Superconducting materials: conventional and unconventional

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Outline

I. Unconventional superconductors

Common features

II. Chronology for new superconductor before cuprates

III. Superconductors discovered after Cuprate Superconductors

*** Unconventional superconductors**

Triangle lattice $Na_xCoO_2 \cdot yH_2O$, Sr_2RuO_4 with p-wave symmetry,

Heavy Fermion, Ferromagnetic SC, Non-centrosymmetry,

*** Superconductors with Tc>20 K**

Intercalated HfNCl, MgB_2, $Ba_{1-x}K_xBiO_3$, Fullerides, Organic superconductors,

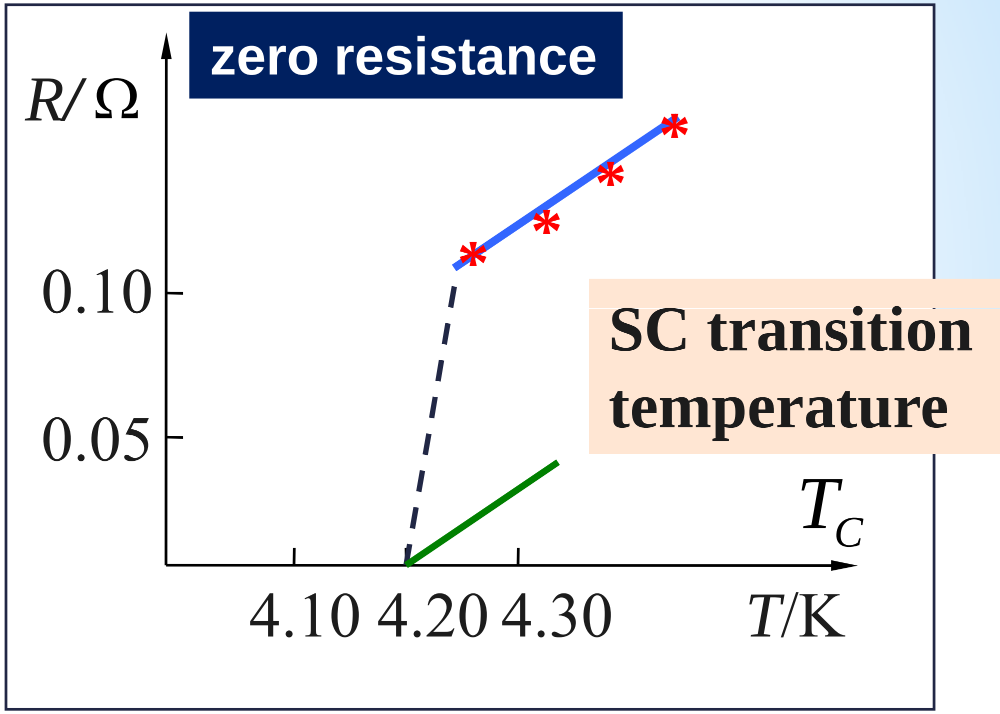
Borocarbides, Iron-pnictides

*** Others and superconductivity induced by different ways**

Liquid gating, pressure, topological superconductor etc.

Discovery of Superconductivity

Heike Kamerlingh Onnes



In 1908, Holland physicist H.K. Onnes successfully liquefied Helium, and a new low temperature region (<4.2K) was then achieved.

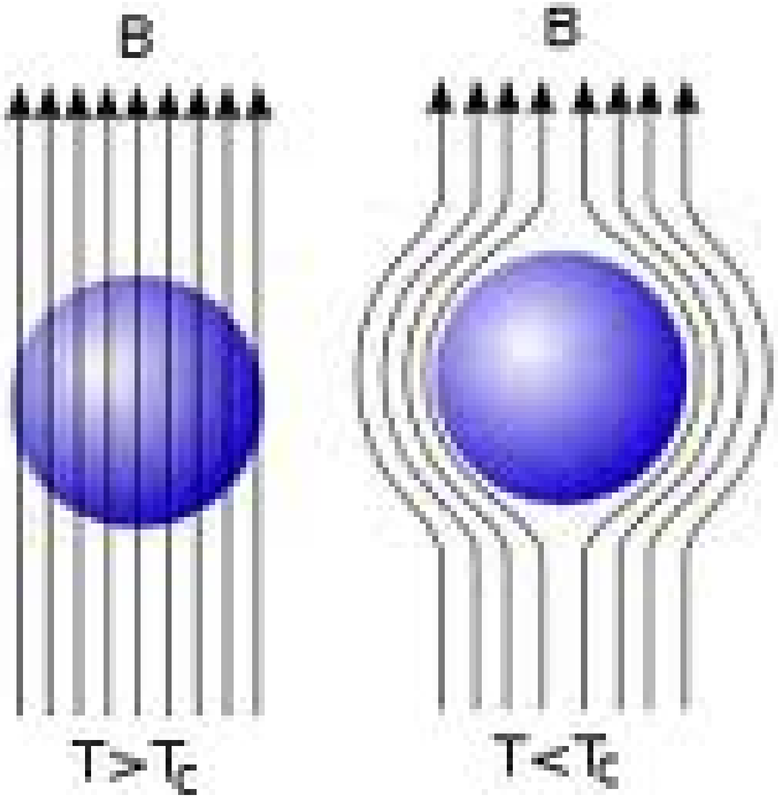
In 1911, he found the resistance of Hg becomes zero as temperature reaches 4.2 K. He named the new state as superconductivity

Nobel award in Physics in 1913

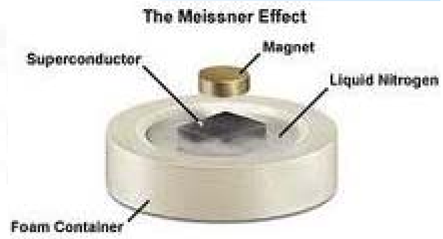
* Perfect Diamagnetism: Meissner Effect

Walter Hans. Meissner

Robert Ochsenfeld



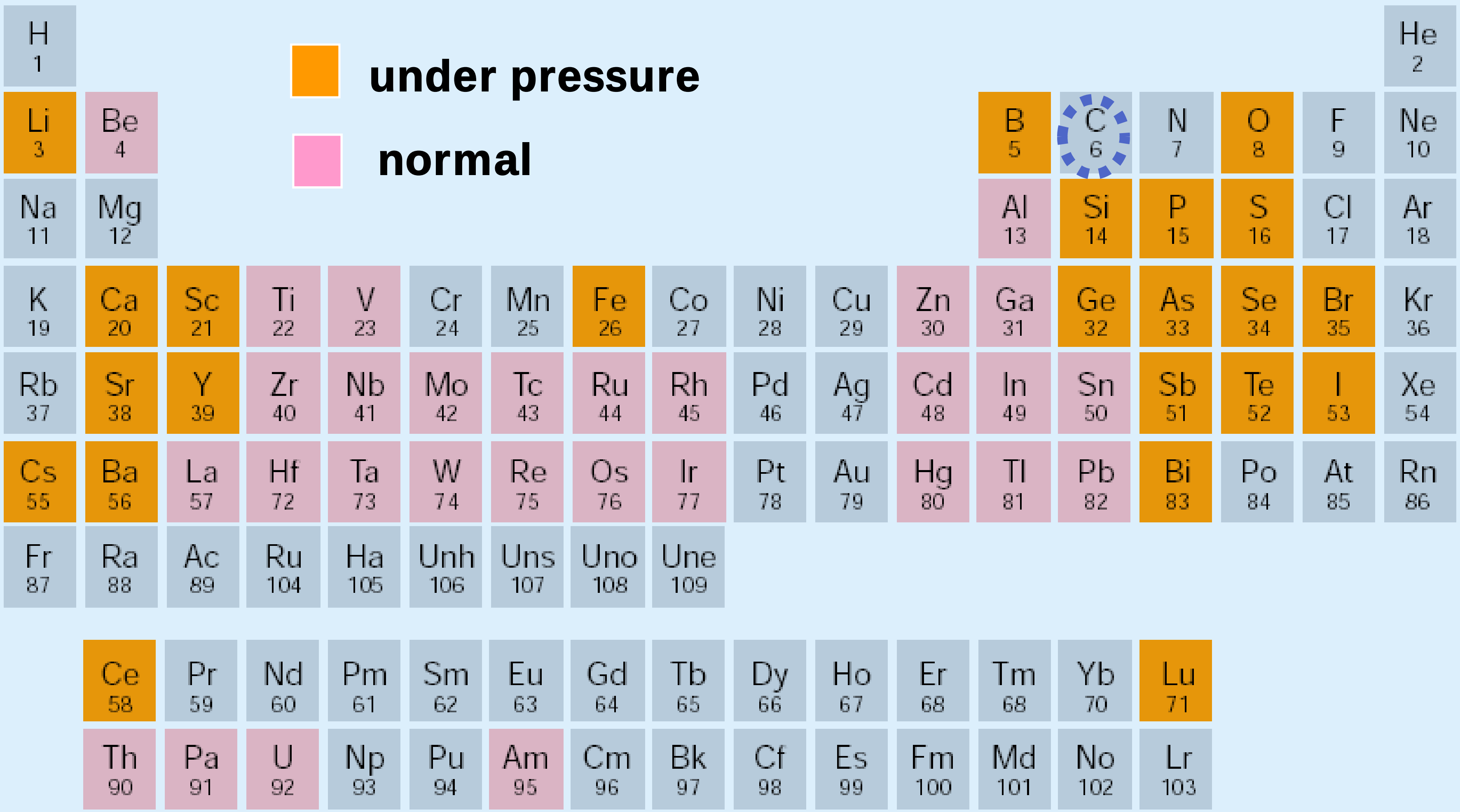
Magnetic suspension



Perfect Diamangetic

1933 W. Hans. Meissner and Robert Ochsenfeld found
Perfect diamagnetism: susceptibility x=−1, Meissner Effect

Elemental Superconductors

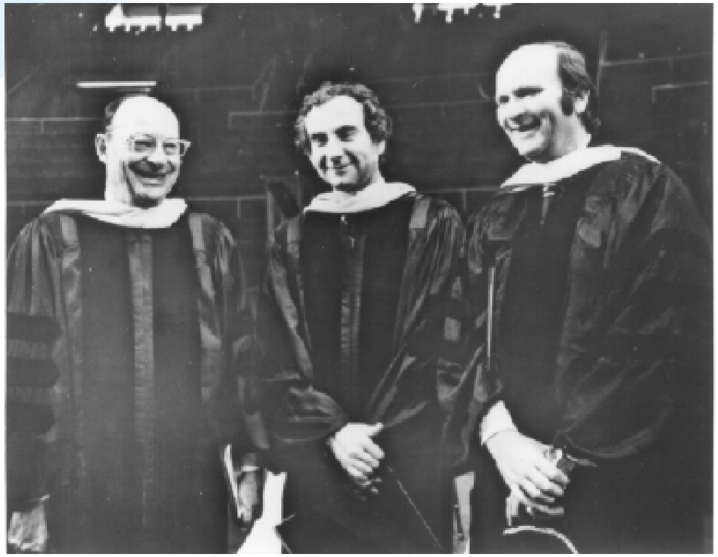


Chronology for new superconductors before cuprates

- In 1911, H. K. Onnes found that Hg exhibited sudden zero resistance at 4.2 K, and defined the new physical state as superconductivity (Nobel award in Physics in 1913).
- In 1913, H. K. Onnes observed SC in Pb below 7.2 K.
- In 1930, metal Nb was found to be superconducting with T_C=9.2 K, which is the highest T_c for pure elemental metals at ambient.
- In 1958, J. Hulm and B. T. Matthias discovered superconductors with *A15* structure and yielded materials with $T_C > 20$ K.
- In 1975, Metal oxide $BaPb_{1-x}Bi_xO_3$ with T_C = 13K.
- In 1979, F. Steglich discovered heavy-fermion superconductor (unconventional).
- In 1980, D. Jerome discovered the first organic superconductor。
- In 1986, K. A. Müller and G. Bednorz discorved the first high-temperature superconductor LaBaCuO with T_C > 30K (Nobel award in Physics in 1987)

Conventional and unconventional superconductivity

Conventional superconductivity: cooper pair mediated by e-p interaction， follows BCS theory McMillan limitation T_c~39 K



Rules of Mathias for discovering conventional superconductors

1. High symmetry is best
2. Peaks in density of states are good
3. Stay away from oxygen
4. Stay away from magnetism
5. Stay away from insulators

B. Matthias

Unconventional superconductivity cannot be explained by BCS theory and Matthias rules: closely related to oxides, magnetism, insulator etc.

Unconventional superconductors

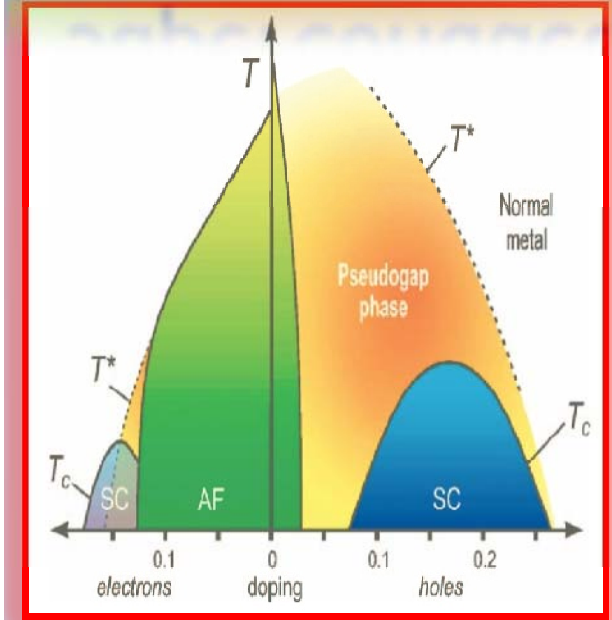
Examples of Superconductors

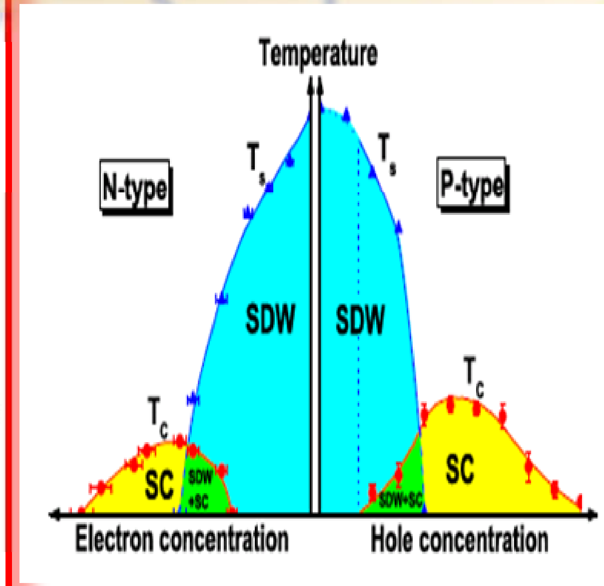
Hg	first superconductor ever discovered	4.1 K
Nb	highest T_c amongst the elements	9.3 K
NbTi	used in superconducting magnets up to ~ 9 T	10 K
Nb_3Sn	used in superconducting magnets up to ~ 20 T	24.5 K
MgB_2	highest T_c amongst "conventional" superconductors	39 K

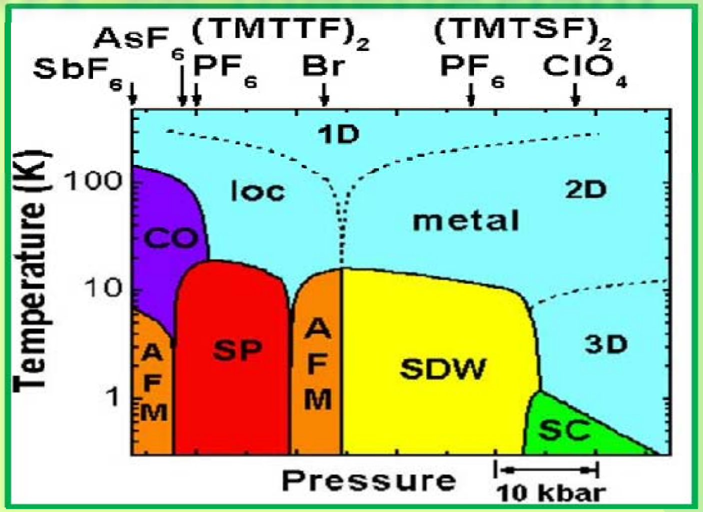
1979

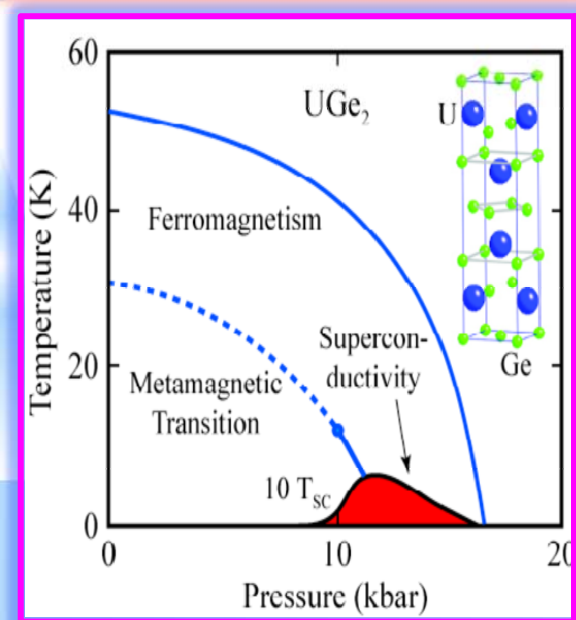
$CeCu_2Si_2$	first of the heavy-fermion superconductors	~0.8 K
$La_{2-x}Ba_xCuO_4$	first of the cuprate superconductors	~35K
$YBa_2Cu_3O_{7-\delta}$	cuprate superconductor with T_c above liquid nitrogen temperatures	92 K
$HgBa_2Ca_2Cu_3O_{8+\delta}$	highest T_c superconductor to date	164 K
Sr_2RuO_4	p-wave superconductor	1.5 K
UGe_2	first ferromagnetic superconductor	0.3 K

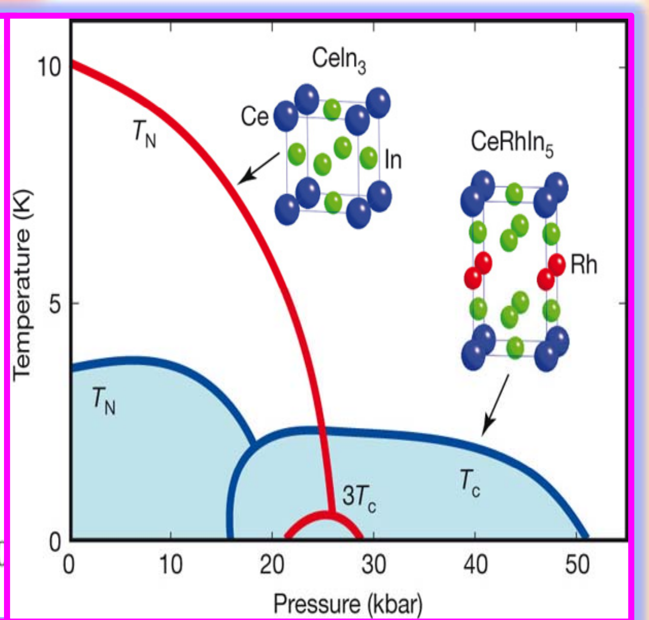
Superconductivity in proximity to magnetism

