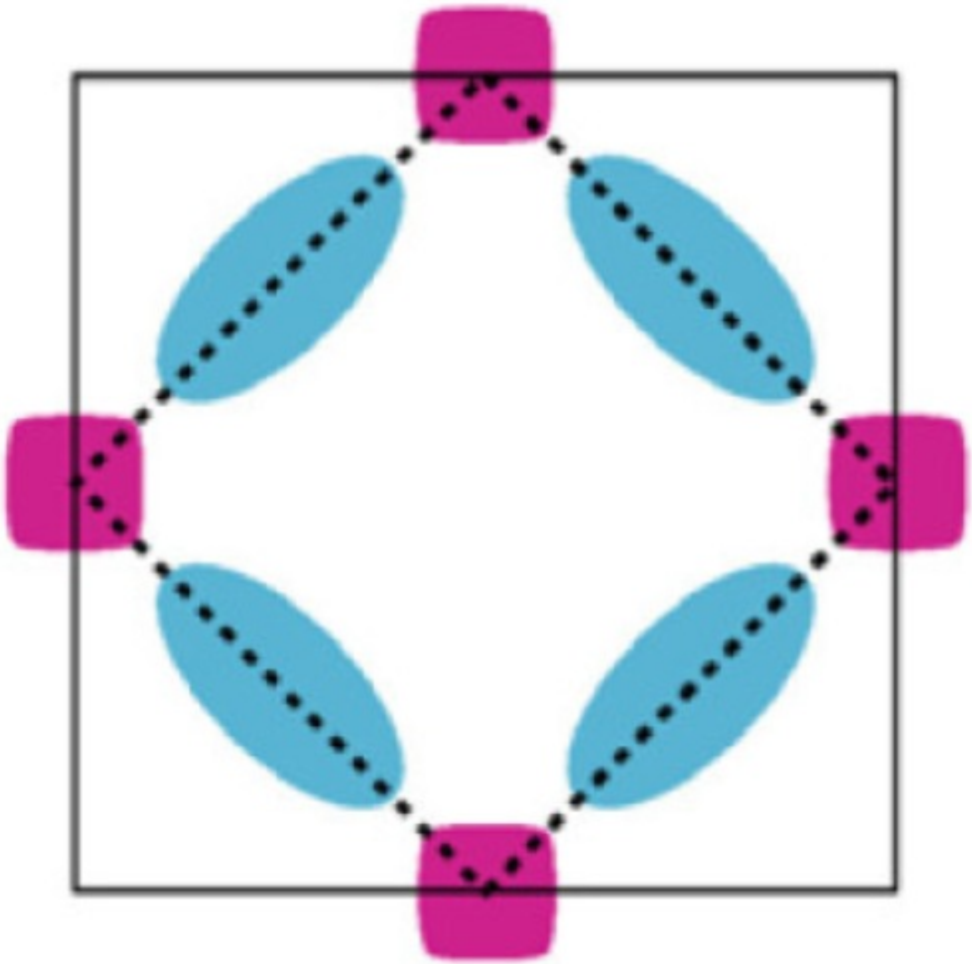
Fermi surface reconstruction

- Add new zone boundary



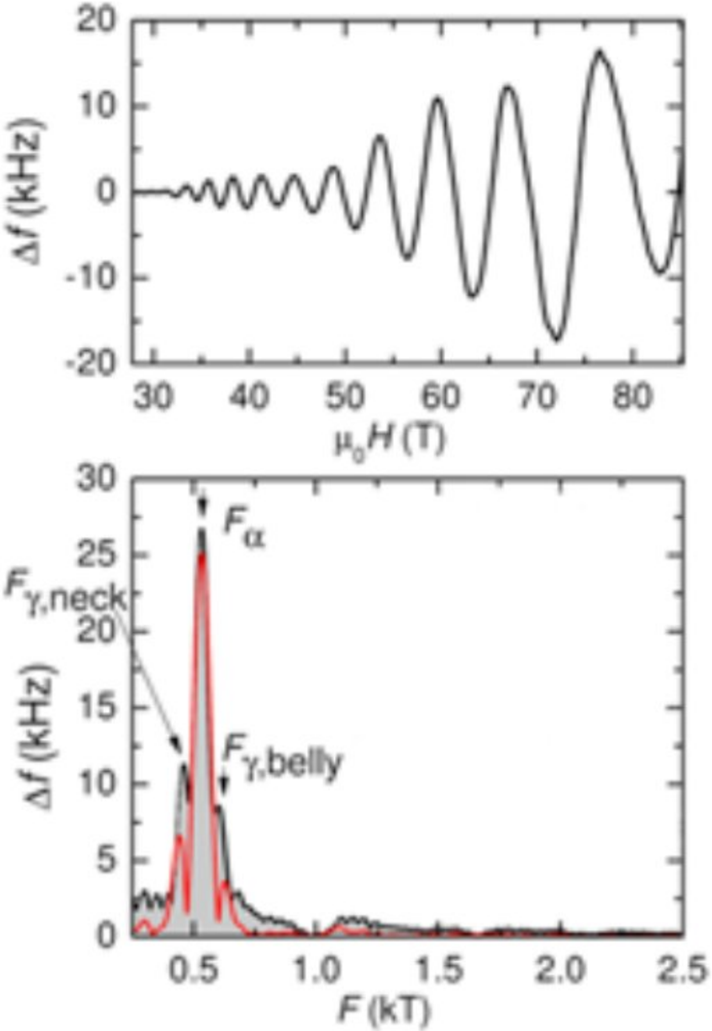
Fermi surface reconstruction

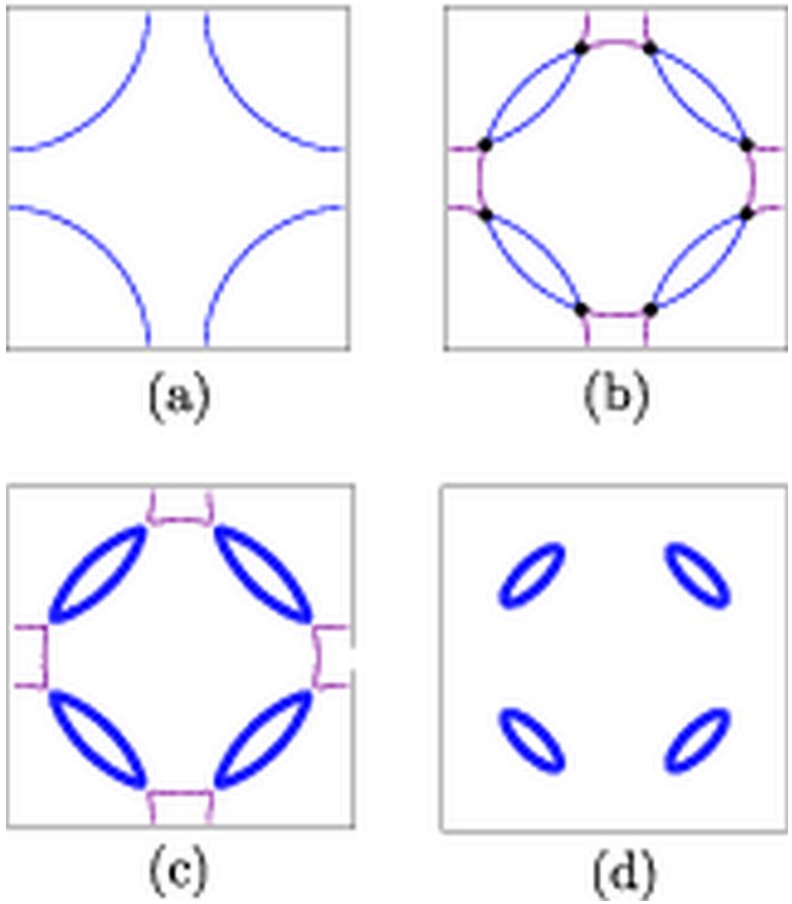
- Much smaller area; hole and electron pockets



Fermi surface reconstruction

- Evidence: Shubnikov–de Haas oscillations





Drude conductivity

$$\sigma(\omega) = \frac{{\omega_p}^2 \tau}{4\pi(1 - i\omega\tau)}$$

- τ - mean free time between collisions.
- $\omega_p = \sqrt{4\pi n e^2/m}$ - plasma frequency

