



# Materials Trends in Different Classes of Superconductors from Heavy Fermion Compounds to Iron Pnictides and Beyond

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## *Three classes of extraordinary superconducting materials*

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- **Three classes of extraordinary superconducting materials discovered within past 3 decades**
  - Heavy fermion f-electron compounds (~1980)  
 $T_c$ 's up to ~several K ( $T_c$  = superconducting critical temperature)
  - Layered copper oxide compounds (cuprates) (~1986)  
 $T_c$ 's up to 133 K (165 K – high pressure!)
  - Iron pnictide and chalcogenide compounds (~2006)  
 $T_c$ 's up to 56 K
- **Striking similarities**
  - “Unconventional” superconductivity (SC) (differs from “conventional” BCS SC)
  - SC often found to “emerge” from a magnetically-ordered phase upon variation of chemical composition (x) or pressure (P)
  - Same electrons involved in magnetism and superconductivity
  - Evidence for pairing of SC'ing electrons via spin fluctuations (cannot exclude possibility of other pairing scenarios, especially for the cuprates)
  - Strongly correlated electron materials
- **Noteworthy differences**
  - Values of  $T_c$ , crystal structures, pseudogap, underlying physics of the normal state, etc.

## *Outline*

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- Historical remarks about development of SC'ing materials
- Heavy fermion f-electron SC's
- Emergence of SC from magnetic order, unconventional SC, and electron pairing via spin fluctuations
- Copper oxide (cuprate) SC's
- Iron pnictide/chalcogenide SC's
- Evidence for strong electronic correlations
- New class of layered SC's based on LnOBiS<sub>2</sub> parent compounds
- Prospects for the future

Emphasis is on experiment, selected examples

## *Outline*

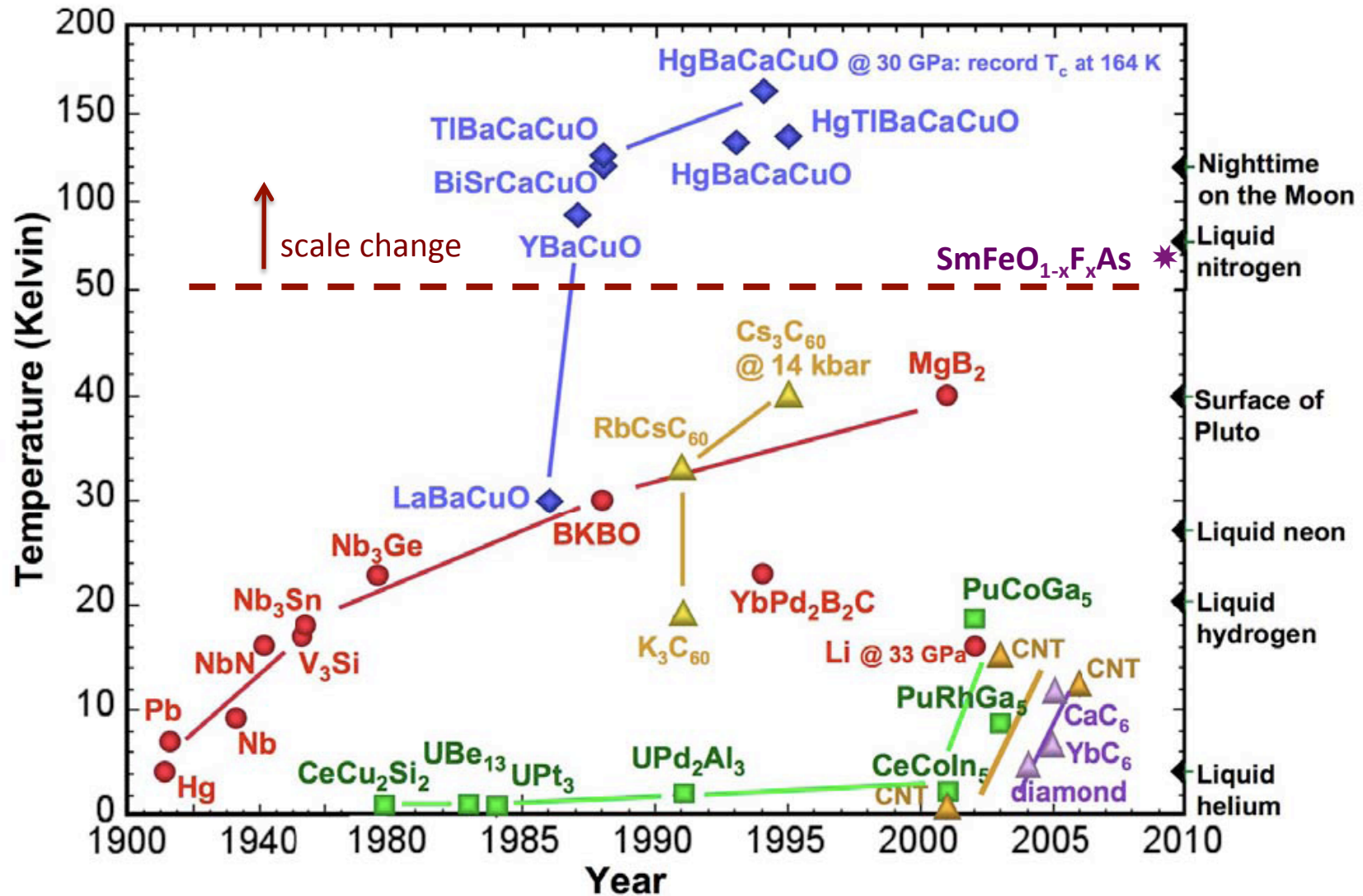
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## $T_c$ vs time for various types of superconducting materials

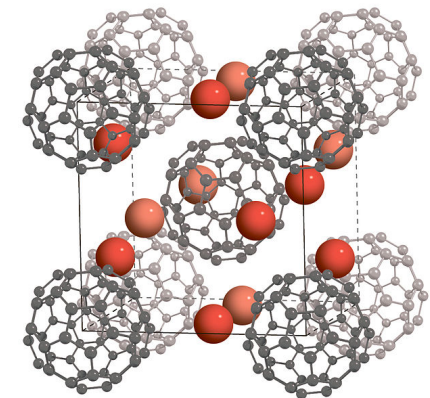
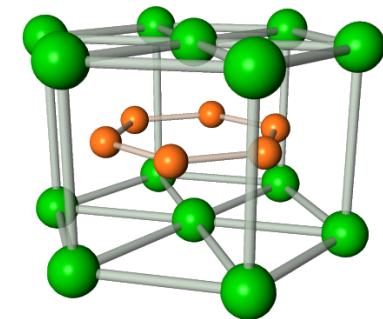
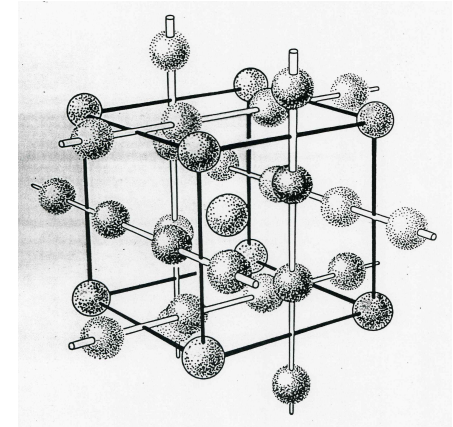
1<sup>st</sup> breakthrough (1986) – cuprates: Max  $T_c \approx 133$  K (165 K - high pressure) (COPPER AGE)

2<sup>nd</sup> breakthrough (2006) – iron pnictides: Max  $T_c \approx 56$  K currently! (IRON AGE)



## Superconducting materials

|                         | MATERIAL                               | $T_c$  |
|-------------------------|--|--------|
| • ALLOYS                | NbTi                                   | 9.6 K  |
| • COMPOUNDS             | NbN                                    | 9.6 K  |
| Borocarbide             | (Lu/Y)Ni <sub>2</sub> B <sub>2</sub> C | 23 K   |
| “A15” Structure         | Nb <sub>3</sub> Sn                     | 18 K   |
| ( $\beta$ -W structure) | Nb <sub>3</sub> Al                     | 18.7 K |
|                         | Nb <sub>3</sub> Ge                     | 23 K   |
| • RECENT                | MgB <sub>2</sub>                       | 39 K   |
| Fullerene               | Cs <sub>2</sub> RbC <sub>60</sub>      | 33 K   |
|                         | + pressure of 15 kbar                  | 40 K   |



- Certain structures favorable for SC; e.g., A15 structure, ThCr<sub>2</sub>Si<sub>2</sub> structure (HF compounds, Fe pnictides)
- History of SC would be very different if discoveries of certain SC'ing materials had been made in a different order! (e.g., MgB<sub>2</sub>!)

## Conventional high $T_c$ superconductors

Guide for searching for conventional high  $T_c$  superconductors

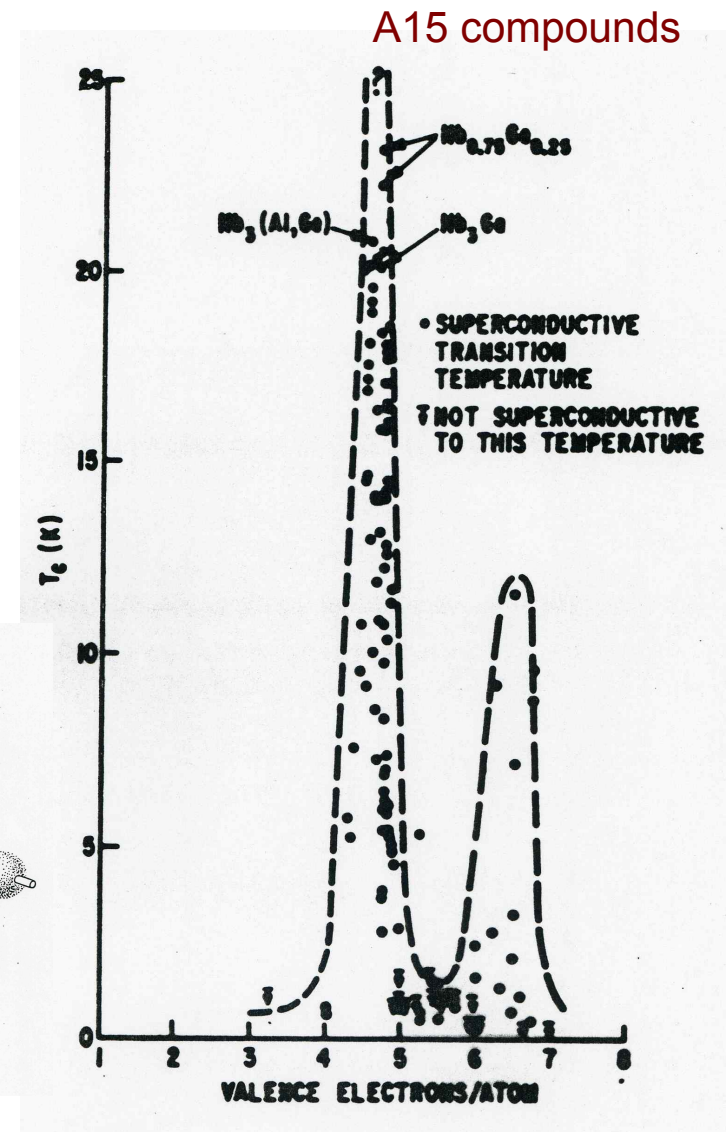
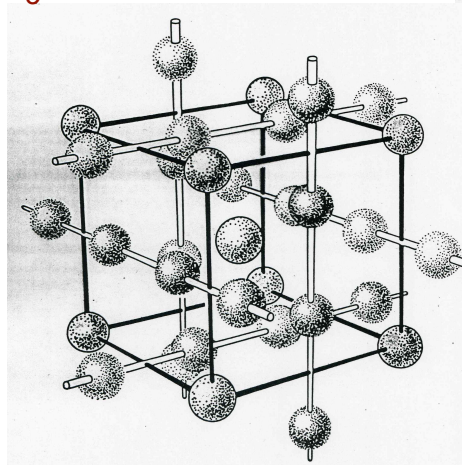
Matthias' "rules" (according to W. E. Pickett – 2001)

- (1) Transition metals are better than simple metals
- (2) Favorable valence electron per atom ratios  $[N(E_F)]$  (5 and 7)
- (3) High symmetry is best, especially cubic
- (4) Avoid oxygen
- (5) Avoid magnetism
- (6) Avoid theorists!



Bernd T. Matthias, 1980

$Nb_3Sn$



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## *Heavy fermion superconductors*

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- Metallic f-electron compounds with enormous electronic specific heat coefficient  $\gamma$  as high as **several J/mol-K<sup>2</sup>!** (Conventional metal:  $\gamma \sim$  several mJ/mol-K<sup>2</sup>)
- Electron effective mass  $m^* \sim 10^2\text{-}10^3 m_e!$
- Based on lanthanide (Ln) and actinide (An) ions with partially-filled f-electron shell and unstable valence: e.g, Ln = Ce, Pr, Yb; An = U, Pu
- Localized f-electron states hybridized with conduction-electron states
- Kondo effect or valence fluctuations  $\Rightarrow$  **strong electronic correlations**
- Characteristic “Kondo” or “valence fluctuation” temperature  $T^*$
- $T \gg T^*$ : Local moment behavior [i.e.,  $\chi(T) \approx N\mu_{\text{eff}}^2/3k_B(T + T^*)$ ]
- $T \ll T^*$ : Nonmagnetic heavy Fermi liquid (FL)

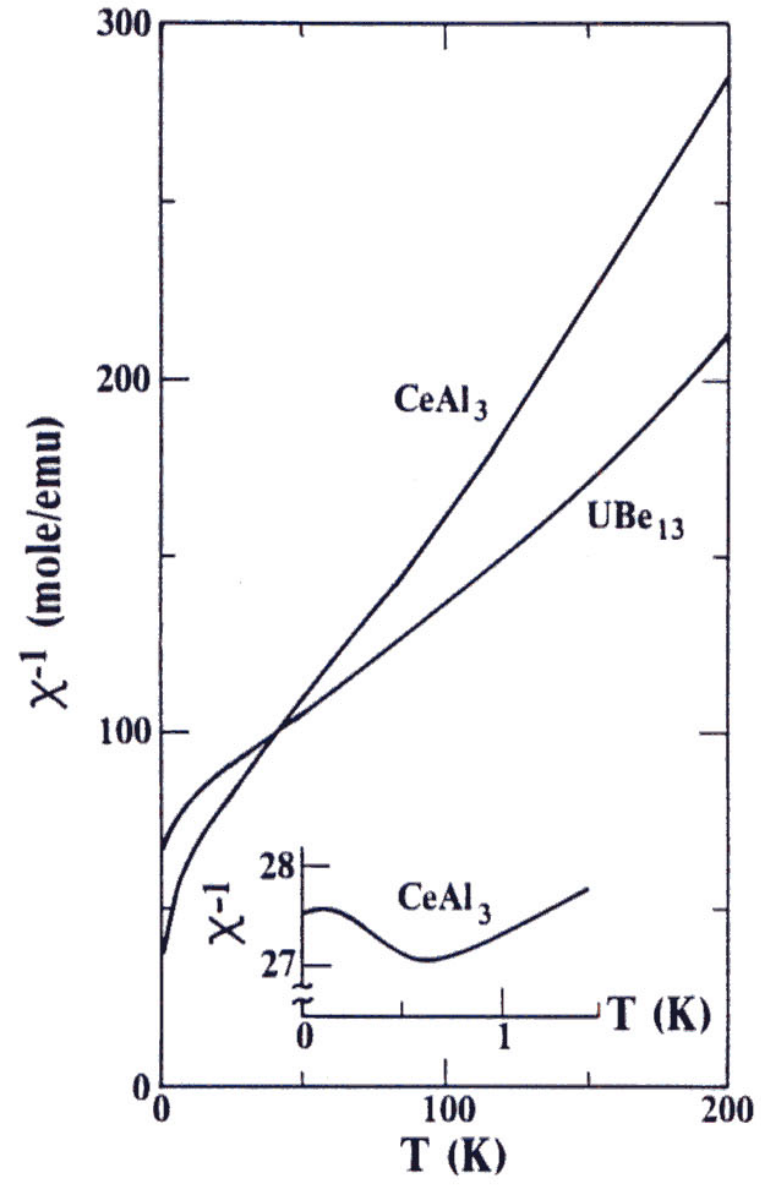
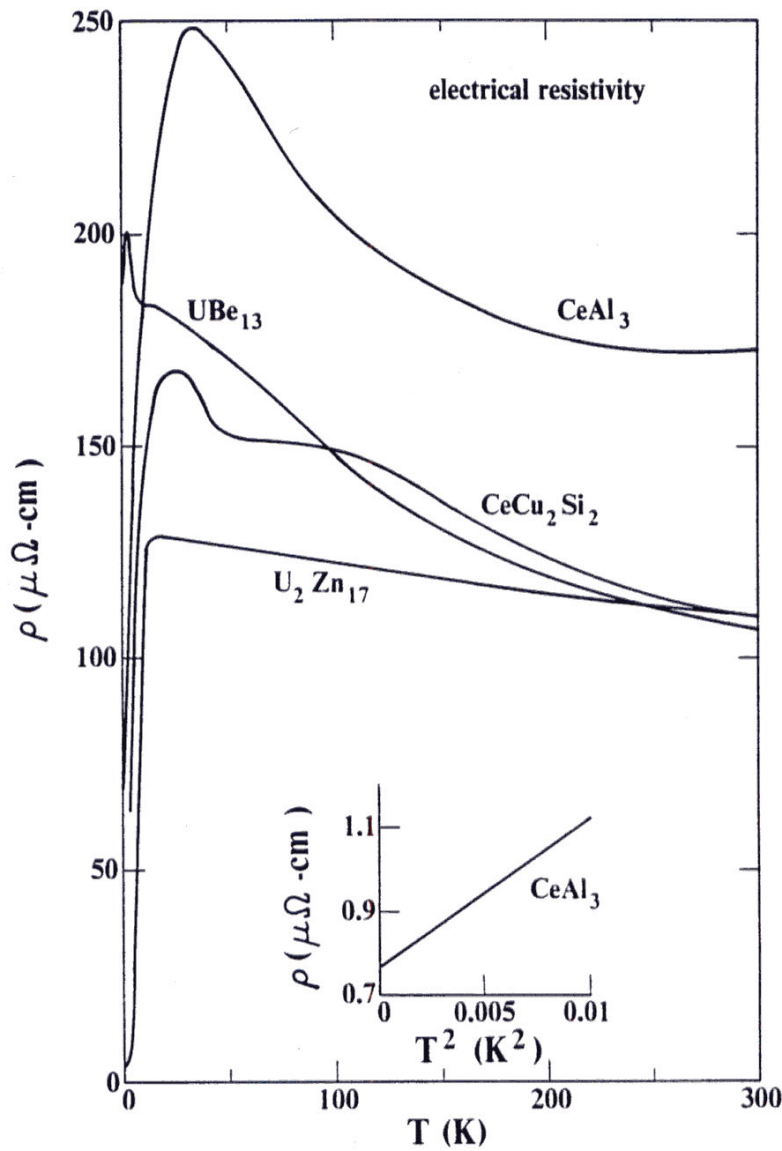
$$\chi(T) \rightarrow \chi_0 \propto m^* \propto 1/T^*$$

$$\gamma(T) = C_e(T)/T \rightarrow \gamma_0 \propto m^* \propto 1/T^* \quad (\text{as high as several J/mol K}^2!)$$

$$R = (\chi_0/\mu_{\text{eff}}^2)/(\gamma_0/\pi^2k_B^2) \approx 1 \quad (\text{Wilson-Sommerfeld ratio})$$