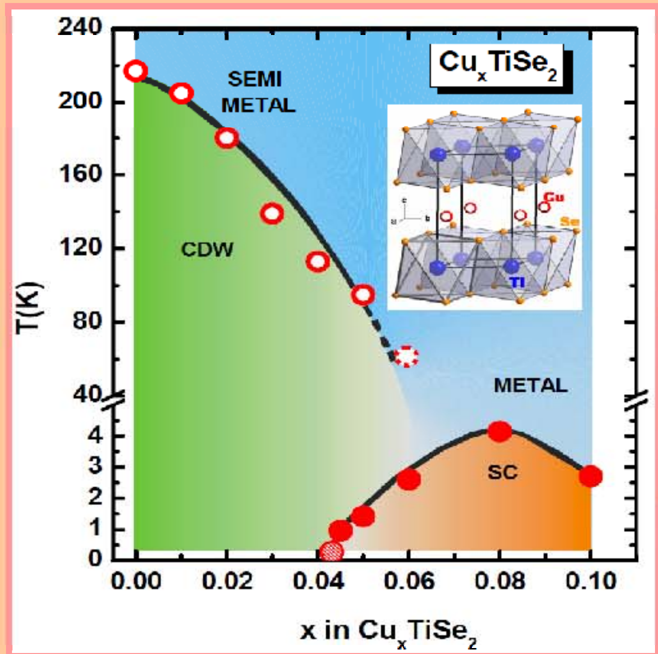




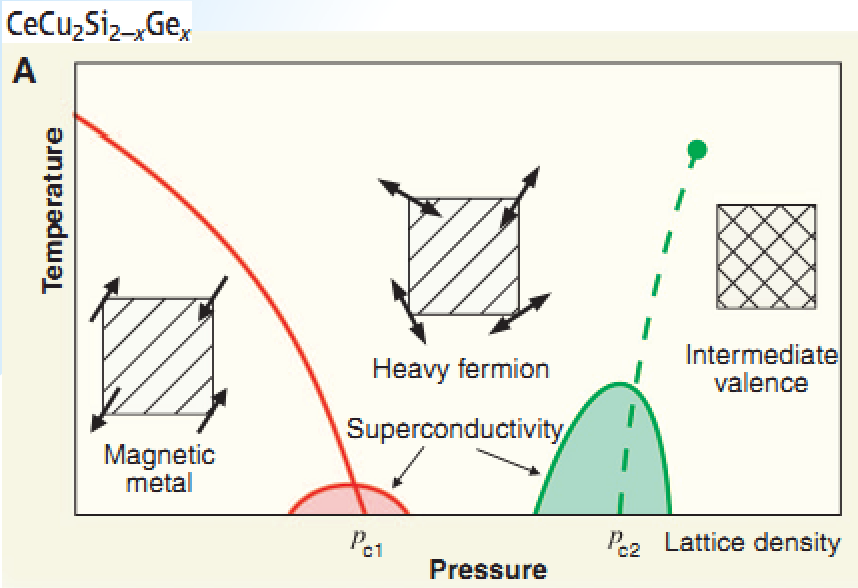


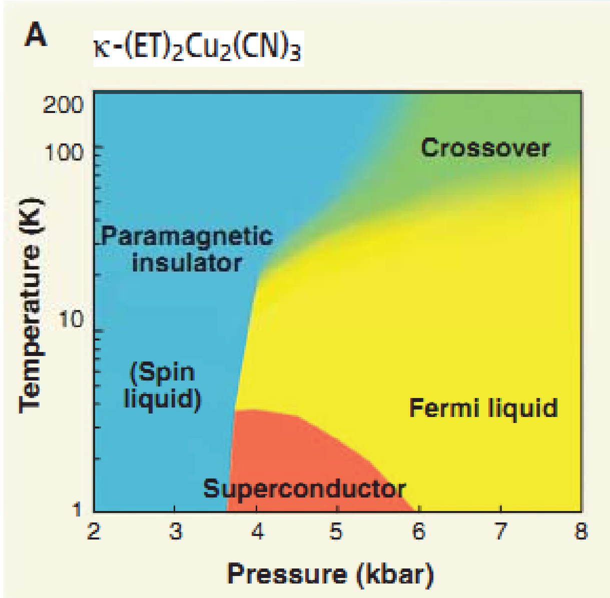


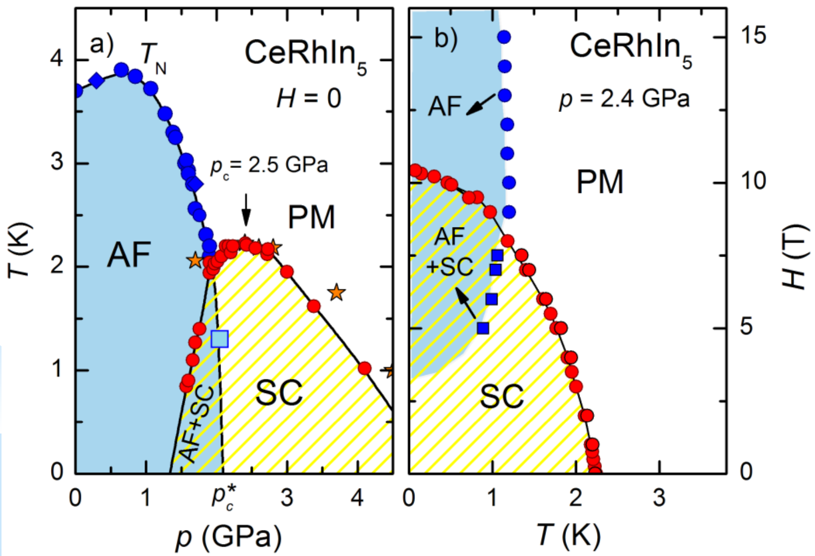


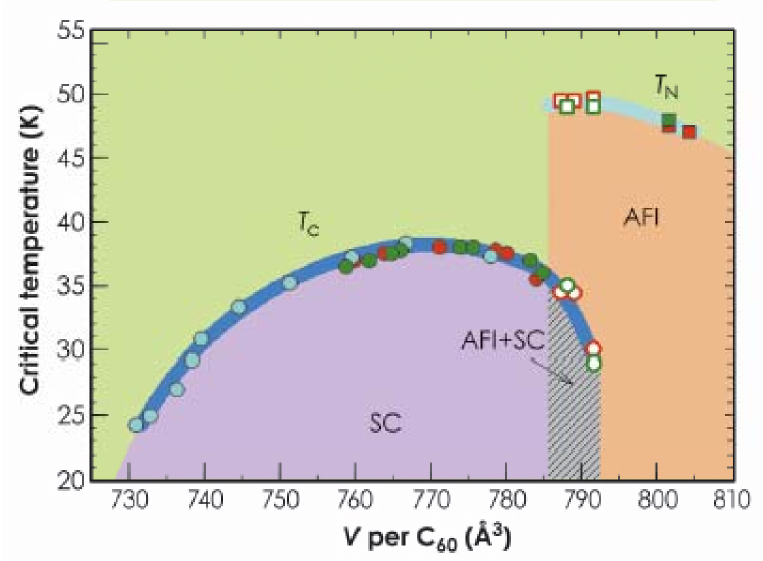


Unconventional superconductivity: external conditions (Pressure)

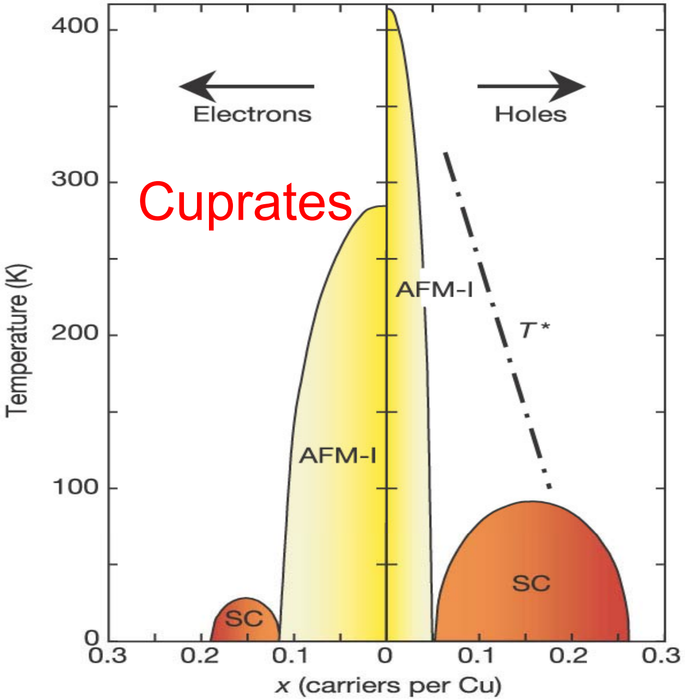


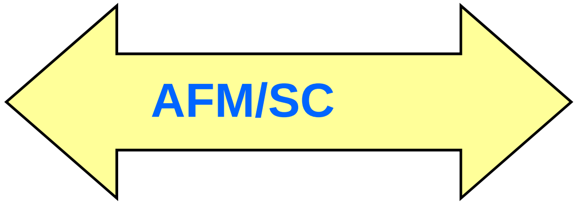


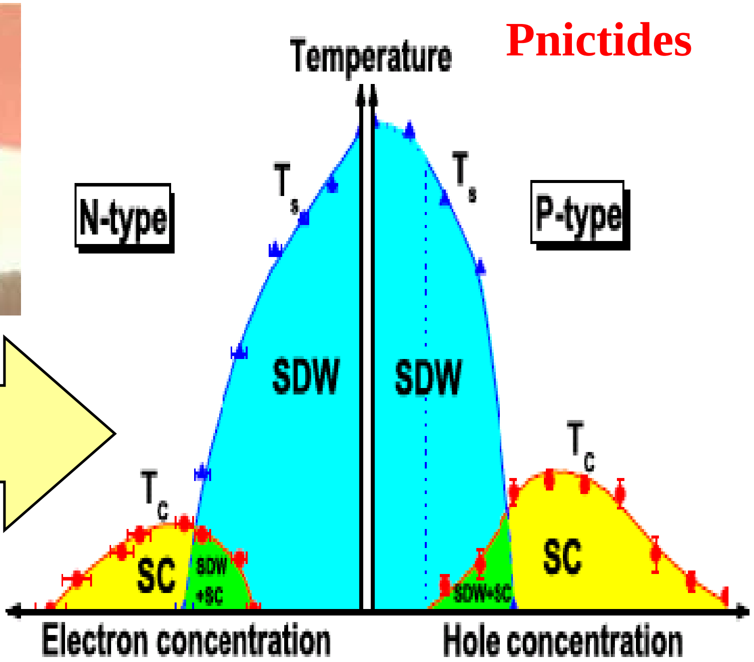




Unconventional Superconductivity
Competing with other ordering state (AFM order)







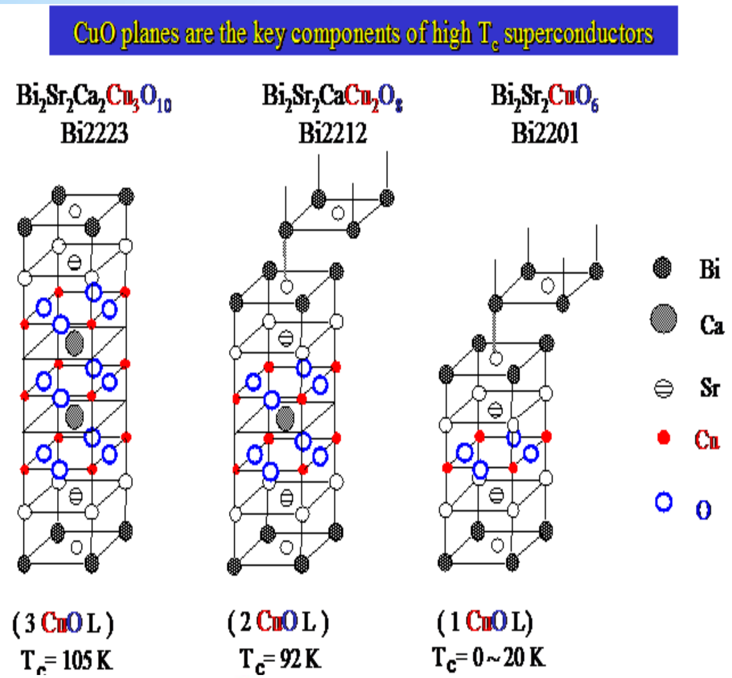
Mott Insulator with s=1/2 **SDW**

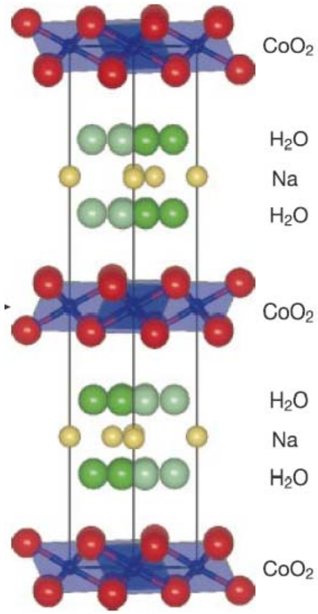
Structure-Magnetism-Superconductivity

Competing between SC and other ordering:

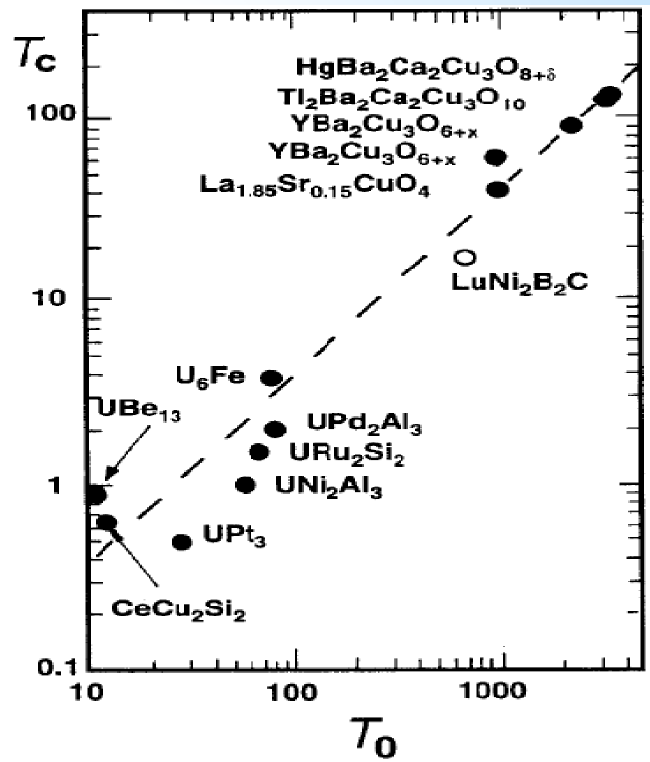
SC/ AFM;	SC/SDW;	SC/CDW
Cuprates;	iron-pnictides;	dicalcogenides

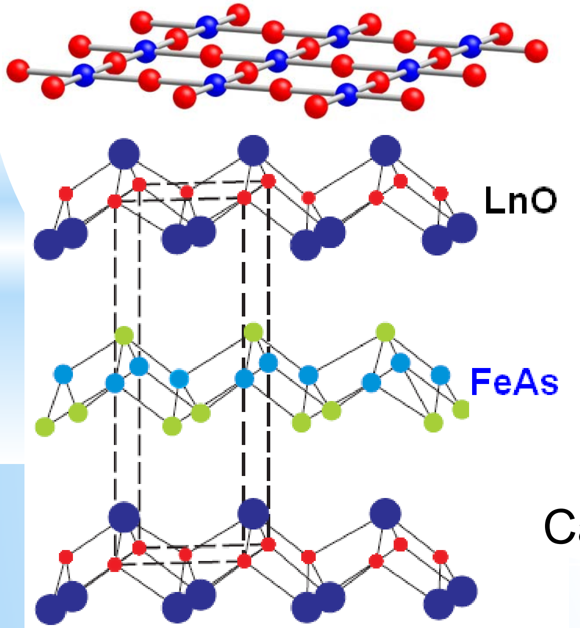
Strong 2D character is very important for unconventional SC

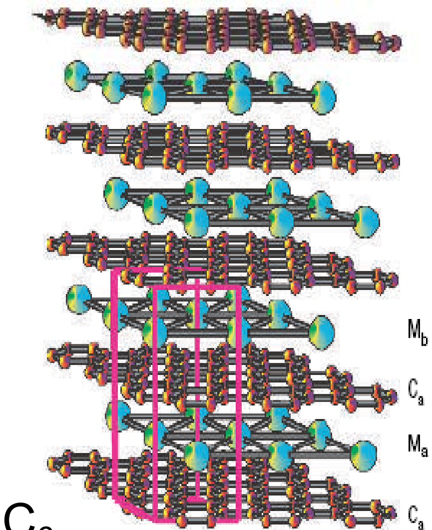




T_C=5K







CaC_6

T_C=6.5-11.5K

***T_0*, spin fluctuation temperature.**

N. Sato, Physica B 259, 634(1999)

Spin fluctuations is enhanced in low-dimensional system.

Mermin-Wegner, PRL (1966);
Hoberberg, PRL (1966);

Chronology for new superconductors after cuprates

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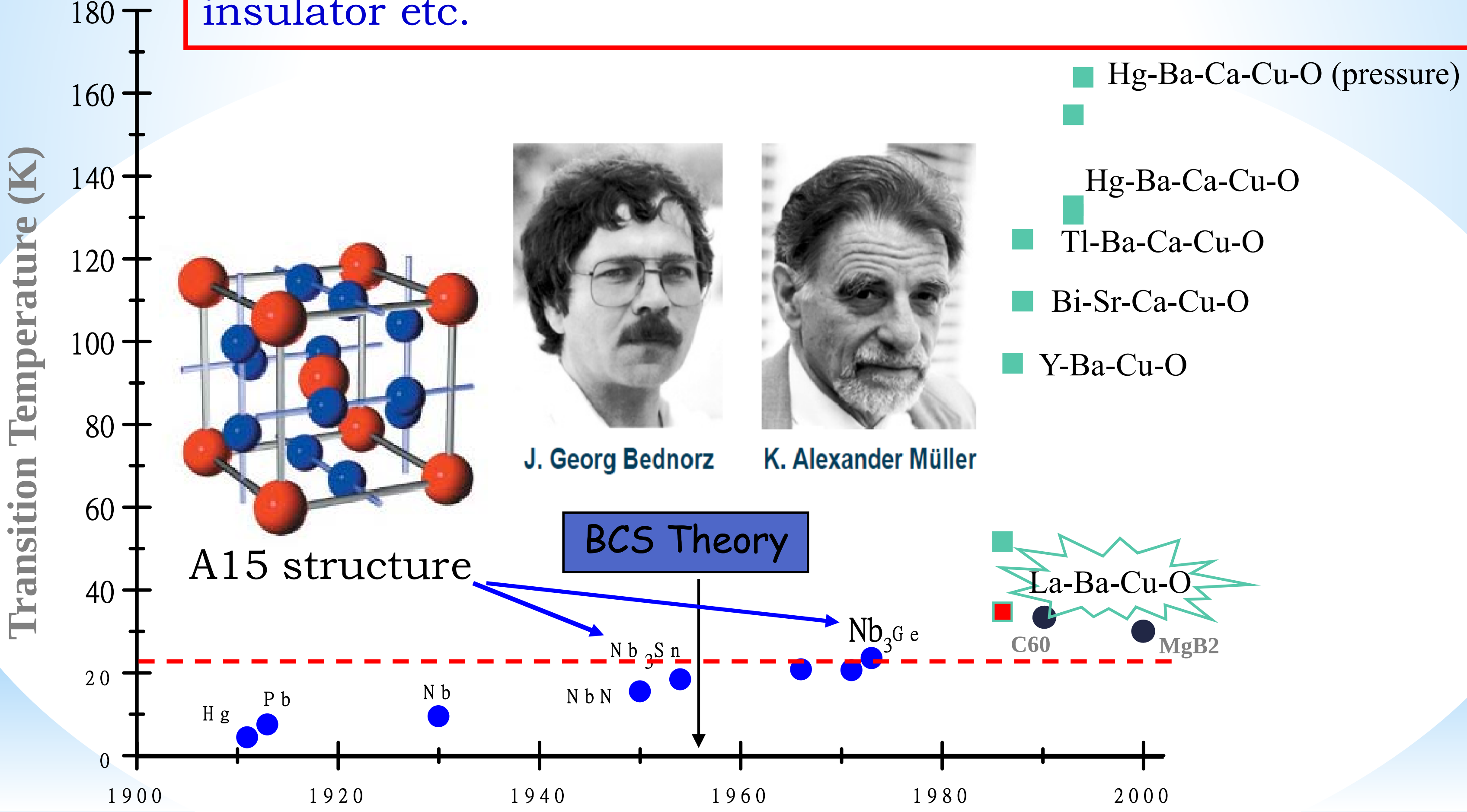
- In 1986, K. A. Müller and G. Bednorz discorved the first high-temperature superconductor LaBaCuO with T_C > 30K (Nobel award in Physics in 1987)
- **In 1987, Zhong-xian Zhao and Paul Ching-wu Chu, independently to each other, discovered $YBa_2Cu_3O_{7-\delta}$ with T_C ~92K, which is the first superconductor with T_c higher than the boiling point of liquid N_2。**

Discovery of unconventional superconductivity

Unconventional superconductivity cannot be explained by BCS theory and Matthias' rules: closely related to oxides, magnetism, insulator etc.