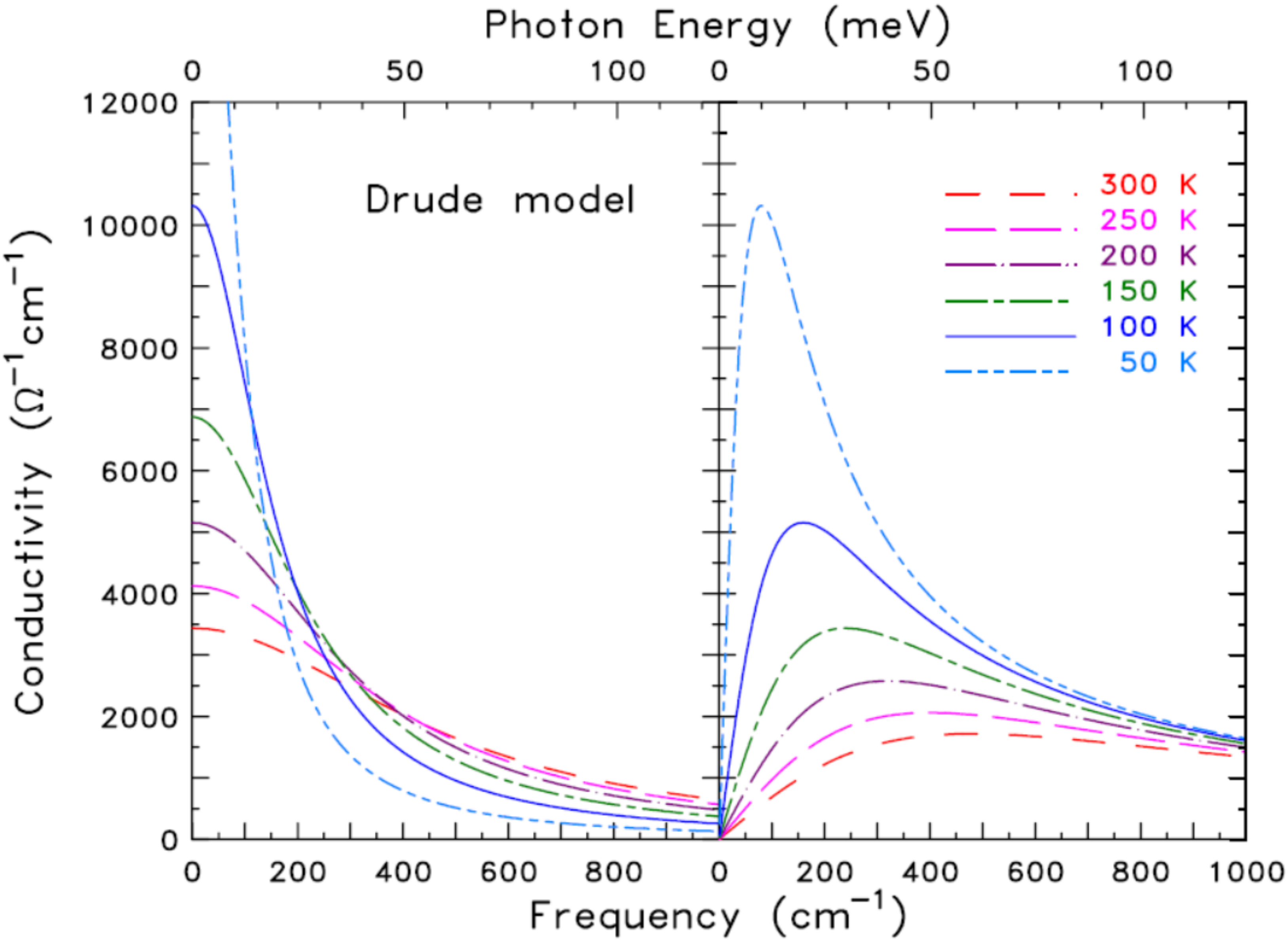
  or oscillator strength or spectral weight
- Real part, $\sigma_{1D}(\omega)$, satisfies sum rule,

$$\int_0^\infty d\omega \sigma_1(\omega) = \frac{\pi}{2}\frac{ne^2}{m} = \frac{{\omega_p}^2}{8}$$