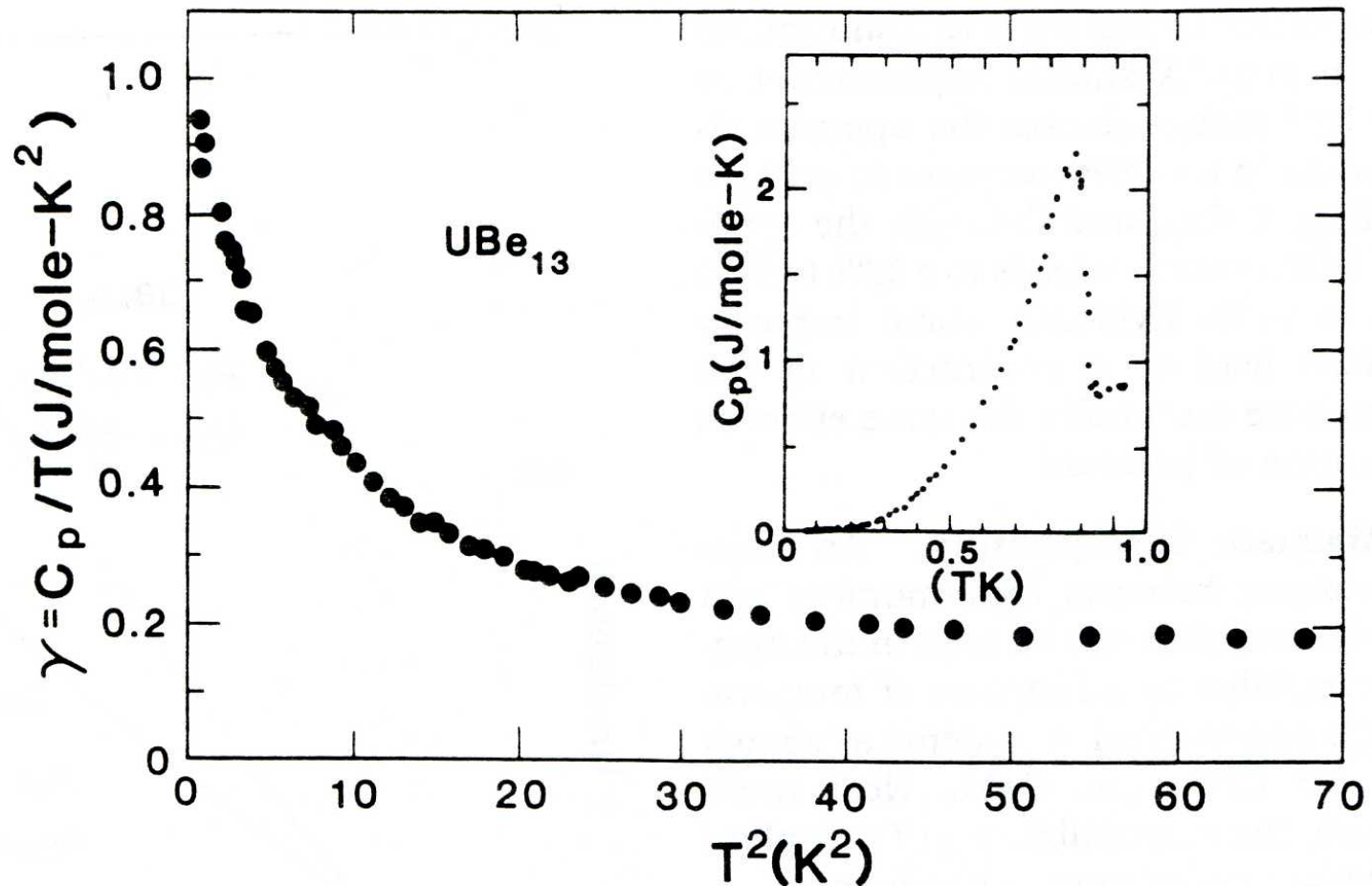
- Narrow resonance in  $N(E)$  near  $E_F$  (Kondo model: “Abrikosov-Suhl resonance”)
- Heavy FL unstable to unconventional SC and magnetic order (RKKY)

## Electrical resistivity and magnetic susceptibility of heavy fermion compounds



After Fisk, Ott, Rice & Smith 86

## Low temperature specific heat of $UBe_{13}$



- $\gamma(0) \approx 1 \text{ J/mol-K}^2 \Rightarrow m^* \approx 10^2 m_e$
- $\Delta C \approx \gamma T_c \Rightarrow$  heavy electrons responsible for large  $\gamma$  are involved in SC!

After D. W. Hess, P. S. Riseborough, J. L. Smith, *Enc. App. Phys.* 7 (93)

## *Heavy fermion superconductors (partial list)*

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*Superconducting at  
atmospheric pressure:*

| <u>Compound</u>                     | <u>T<sub>c</sub> (K)</u> |
|-------------------------------------|--------------------------|
| CeCoIn <sub>5</sub>                 | 2.3                      |
| CeCu <sub>2</sub> Si <sub>2</sub> * | 0.49                     |
| CeIrIn <sub>5</sub>                 | 0.4                      |
| U <sub>6</sub> Fe                   | 3.7                      |
| UPd <sub>2</sub> Al <sub>3</sub> *  | 2.0                      |
| URu <sub>2</sub> Si <sub>2</sub> *  | 1.5                      |
| UNi <sub>2</sub> Al <sub>3</sub> *  | 1.0                      |
| UBe <sub>13</sub>                   | 0.85                     |
| UPt <sub>3</sub> *                  | 0.55                     |
| URhGe*                              | 0.4                      |
| PrOs <sub>4</sub> Sb <sub>12</sub>  | 1.8                      |

\* *Magnetic order*

## *Heavy fermion superconductors (partial list)*

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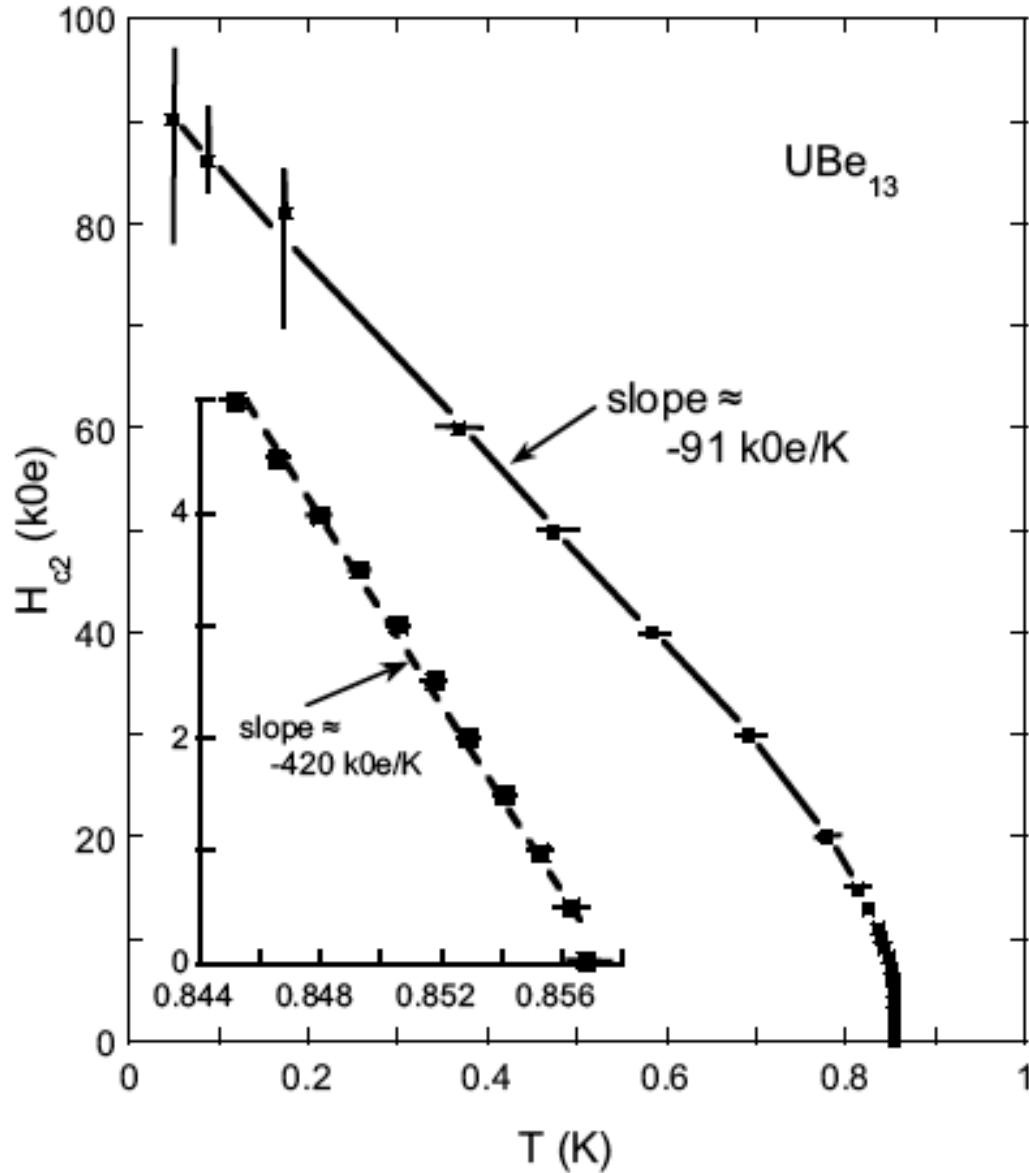
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| URhGe*                              | 0.4                      |
| PrOs <sub>4</sub> Sb <sub>12</sub>  | 1.8                      |

### *Superconducting under pressure:*

| <u>Compound</u>                     | <u>T<sub>c</sub> (K)</u> | <u>P (kbar)</u> |
|-------------------------------------|--------------------------|-----------------|
| CeRhIn <sub>5</sub> *               | 2.2                      | 21              |
| Ce <sub>2</sub> RhIn <sub>8</sub> * | 2                        | 23              |
| CeCu <sub>2</sub> Ge <sub>2</sub> * | ~2                       | 165             |
| CePd <sub>2</sub> Si <sub>2</sub> * | 0.43                     | 28              |
| CeRh <sub>2</sub> Si <sub>2</sub> * | 0.26                     | 11              |
| CeNi <sub>2</sub> Ge <sub>2</sub>   | 0.23                     | 23              |
| CeIn <sub>3</sub> *                 | 0.17                     | 25              |
| UGe <sub>2</sub> *                  | 0.7                      | 10              |

\* *Magnetic order*

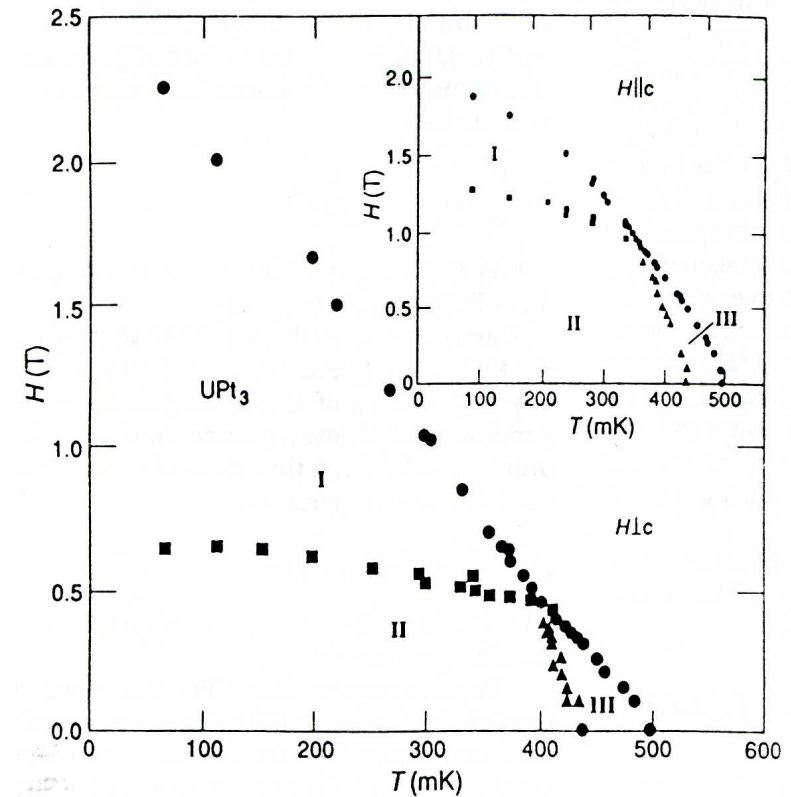
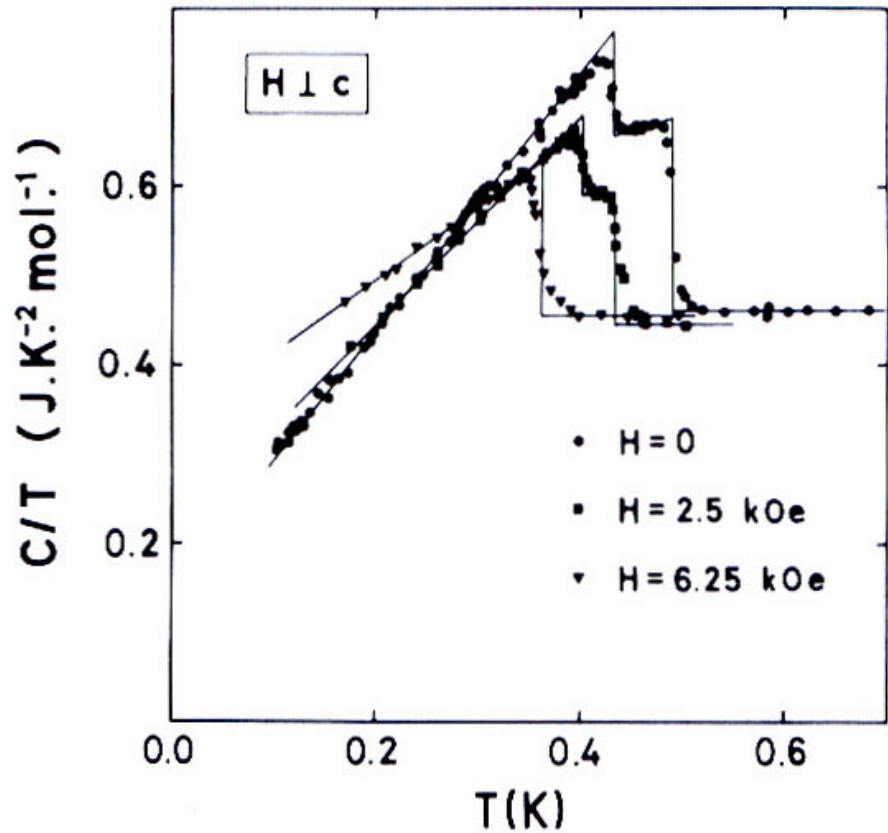
## Upper critical field of $UBe_{13}$



- Upper critical field  $H_{c2}(T)$ :
- Unusual shape
- Enormous initial slope  
 $(dH_{c2}/dT)_{T_c} \propto \rho\gamma$   
 $\Rightarrow m^* \approx 300 m_e$
- Orbital critical field  
 $H_{c2}^*(0) \approx 250$  kOe
- Paramagnetic limiting  
 $H_p = 18.4 T_c$  [kOe]  $\approx 16$  kOe  
(w/o spin-orbit scattering)

*M. B. Maple et al., PRL 54 '85*

## Multiple superconducting phases in $UPt_3$



- $C(H,T) \Rightarrow$  two distinct SC'ing transitions  
*Hasselbach, Taillefer, Flouquet (89)*
- $H - T$  phase diagram (sound velocity)  
 $\Rightarrow$  three distinct SC'ing phases  
*Adenwalla et al. PRL 65 (90)*

- Coupling between multicomponent SC'ing OP & AFM OP
- AFM:  $T_N \approx 5$  K  
 $\mu \approx 0.02 \mu_B/U$  (basal plane)  
*Aeppli et al. JMMM 76 & 77 (88)*

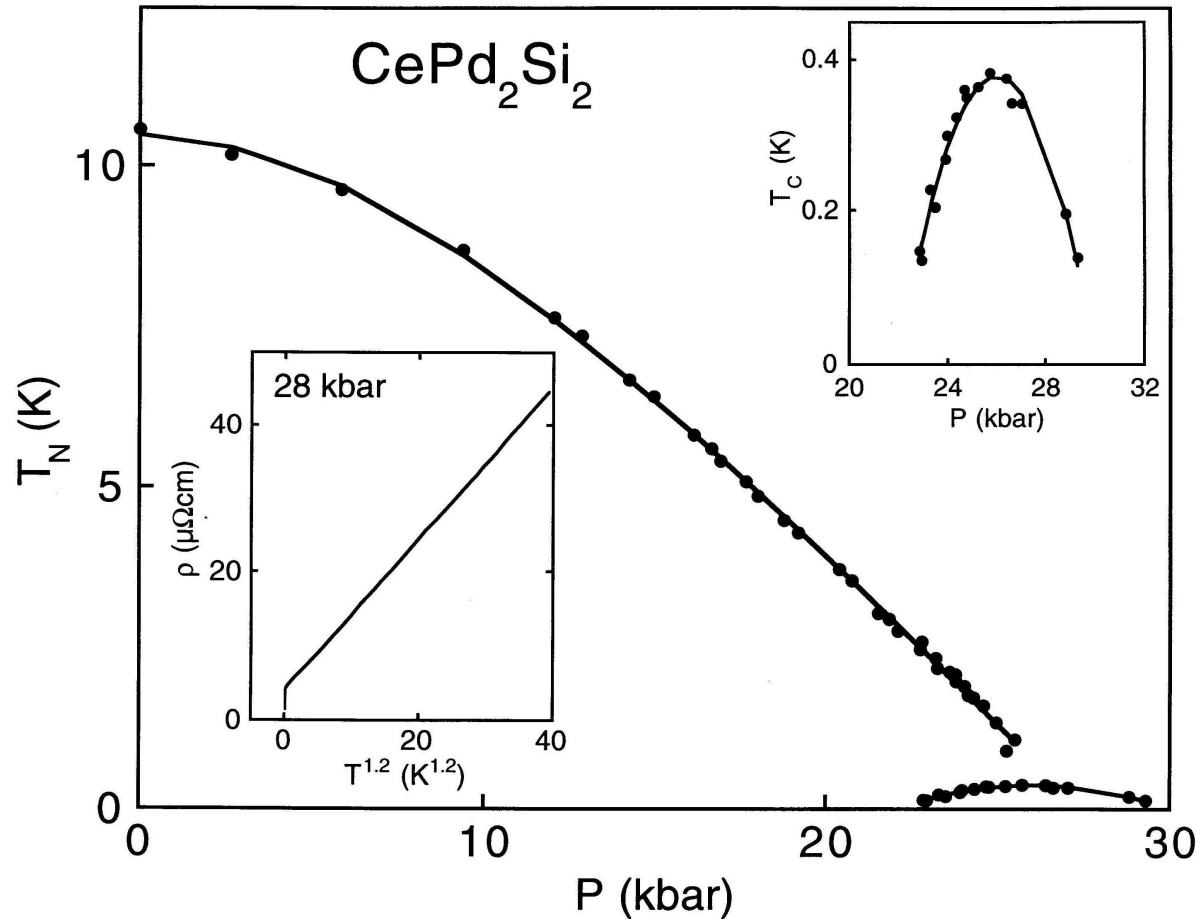
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## Superconductivity near pressure-induced AFM QCP



AFM QCP:

$P_c \approx 28$  kbar

NFL behavior:

$\rho(T) \approx \rho_0 + AT^{1.2}$

( $T_c \leq T \leq 40$  K)

SC'ing dome:

$T_c(\text{max}) \approx 0.4$  K

Similar behavior  
for  $\text{CeIn}_3$  under  $P$

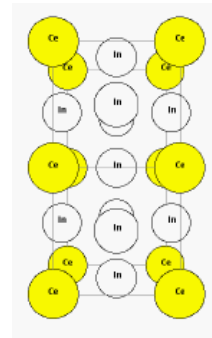
*Julian, Lonzarich et al. (98)*

Suggests AFM spin fluctuations responsible for  
NFL behavior in  $\rho(T)$  and SC'ing electron pairing