Conventional SC: Phonons mediated superconductivity

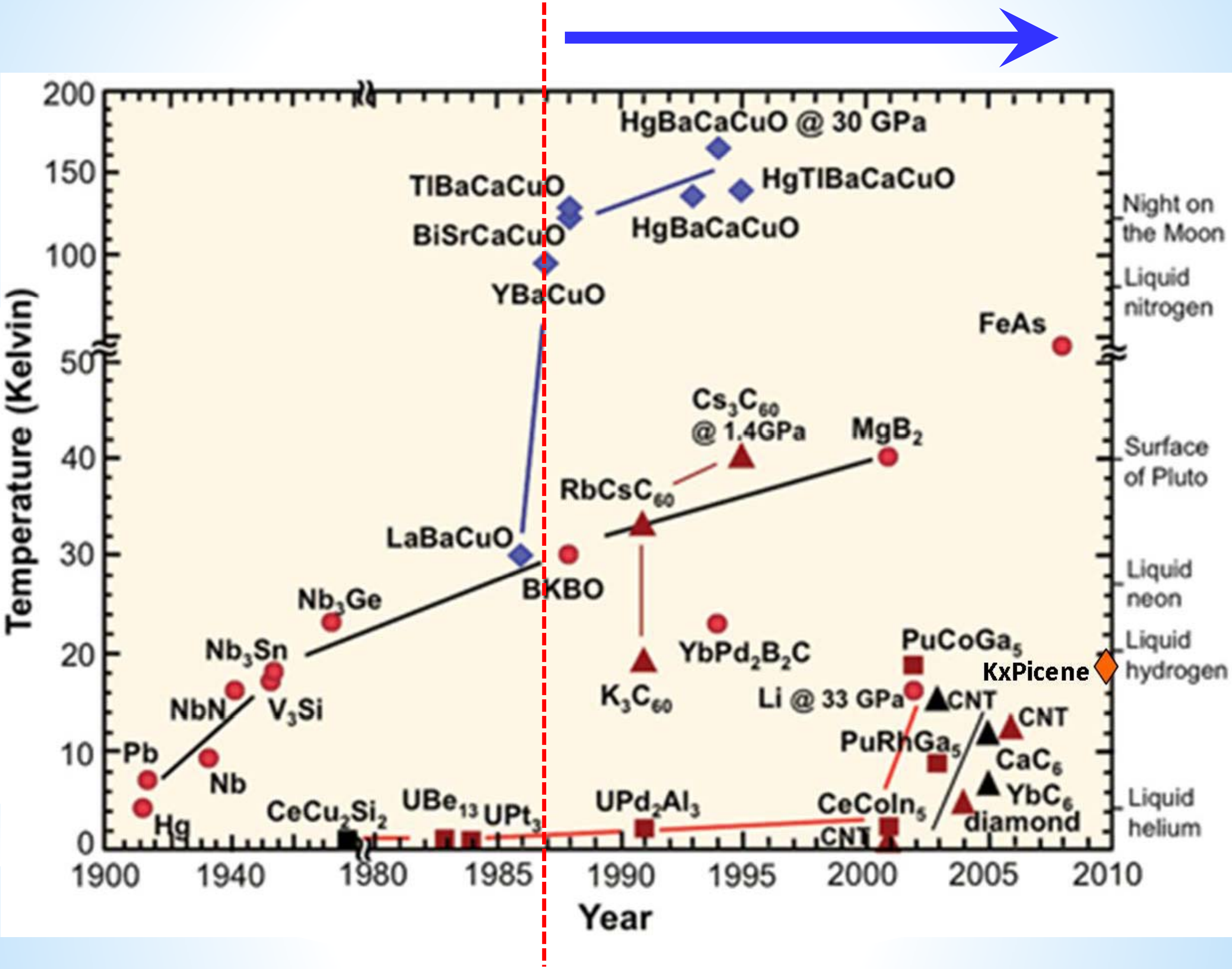
Year of Discovery

HTSC: New mechanism?

Chronology for new superconductors

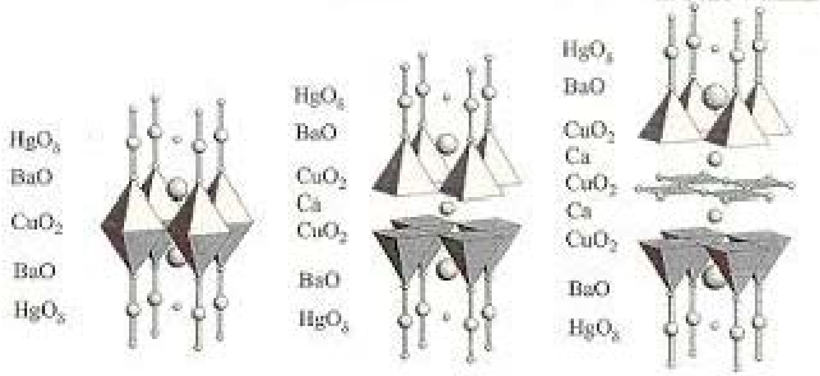
- In 1988, H. Maeda *et al.* discovered $Bi_2Sr_2Ca_2Cu_3O_{10}$ with T_C ~110K
- In 1988, Sheng and Herman discovered $Tl_2Ba_2Ca_2Cu_3O_{10}$ with T_C ~125K
- In 1991, R. C. Haddon *et al.* observed SC in K_3C_{60} with T_C=18K
- **In 1993, K. Tanigaki *et al.* observed SC in $RbCs_2C_{60}$ with T_C=33 K**
- In 1993, A. Schilling *et al.* discovered $HgBa_2Ca_2Cu_3O_8$ with T_C ~134 K。$HgBa_2Ca_2Cu_3O_8$ keeps the record of highest Tc，and has T_C ~ 164 K under high pressure 。
- **In 1995, T. T. M. Palstra *et al.* observed SC under high pressure in Cs_3C_{60} with *T_C=38K***
- **In 2001, J. Nagamatsu *et al.* observed SC in intermetallic MgB_2 with *T_C ~39K*, which keeps the record for highest Tc of intermetallic compounds。**
- In 2008年，H. Hosono *et al.* observed T_c in $LaFeAsO_{1-x}F_x$ reached 26K，subsequently, **X. H. Chen and N. L. Wang et al. found T_c in $SmFeAsO_{1-x}F_x$ and $CeFeAsO_{1-x}F_x$ exceeded the McMillan limit (40 K)， Z. X. Zhao *et al.* found T_C~55K in $SmFeAsO_{1-x}F_x$, which is highest Tc in this type of superconductors, demonstrating FeAs-based compounds are the second type of high-temperature superconductor after cuprates 。**
- **In 2010, Y. Kubozono *et al.* discovered that K-doped Picene shows T_C~18 K, renewing the record of highest Tc in organic superconductivity。**

Chronology for new superconductors



Copper Oxide Superconductors

Hg-Family	Abbrev.	T_c
$HgBa_2Ca_3Cu_4O_{10+\delta}$	Hg-1234	125 K
$HgBa_2Ca_2Cu_3O_{8+\delta}$	Hg-1223	134 K (164 K @ 30GPa) – Record holder
$HgBa_2CuO_{4+\delta}$	Hg-1201	95 K
Tl-Family		
$Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$	Tl-2223	128 K
$Tl_2Ba_2CaCu_2O_{6+\delta}$	Tl-2212	118 K
$Tl_2Ba_2CuO_{6+\delta}$	Tl-2201	95 K (can be highly overdoped)
$TlBa_2Ca_3Cu_4O_{11+\delta}$	Tl-1234	112 K
$TlBa_2Ca_2Cu_3O_{9+\delta}$	Tl-1223	120 K
$TlBa_2CaCu_2O_{7+\delta}$	Tl-1212	103 K
Bi-Family		
$Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$	Bi-2223	110 K
$Bi_2Sr_2CaCu_2O_{8+\delta}$	Bi-2212	91 K (photoemission/tunneling –cleaves)
$Bi_2Sr_2CaCu_2O_{8+\delta}$	Bi-2201	35 K
Y-Family		
$YBa_2Cu_3O_{7+\delta}$	Y-123	94 K (cleanest – most highly studied)
$Y_2BaCu_4O_{7+\delta}$	Y-124	82 K
La-Family		
$La_{2-x}Sr_xCuO_{4+\delta}$	LaSr-214	40 K (full doping range)
$La_{2-x}Ba_xCuO_{4+\delta}$	LaBa-214	30 K (1st cuprate superconductor)
Others		
$Ca_{1-x}Sr_xCuO_2$		110 K
$Nd_{2-x}Ce_xCuO_{4+\delta}$		30K



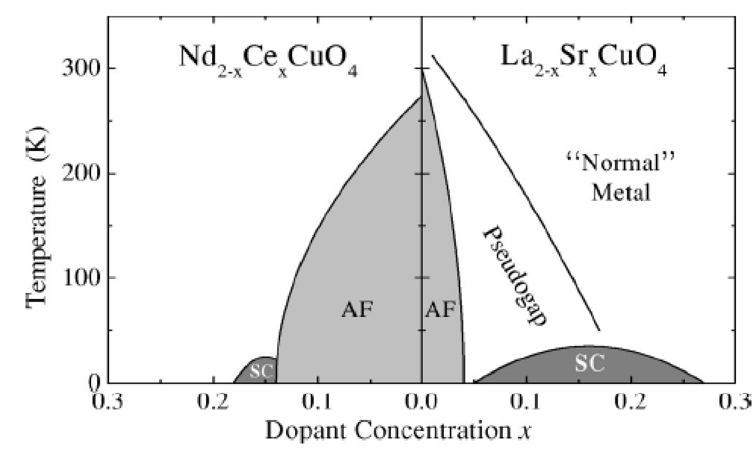
Hg-1201, Hg-1212, Hg-1223

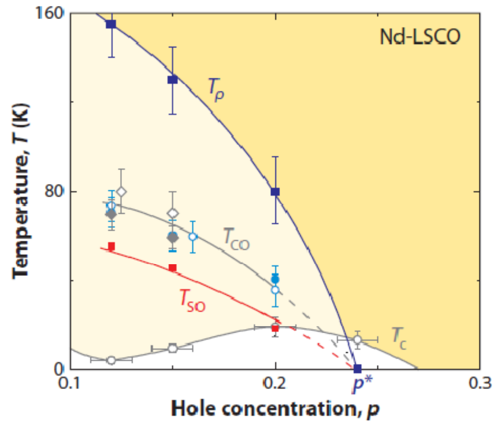
High-Tc superconducting cuprates

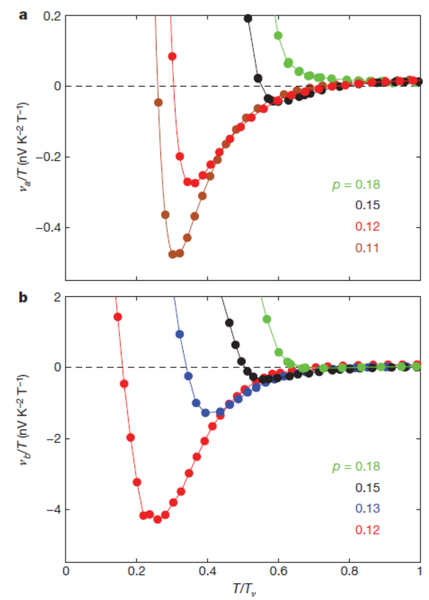
H. Eisaki et al., PRB **69**, 064512 (2004)

T_c increases with raising the number of CuO_2 plane

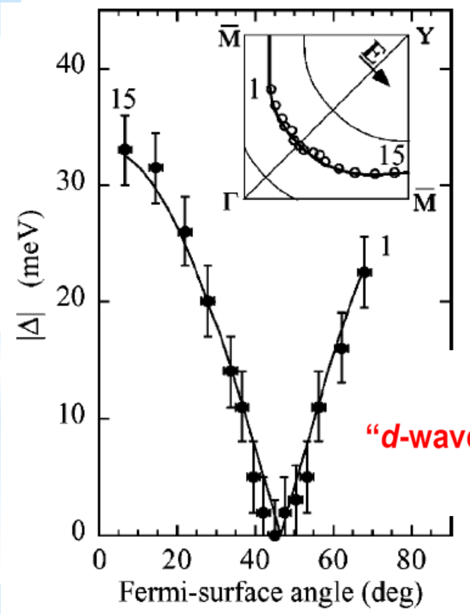
Phase diagram and d-wave pairing symmetry

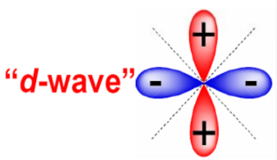


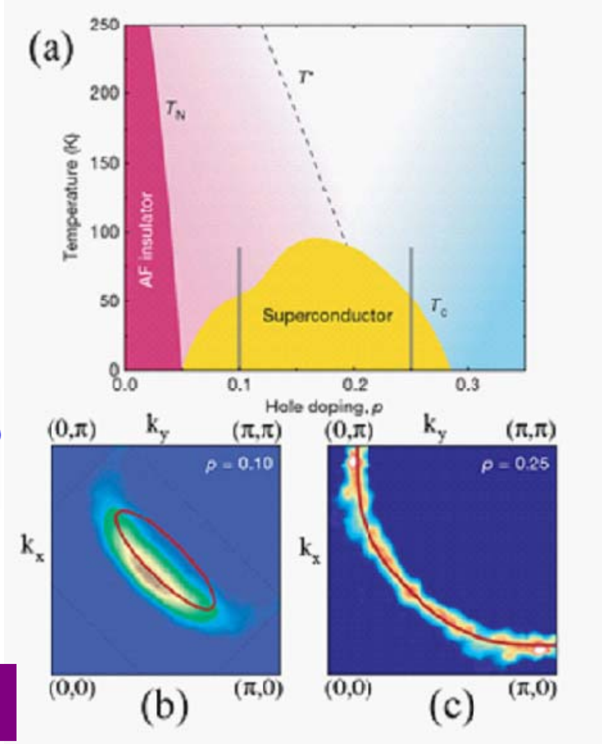


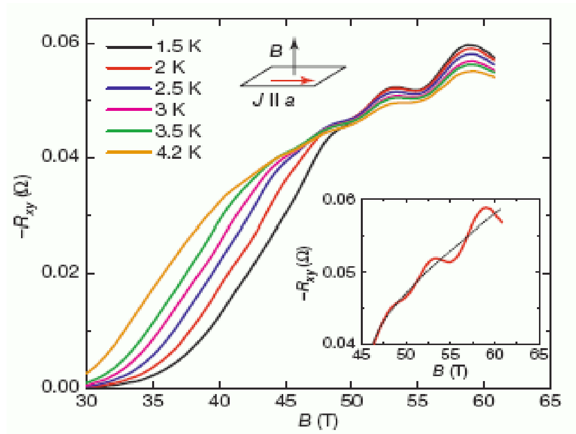


赝能隙：平移对称性破缺





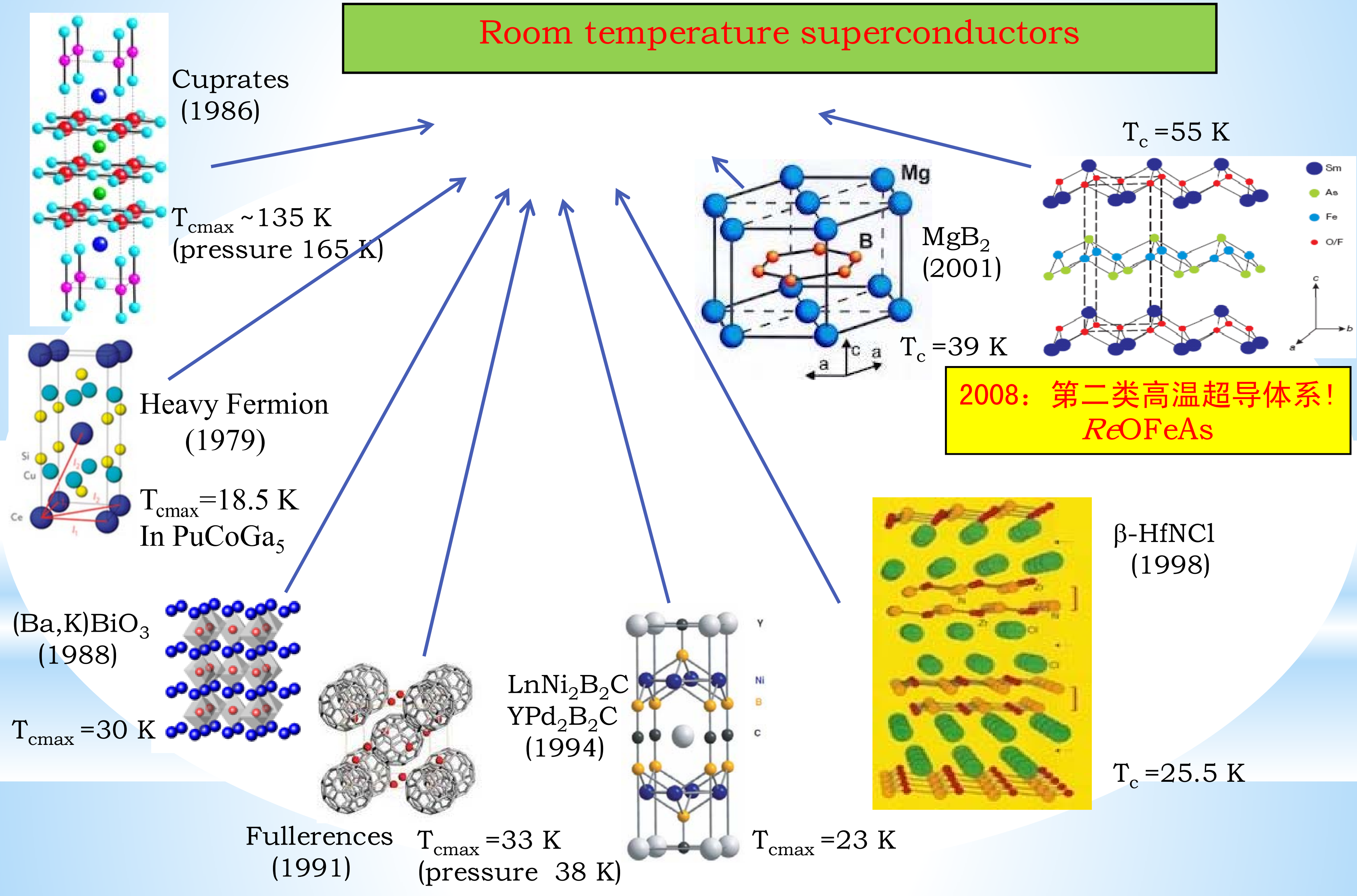




d-wave pairing from ARPES

Quantum oscillations in $YBa_2Cu_3O_{6.5}$: Fermi pocket

Typical superconductors and their Tc



Superconductors discovered after Cuprate Superconductors

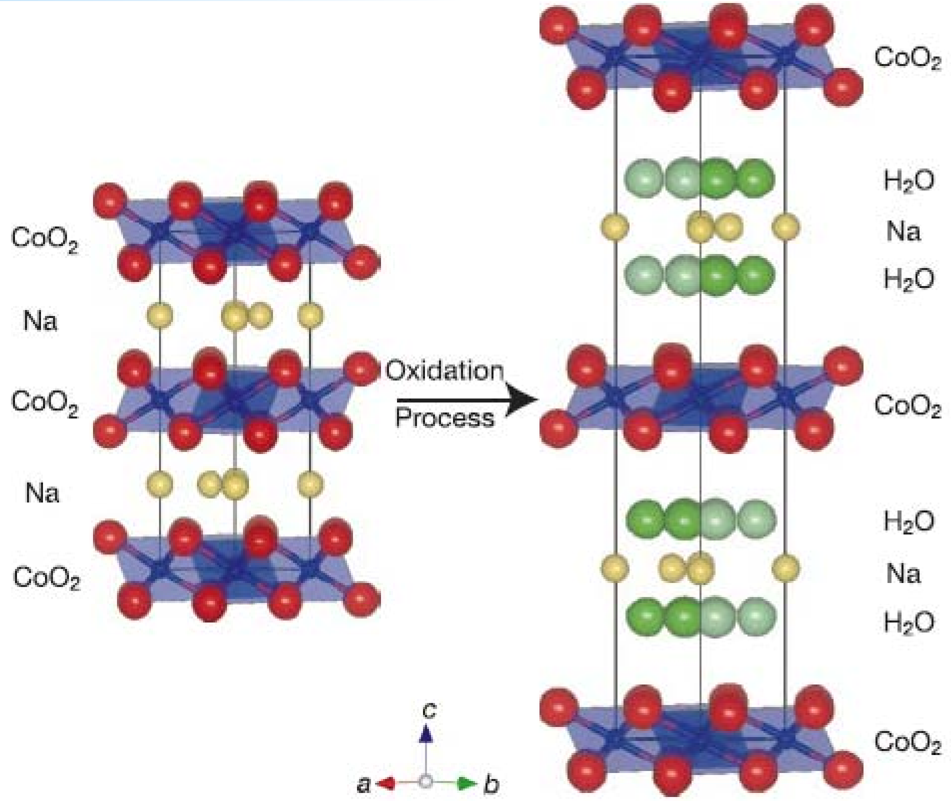
* Unconventional superconductors

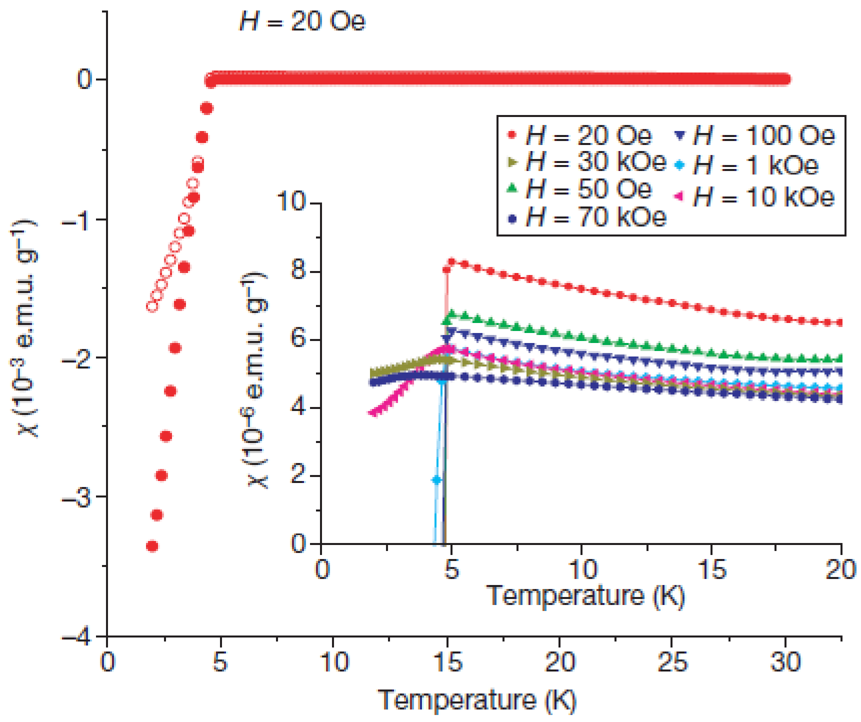
Triangle lattice $Na_xCoO_2 \cdot yH_2O$, Sr_2RuO_4 with p-wave symmetry,

Heavy Fermion, Ferromagnetic SC, Non-centrosymmetry.