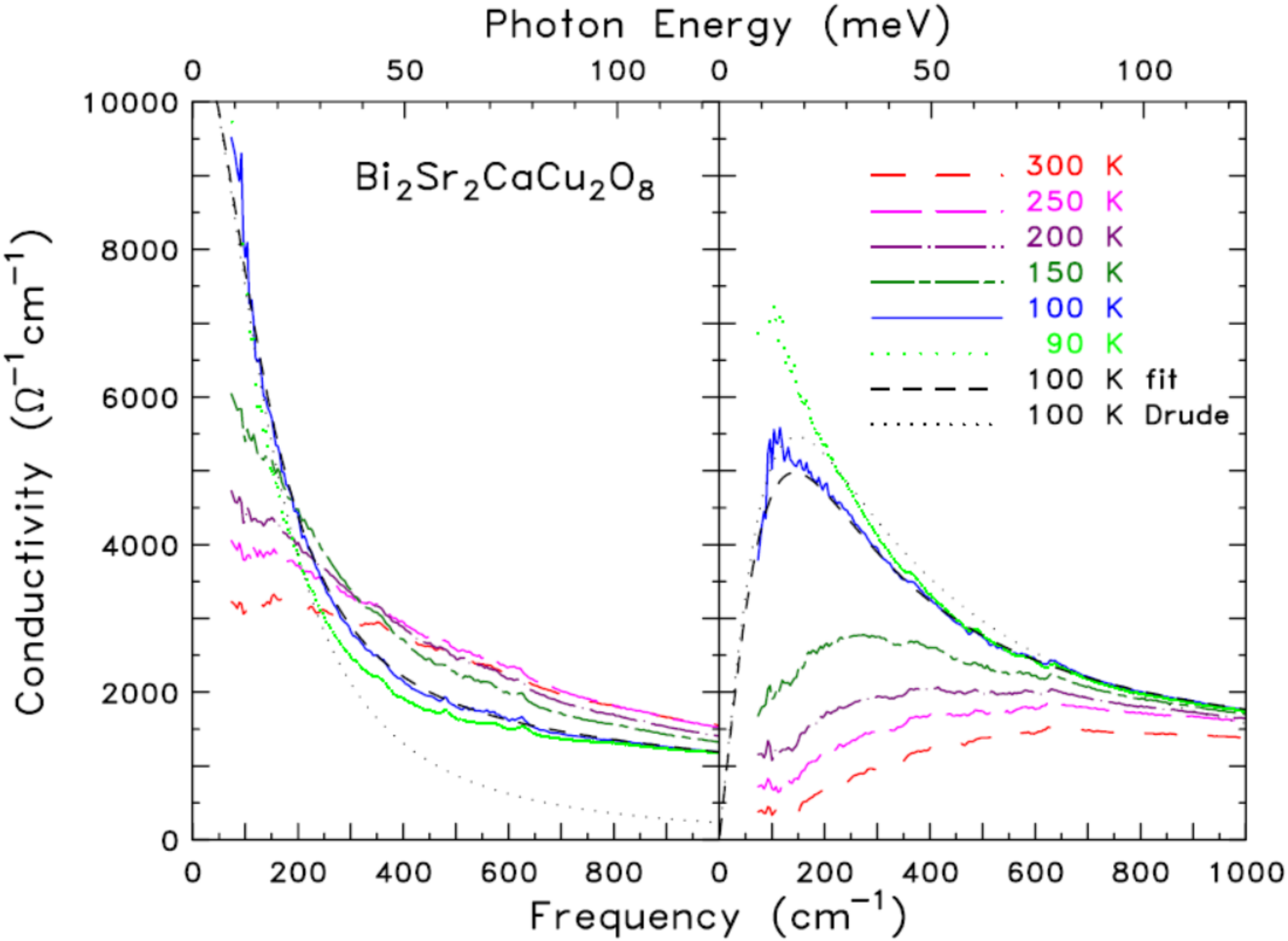
- Expect n constant, τ varies with condition

  (purity, temperature ….)