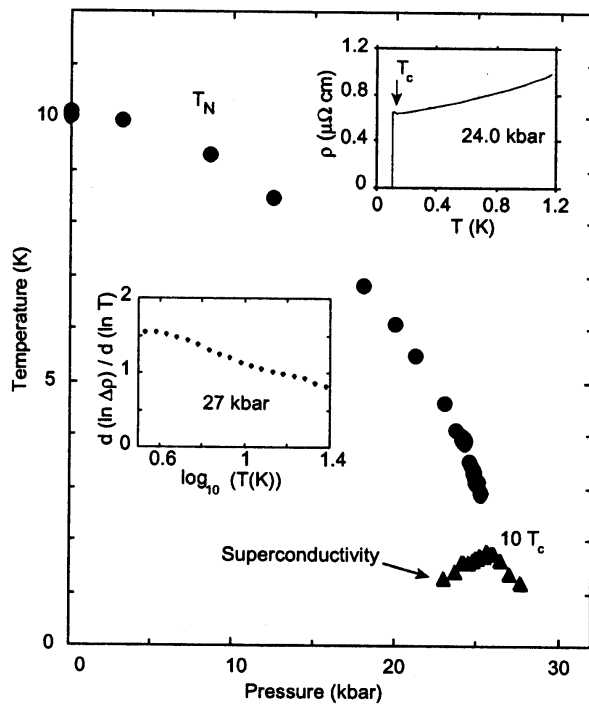
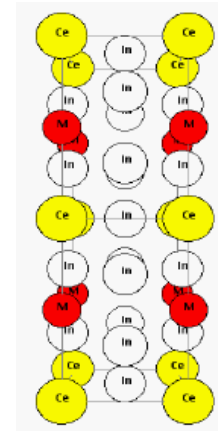
## Emergence of SC near AFM QCP in $CeIn_3$ and $CeRhIn_5$

M = Co, Rh, Ir (isovalent)  
 “Layered” version of  $CeIn_3$   
 $CeRhIn_5$ :  $T_N = 3.8$  K (AFM)  
 $CeCoIn_5$ :  $T_c = 2.3$  K (SC)  
 $CeIrIn_5$ :  $T_c = 0.4/1.0$  K (SC)

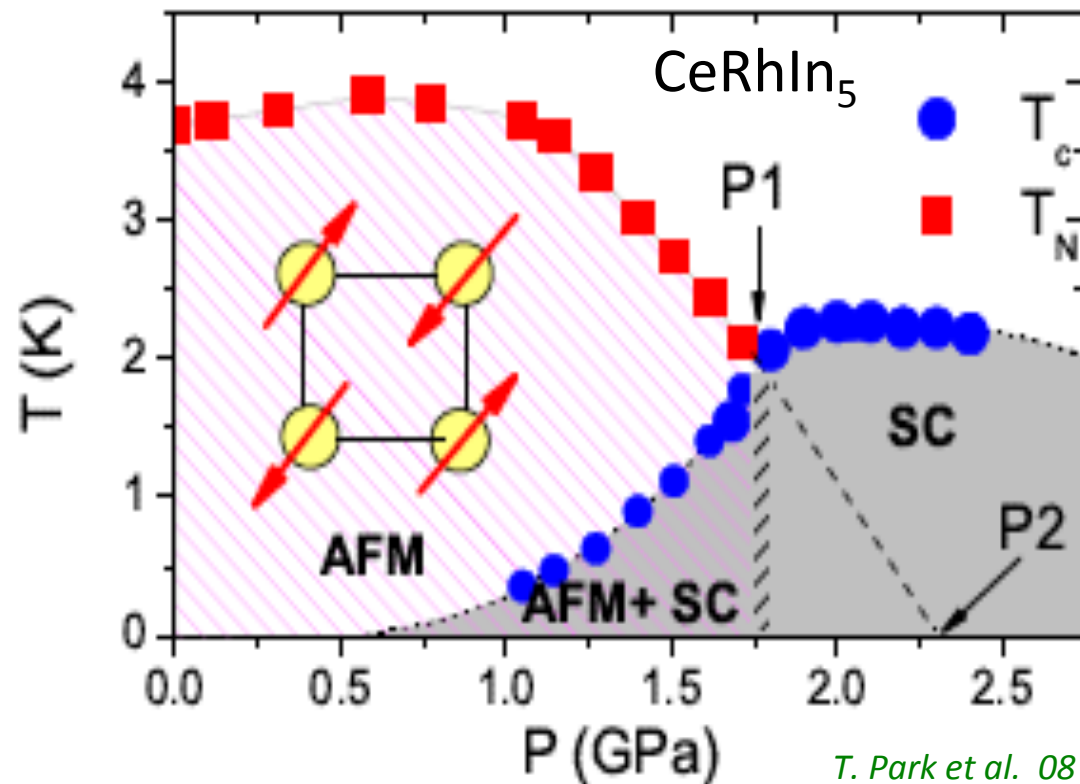
$CeIn_3$



$CeMIn_5$



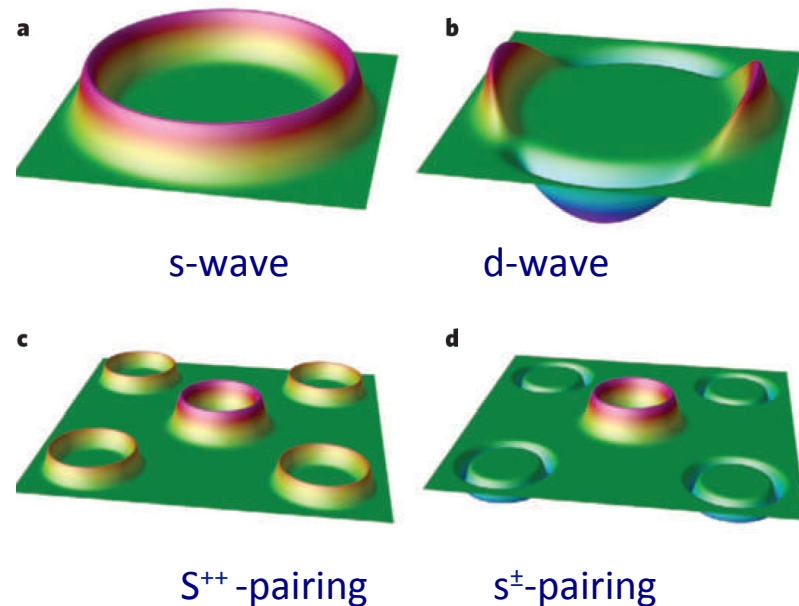
Mathur et al., Nature **394**, 39 (98)



T. Park et al. 08

## Electron pairing scenarios in superconductors

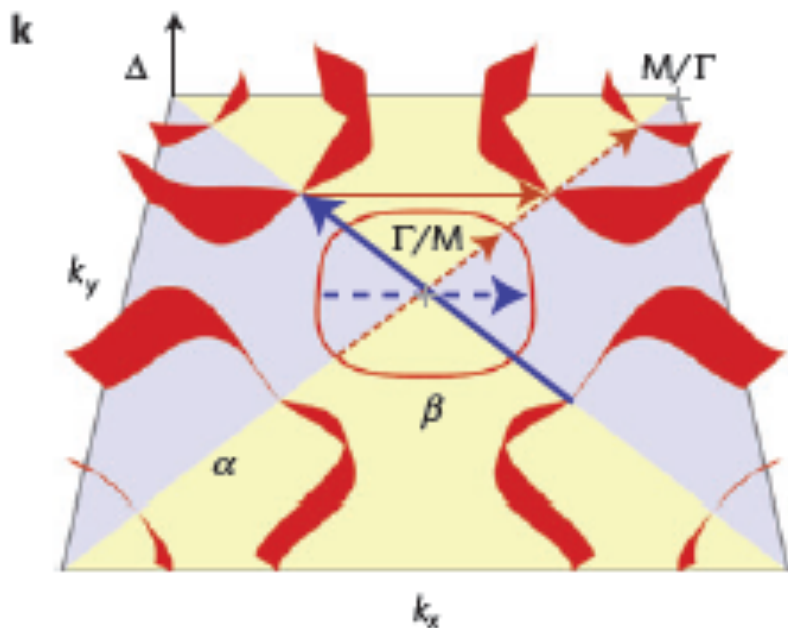
- Consider singlet spin pairing:  $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$
- Superconducting energy gap  $\Delta(\mathbf{k})$ :
  - s-wave – conventional BCS  
Nearly isotropic (nodeless) energy gap  
(e.g., Pb, Sn, Al)
  - d-wave – unconventional  
Anisotropic (nodal) energy gap  
(e.g., HF f-electron SC's, cuprate SC's)
  - $s^{++}$ -wave – two band s-wave, same sign  
(e.g.,  $\text{MgB}_2$ )
  - $s^{\pm}$ -wave – two band s-wave, opposite sign  
(e.g., Fe-pnictides?)



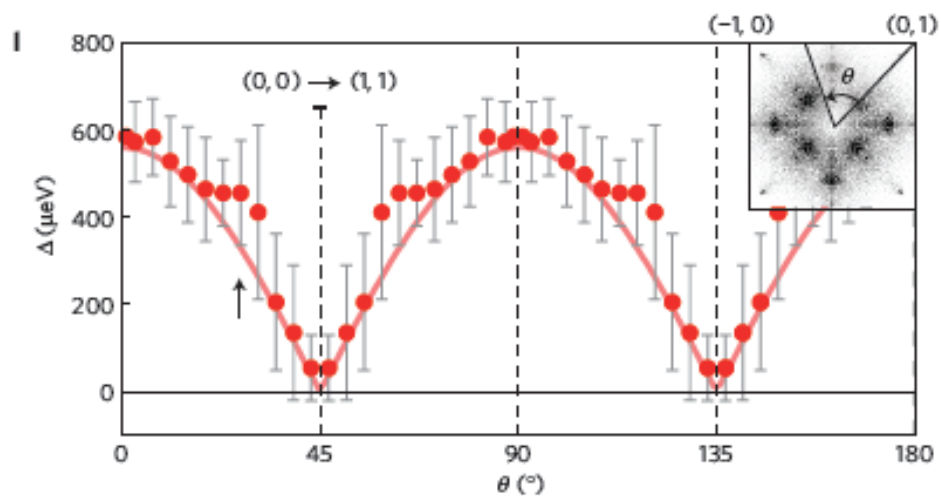
After I. I. Mazin, *Nature* **464**, 183 (10)

- Pairing of SC'ing electrons via spin fluctuations [Review: D. J. Scalapino RMP **84**,1383 (12)]
  - Suppression of AFM or SDW order by chemical substitution or pressure  
 $\Rightarrow$  spin fluctuations peaked at ordering wave vector  $\mathbf{Q}$
  - Repulsive interaction involving spin fluctuations rendered attractive via sign change in gap [ $\text{Sgn } \Delta(\mathbf{k} + \mathbf{Q}) = -\text{Sgn } \Delta(\mathbf{k})$ ]  $\Rightarrow$  d-wave or  $s^{\pm}$ -wave pairing
  - Spin resonance peak at  $\mathbf{k} = \mathbf{Q}$  observed in INS experiments in SC'ing phase

## Superconducting energy gap $\Delta(\mathbf{k})$ of CeCoIn<sub>5</sub> (STM)



- Fermi surfaces and energy gaps of CeCoIn<sub>5</sub> modeled using heavy QPI
- Primary gap occurs on high- $\mathbf{k}$   $\alpha$ -band with lines of gap-nodes along  $\mathbf{k} = (0,0) \rightarrow (\pm 1, \pm 1)\pi/a_0$  directions ( $d_{x^2-y^2}$  symmetry)
- Zero gap is shown on  $\beta$  sheet, but thermodynamic studies show both  $\alpha$  and  $\beta$  bands gapped at lowest T



Measured  $|\Delta(\theta_q)|$  compared with simplest multi-band gap structure  $\Delta_\beta(\theta_k) \approx 0$  and  $\Delta_\alpha(\theta_k)\cos(2\theta_k)$  with  $A = 600 \mu\text{eV}$

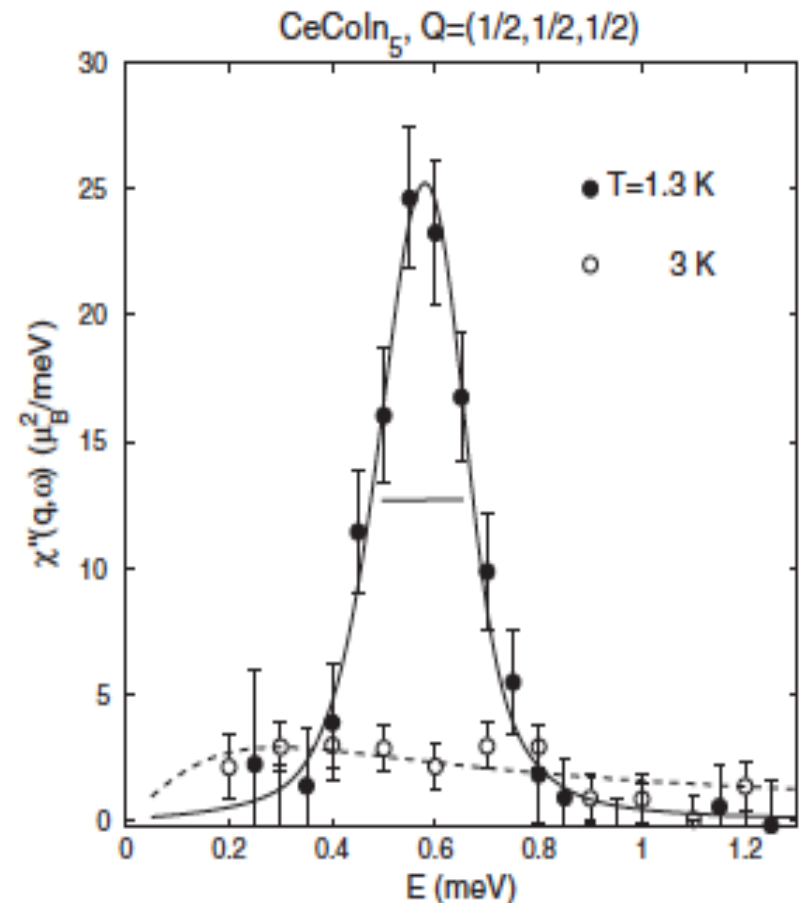
*M. P. Allan et al., Nature Phys. (13)*

## Neutron spin resonance in the superconducting state

- Neutron spin resonance in SC'ing state at AFM or SDW wave vector  $\mathbf{Q}$
- First observed in cuprates (e.g., *Rossat-Mignod et al. '91; Mook et al. '93; Fong et al. '95, '99*)
- Spin-flip INS rate  $\propto \chi''(\mathbf{Q}, \omega)$
- Requires gap sign change between regions on FS separated by momentum  $\mathbf{Q}$  which contribute significantly to spin scattering:

$$[\text{Sgn}\Delta(\mathbf{k} + \mathbf{Q}) = - \text{Sgn} \Delta(\mathbf{k})]$$

(e.g., *Bulut, Scalapino, Scalletar '92; Monthoux, Scalapino '94*)



INS spin resonance in normal (dashed) & SC'ing (solid) states for HF compound CeCoIn<sub>5</sub> ( $T_c = 2.3$  K) *Stock et al. '08*

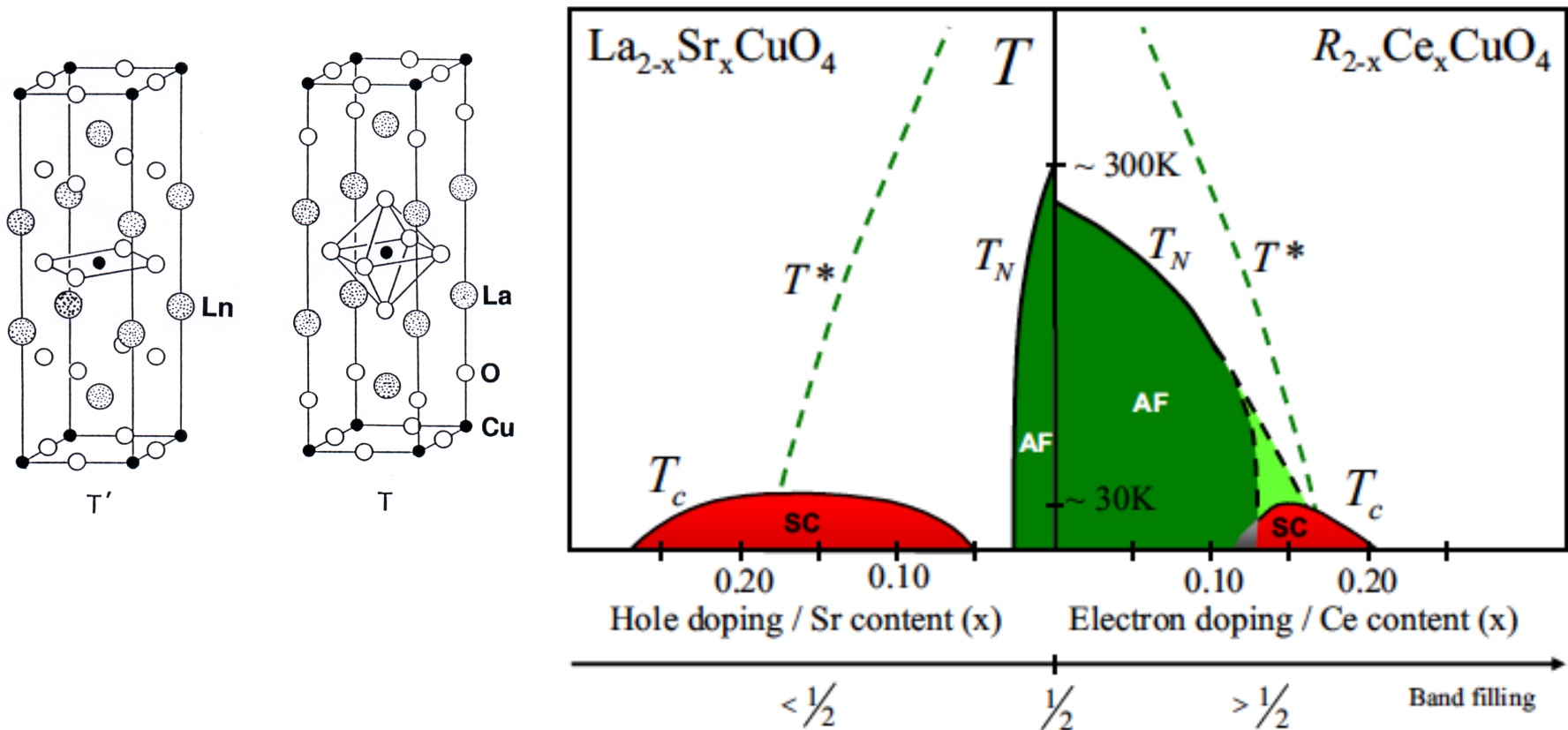
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## Electron- and hole-doped cuprate superconductors

- Parent compound – antiferromagnetic (AFM) Mott insulator
- Chemical substitution  $\Rightarrow$  generates electrons or holes in  $\text{CuO}_2$  planes and suppresses AFM order  $\Rightarrow$  superconducting metal with high  $T_c$

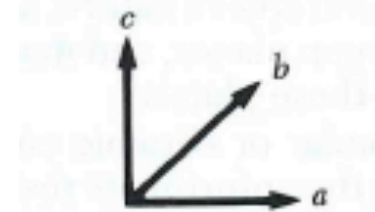


After N. P. Armitage, P. Fournier, R. L. Greene, *RMP* **82**, 2421 (2012)

## Crystal structures of high $T_c$ cuprate superconductors

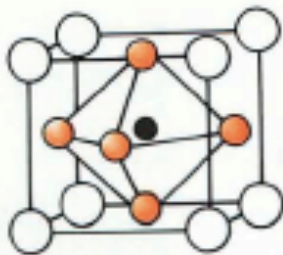
- Layered perovskite-like crystal structure
- Charge carriers move in  $\text{CuO}_2$  plane

$\text{YBa}_2\text{Cu}_3\text{O}_7$ :  $T_c = 92 \text{ K}$

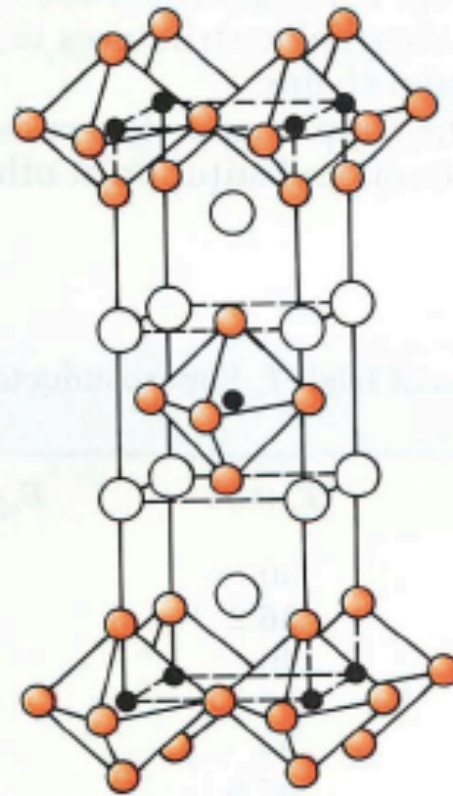


$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ :  $T_c \approx 40 \text{ K}$