Superconductivity at 5 K in $Na_xCoO_2 \cdot yH_2O$

strong correlations and unconventional SC



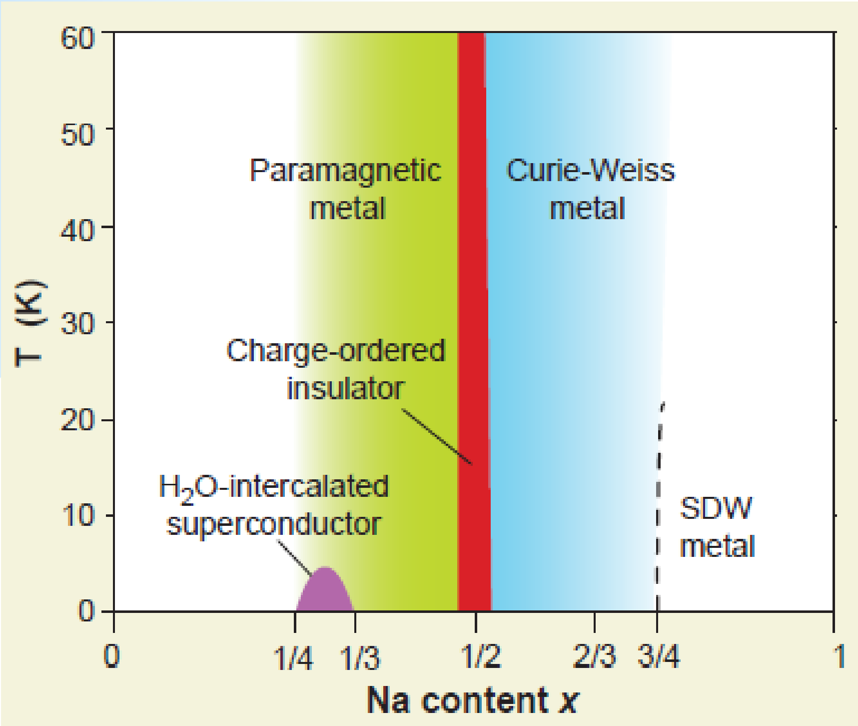


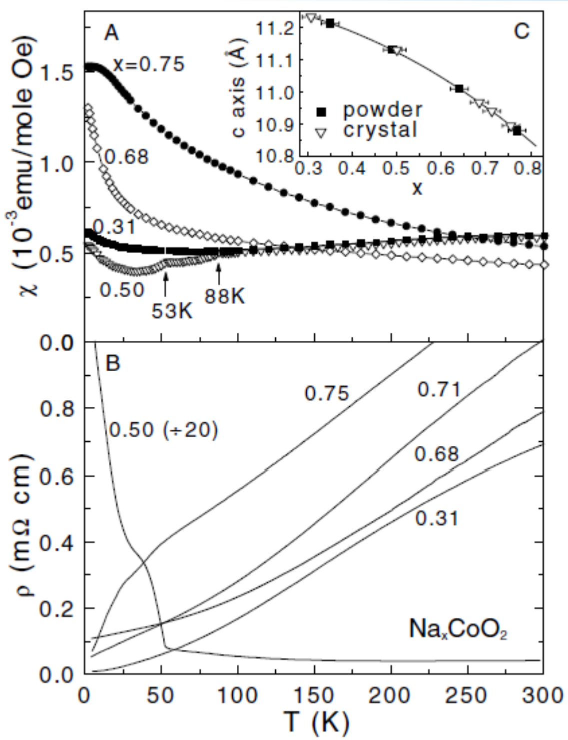
T_c ~ 5K

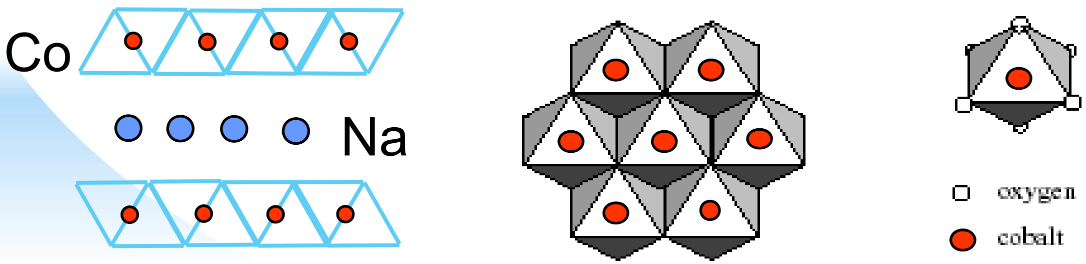
K. Takada et al., *Nature* **422**, 53(2003)

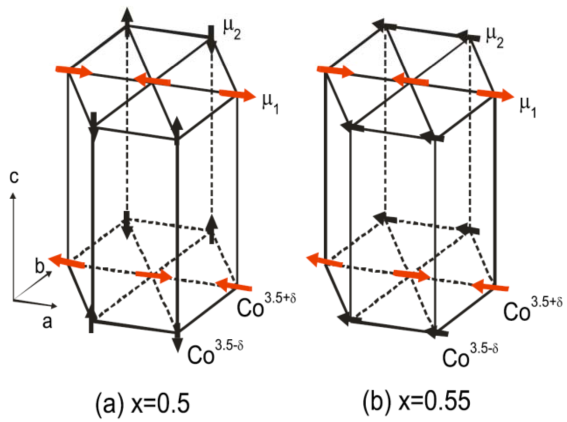
$Na_xCoO_2 \cdot yH_2O$:

strong correlations and unconventional SC





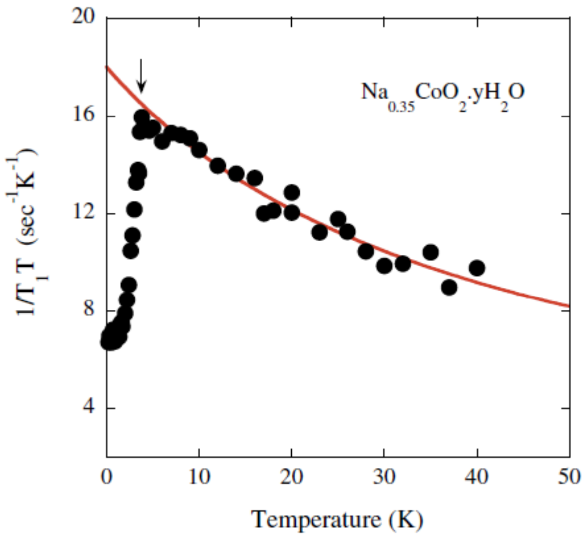




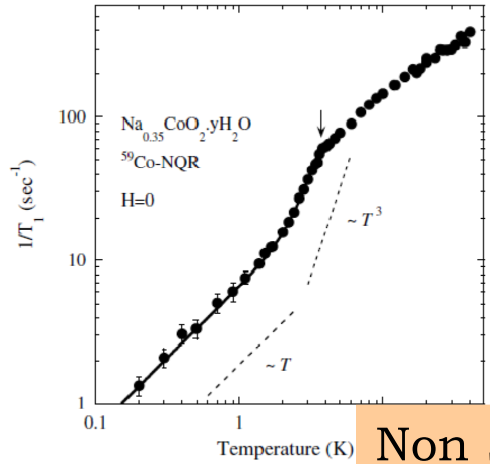
Triangle Lattice

$Na_xCoO_2 \cdot yH_2O$:

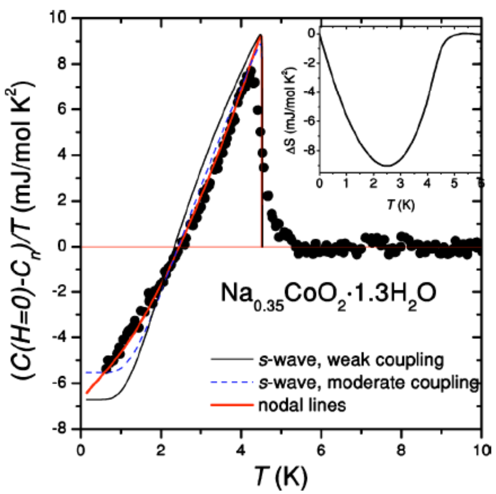
strong correlations and unconventional SC



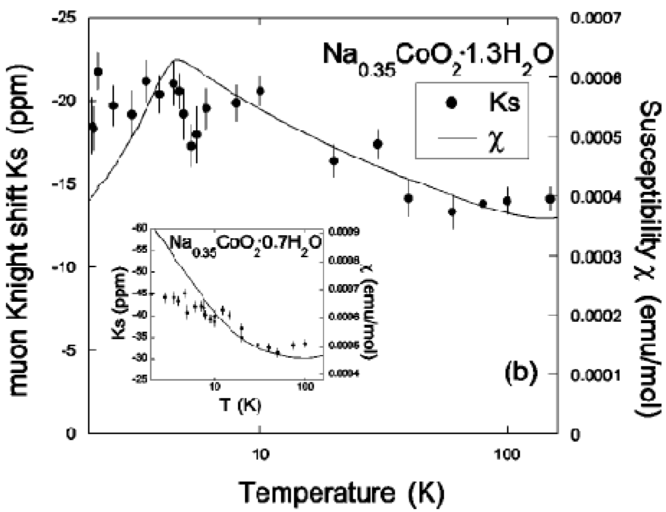
$1/T_1T = C/(T-\theta)$, $\theta = -42K$
2D AFM correlation



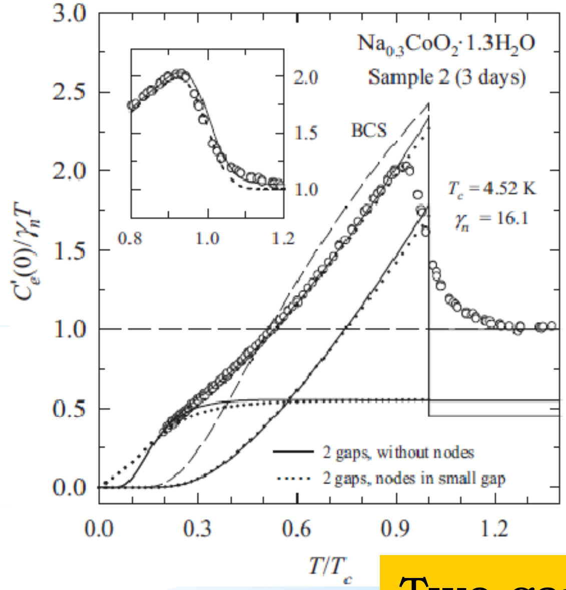
Non *s*-wave



Nodes in gap?



Spin-triplet?

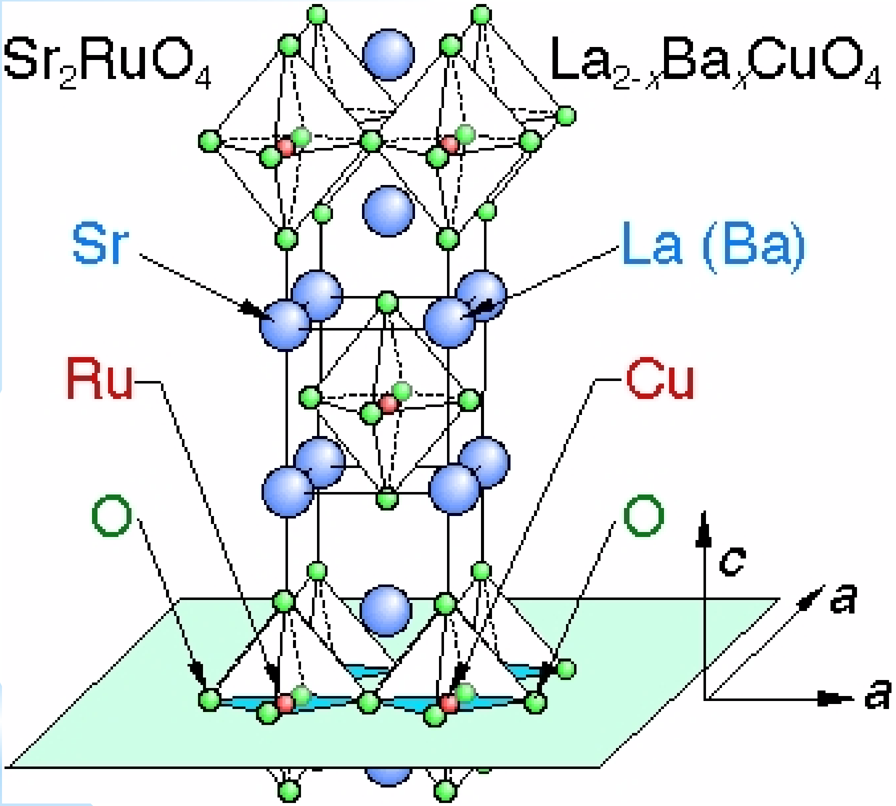


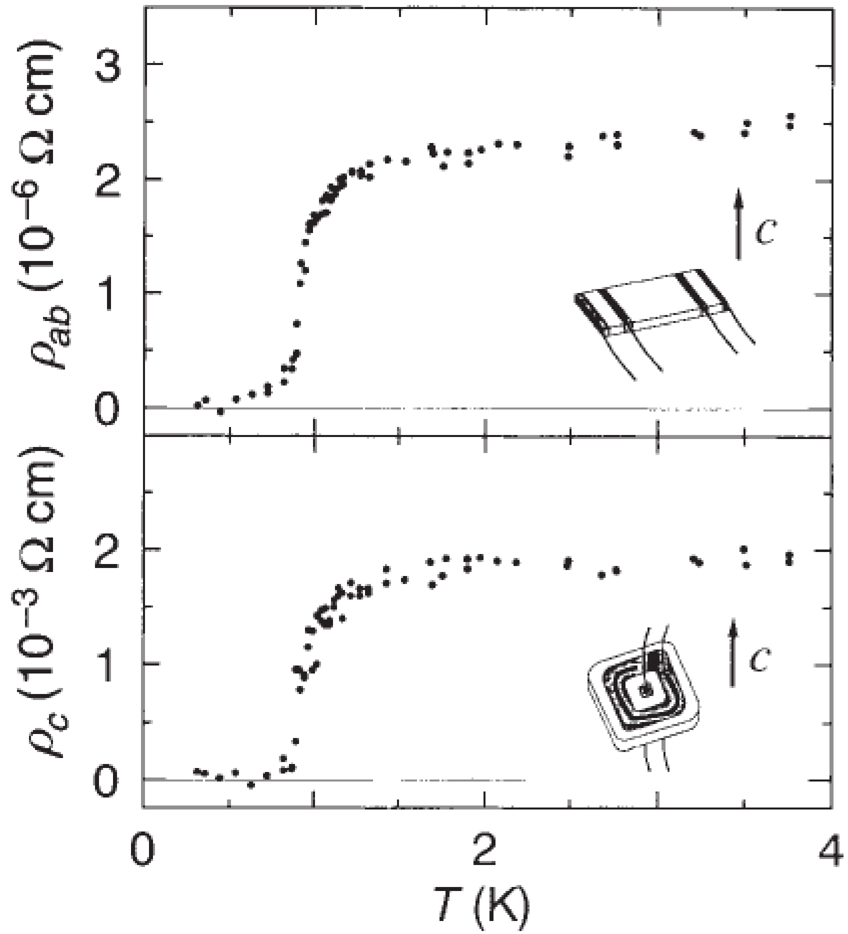
Two gaps?

Mazin and Johannes
Nat. Phys. 1, 91 (2005)

Superconductivity in Sr_2RuO_4

chiral spin-triplet p-wave pairing?

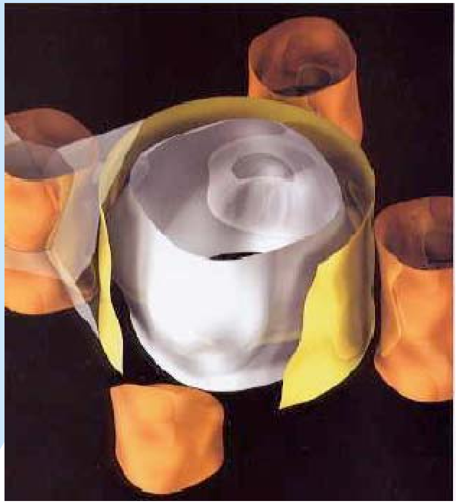




Y. Maeno et al. *Nature* (1994)

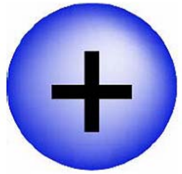
Sr_2RuO_4:

chiral spin-triplet p-wave pairing?