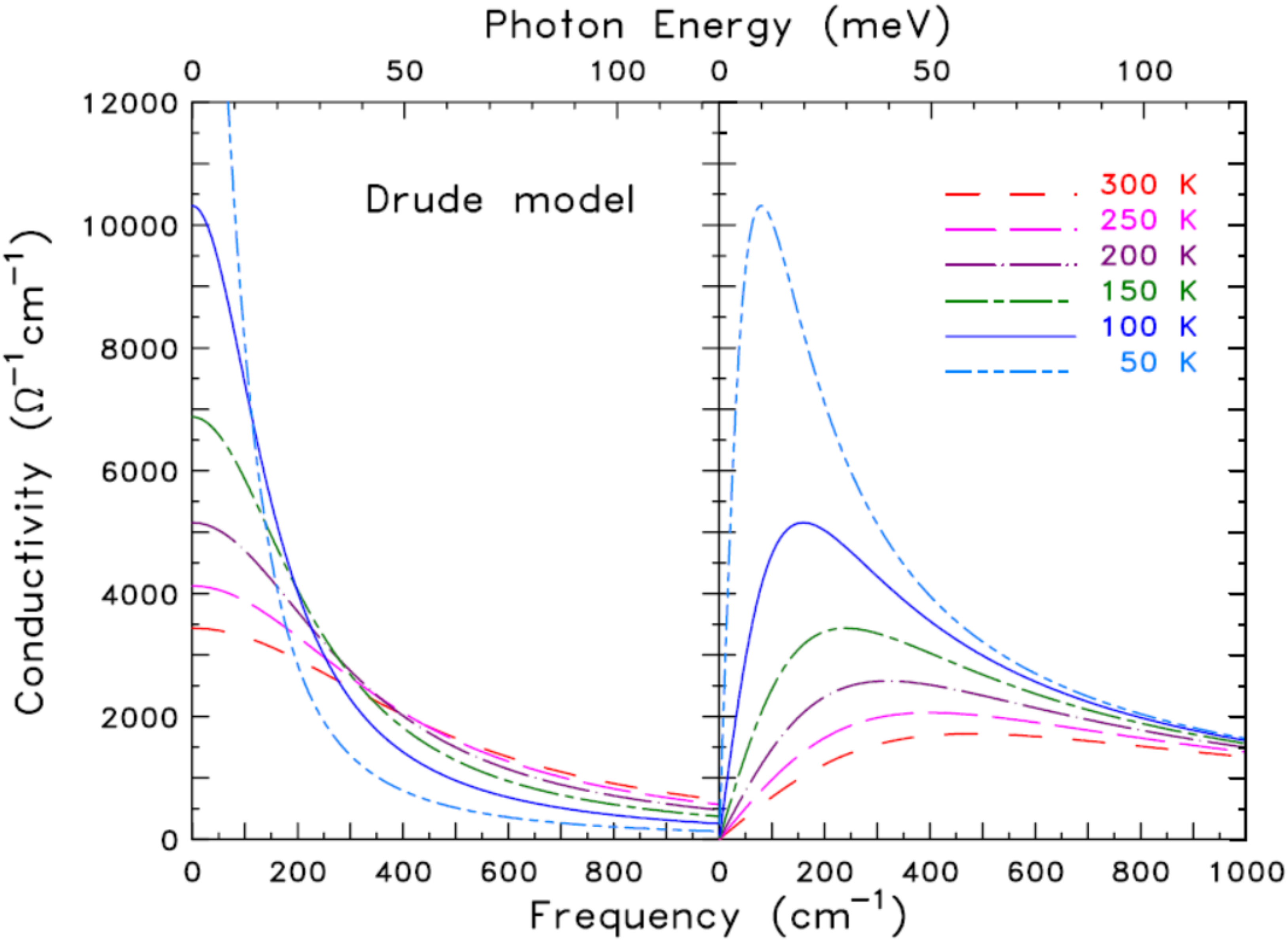
$\sigma_1(\omega)$ and $\sigma_2(\omega)$ from the Drude model