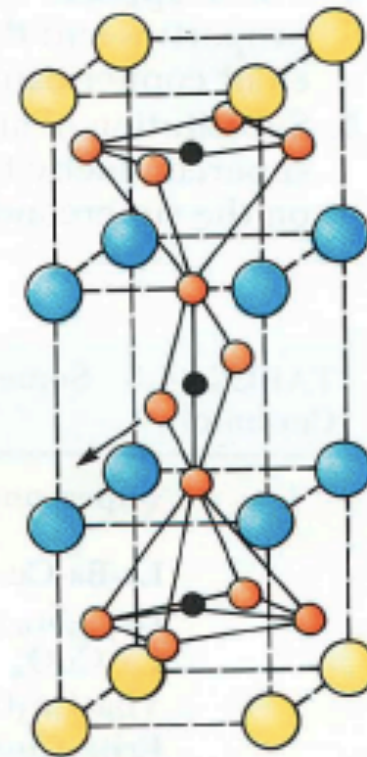
- = Cu
- = La
- = Oxygen
- = Yttrium
- = Barium



$\text{LaCuO}_0$   
Perovskite



$\text{La}_2\text{CuO}_4$   
Layered perovskite



$\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$   
Oxygen defect  
Perovskite

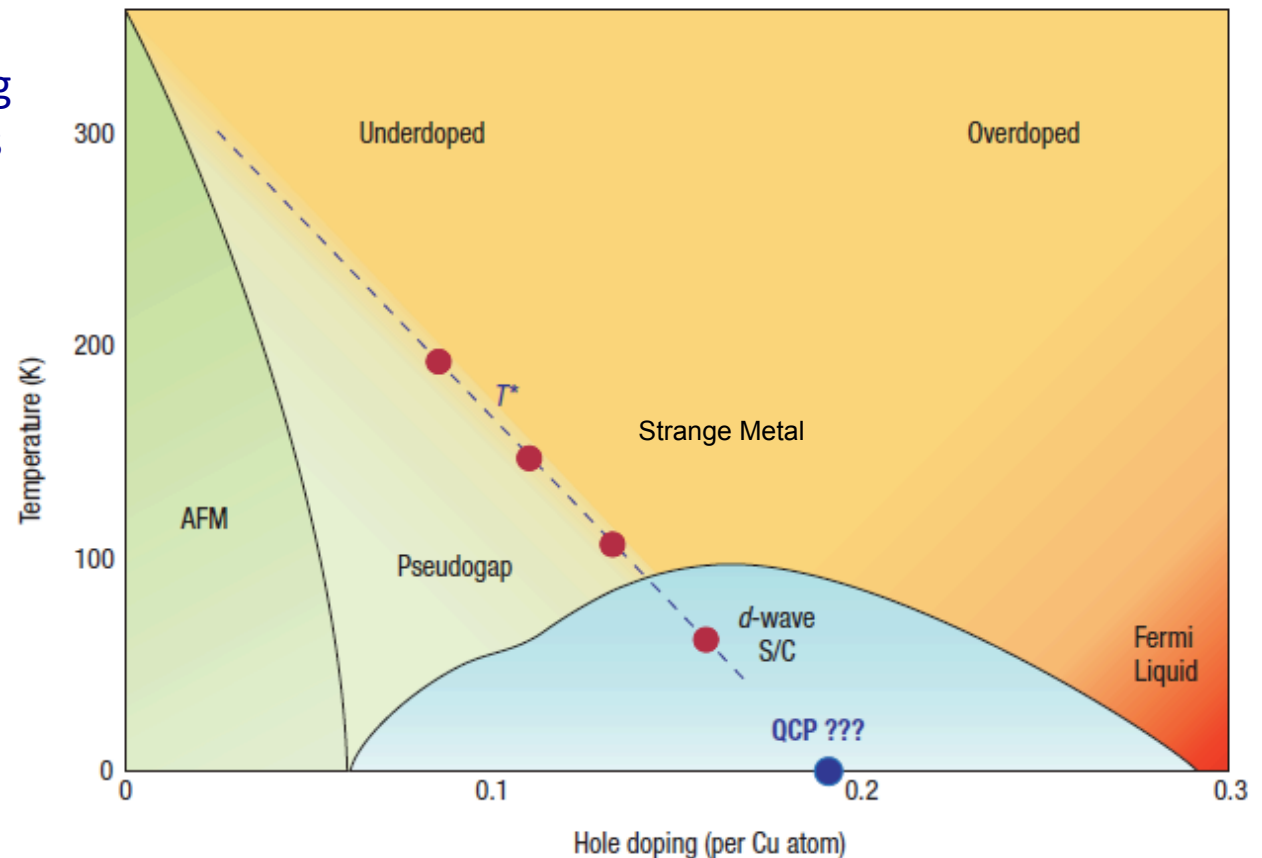


## Generalized phase diagram for hole-doped cuprates

Generalized T – hole doping  
phase diagram for cuprates

After D. M. Broun, *Nature  
Physics* **4**, 178 (2008)

Pseudogap (PG) phase:  
Anomalous properties  
in transport, magnetic,  
thermodynamic, and  
optical properties at  $T^*$   
(pseudogap temperature)



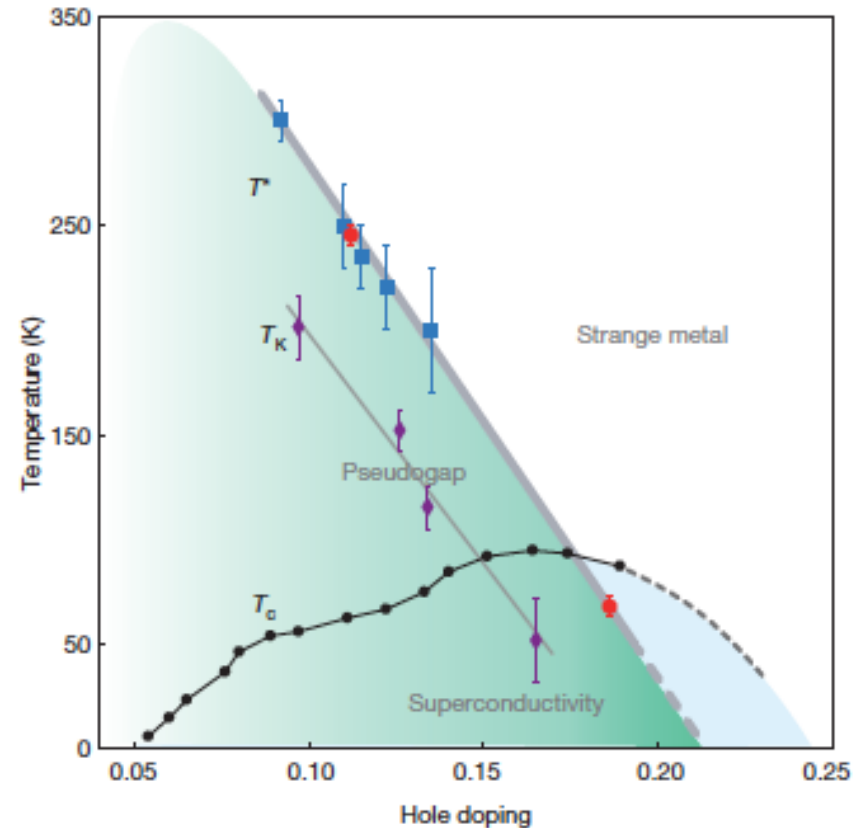
Two major approaches to describe PG phase:

- (1)  $T^*$  represents crossover into state of preformed pairs with d-wave gap symmetry
- (2)  $T^*$  marks transition into distinct phase with broken symmetry that terminates at a QCP, typically inside SC'ing dome; e.g., CDW order, charge current loops

Recent experiments seem to favor alternative (2)

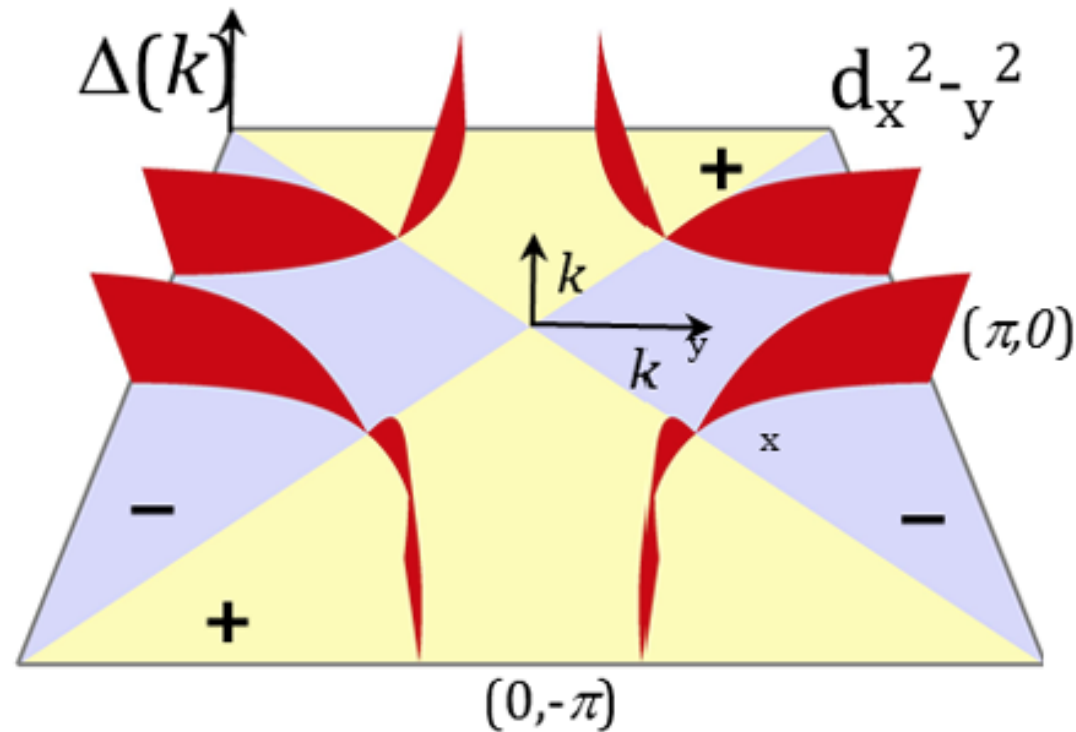
## Evidence for symmetry breaking in pseudogap state

- Broken time reversal symmetry (TRS)
  - Polarized neutron diffraction
    - *B. Faqué et al., PRL (06)*
    - *Kaminski et al., Nature (02)*
    - *Y. Li et al., Nature (08)*
  - Polar Kerr effect
    - *J. Xia et al., PRL (08)*
- Broken rotational symmetry
  - Electrical resistivity
    - *Y. Ando et al., PRL (02)*
  - Inelastic neutron scattering (INS)
    - *C. Stock et al., PRB (04)*
    - *V. Hinkov et al., Nature Phys. (07)*
    - *V. Hinkov et al., Science (08)*
  - STM
    - *Y. Kohsaka et al., Science (07)*
    - *Y. Kohsaka et al., Nature (08)*
  - Nernst effect
    - *R. Daou et al., Nature (10)*
- Phase transition
  - RUS measurements
    - *A. Shekhter et al., Nature (13)*



After *A. Shekhter et al., Nature (13)*  
Blue squares – neutron diffraction  
Red circles – RUS  
Purple diamonds – Kerr rotation  
(onset of charge order – x-ray study)  
*J. Chang et al., Nature Phys. (12)*

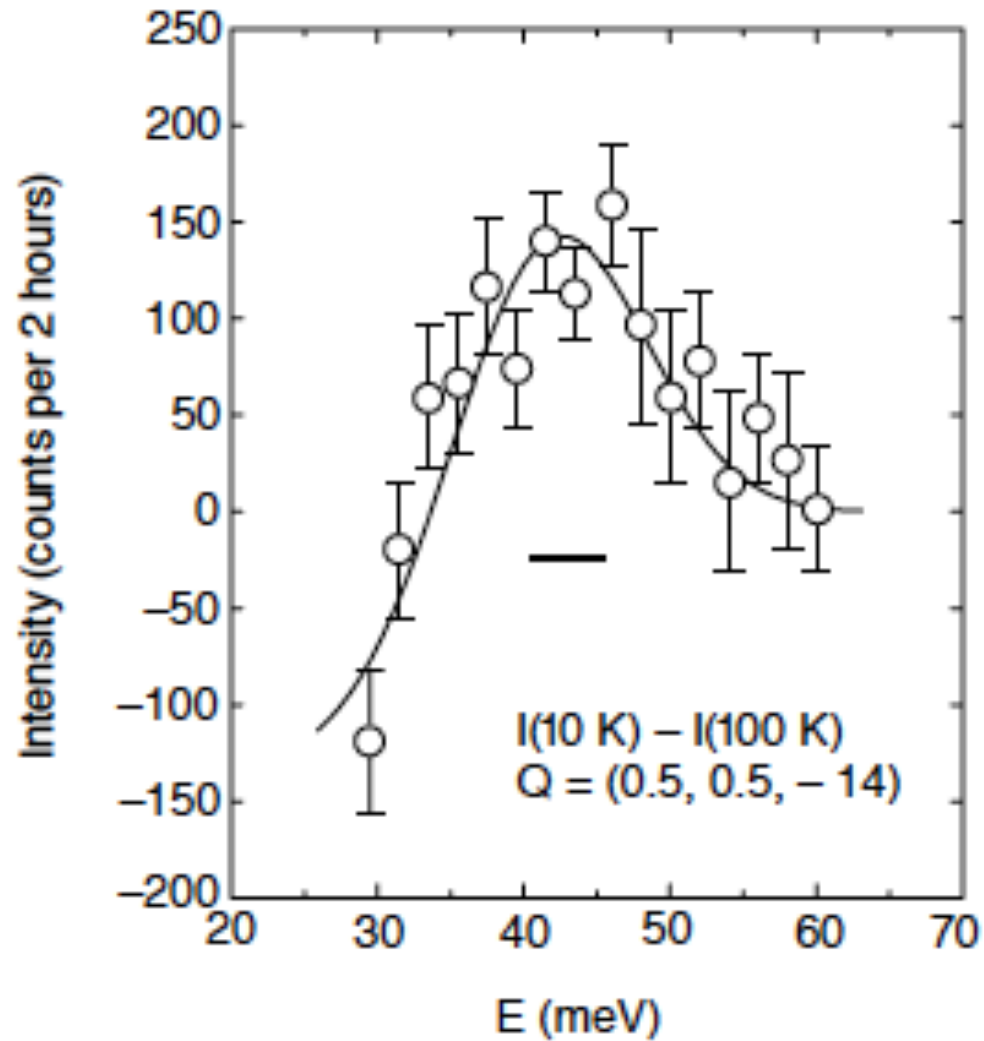
## Superconducting energy gap $\Delta(k)$ of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (STM)



After J. C. Davis (14); Y. Kohsaka et al.,  
*Nature* **454**, 1072 (08)

- Interaction mediated by AFM spin fluctuations peaked at momenta near  $(\pi, \pi)$
- Links fermions in different “hot regions” of the BZ near  $(0, \pi)$ ,  $(\pi, 0)$
- Overall sign of interaction is positive (repulsive)
- d-wave gap changes sign between “hot regions”  $\Rightarrow$  d-wave component is attractive

## Neutron spin resonance in the superconducting phase



$I(10\text{ K}) - I(100\text{ K})$  for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$   
at wave vector  $Q = (\pi/a, \pi/a)$  showing  
spin resonance at  $\sim 43\text{ meV}$  ( $T_c = 91\text{ K}$ )  
*Fong et al. '99*

## *Outline*

---

- Historical remarks about development of SC'ing materials
- Heavy fermion f-electron SC's
- Emergence of SC from magnetic order, unconventional SC, and electron pairing via spin fluctuations
- Copper oxide (cuprate) SC's
- Iron pnictide/chalcogenide SC's
- Evidence for strong electronic correlations
- New class of layered SC's based on  $\text{LnOBiS}_2$
- Prospects for the future

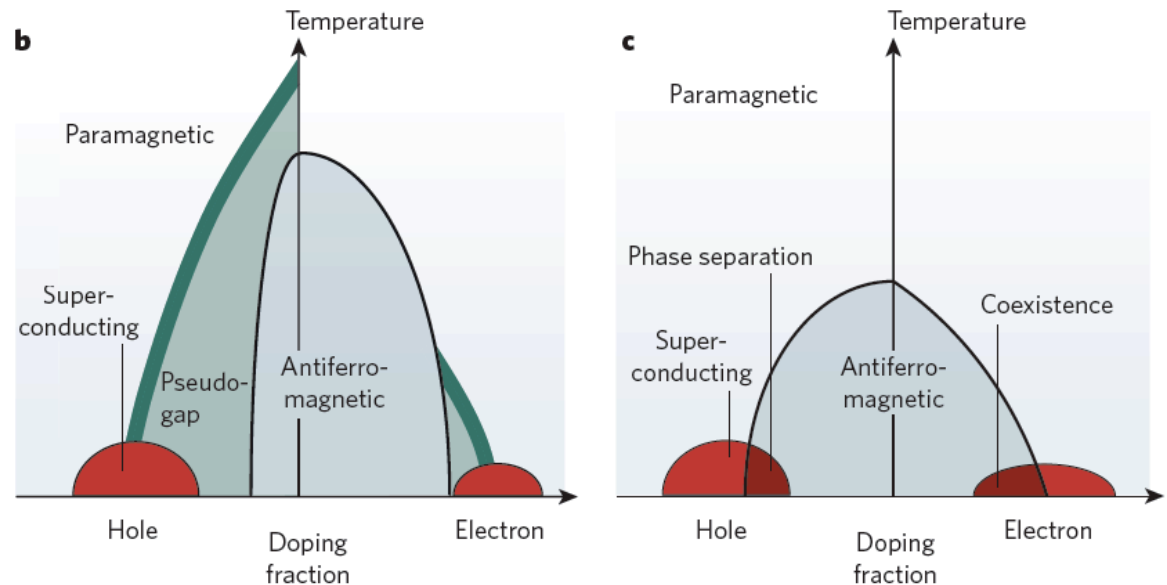
## High $T_c$ superconductivity in Fe pnictides/chalcogenides

- Similarities to cuprates
  - “Layered” structures – FePn or FeCh layers and filler layers (charge reservoirs)
  - Proximity to magnetically ordered phase
- Differences from cuprates
  - Undoped parent compound is poor metal with AFM (SDW-type) order involving Fe  $\mu$ 's (rather than AFM Mott insulator)
  - Electronic correlations weaker than in cuprates
- Symmetry of SC'ing OP: clues regarding electron pairing mechanism

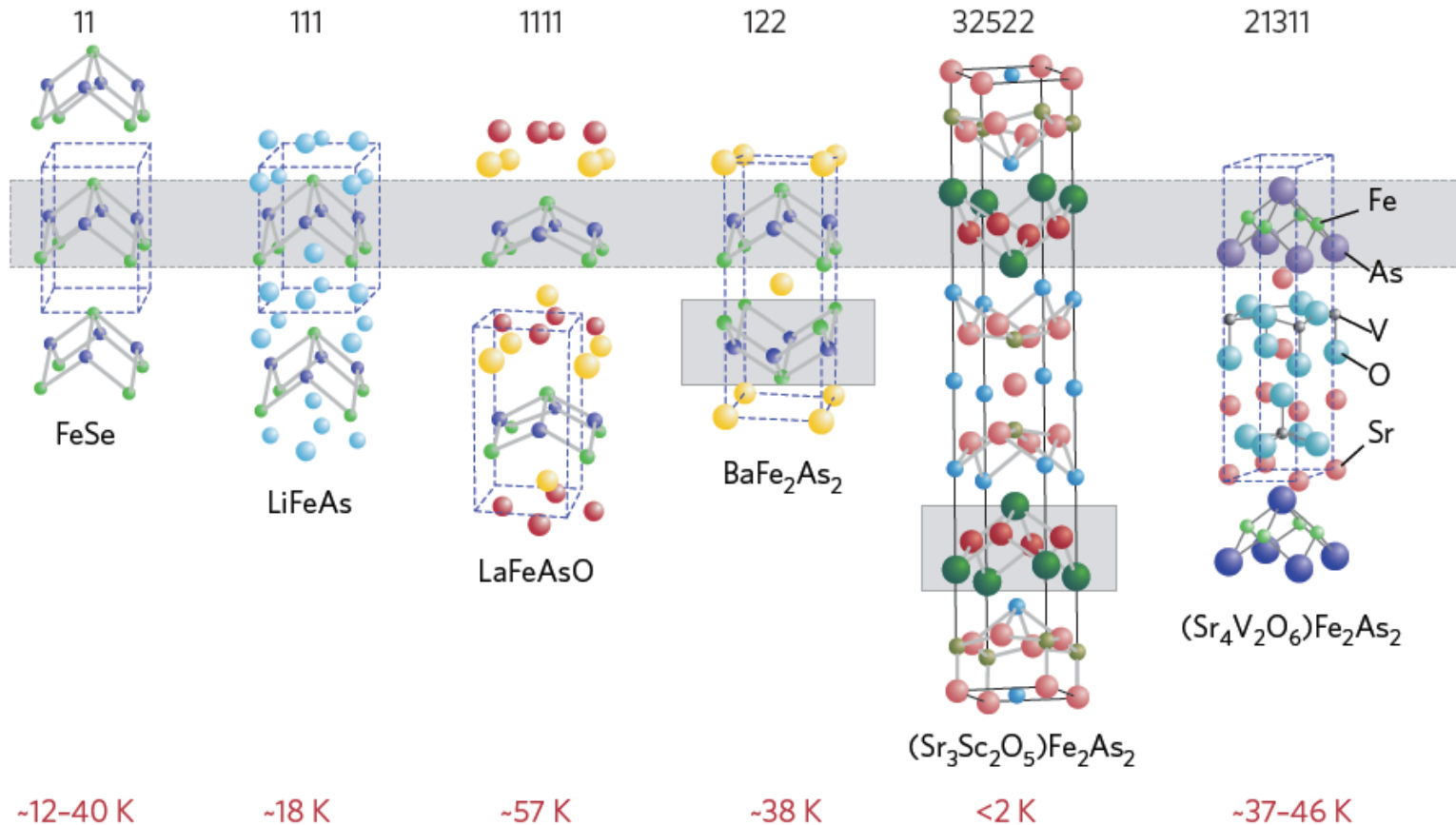
Depending on SC'ing material, evidence for

- Nodal gap – d-wave
- Nodeless gap –  $s^\pm$
- Pairing mechanism: spin fluctuations (assisted by phonons?)