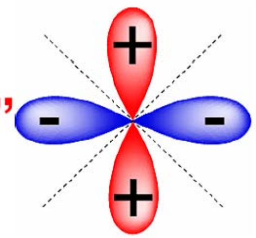
Fermi surface sheets

“*s*-wave”



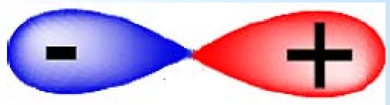
S = 0 singlet
L = 0 *s*-wave

“*d*-wave”



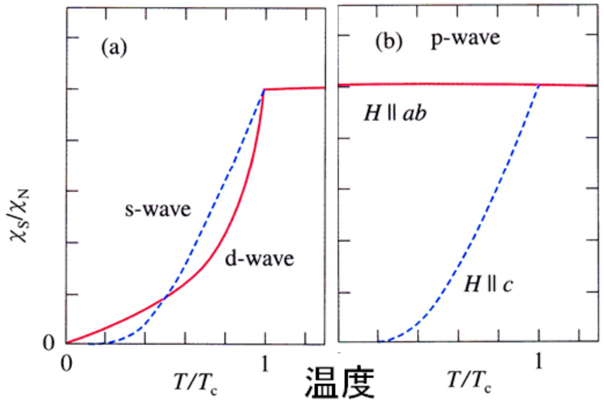
S = 0 singlet
L = 2 *d*-wave

“*p*-wave”

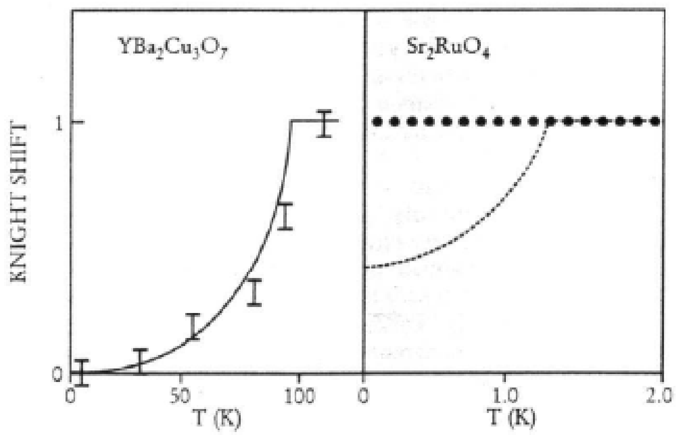


S = 1 triplet
L = 1 *p*-wave

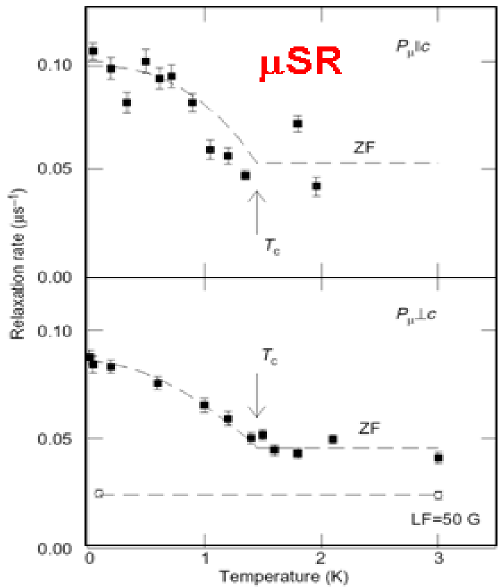
Tc = 1.5 K
Unconventional SC



单重态 三重态

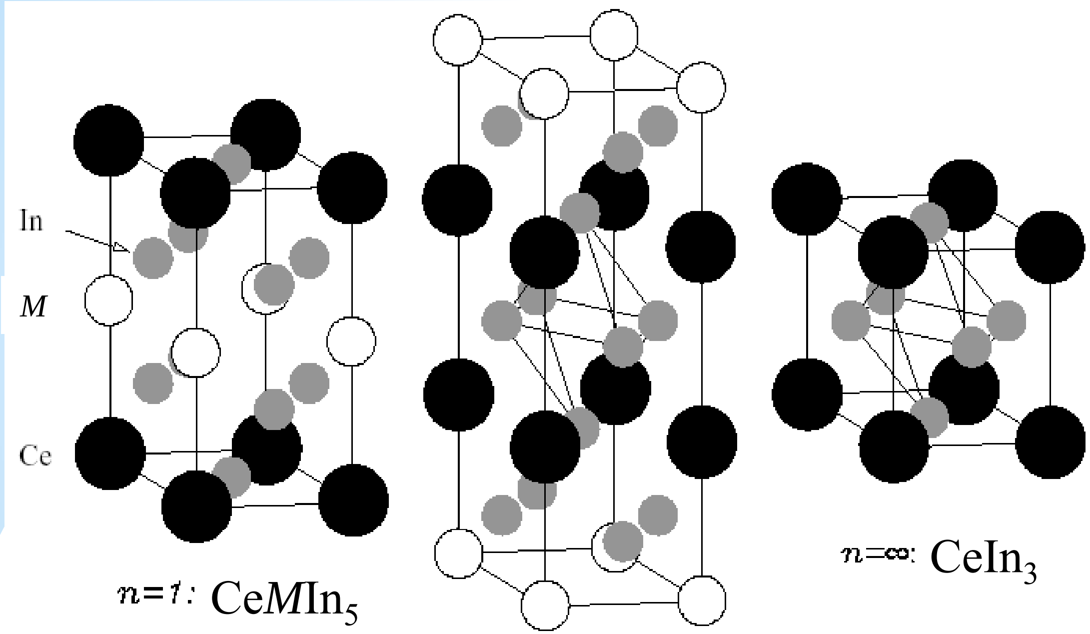


Ishida et al., *Nature* (1998)



G.M. Luke *et al.*, Nature **394**, 558 (1998)

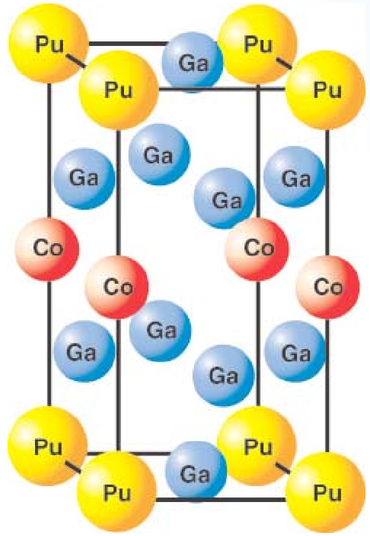
Heavy fermion superconductors discovered after YBCO



n=1: $CeMIn_5$

n=2: Ce_2MIn_8

n=∞: $CeIn_3$



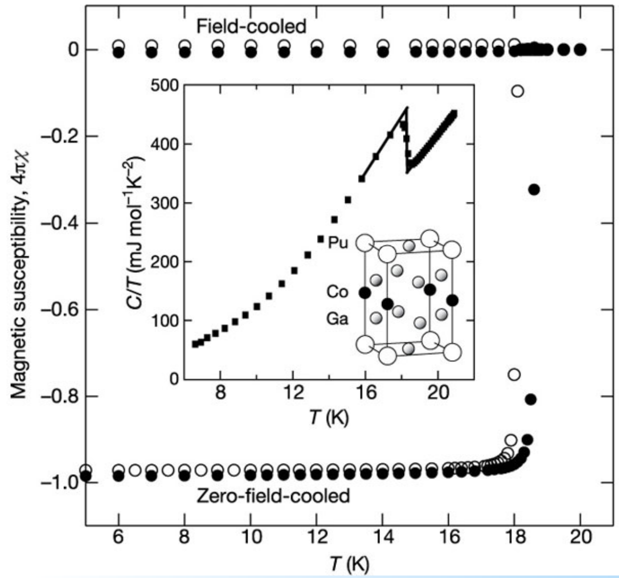
$PuCoGa_5$
Tc~18.5K
Highest among HF

J. L. Sarrao et al.
Nature (2002)

M = Co, Rh, Ir (isovalent)

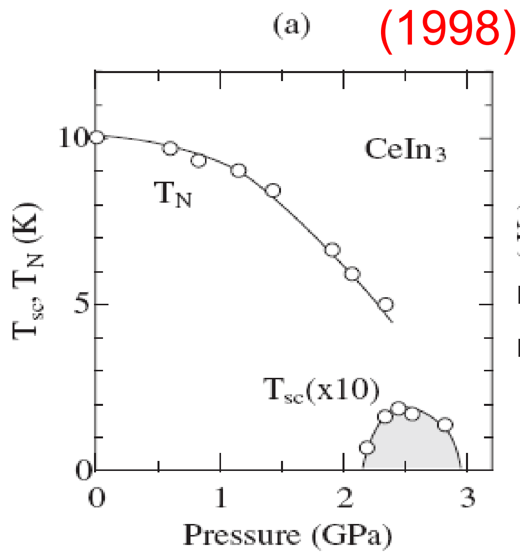
$Ce_nM_mIn_{3n+2m}$ structure

Consists of $CeIn_3$ and MIn_2 layers
quasi 2-dimension

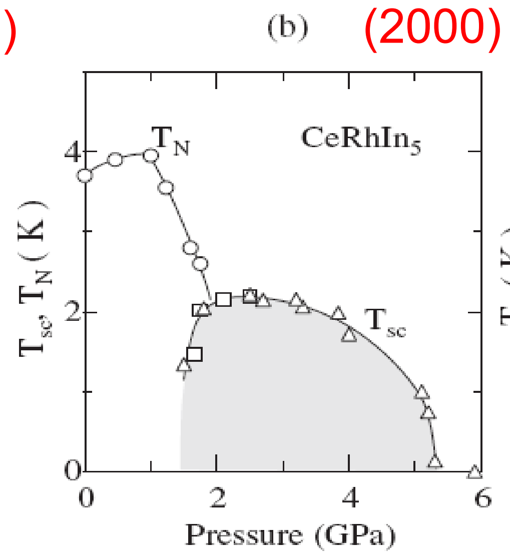


$CeRhIn_5$ @ pressure H. Hegger et al. *PRL* **84**, 4986 (2000)
$CeIrIn_5$ C. Petrovic et al. *EPL*, **53**, 354 (2001)
$CeCoIn_5$ C Petrovic et al. *J. Phys. Cond. Mat.* **13**, L337 (2001)

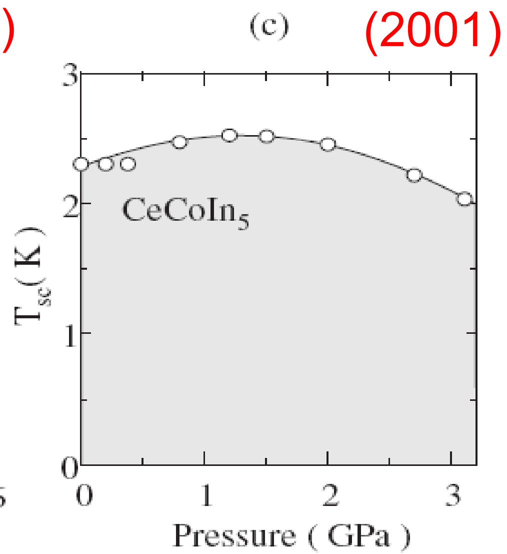
Competition between SC and magnetism



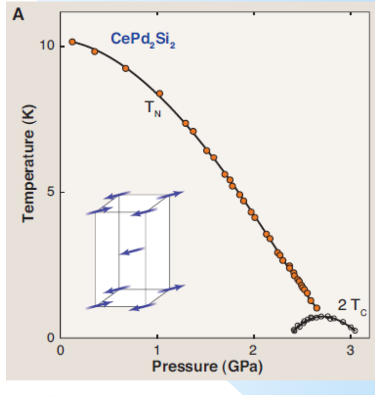
Low T_C

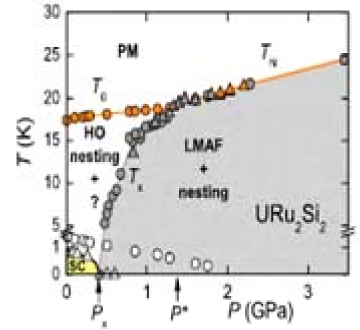


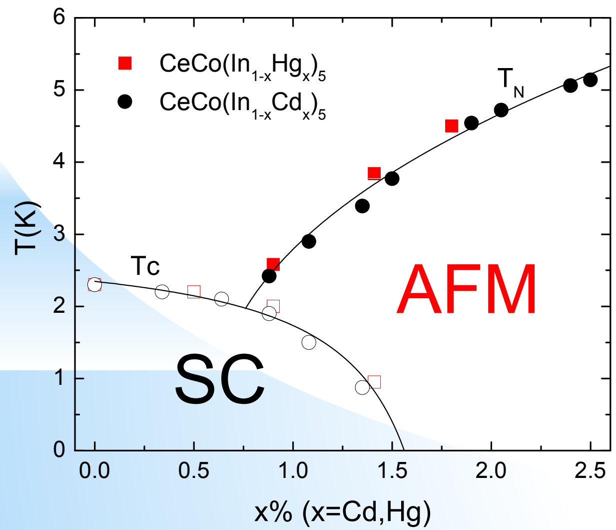
Coexistence of SC and Magnetism

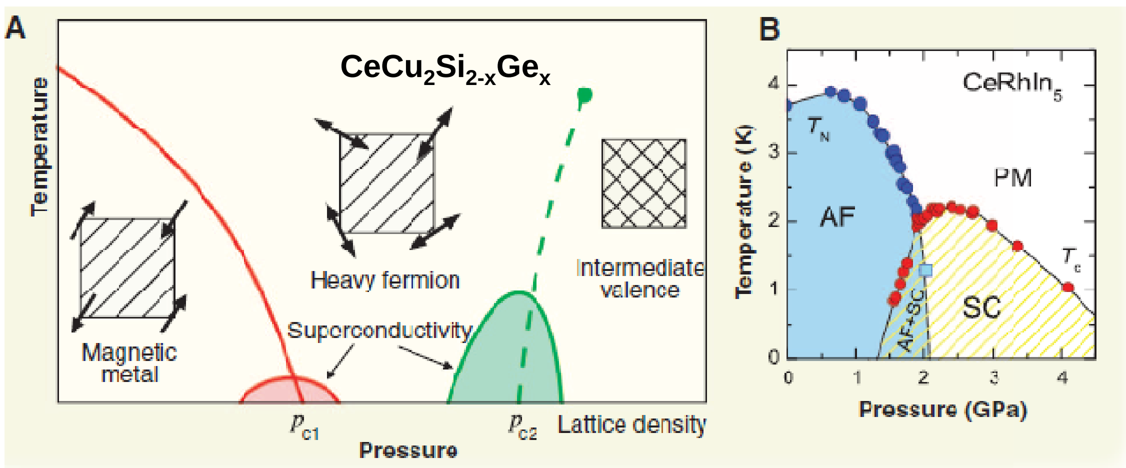


No magnetic order

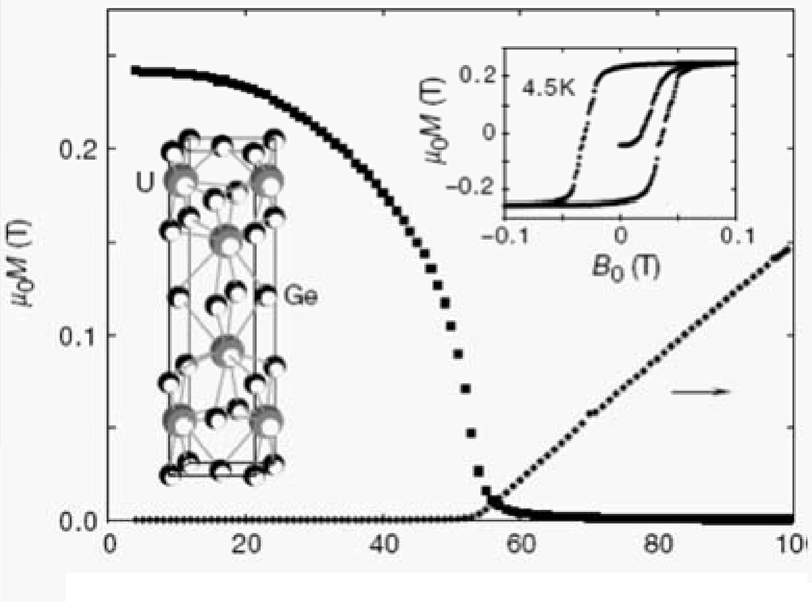


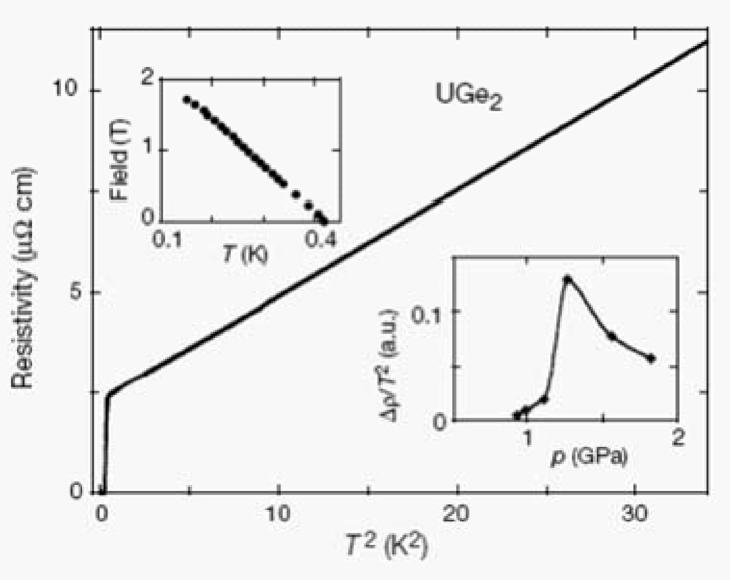


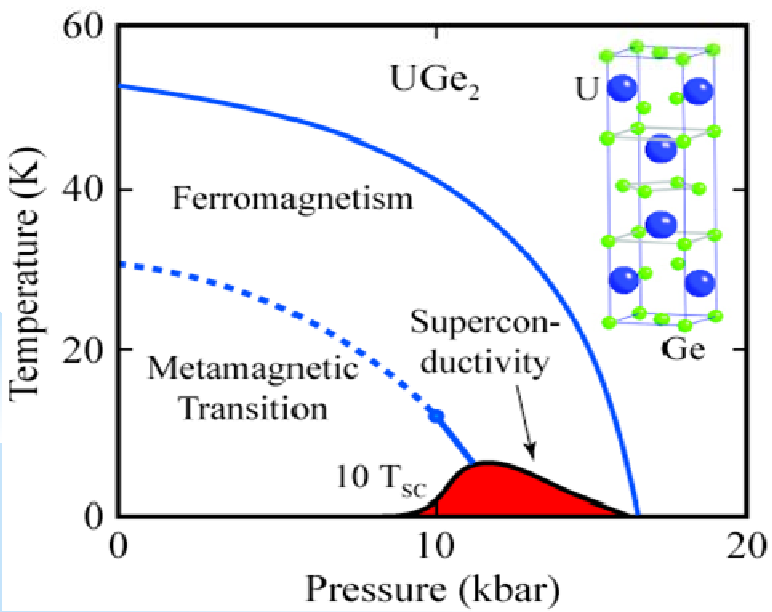




Ferromagnetic superconductors







S.S. Saxena et al., *Nature* **406**, 587 (2000)

UGe_2

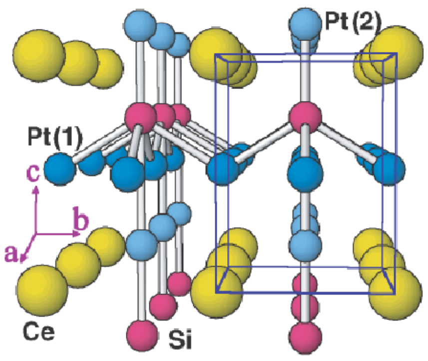
URhGe

UCoGe

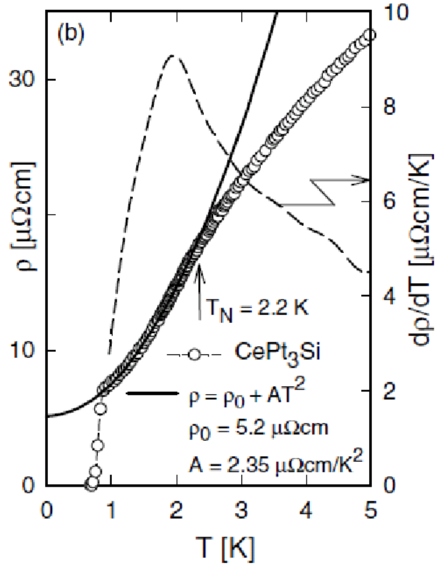
Maybe $ZrZn_2$

Non-centrosymmetric superconductors

$CePt_3Si$



No inversion symmetry along c-axis



E. Bauer et al, PRL 2004

T_c = 0.75 K

With inverse center：

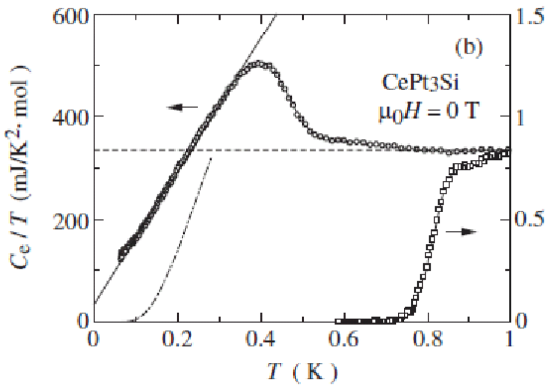
$$P\Psi(r) = \pm\Psi(r)$$ (P is parity operator)

$$P\Delta(r,s) = \pm\Delta(r,s)$$

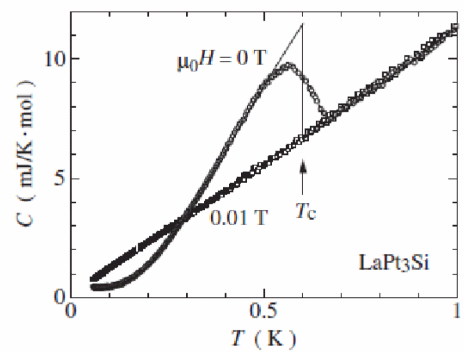
Pairing symmetry could be spin-singlet or spin-triplet