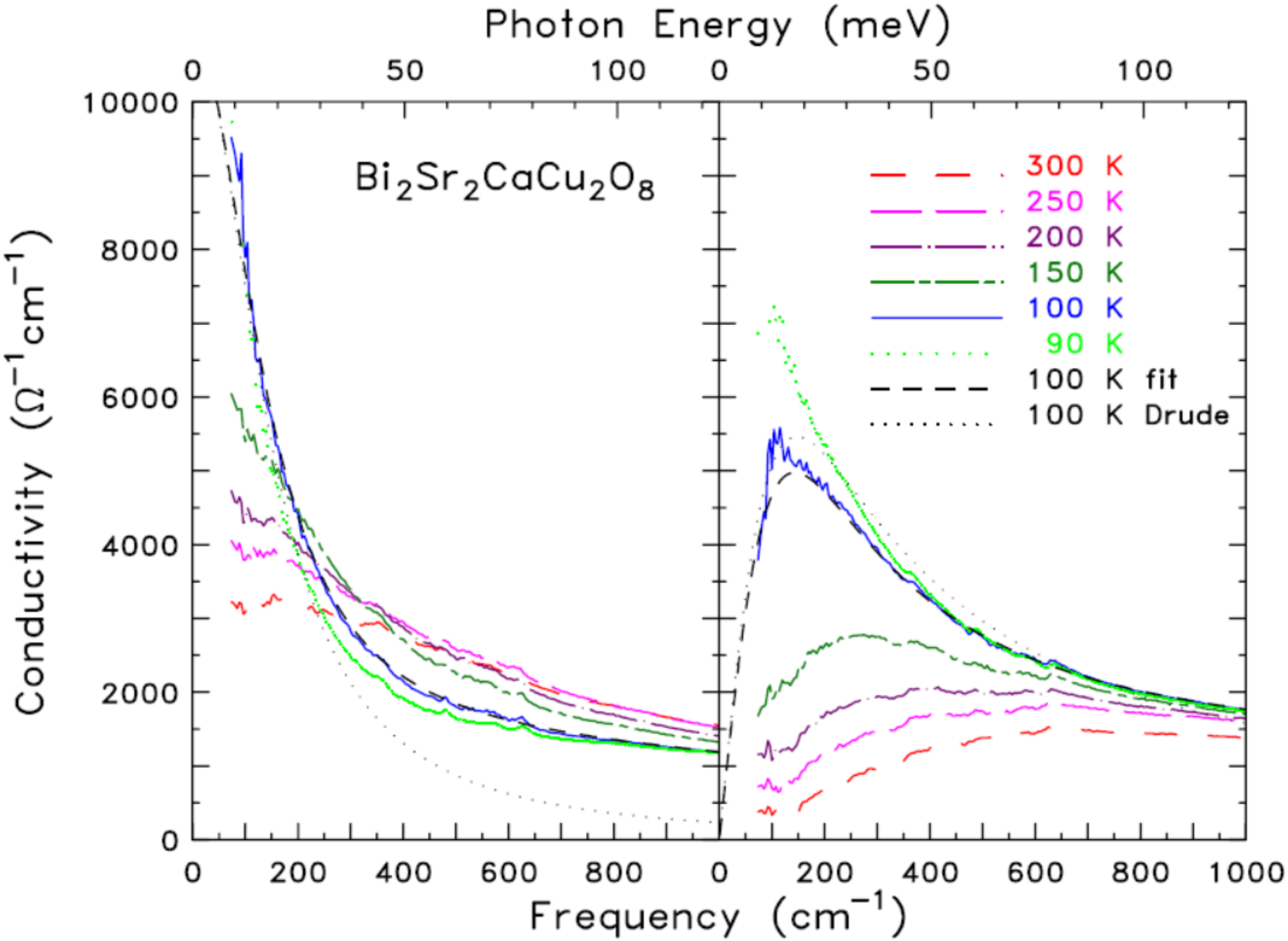
BSCO 2212 conductivity



Looks like Drude model



BSCO 2212 conductivity



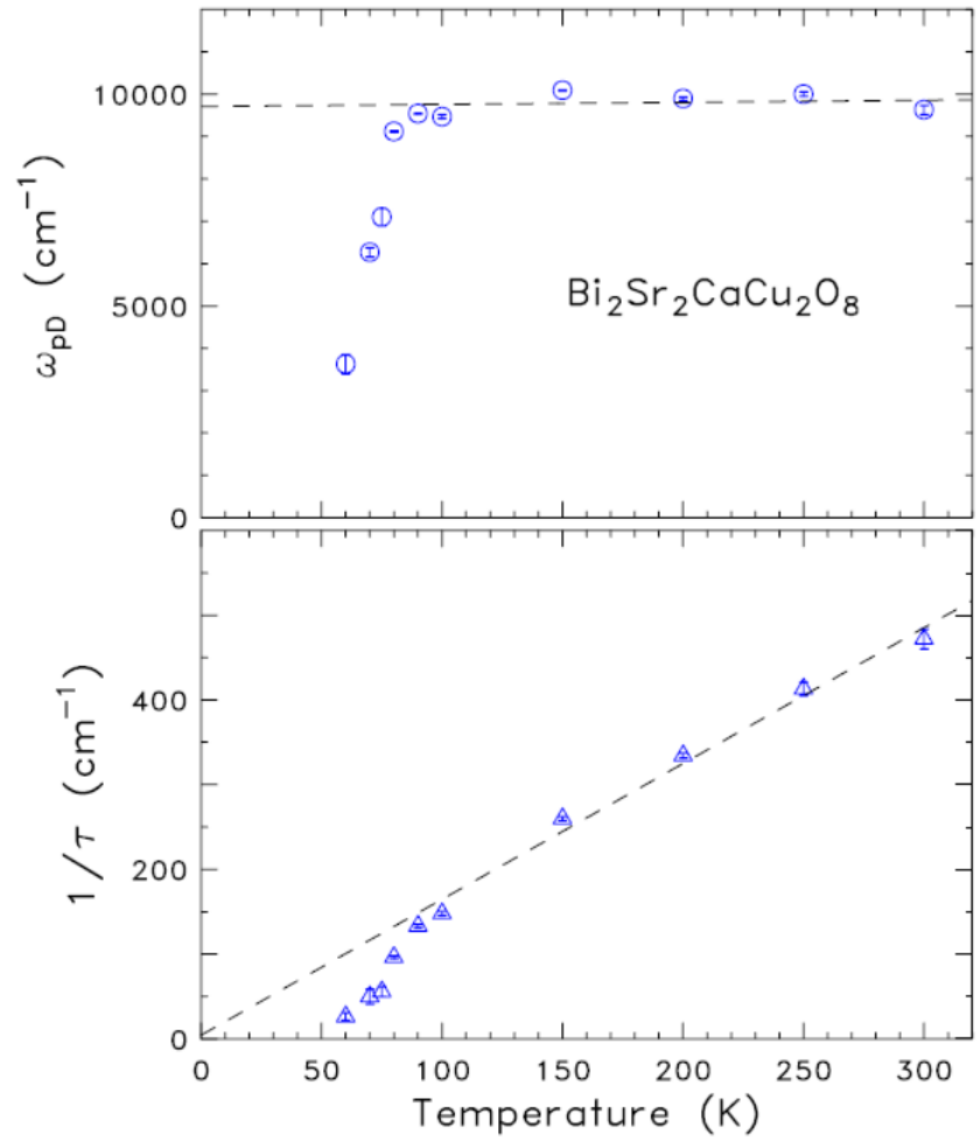
Temperature dependence of $1/\tau$ and ω_p