*I. I. Mazin, Nature 464, 183 (10)*

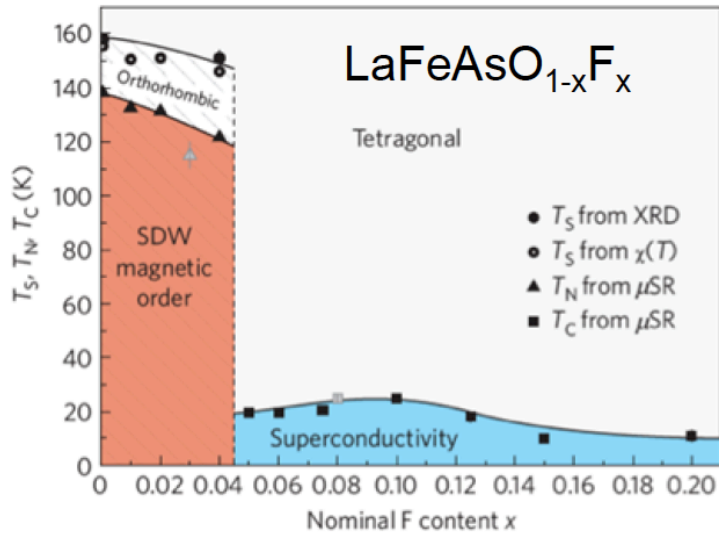


## Transition metal pnictide/chalcogenide structures

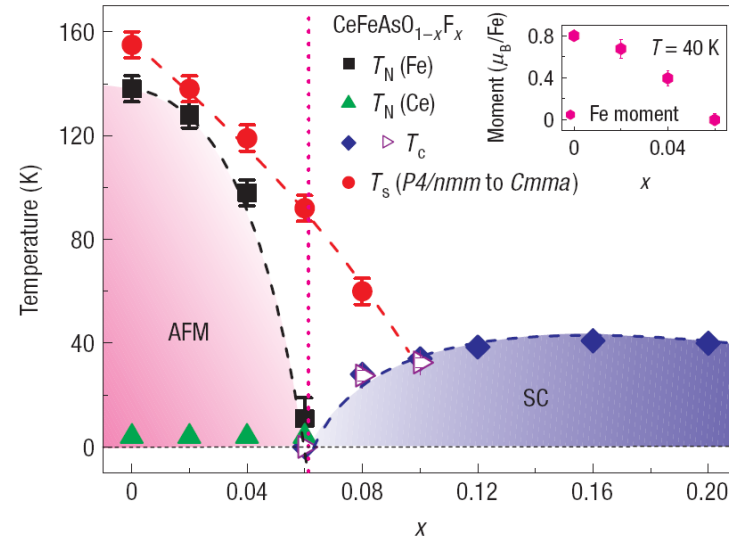


- Multinary compounds with different structures that contain TPn and TCh layers
- Many chemical substitutions possible → enormous number of compounds!!
- Opportunity to search for high  $T_c$  SC and other ordered phases
- High  $T_c$  SC often found in proximity of other ordered phases

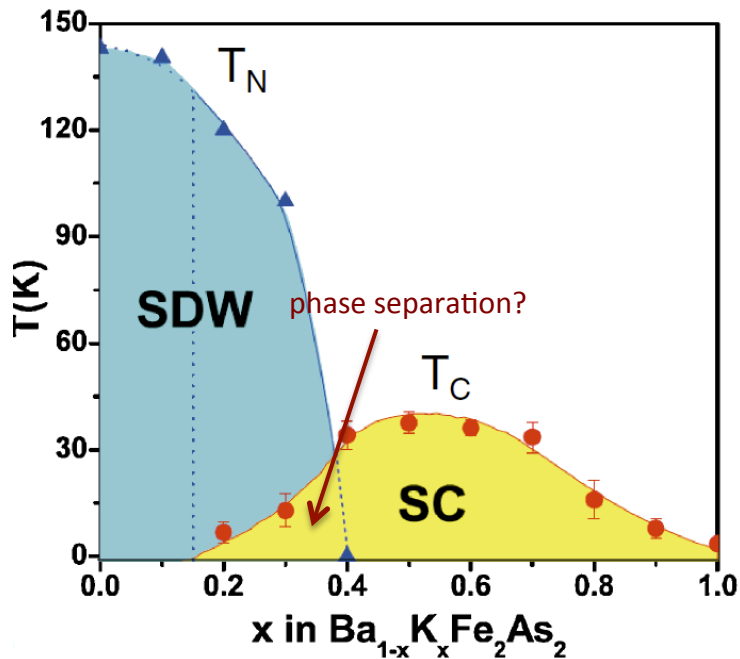
## $T - x$ phase diagrams of Fe pnictide systems



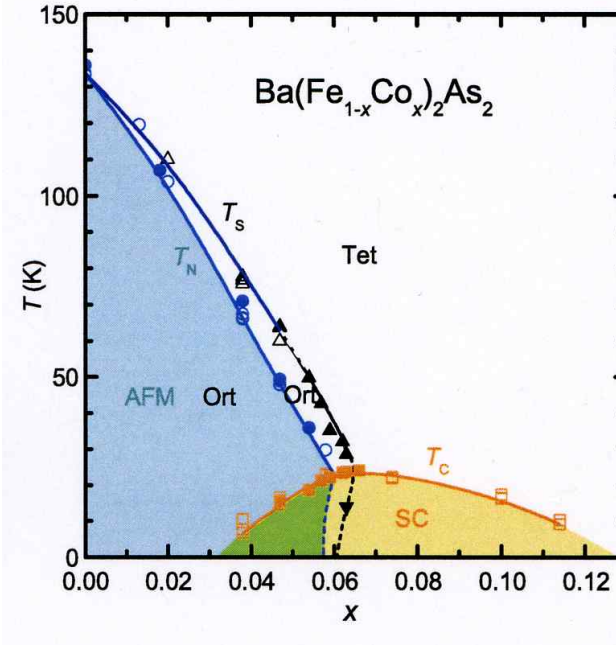
H. Luetkens et al., *Nature Materials* **8**, 305 (2009)



J. Zhao et al., *Nature Materials* **7** (2008)



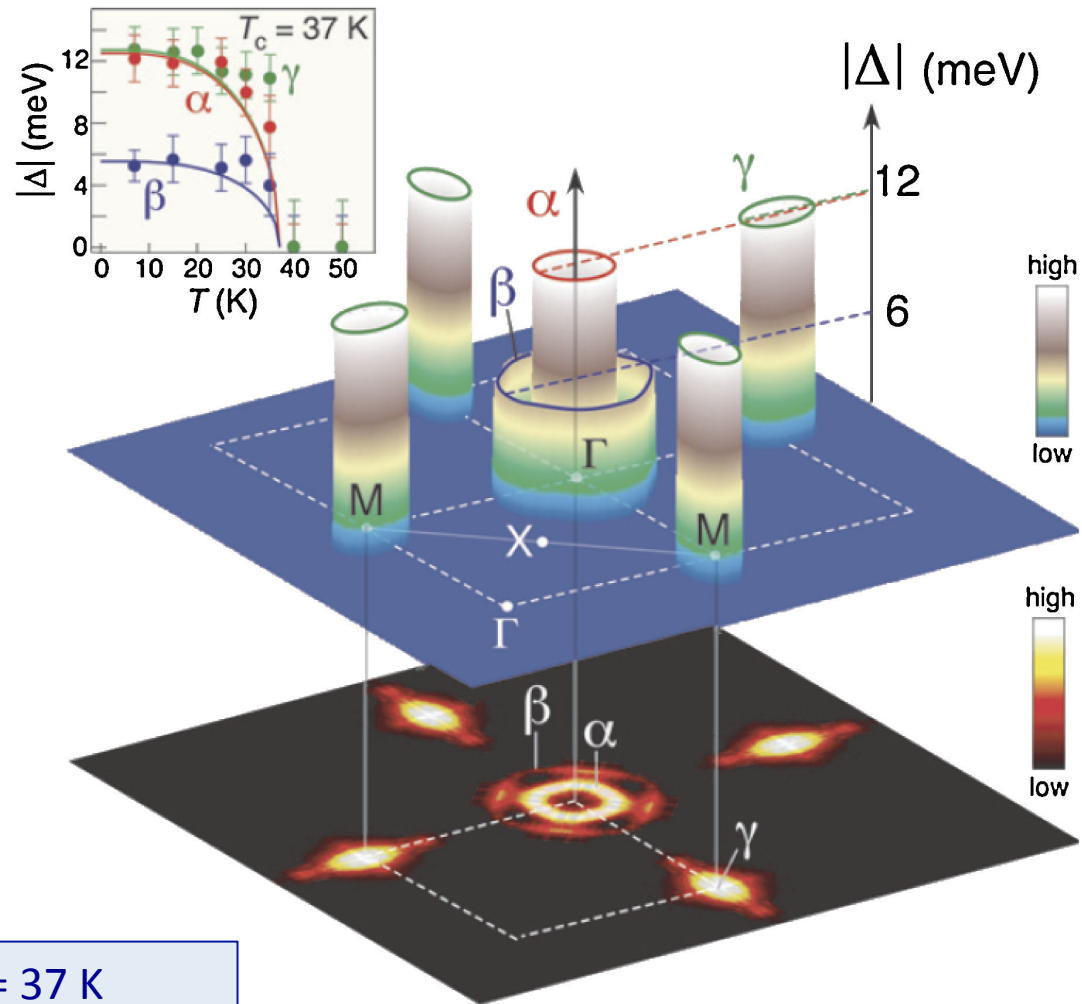
H. Chen et al., *Europhys. Lett.* **85**, 17006 (2009)



S. Nandi et al., *PRL* **104**, 057006 (2010)



## Fermi surface and superconducting gap of $Ba_{0.6}K_{0.4}Fe_2As_2$ from ARPES



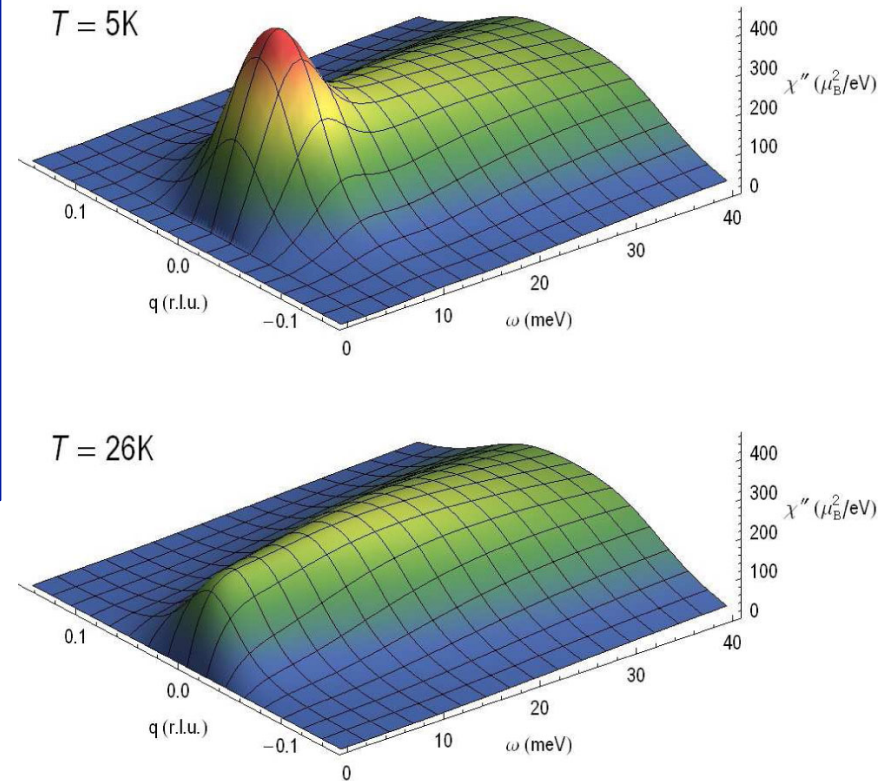
- $Ba_{0.6}K_{0.4}Fe_2As_2$ :  $T_c = 37$  K
- SC'ing energy gap  $\Delta$  on  $\alpha$ ,  $\beta$ ,  $\gamma$  FS sheets measured at 15 K
- Inset: T-dependence of  $\Delta$

*H. Ding et al., Europhys. Lett. (08)*

## Neutron scattering resonance in SCing state

- Fe pnictide parent compounds: SDW with wave vector close to FS nesting wave vector
- Suppression of SDW by substitution of nonmagnetic element produces SC
- Neutron scattering resonance at wave vector of SDW in SC'ing state observed by means of INS
- Resonance associated with scattering between different regions of the FS with opposite sign of SC'ing OP

Ba(Fe<sub>0.925</sub>Co<sub>0.075</sub>)<sub>2</sub>As<sub>2</sub> single crystal  
(T<sub>c</sub> = 25 K)



*D. S. Inosov et al., Nature Phys. 6,178 (2010)*

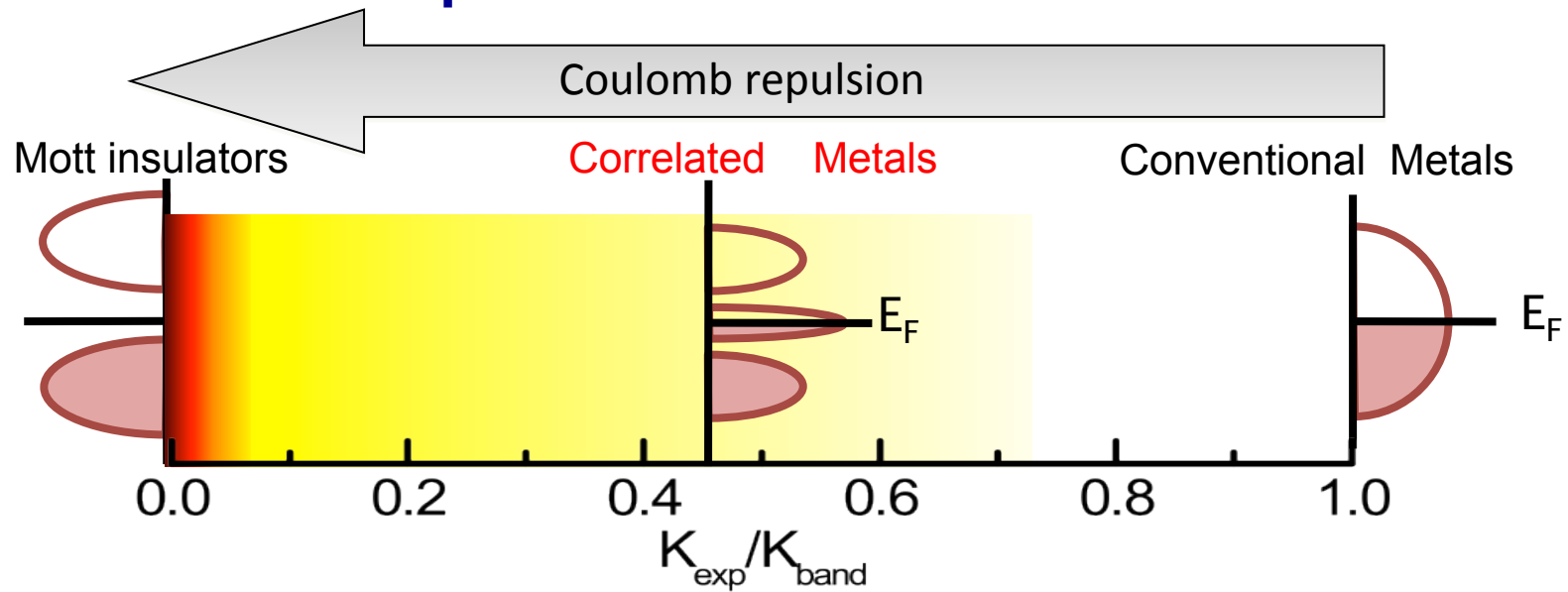
- $\chi''$  of Ba(Fe<sub>0.925</sub>Co<sub>0.075</sub>)<sub>2</sub>As<sub>2</sub> single crystal in SCing (top) and normal (bottom) states vs 2D in-plane wave vector  $q = |Q - Q_{AF}|$  and  $\omega$  [ $Q_{AF} = (1/2, 1/2, L)$  r.l.u.]