Without inverse center, spin-singlet or spin-triplet can be mixed

Line-nodes in $CePt_3Si$



nodeless in $LaPt_3Si$



Magnetic: $CePt_3Si$ (AF and SC coexist)

$CeRhSi_3$, $CeIrSi_3$, UIr

(AF @1bar, SC under P)

magnetism plays important role in the SC

Non-magnetic: Li_2Pd_3B, Li_2Pt_3B

$Rh(Ir)_2Ga_9$, NaAlSi, Al_3Mg_2

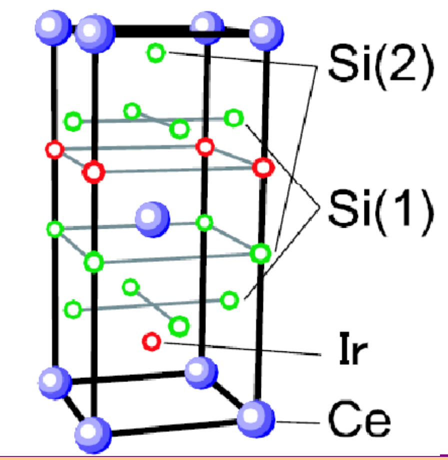
$Mg_{10}Ir_{19}B_1$, Re_3W, Mo_3Al_2C

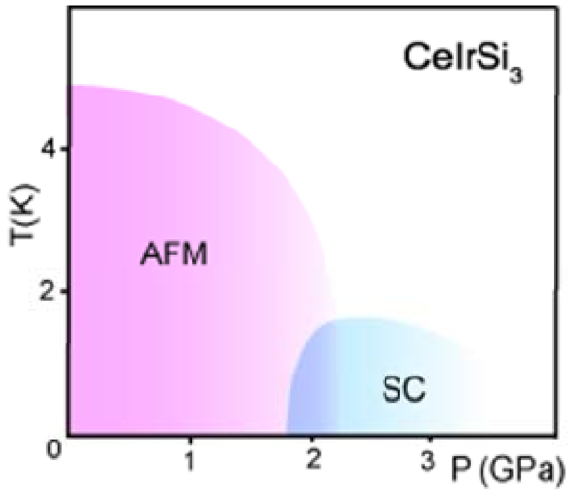
pure effect of broken inversion-symmetry

Non-centrosymmetric superconductors:

Heavy Fermion

$CeIrSi_3$



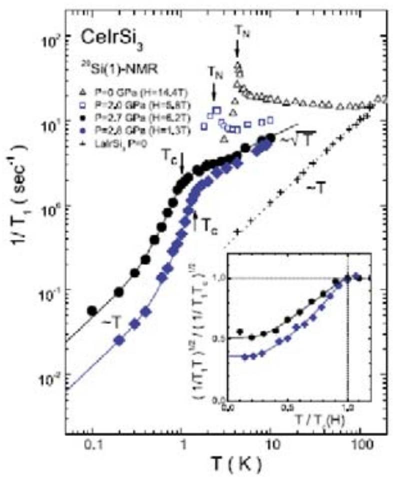


LnPt_3Si or *Ln*$IrSi_3$ (Ln = Ce, La):

Same structure;
Similar spin-orbit coupling;

Different pairing symmetry.

node in $CeIrSi_3$



Superconducting state

$$\frac{1}{T_1} \sim T^3 \qquad (T < T_c)$$

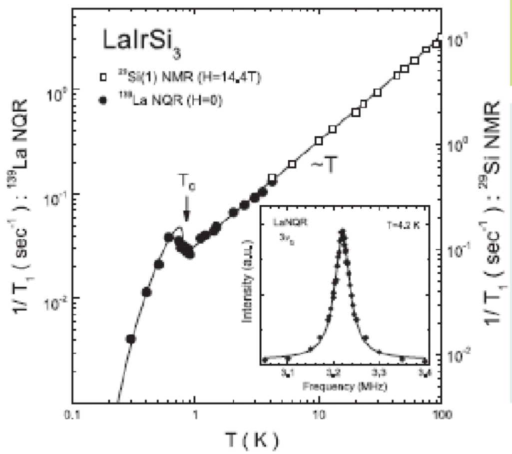
→ Line node gap
with $2\Delta/k_BT_c$~4.6
No coherence peak

$$\frac{1}{T_1} \sim T \qquad (T << T_c)$$

→ Residual DOS at E_F
N_{res}/N_0~52% @6.2T
~37% @1.3T

→Unconventional SC state

nodeless in $LaIrSi_3$



Normal state

$$\frac{1}{T_1} \sim T$$

Korringa's relation
→ Fermi liquid state

Superconducting state

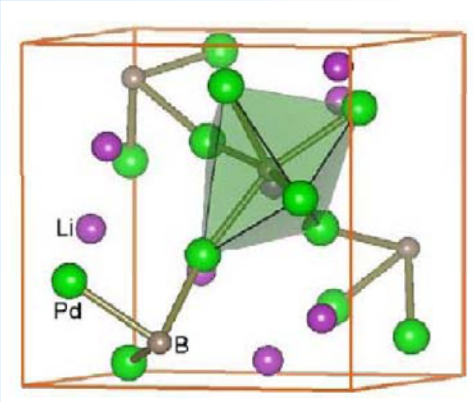
$$\frac{1}{T_1} \sim \exp(-\Delta / k_BT) \qquad (T < T_c)$$

→ Isotropic gap
with $2\Delta/k_BT_c$~ 3.1
→ Coherence peak

→ Conventional BCS state

Non-centrosymmetric superconductors:

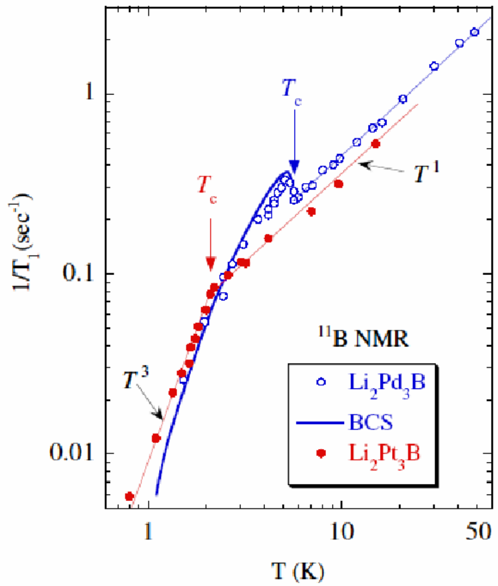
Weakly correlated systems



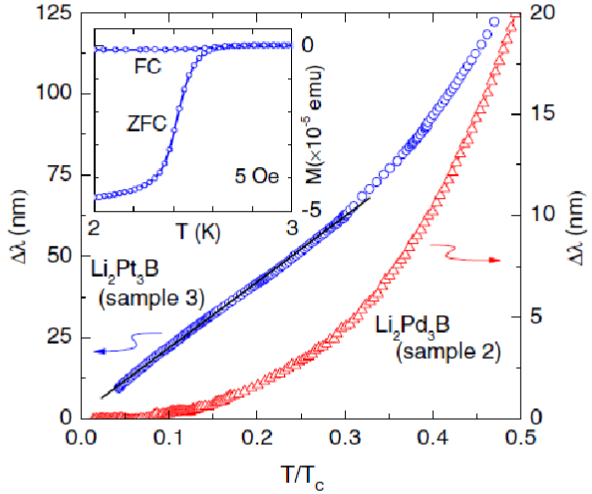
Li_2Pd_3B

Li_2Pt_3B

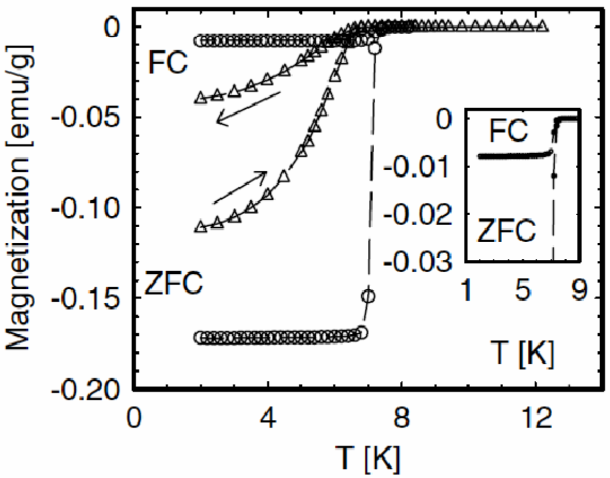
Li_2Pd_3B

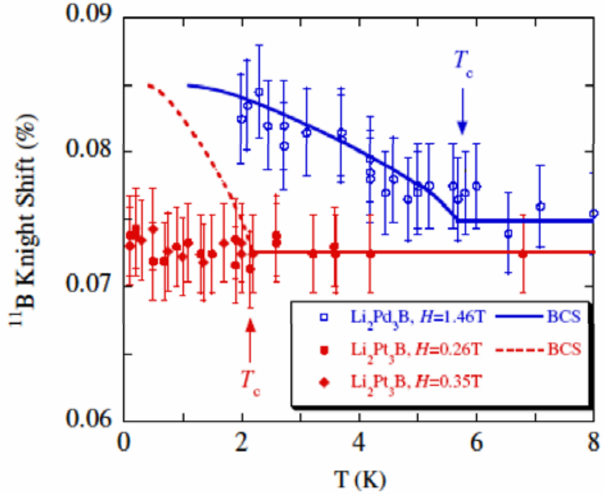


Penetration depth



H. Q. Yuan *et al*, PRL **97**, 017006 (2006)





Li_2Pd_3B: *s*-wave

Li_2Pt_3B:line nodes

Li_2Pd_3B: spin-singlet

Li_2Pt_3B: spin-triplet

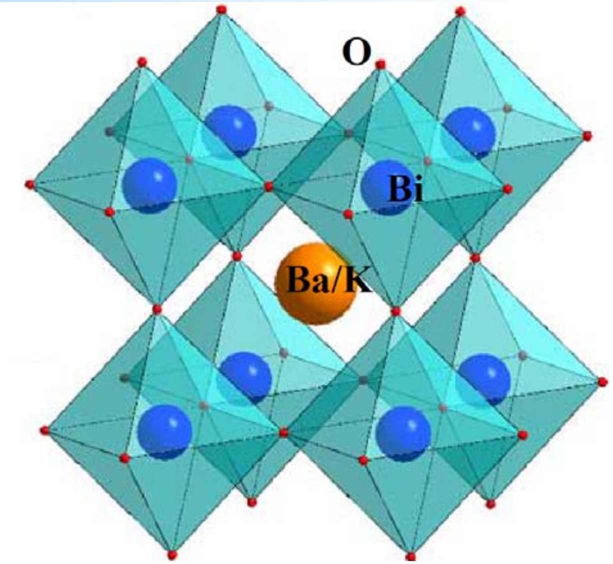
Superconductors discovered after Cuprate Superconductors

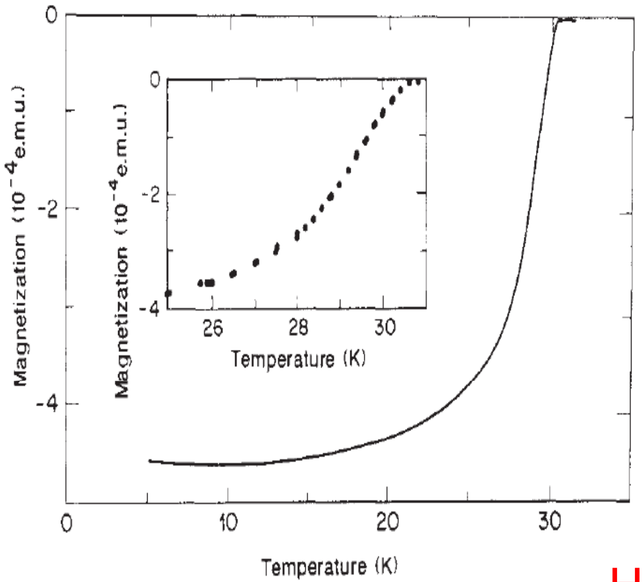
* Superconductors with Tc>20 K

Intercalated HfNCl, MgB_2, $Ba_{1-x}K_xBiO_3$, Fullerides,

Organic superconductors, Borocarbides, Iron-pnictides

First copper-free superconductor with T_C>30 K

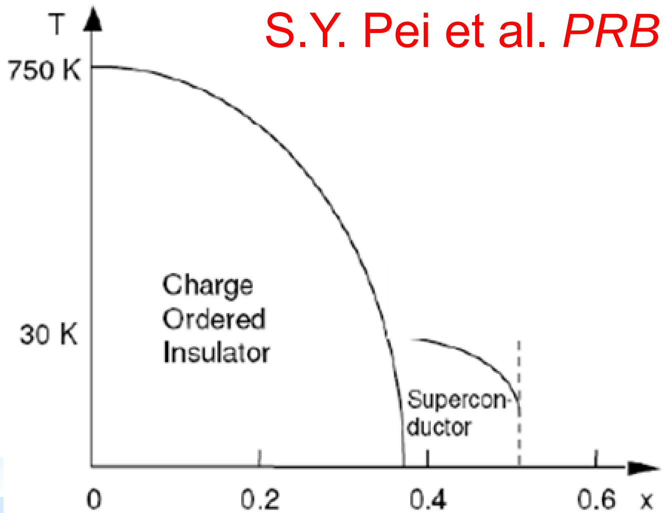




$Ba_{1-x}K_xBiO_3$

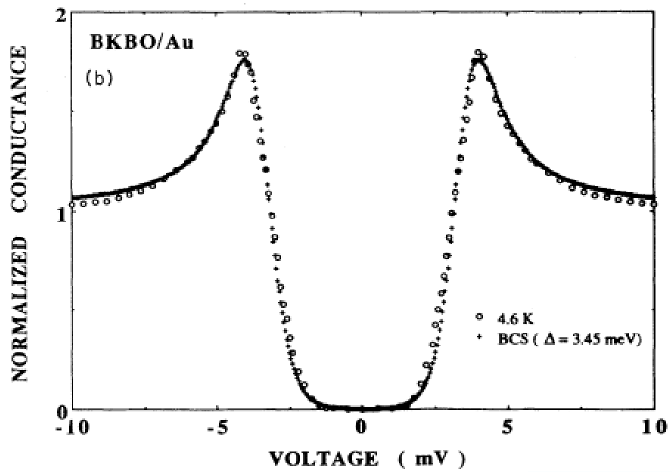
R. J. Cava et al,
***Nature* 322, 814 (1988)**

S.Y. Pei et al. *PRB* (1990)



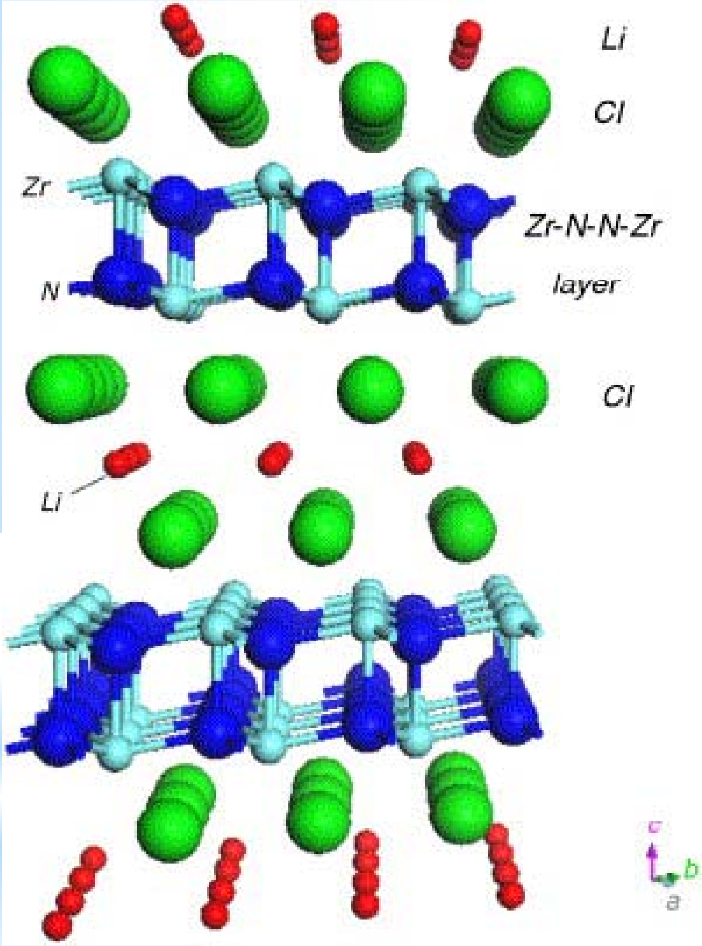
Superconductivity suddenly emerges as CDW disappears

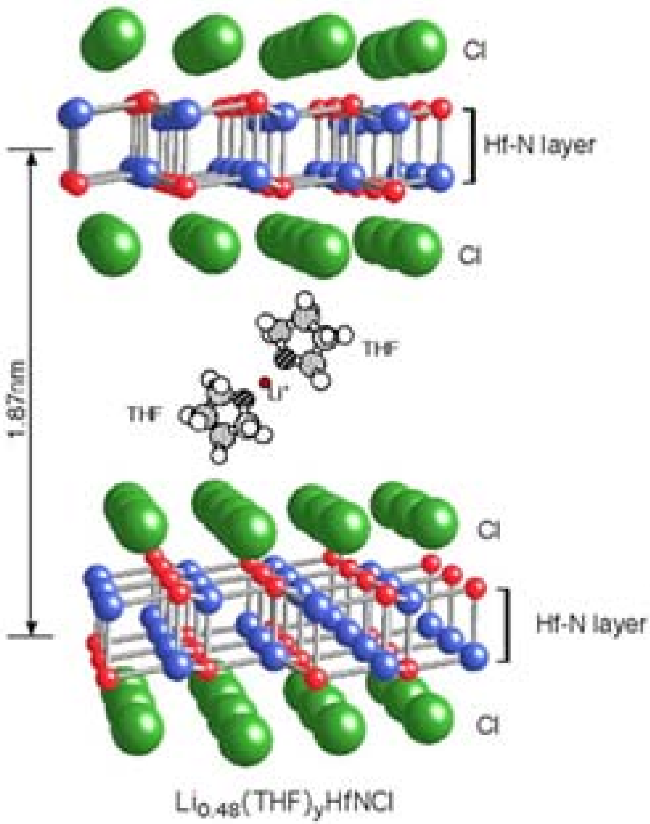
H. Sato et al. *PRB* (1993)