- $1/\tau$: linear in T

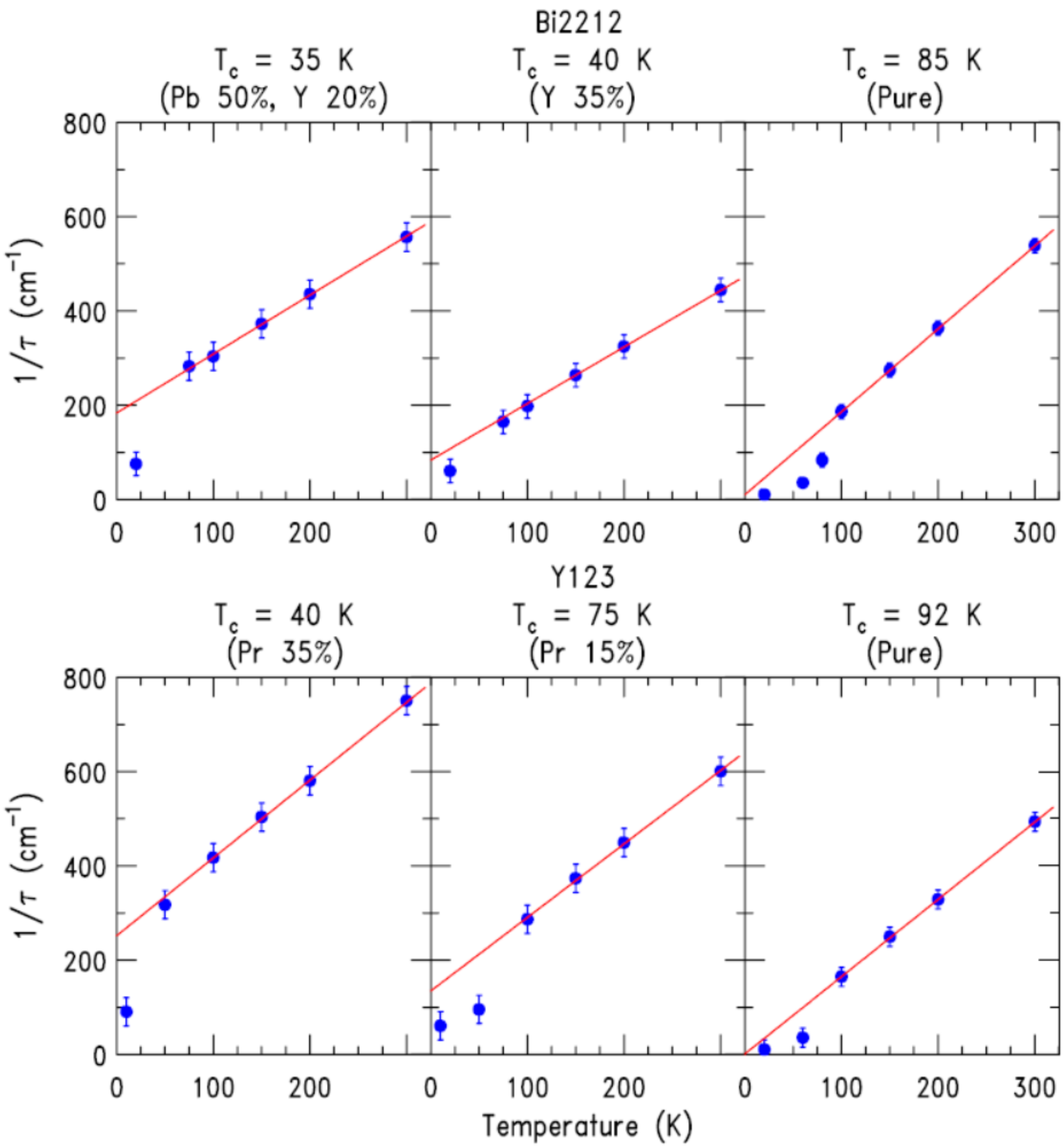
- Generally

$$\frac{\hbar}{\tau} = 2\pi\lambda k_B T + \frac{\hbar}{\tau_0}$$

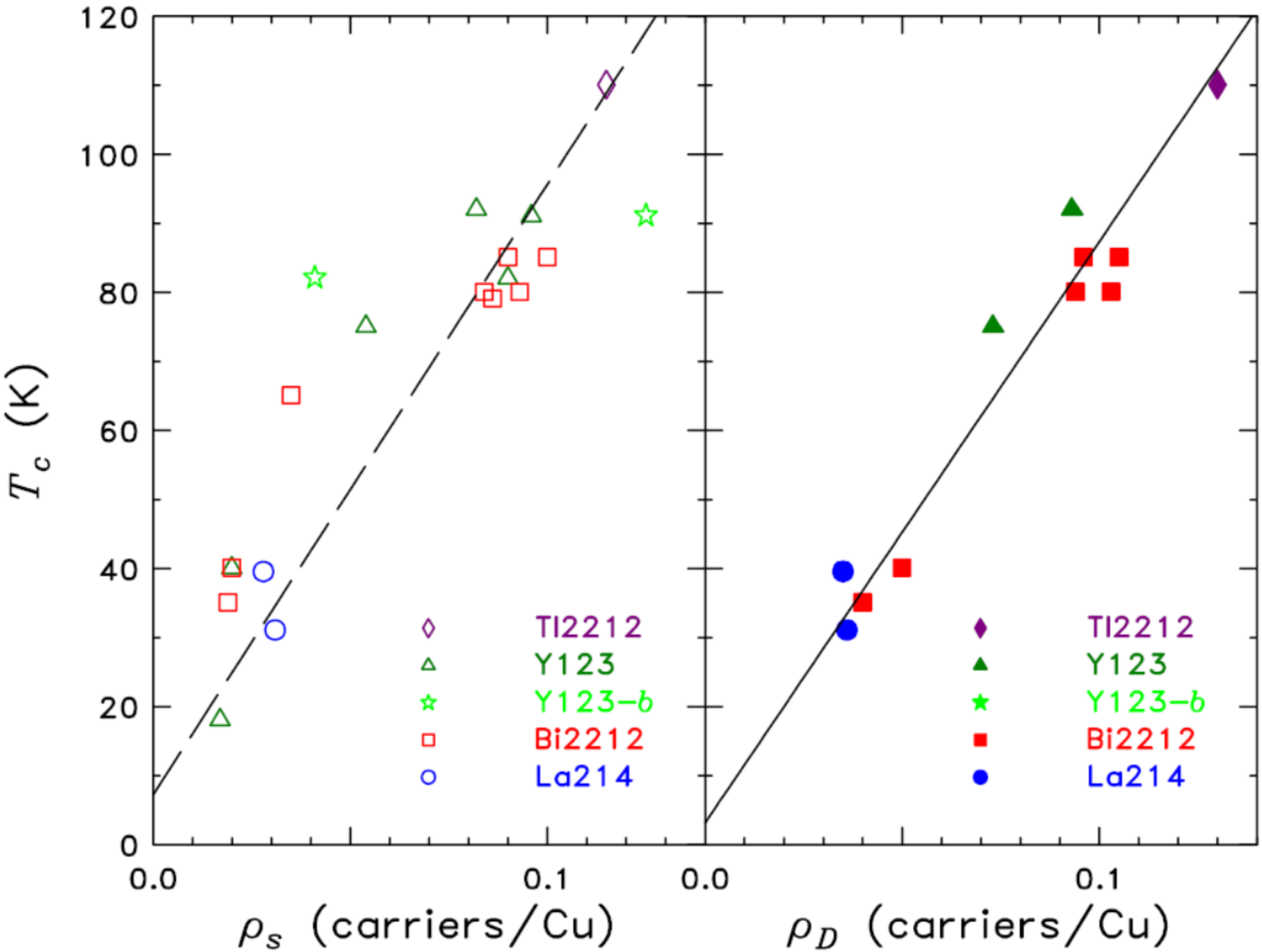
- $\lambda = 0.37$



$1/\tau$ is linear in T, with $\lambda = 0.35 \pm 0.04$



Most of the Drude weight joins the superfluid



Conclusions

- Only about 20% of doping-induced spectral weight condenses into the superfluid

Material	$\vec{E}\|$	T_c	ρ_{eff}	ρ_s	$\frac{\rho_s}{\rho_{eff}}$	ρ_{Drude}	$\frac{\rho_s}{\rho_{Drude}}$
$La_2CuO_{4.12}$	ab	40	0.15	0.028	0.19	0.035	0.80
$Bi_2Sr_2CaCu_2O_8$	a	85	0.40	0.10	0.25	0.105	0.95
$Bi_2Sr_2CaCu_2O_8$	b	85	0.44	0.090	0.20	0.096	0.94
$YBa_2Cu_3O_7$	a	91	0.44	0.096	0.22	0.104	0.92
$Tl_2Ba_2CaCu_2O_8$	ab	110	0.54	0.115	0.21	0.13	0.88

- Almost all the Drude contribution (assuming the description is correct) condenses

The end

Kramers-Kronig analysis of reflectance: High-frequency extensions matter

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Use of x-ray scattering functions in Kramers-Kronig analysis of reflectance

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Kramers-Kronig analysis is commonly used to estimate the optical properties of new materials. The analysis typically uses data from far infrared through near ultraviolet (say 40–40 000 cm^{-1} or 5 meV–5 eV) and uses extrapolations outside the measured range. Most high-frequency extrapolations use a power law, $1/\omega^n$, transitioning to $1/\omega^4$ at a considerably higher frequency and continuing this free-carrier extension to infinity. The midrange power law is adjusted to match the slope of the data and to give pleasing curves, but the choice of power (usually between 0.5 and 3) is arbitrary. Instead of an arbitrary power law, it is better to use x-ray atomic scattering functions such as those presented by Henke and co-workers. These basically treat the solid as a linear combination of its atomic constituents and, knowing the chemical formula and the density, allow the computation of dielectric function, reflectivity, and other optical functions. The "Henke reflectivity" can be used over photon energies of 10 eV to 34 keV, after which a $1/\omega^4$ continuation is perfectly fine. The bridge between experimental data and the Henke reflectivity as well as two corrections made to the latter are discussed.

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