## *Outline*

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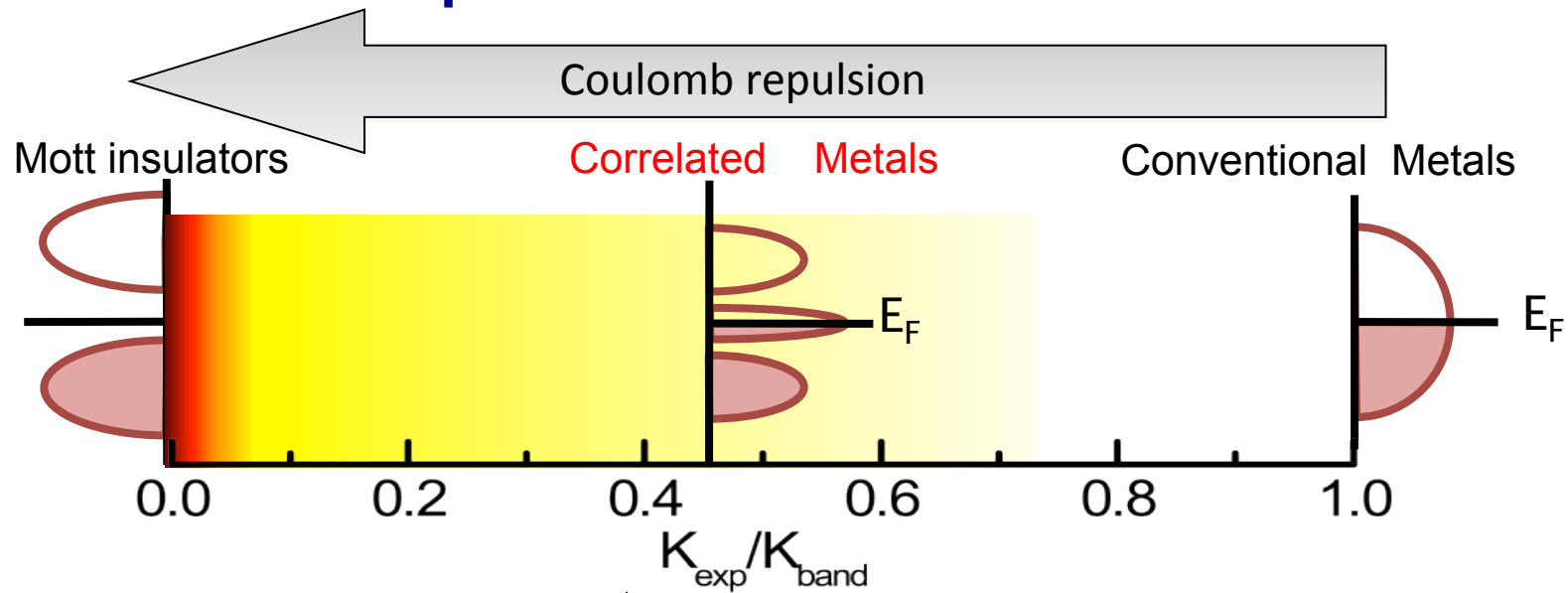
- Historical remarks about development of SC'ing materials
- Heavy fermion f-electron SC's
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- Copper oxide (cuprate) SC's
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- **Evidence for strong electronic correlations**
- New class of layered SC's based on  $\text{LnOBiS}_2$
- Prospects for the future

## An IR probe of electronic correlations



*M.Qazilbash J. Hamlin, R. E. Baumbach, L. Zhang, D.J. Singh, M.B. Maple, and D.N. Basov et al. Nature-Physics 5, 647 (2009)*  
*A.J. Millis et al. PRB 72, 224517 (2005)*

## An IR probe of electronic correlations

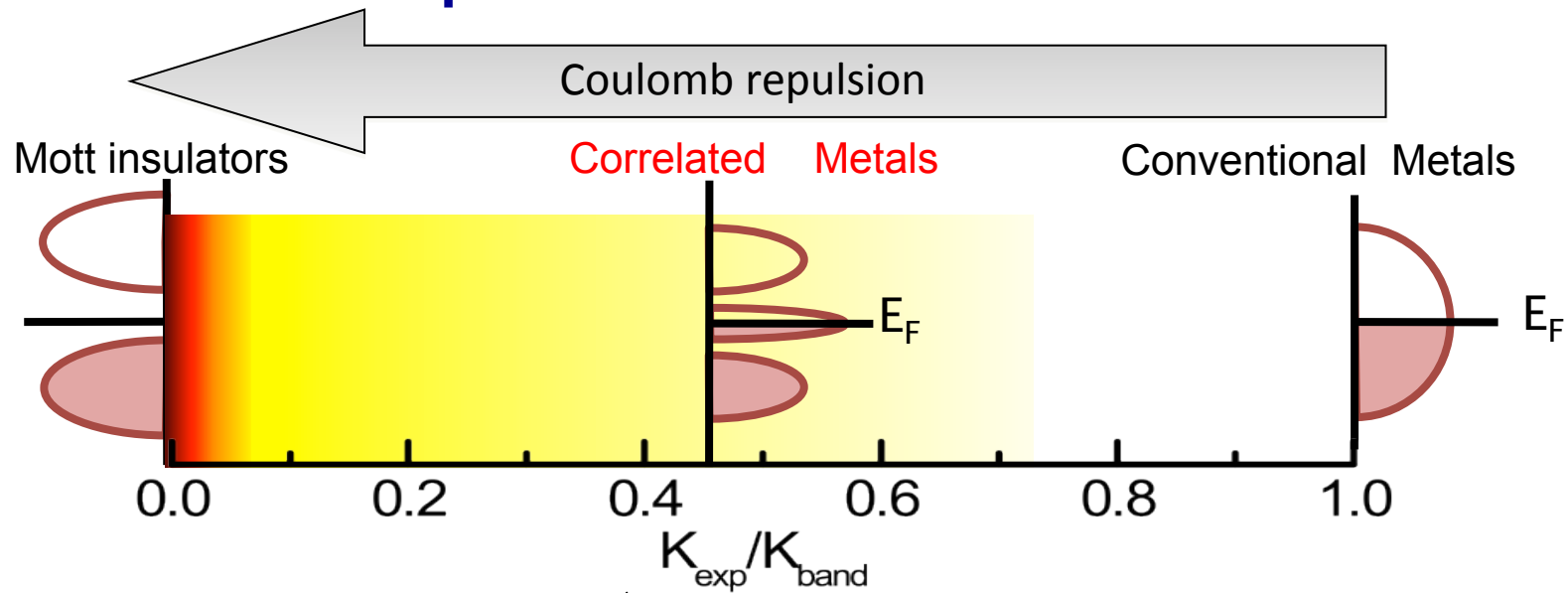


Paul Drude

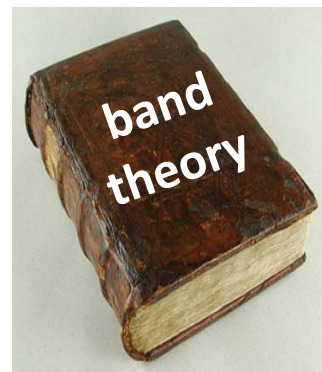
$$K_{\text{exp}} = \int \sigma_1^{\text{Drude}}(\omega) d\omega$$

M.Qazilbash J. Hamlin, R. E. Baumbach, L. Zhang, D.J. Singh, M.B. Maple, and D.N. Basov et al. *Nature-Physics* 5, 647 (2009)  
A.J. Millis et al. *PRB* 72, 224517 (2005)

## An IR probe of electronic correlations



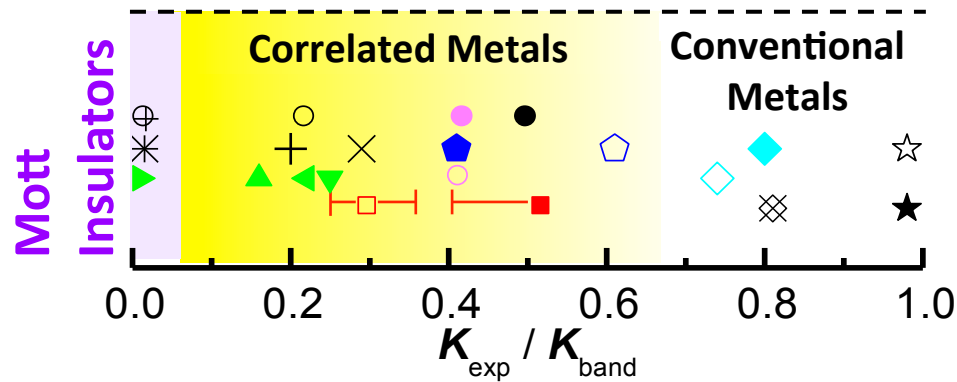
Paul Drude



$$K_{\text{exp}} = \int \sigma_1^{\text{Drude}}(\omega) d\omega$$

M.Qazilbash J. Hamlin, R. E. Baumbach, L. Zhang, D.J. Singh, M.B. Maple, and D.N. Basov et al. *Nature-Physics* 5, 647 (2009)  
 A.J. Millis et al. *PRB* 72, 224517 (2005)

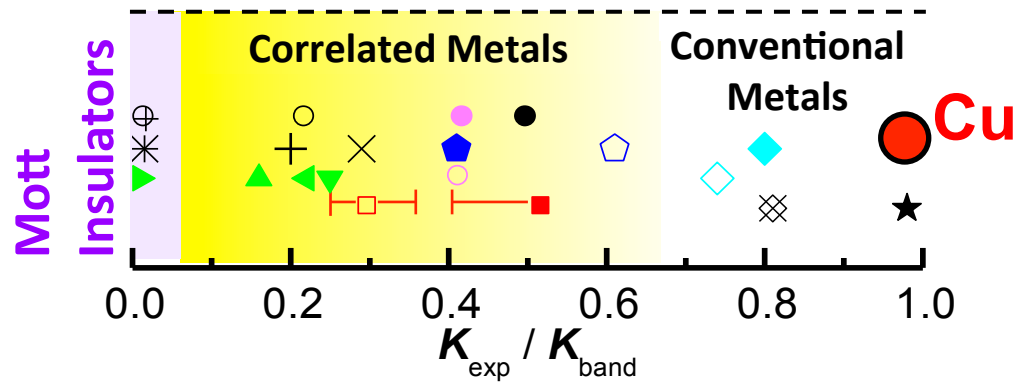
## Electronic correlations in pnictides



- |  |   |
|--|---|
| $\blacksquare$ LaFePO  | $\bullet$ VO <sub>2</sub> (rutile metal)                |
| $\square$ BaFe <sub>2</sub> As <sub>2</sub>                                      | $\circ$ V <sub>2</sub> O <sub>3</sub> (metal)           |
| $\blacktriangleright$ La <sub>2</sub> CuO <sub>4</sub>                           | $\bullet$ $\kappa$ -(BEDT-TTF)Cu[N(CN) <sub>2</sub> ]Br |
| $\blacktriangle$ La <sub>2-x</sub> Sr <sub>x</sub> CuO <sub>4</sub> (x=0.1)      | $\circ$ $\kappa$ -(BEDT-TTF)Cu(SCN) <sub>2</sub>        |
| $\blacktriangleleft$ La <sub>2-x</sub> Sr <sub>x</sub> CuO <sub>4</sub> (x=0.15) | $\blacklozenge$ Sr <sub>2</sub> RuO <sub>4</sub>        |
| $\blacktriangleright$ La <sub>2-x</sub> Sr <sub>x</sub> CuO <sub>4</sub> (x=0.2) | $\blacklozenge$ SrRuO <sub>3</sub>                      |
| $\ast$ Nd <sub>2</sub> CuO <sub>4</sub>  | $\diamond$ CrO <sub>2</sub>                             |
| $+$ Nd <sub>2-x</sub> Ce <sub>x</sub> CuO <sub>4</sub> (x=0.1)                   | $\blacklozenge$ Cr                                      |
| $\times$ Nd <sub>2-x</sub> Ce <sub>x</sub> CuO <sub>4</sub> (x=0.15)             | $\otimes$ MgB <sub>2</sub>                              |
| $\oplus$ NiO   | $\star$ Ag $\star$ Cu                                   |

M.Qazilbash J. Hamlin, R. E. Baumbach, L. Zhang, D.J. Singh, M.B. Maple, and D.N. Basov et al. *Nature-Physics* 5, 647 (2009)  
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## Electronic correlations in pnictides

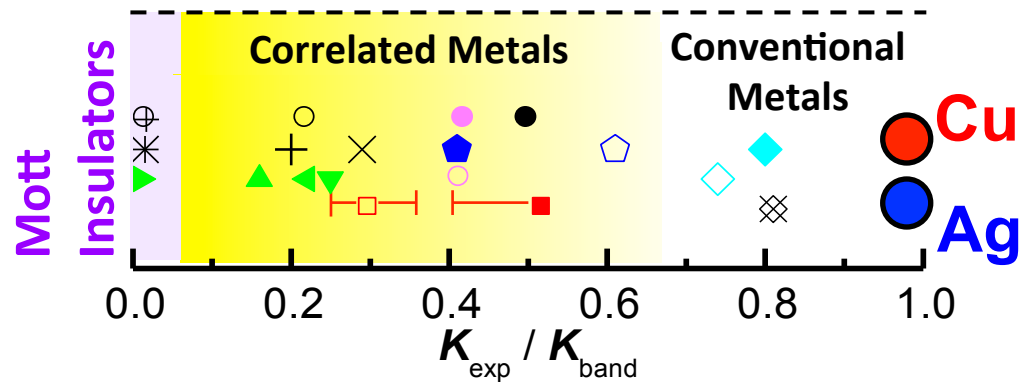


- |   |   |
|---|---|
| ■ LaFePO  | ● VO <sub>2</sub> (rutile metal)        |
| □ BaFe <sub>2</sub> As <sub>2</sub>                           | ○ V <sub>2</sub> O <sub>3</sub> (metal) |
| ▶ La <sub>2</sub> CuO <sub>4</sub>                            | ● κ-(BEDT-TTF)Cu[N(CN) <sub>2</sub> ]Br |
| ▲ La <sub>2-x</sub> Sr <sub>x</sub> CuO <sub>4</sub> (x=0.1)  | ○ κ-(BEDT-TTF)Cu(SCN) <sub>2</sub>      |
| ◀ La <sub>2-x</sub> Sr <sub>x</sub> CuO <sub>4</sub> (x=0.15) | ◆ Sr <sub>2</sub> RuO <sub>4</sub>      |
| ▼ La <sub>2-x</sub> Sr <sub>x</sub> CuO <sub>4</sub> (x=0.2)  | ◇ SrRuO <sub>3</sub>                    |
| * Nd <sub>2</sub> CuO <sub>4</sub>                            | ◇ CrO <sub>2</sub>                      |
| + Nd <sub>2-x</sub> Ce <sub>x</sub> CuO <sub>4</sub> (x=0.1)  | ◆ Cr                                    |
| × Nd <sub>2-x</sub> Ce <sub>x</sub> CuO <sub>4</sub> (x=0.15) | ⊗ MgB <sub>2</sub>                      |
| ⊕ NiO   | ★ Ag ☆ Cu                               |

M.Qazilbash J. Hamlin, R. E. Baumbach, L. Zhang, D.J. Singh, M.B. Maple, and D.N. Basov et al. *Nature-Physics* 5, 647 (2009)  
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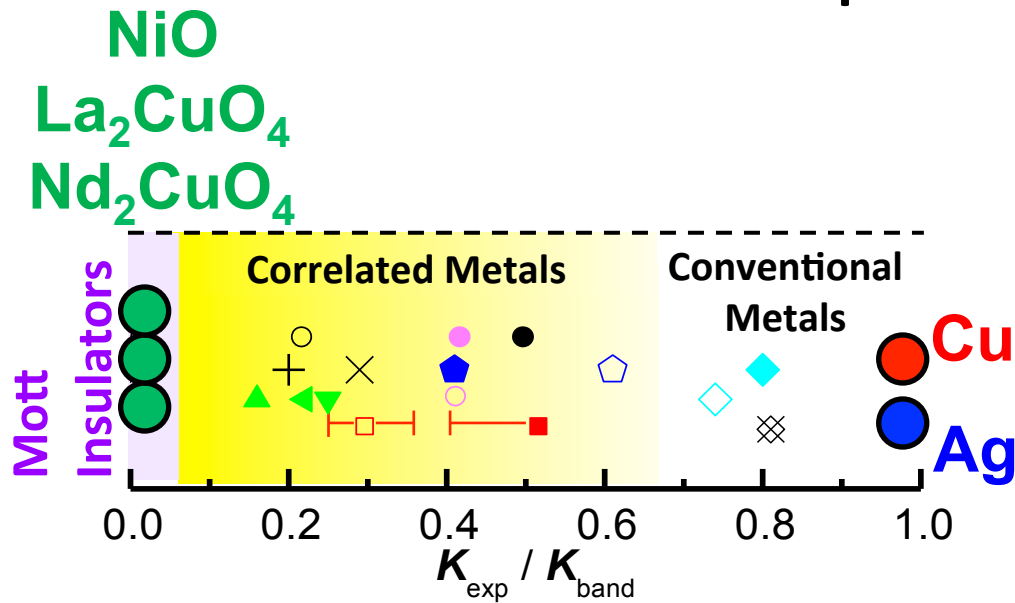
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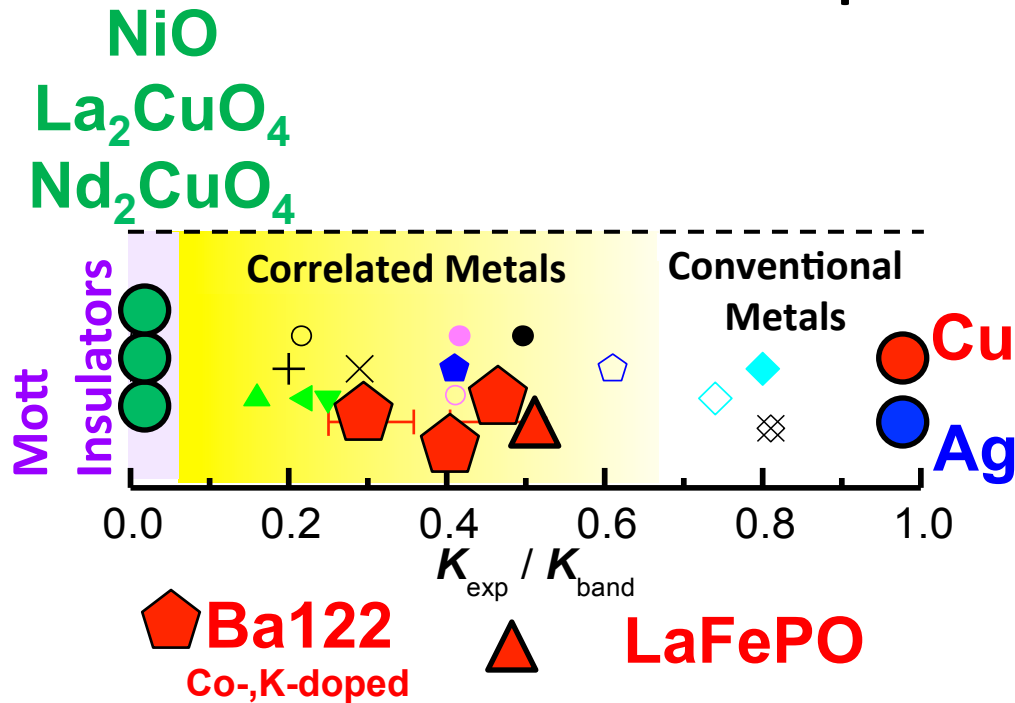
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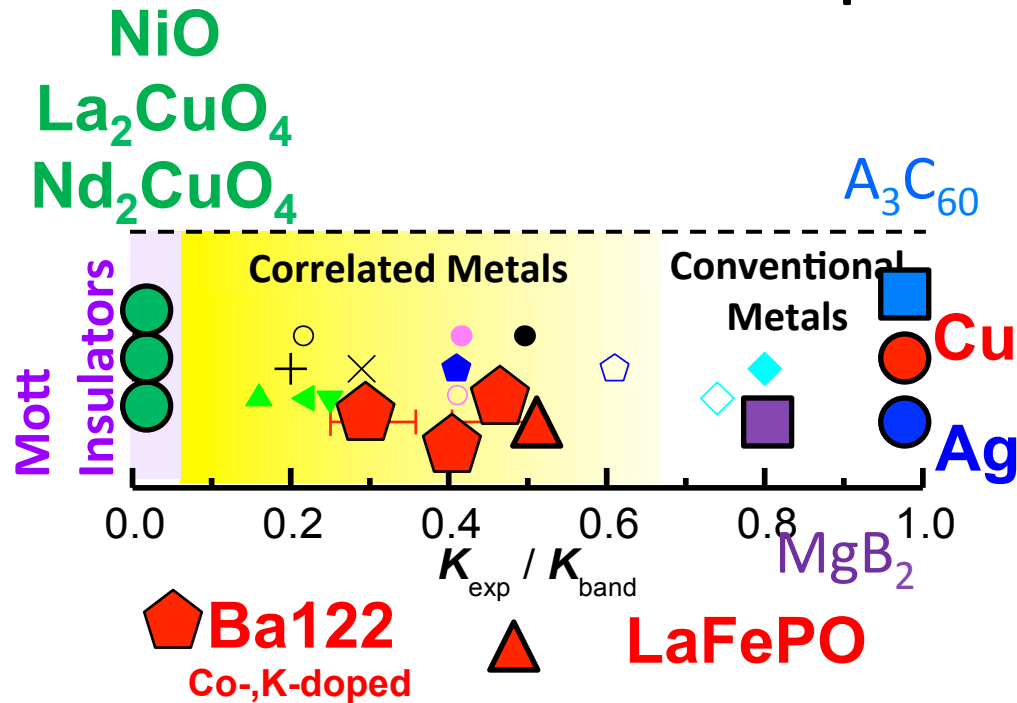
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M.Qazilbash J. Hamlin, R. E. Baumbach, L. Zhang, D.J. Singh, M.B. Maple, and D.N. Basov et al. *Nature-Physics* 5, 647 (2009)  
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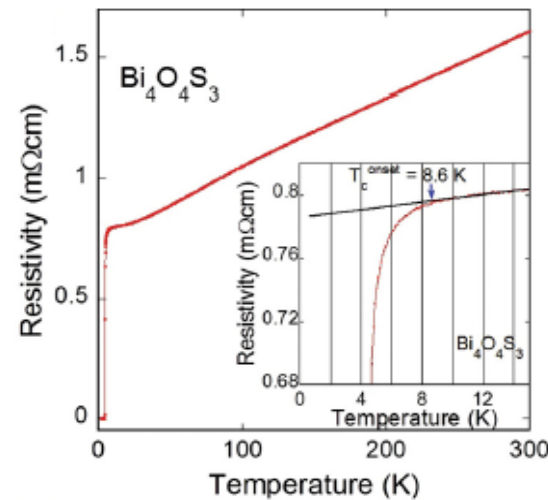
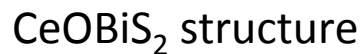
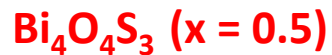
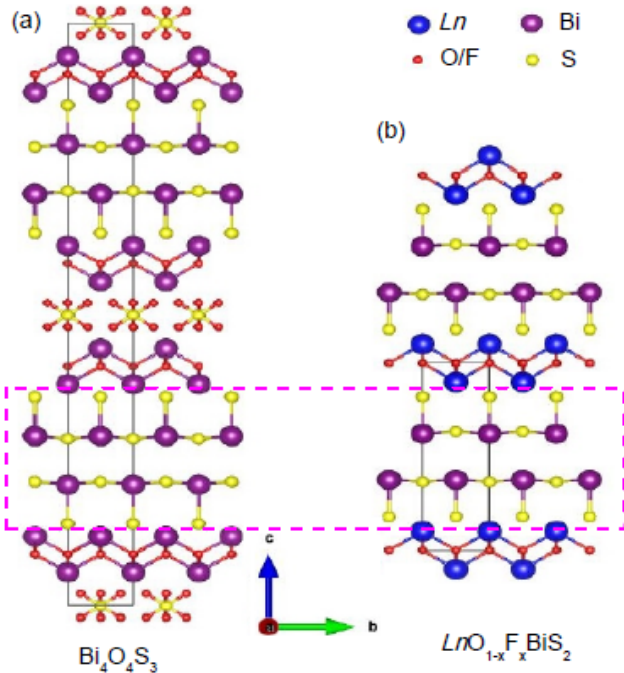
M.Qazilbash J. Hamlin, R. E. Baumbach, L. Zhang, D.J. Singh, M.B. Maple, and D.N. Basov et al. *Nature-Physics* 5, 647 (2009)  
 A.J. Millis et al. *PRB* 72, 224517 (2005)