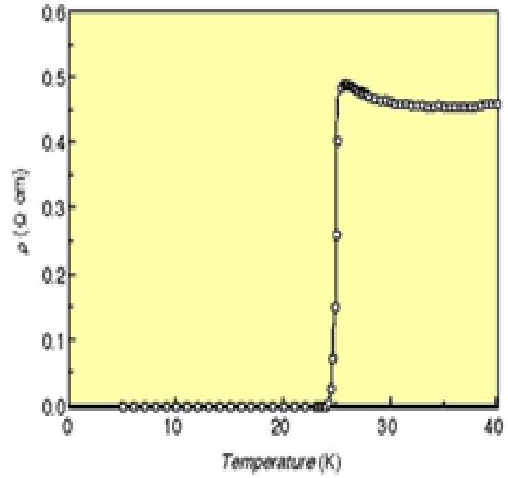


Good fit for tunneling spectrum in BCS theory with λ=1

Intercalated ZrNCl and HfNCl



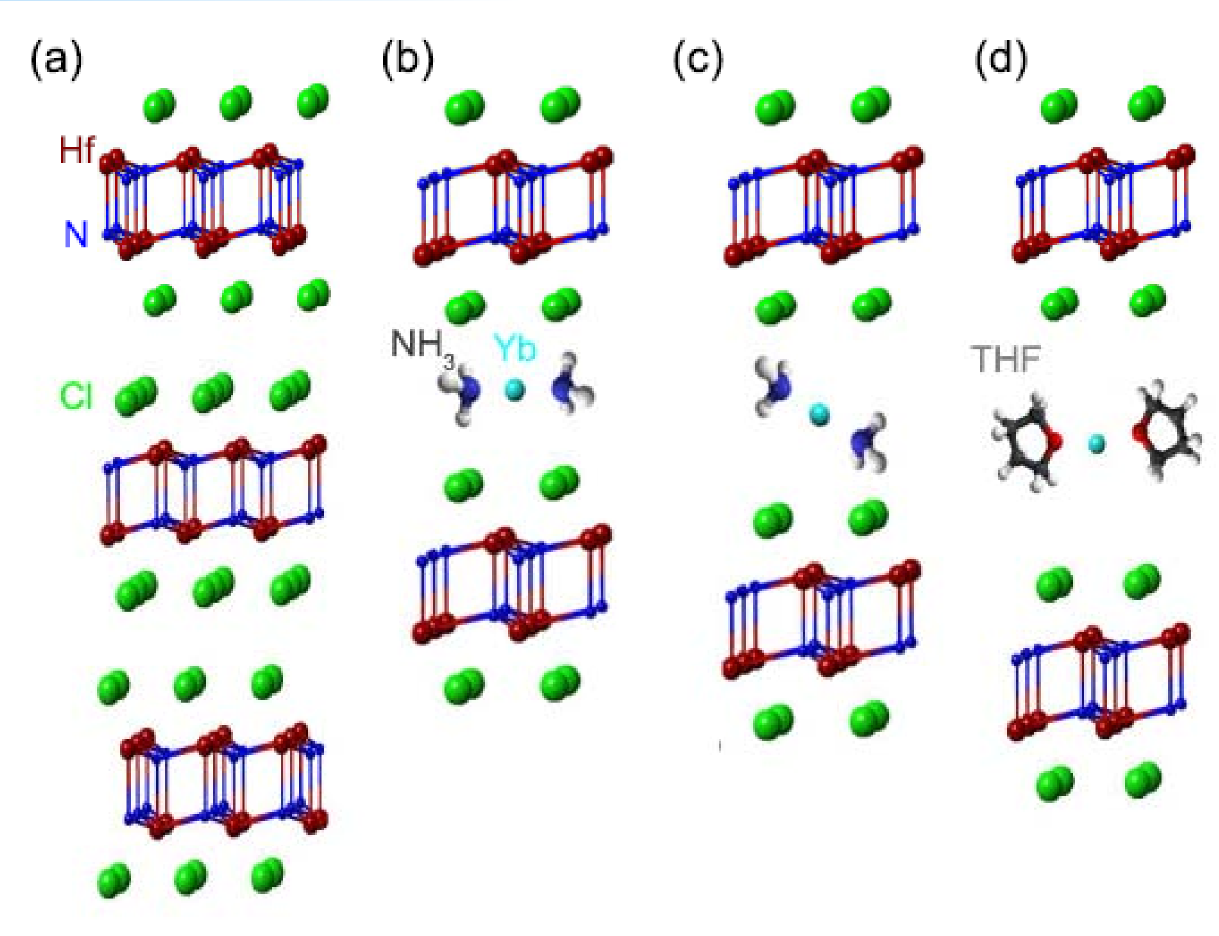


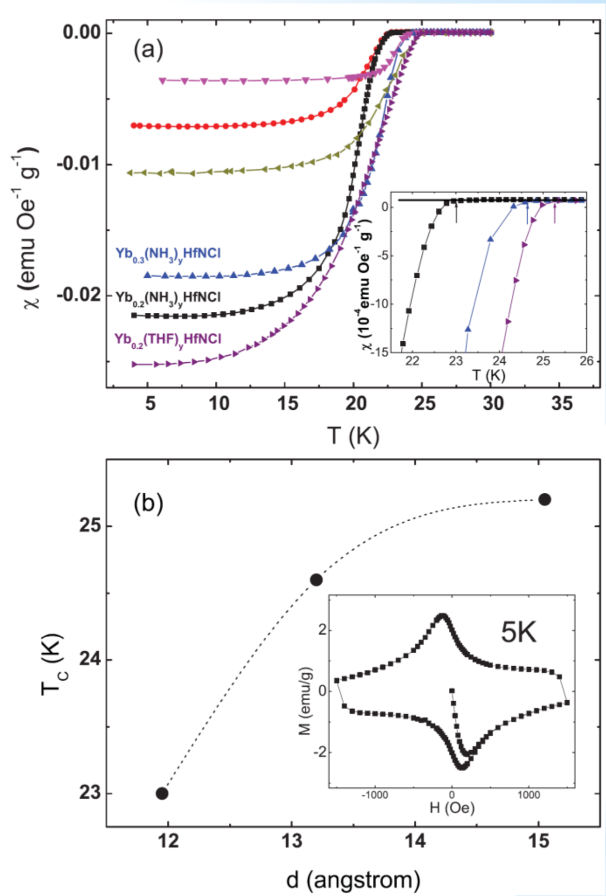


T_c ~ 25.5 K

S. Yamanaka et al., *Nature* **392**, 580 (1998)

Superconductivity and Structure of HfNCl, $Yb_{0.2}(NH_3)_yHfNCl$, $Yb_{0.2}(NH_3)_yHfNCl$ and $Yb_{0.2}(THF)_yHfNCl$

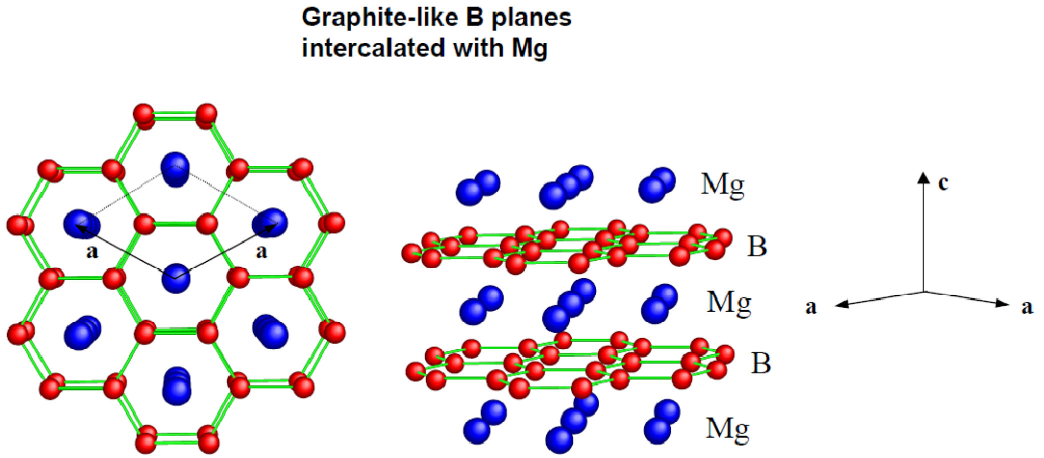


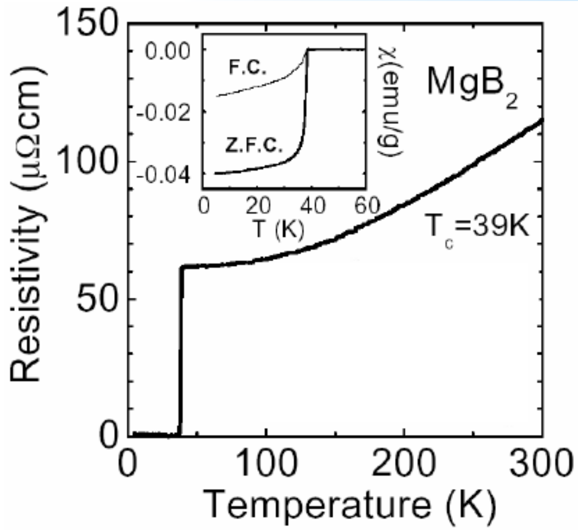


G. J. Ye, X. H. Chen et al., *PRB* (2012)

Tc=25.2 K

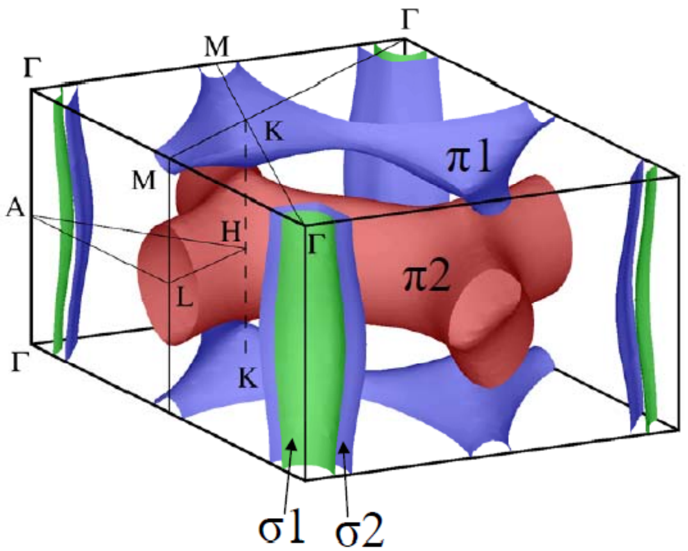
Highest Tc (39K) in the e-p mediated superconductors: MgB_2

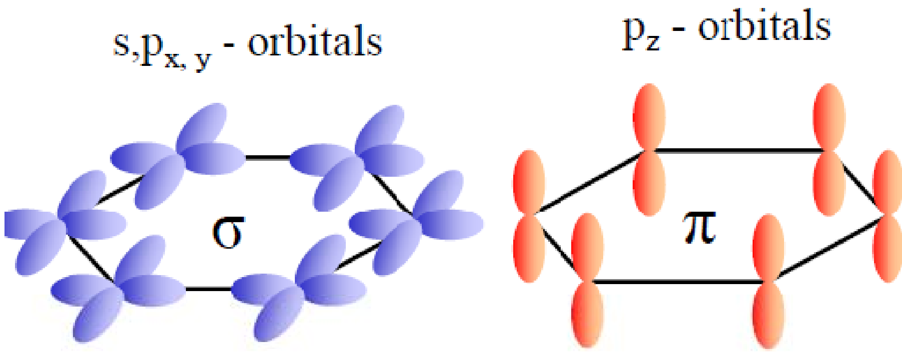




J. Nagamatsu *et al.*, Nature 410, **63** (2001)

Fermi surface

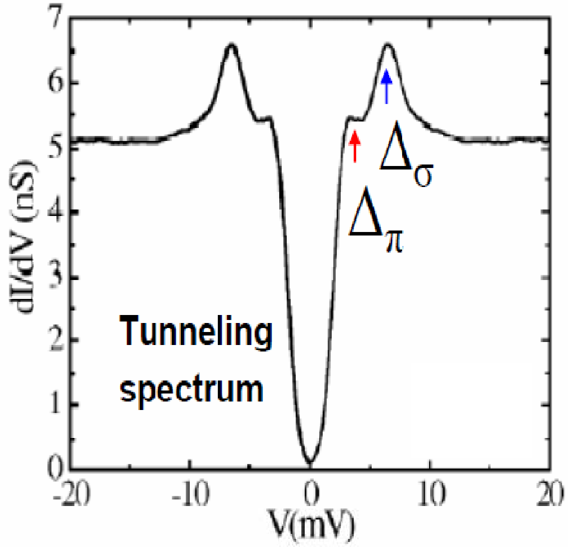




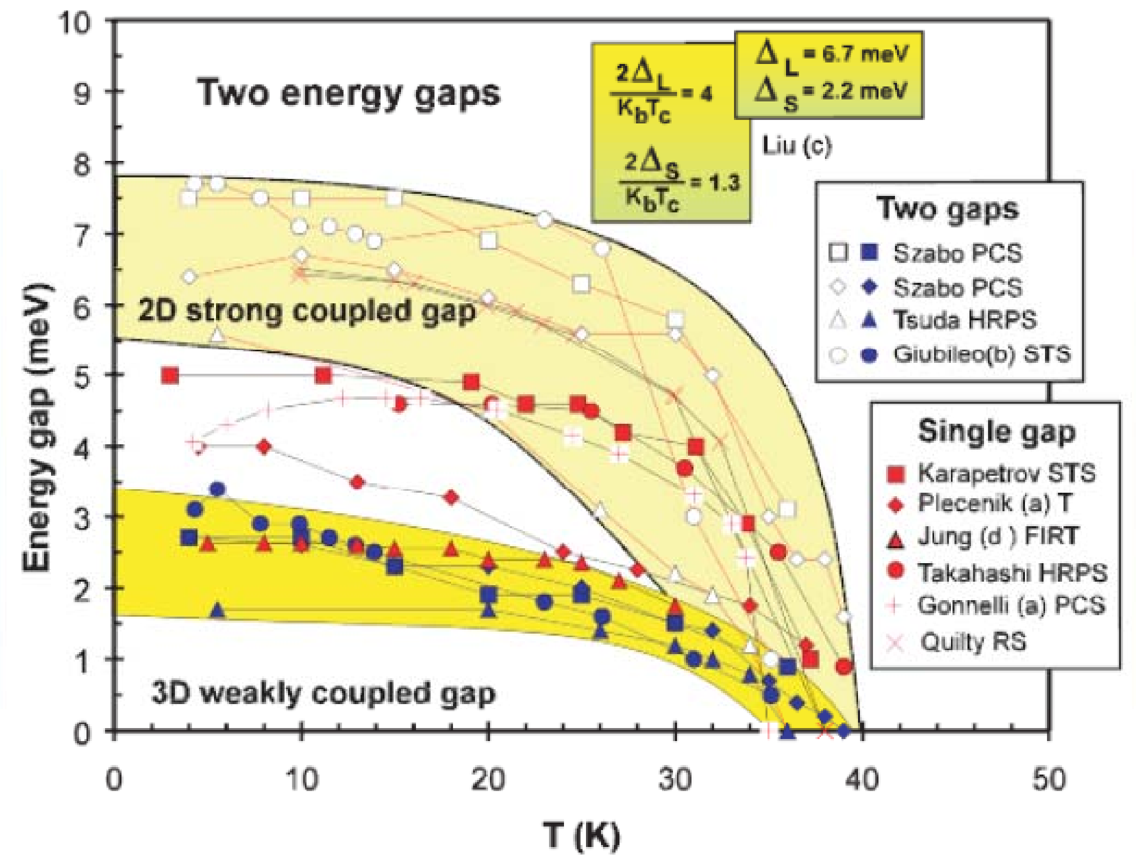
2D σ-bands

3D π-bands

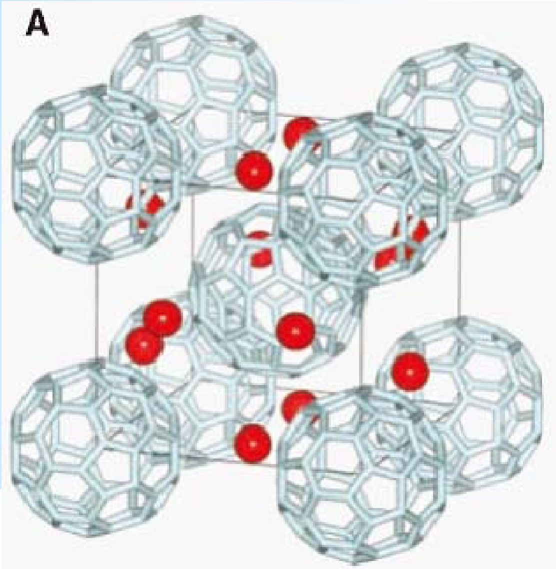
The first determined two-gap superconductor



M. Iavarone *et al*, Phys. Rev. Lett. 89, 187002 (2001)



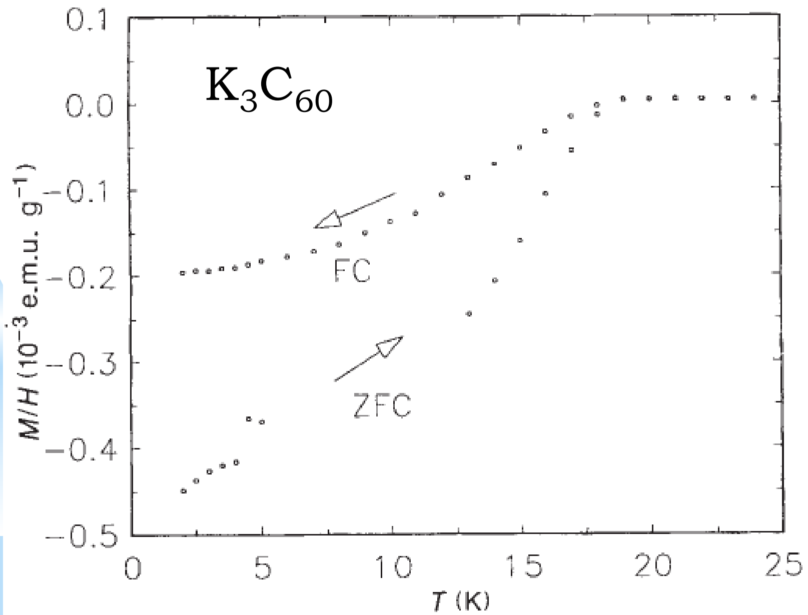
Fullerene superconductors



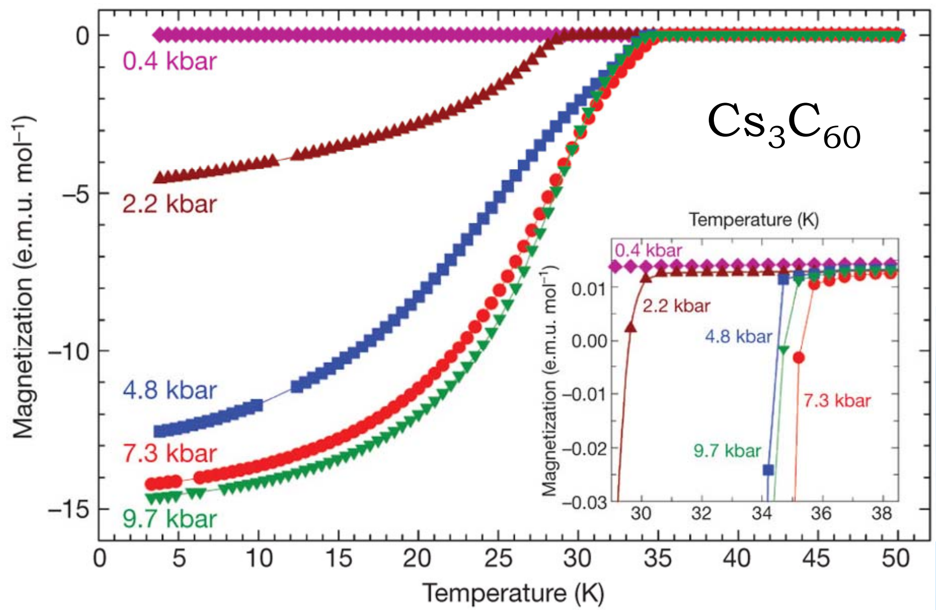
Fullerene superconductors:

K_3C_{60} : 19.3 K
Cs_2RbC_{60}: 33 K
CsK_2C_{60}: 24 K
Cs_3C_{60}: 38 K (1.43 GPa)
$NH_3K_3C_{60}$: 28 K
$Sm_{2.75}C_{60}$: 8 K
Rb_x(OMTTF)C_{60} (benzene): 26 K
K_x(OMTTF)C_{60} (benzene): 18.8 K

Rb_3C_{60}: 29.6 K
RbK_2C_{60}: 27 K
$RbNa_2C_{60}$: 3.5 K
$RbTl_{1.5}C_{60}$: 27.5 K
$Na_3N_3C_{60}$: 15 K