## *Outline*

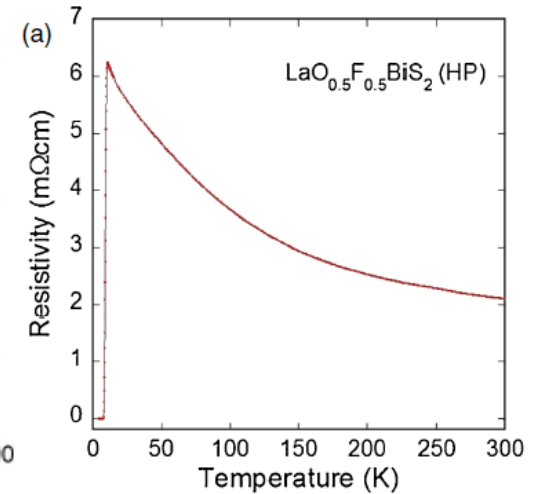
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- Prospects for the future

## Superconductivity in $\text{BiS}_2$ -based materials



Mizuguchi et al., *PRB*  
**86**, 220510(R) (2012)

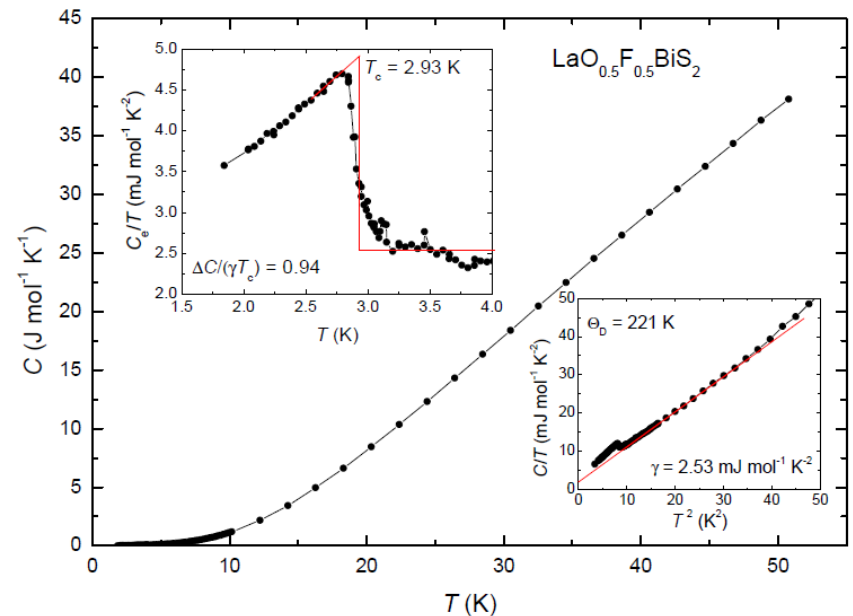
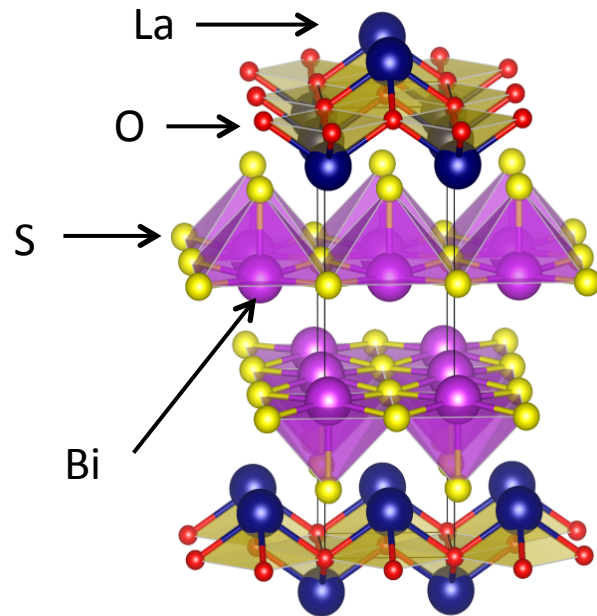
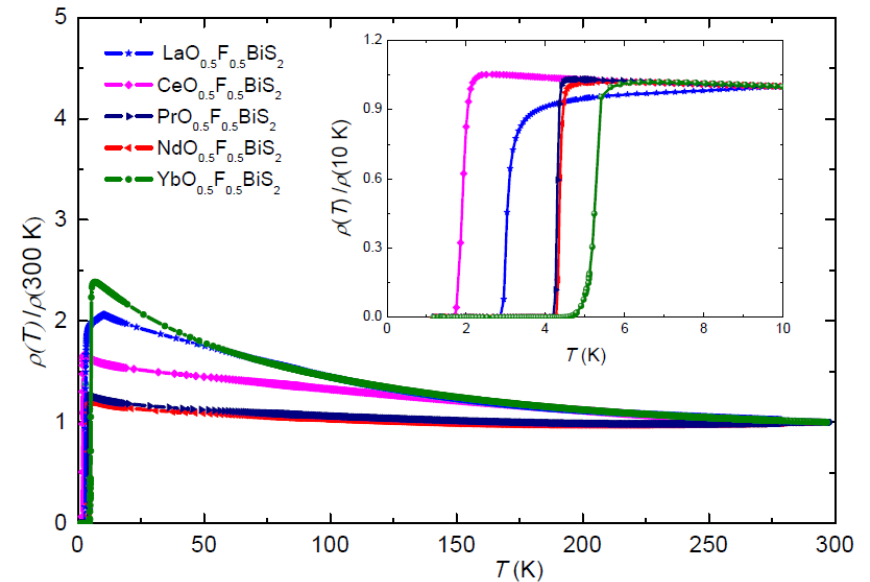


Mizuguchi et al., *JPSJ*  
**81**, 114725 (2012)

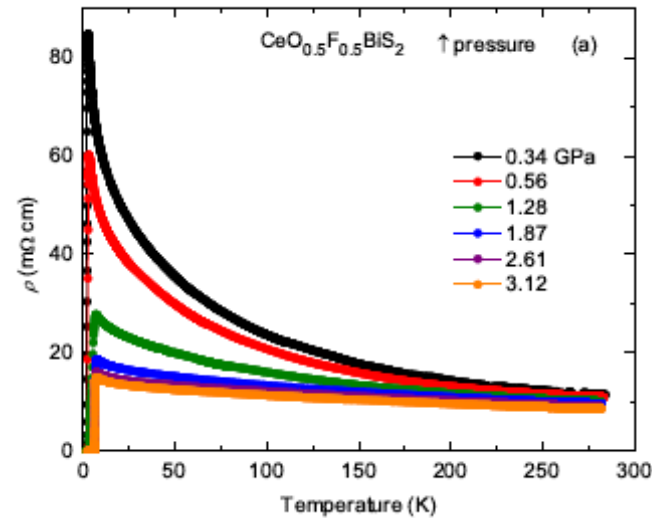
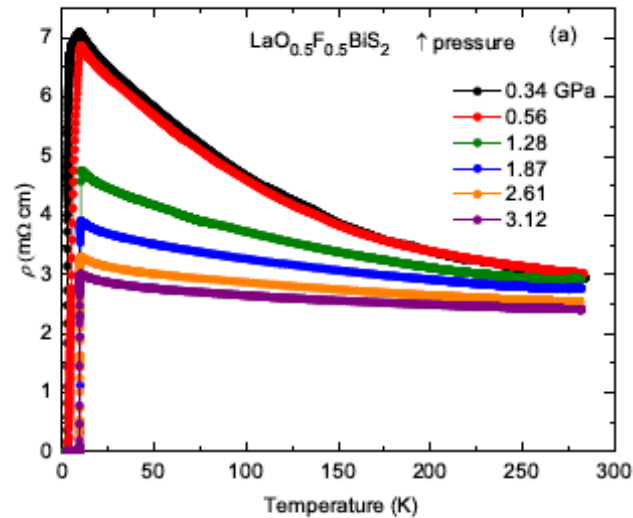
| Material                                     | $T_c$        | Reference   |
|--|--------------|---|
| $\text{Bi}_4\text{O}_4\text{S}_3$            | 4.7 K        | Mizuguchi et al., <i>PRB</i> <b>86</b> , 220510(R) (2012)                     |
| $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ | 10.6 K/3.1 K | Mizuguchi et al., <i>JPSJ</i> <b>81</b> , 114725 (2012)                       |
| $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ | 1.89 K       | Yazici et al., and Xing et al., <i>PRB</i> <b>86</b> , 214518 (2012)          |
| $\text{PrO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ | 4.29 K       | Yazici et al. and Jha et al., <i>J. SC. Nov. Mag.</i> <b>26</b> , 499 (2013)  |
| $\text{NdO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ | 4.37 K       | Yazici et al. and Demura et al., <i>J. Phys. Soc. Jpn.</i> , <b>82</b> (2013) |
| $\text{YbO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ | 5.30 K       | Yazici et al., <i>Phil. Mag.</i> <b>93</b> , 673 (2013)                       |

## Superconductivity in $\text{LnO}_{1-x}\text{F}_x\text{BiS}_2$ compounds

- SC of  $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2 - T_c \approx 8.5$  K (HP synthesis)  
*Mizuguchi et al., JPSJ 81, 114725 (2012)*
- SC of  $\text{LnO}_{0.5}\text{F}_{0.5}\text{BiS}_2$  for  $\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Yb}$   
 (electron doping via F substitution)  
*Yazici et al., Phil. Mag. 93, 673 (2013)*
- SC of  $\text{LnOBiS}_2$  induced by electron doping  
 via substitution of tetravalent Ti, Zr, Hf, Th  
*Yazici et al., PRB 87, 174512 (2013)*

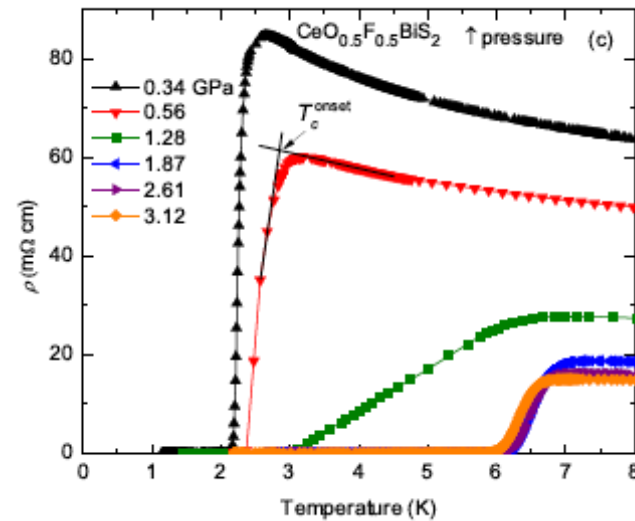
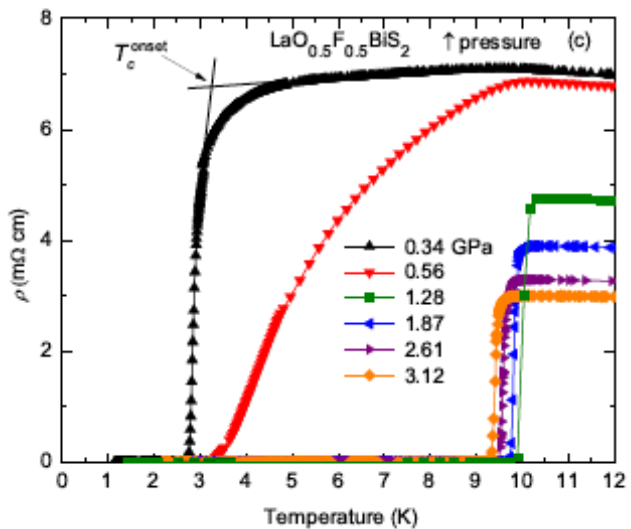


## Electrical resistivity of $\text{LnO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ ( $\text{Ln} = \text{La}, \text{Ce}$ ) under pressure



Left panel:  
 $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$

Right panel:  
 $\text{CeO}_{0.5}\text{F}_{0.5}\text{BiS}_2$

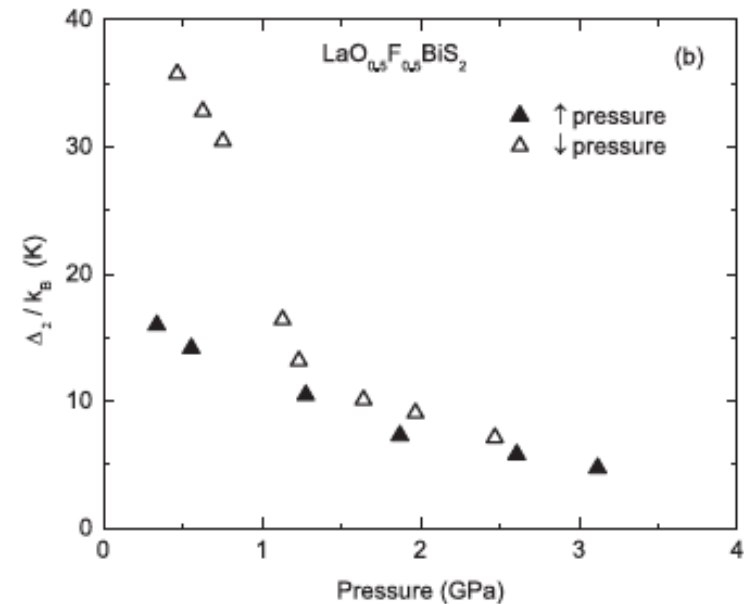
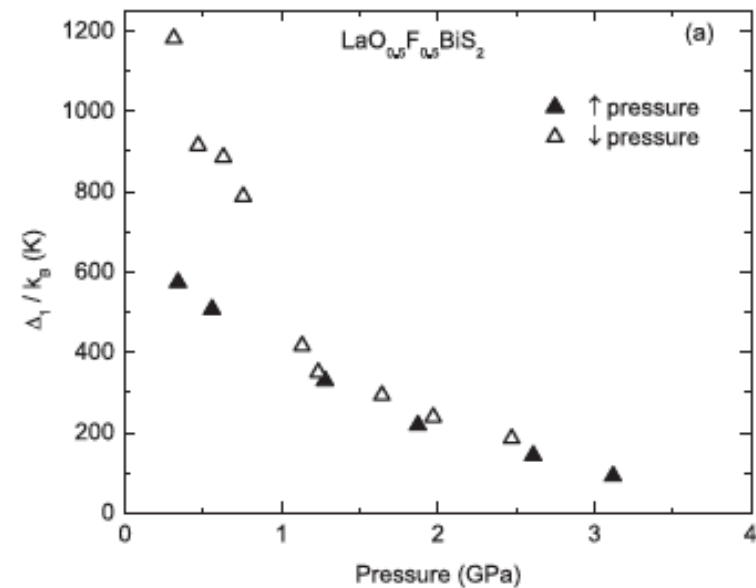
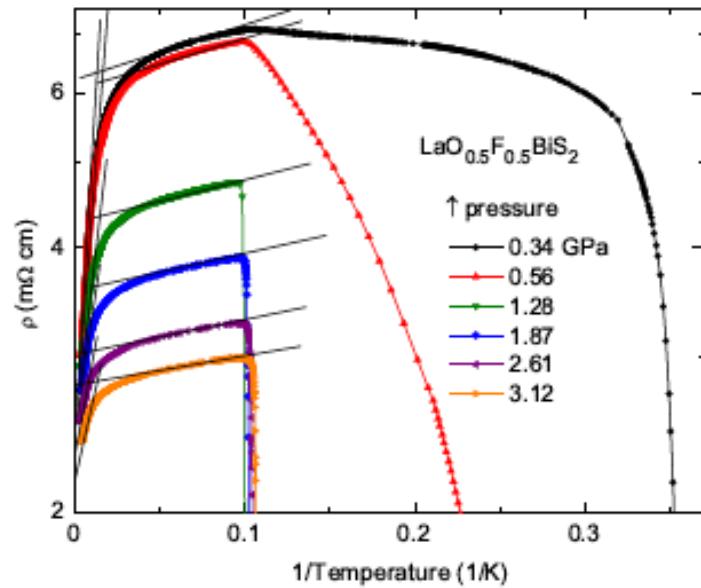


*C. T. Wolowiec et al., Phys. Rev. B **88**, 064503 (2013)*

- Reversible semiconductor-metal transition under  $P$
- Reversible transition between low and high  $T_c$  superconducting phases under  $P$

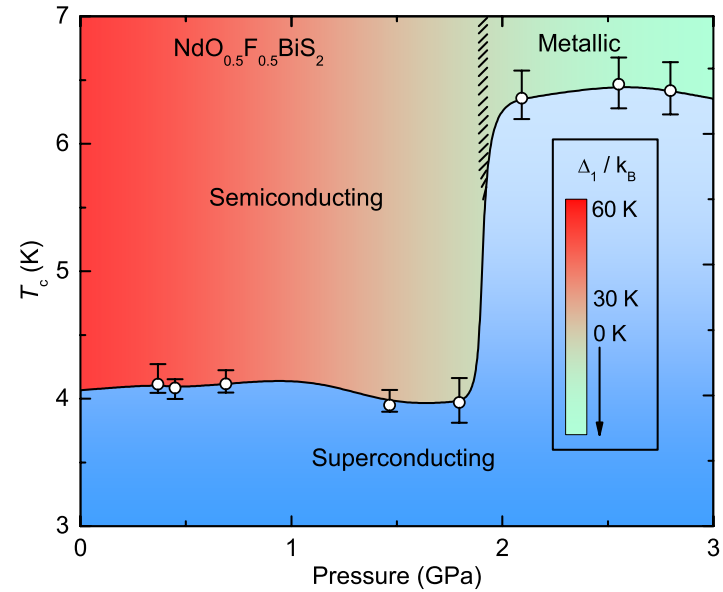
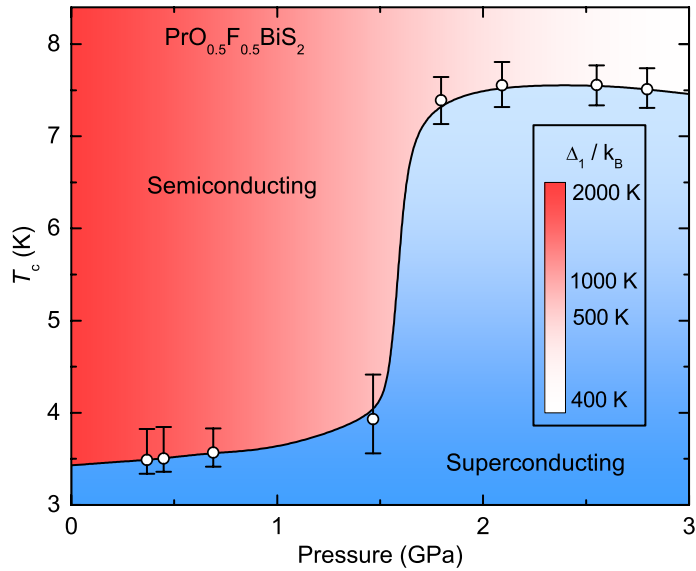
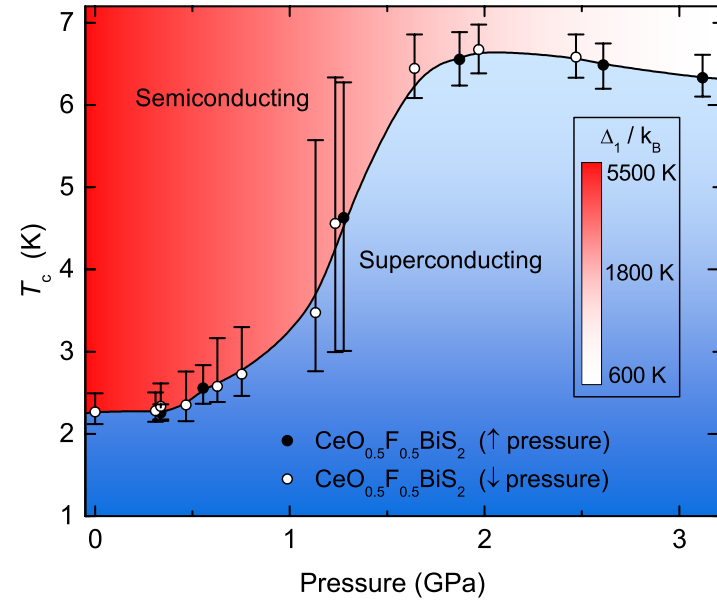
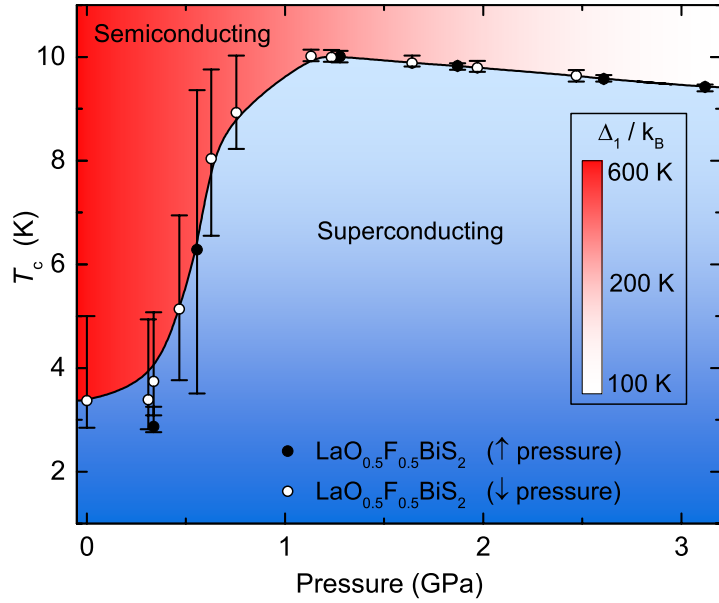


## Semiconducting energy gaps for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$

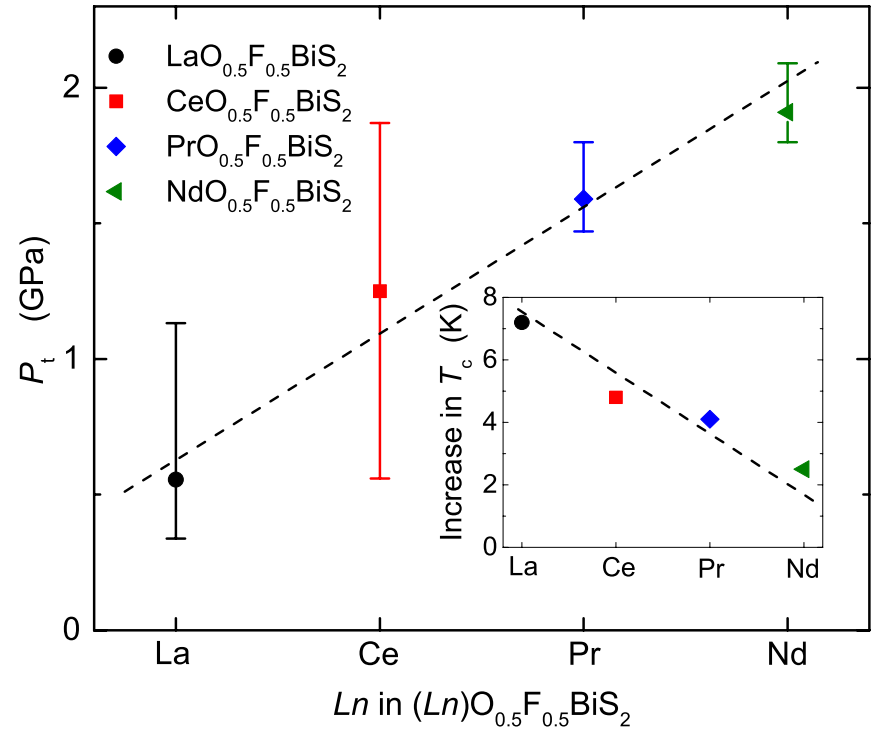
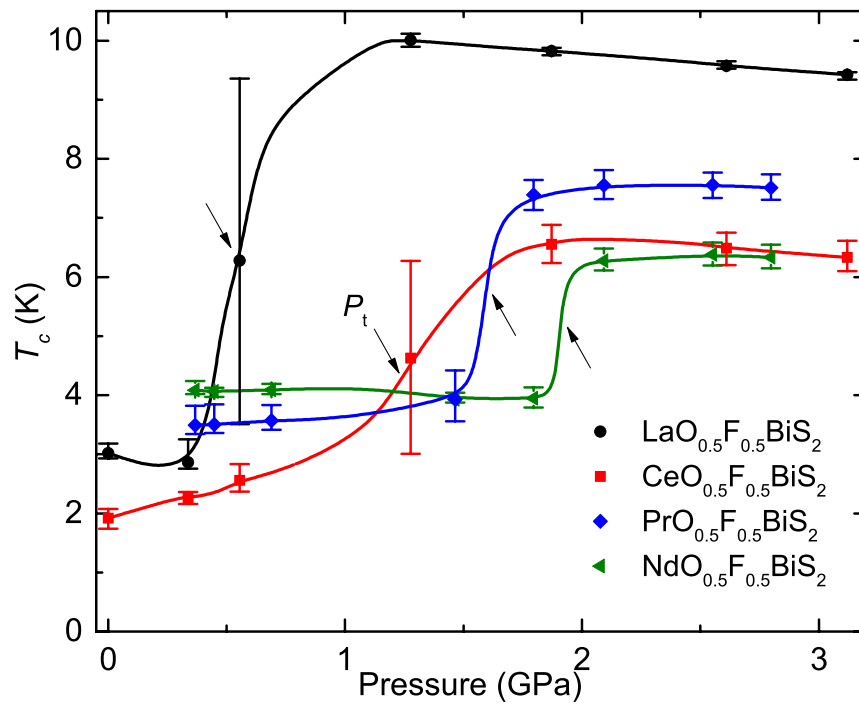


- $\rho(T) = \rho_0 \exp(\Delta/T) \Rightarrow \ln[\rho(T)] = \ln(\rho_0) + \Delta/T$
- Extract  $\Delta$  from plot of  $\ln[\rho(T)]$  vs  $1/T$
- $\Delta_1 \approx 600$  K and  $\Delta_2 \approx 17$  K for  $P = 0.34$  GPa
- $\Delta_1$  and  $\Delta_2$  both decrease rapidly with  $P$  and exhibit kink near  $P_t \approx 1.2$  GPa
- $\Delta_1$  – intrinsic?  $\Delta_2$  – impurity level?
- $\Delta_1, \Delta_2$  hysteretic –  $P < P_t$ ; reversible –  $P > P_t$
- Similar results: *H. Kotegawa et al., J. Phys. Soc. Jpn. 81, 103702 (2012)*

## Pressure dependence of $T_c$ and $\Delta_1$ for $\text{LnO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ ( $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$ )



## Transition pressure $P_t$ vs rare earth atomic number

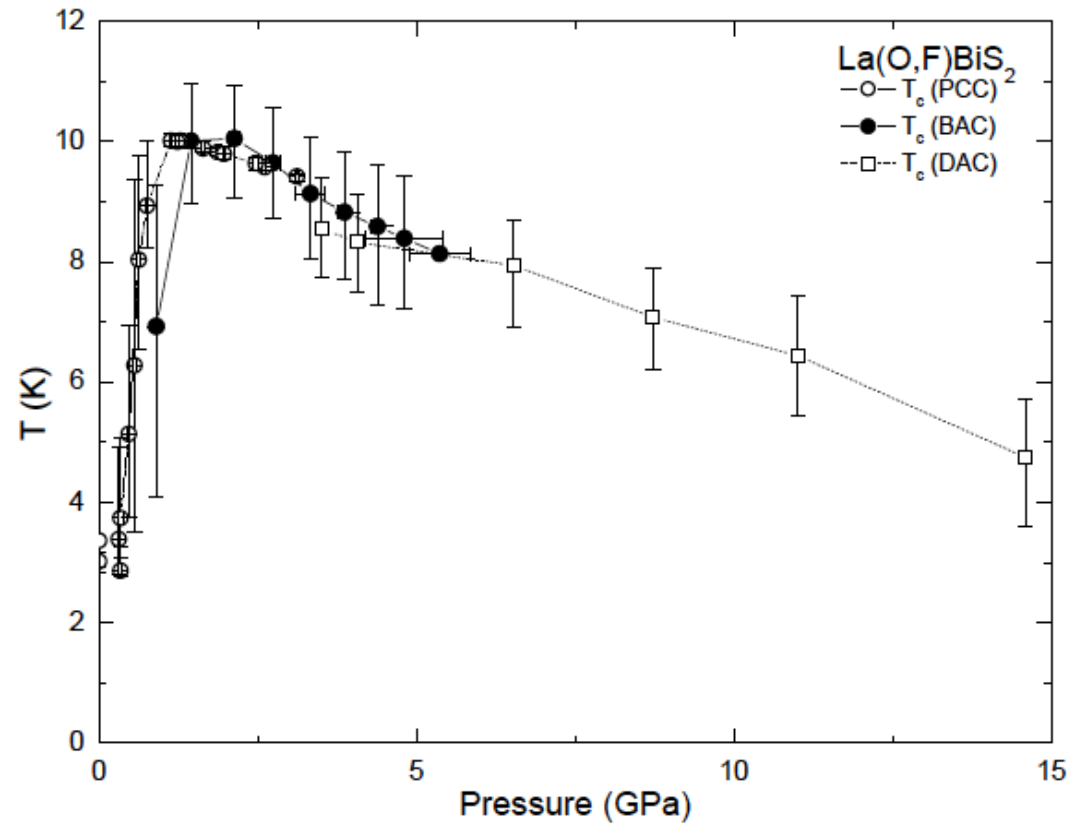
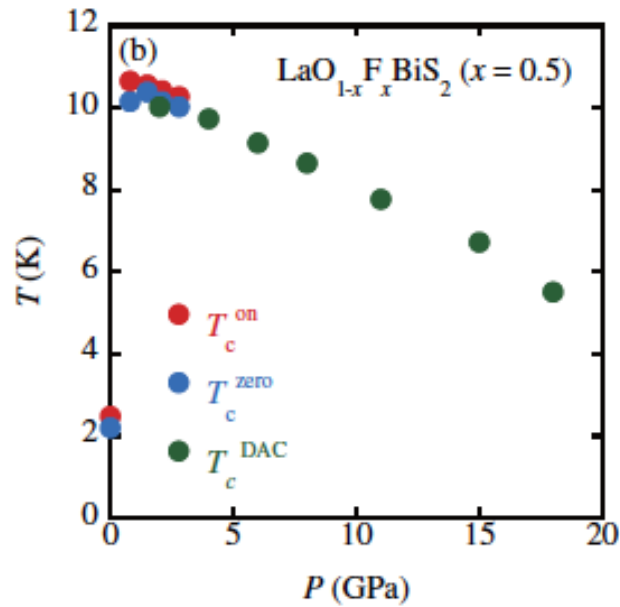
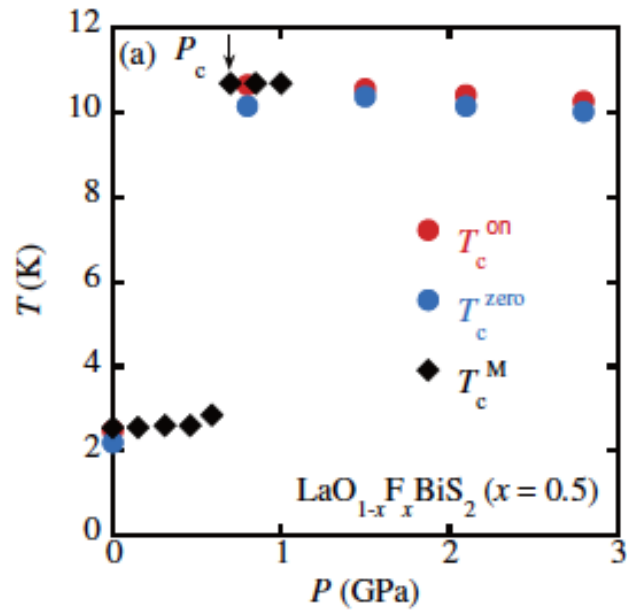


- $P_t$  increases with  $Ln$  atomic number
- Increase in  $T_c$  at  $P_t$  decreases with  $Ln$  atomic number
- Conjecture: Structural transition occurs at  $P_t$
- Evidence of structural transition at  $P_t \approx 1$  GPa in  $LaO_{0.5}F_{0.5}BiS_2$

*R. Kumar et al., 2013*

*T. Tomita et al., JPSJ 83, 063704 (2014)*

## Pressure dependence of $T_c$ of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ to 20 GPa



*C. A. McElroy et al. (2013) (UCSD)*

*T. Tomita et al., JPSJ 83, 063704 (2014)*

## *Outline*

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- Historical remarks about development of SC'ing materials
- Heavy fermion f-electron SC's
- Emergence of SC from magnetic order, unconventional SC, and electron pairing via spin fluctuations
- Copper oxide (cuprate) SC's
- Iron pnictide/chalcogenide SC's
- Evidence for strong electronic correlations
- New class of layered SC's based on LnOBiS<sub>2</sub>
- Prospects for the future

## *Summary*

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- Brief survey of the basic properties of heavy fermion f-electron, cuprate, and iron pnictide/chalcogenide materials
- “Unconventional” SC often found to “emerge” from a magnetically-ordered phase upon variation of chemical composition or pressure
- Evidence for pairing of SC’ing electrons via spin fluctuations
- Cannot exclude other pairing scenarios, especially for the cuprates
- No “smoking gun” test for pairing mechanisms – need preponderance of evidence!
- Correlated electron materials
- New class of layered SC’s based on LnOBiS<sub>2</sub> parent compounds
- Have not discussed emergence of SC from other spin and charge ordered phases (e.g., FM – UGe<sub>2</sub>; CDW – LnTe<sub>3</sub>; quadrupolar order – PrOs<sub>4</sub>Sb<sub>12</sub>; “hidden order” – URu<sub>2</sub>Si<sub>2</sub>)

## *Prospects for the future*

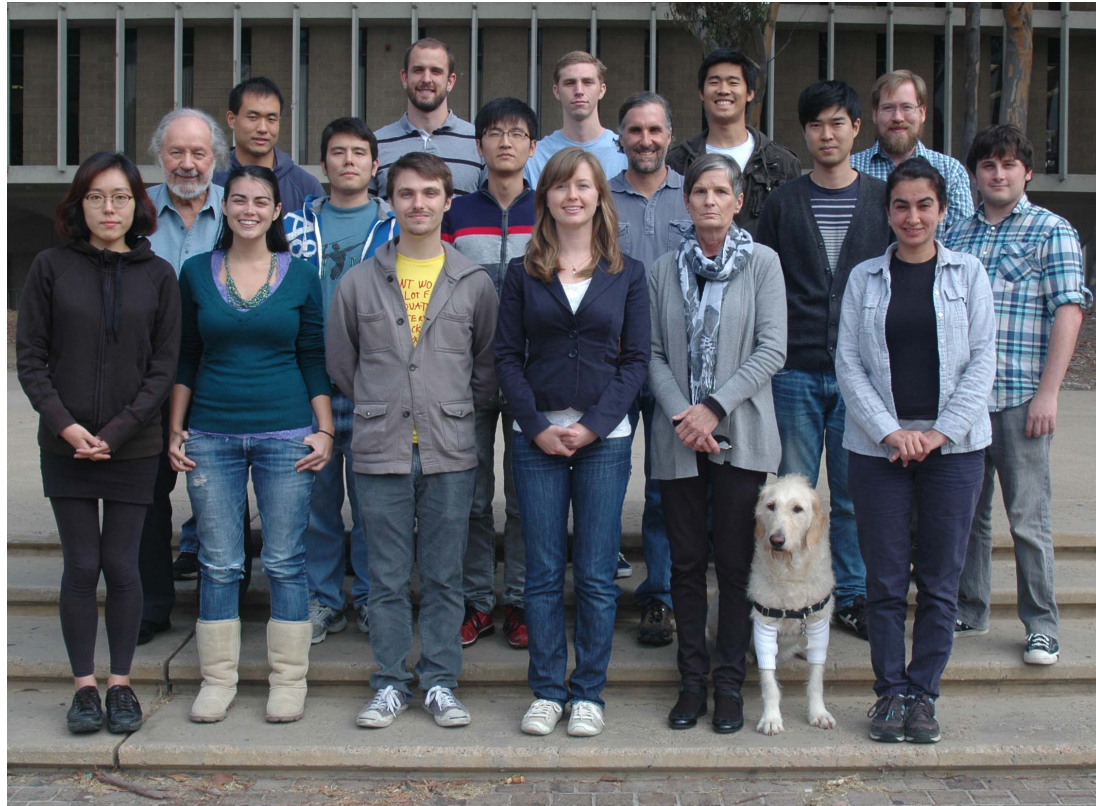
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- Many new superconducting materials with high (and, hopefully, higher!) values of  $T_c$  remain to be discovered
- Superconductivity near room temperature no longer seems impossible!
- Where should one look for new high  $T_c$  superconductors?
- A new set of guiding principles to replace Matthias' "rules" is suggested by the superconductors with the highest values of  $T_c$  ( $> 40$  K)
- One might look for:
  - ✦ Correlated electron materials
  - ✦ Complex materials containing many different types of atoms
  - ✦ Materials containing elements with partially-filled d- and f-electron shells
  - ✦ Materials containing oxygen
  - ✦ Materials with layered crystal structures with low symmetry
  - ✦ Materials that exhibit magnetism
  - ✦ Probably not a good idea to avoid theorists

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*END*