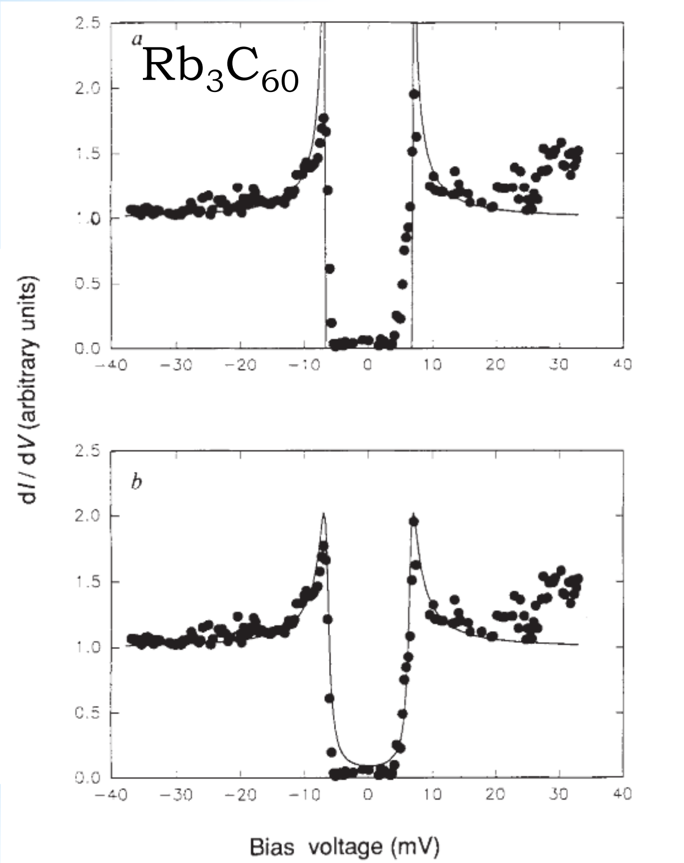


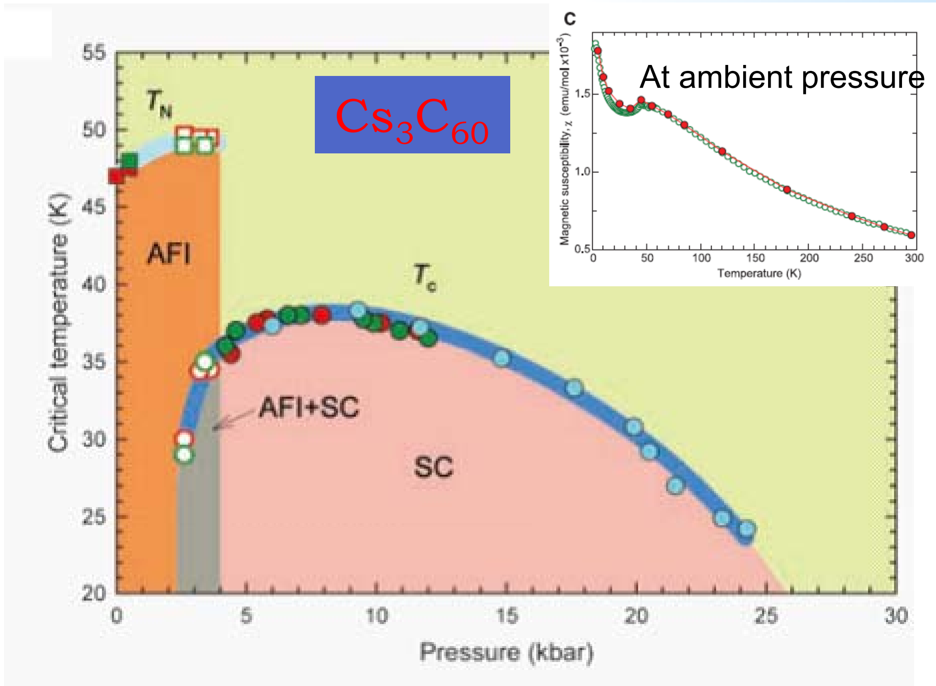
R.C. Haddon et al. *Nature* **350**, 320 (1991)



T.T.M. Palstra et al. *Solid State Commun.* **93**, 327 (1995)

Superconductivity: Conventional or unconventional?





1. SC emerges from AFI;
2. T_c raises and then drop with increasing P

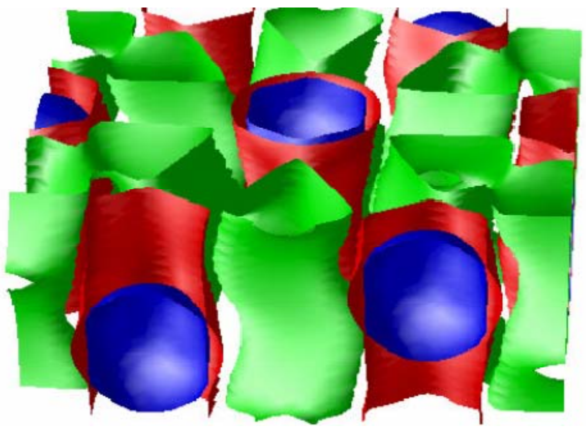
STM spectrum: Good fit in BCS thoery

Z. Zhang et al. *Nature* **353**, 333 (1991)

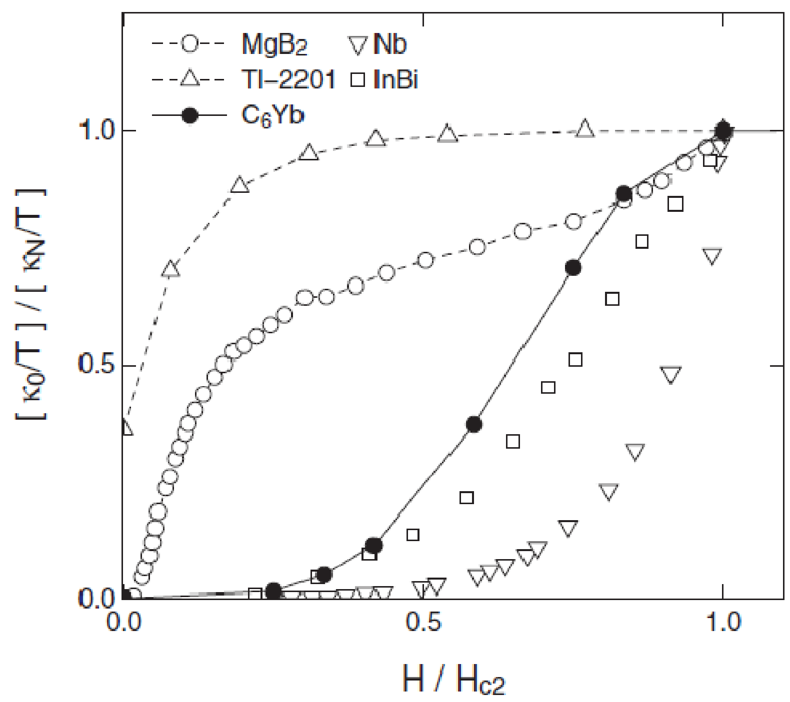
Y. Takabayashi et al. *Science* **323**, 1585 (2009)

Metal-intercalated graphite superconductors

KC_8 T_c = 0.125-0.55K
RbC_8 T_c = 0.020-0.151 K
CsC_8 T_c = 0.020-0.135 K
YbC_6 T_c = 5 K
CaC_6 T_c = 11.5 K (15.1 K@8GPa)



Multiband nature

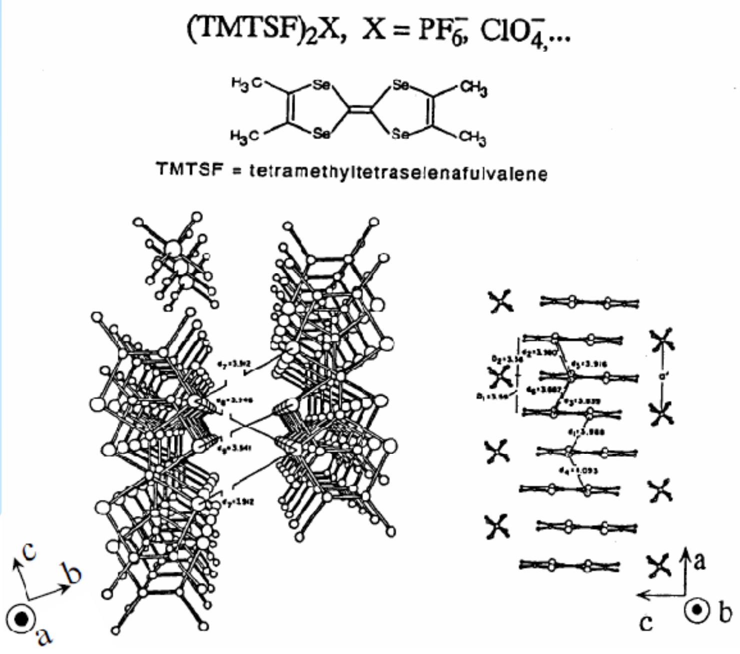


Isotropic *s*-wave

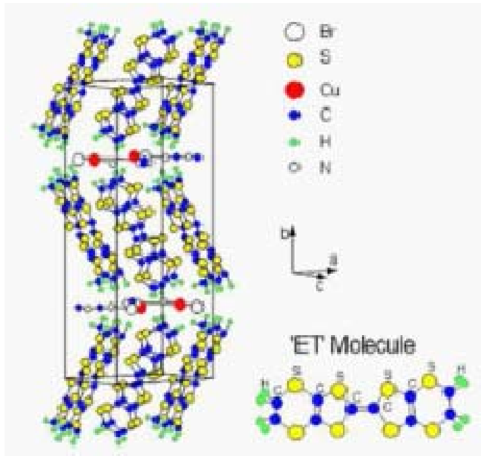
M. Sutherland et al., *PRL* **98**, 067003 (2007)

Organic superconductors

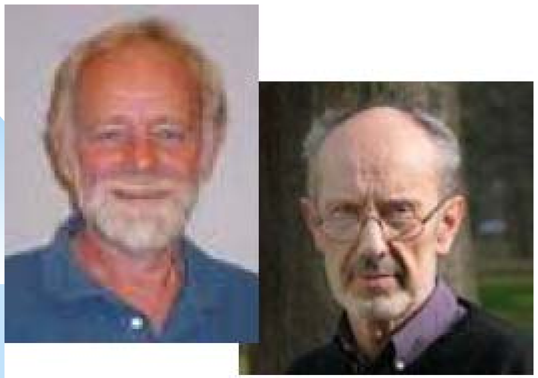
Tc= 14.2 K highest Tc



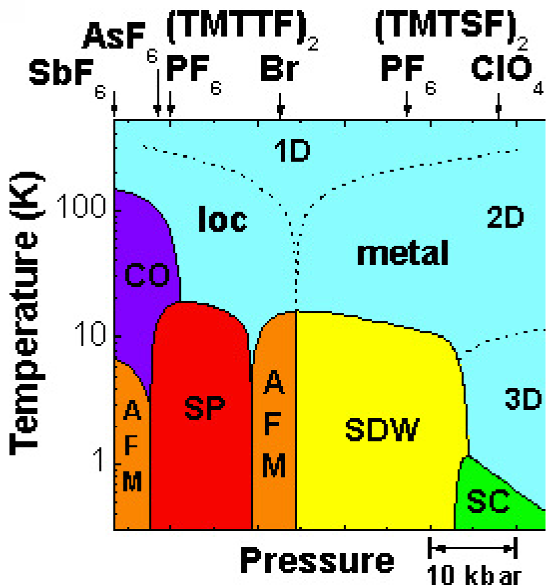
1979

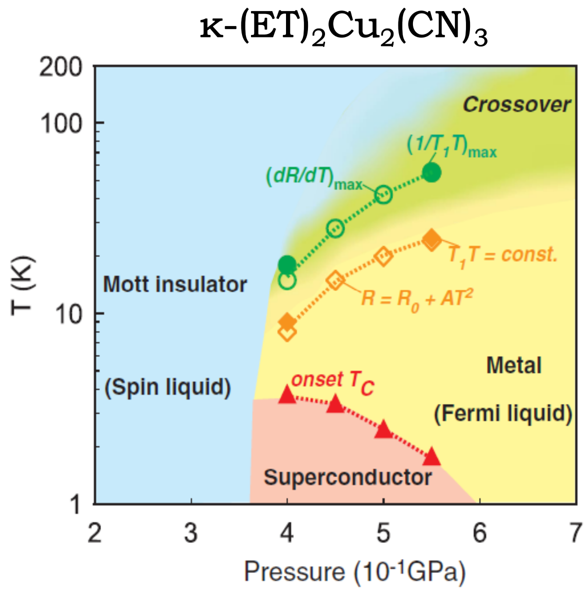


κ-(ET)2Cu2(CN)3



Bechgaard and Jerome

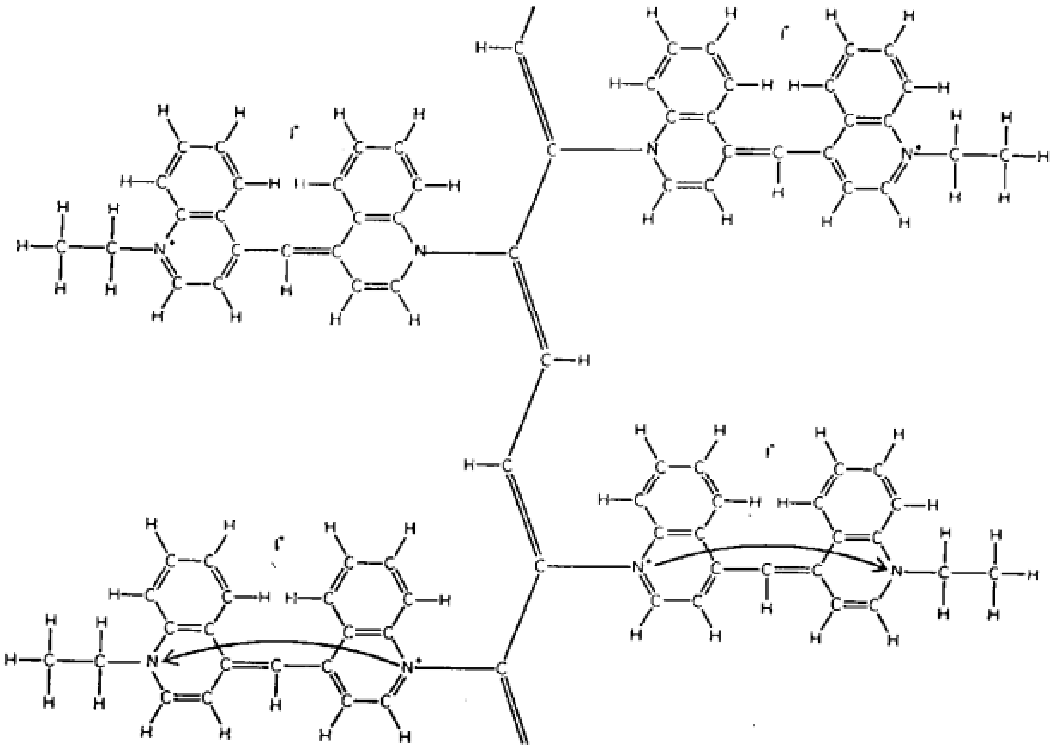


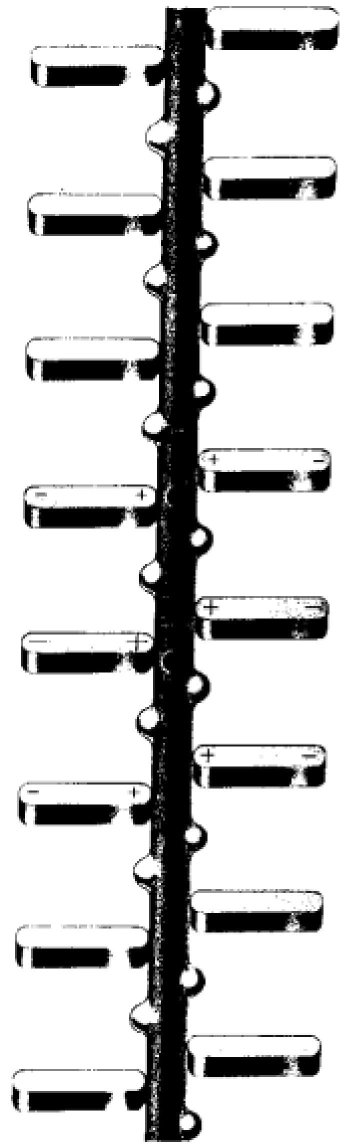


SCIENTIFIC AMERICAN FEBRUARY 1965 VOLUME 212 NUMBER 2

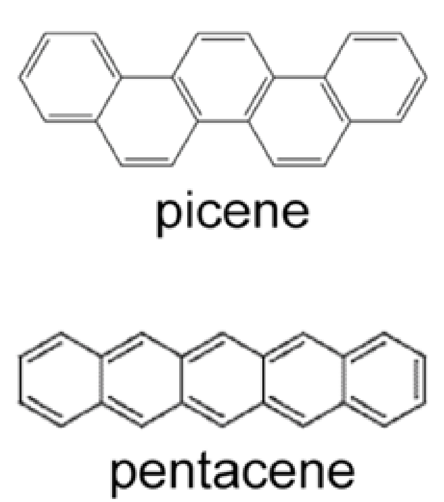
SUPERCONDUCTIVITY AT ROOM TEMPERATURE

IT HAS NOT YET BEEN ACHIEVED, BUT THEORETICAL STUDIES SUGGEST THAT IT IS POSSIBLE TO SYNTHESIZE ORGANIC MATERIALS THAT, LIKE CERTAIN METALS AT LOW TEMPERATURES, CONDUCT ELECTRICITY WITHOUT RESISTANCE

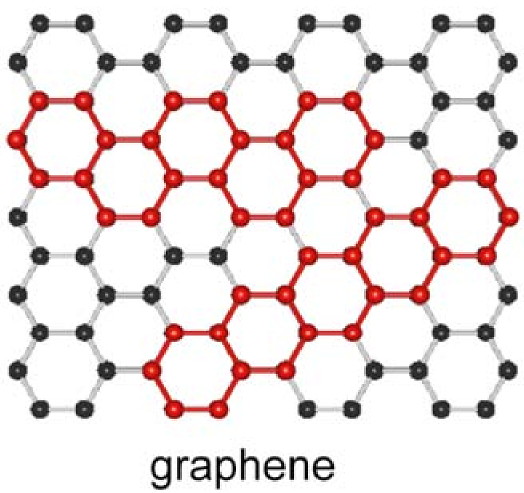




* picene molecule



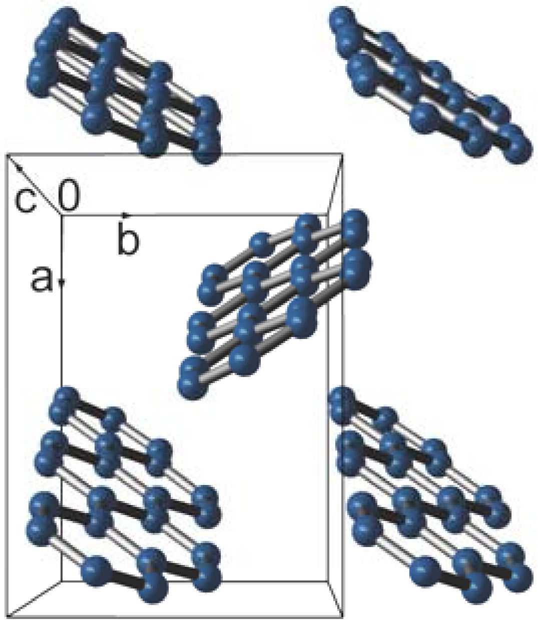
$C_{22}H_{14}$

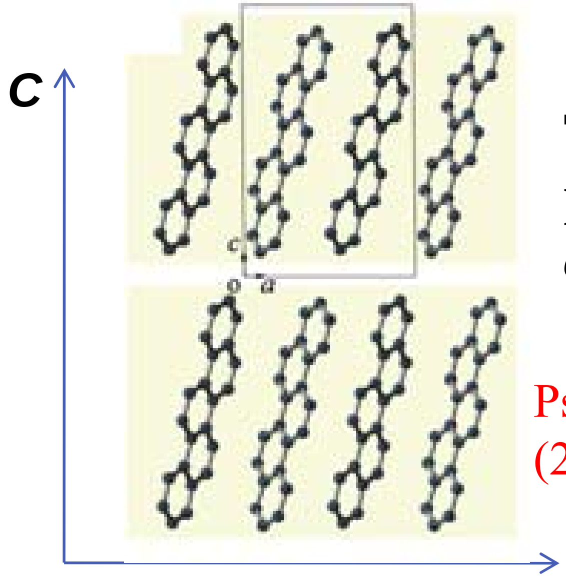


phenacene type

acene type

Fragment of graphene sheet



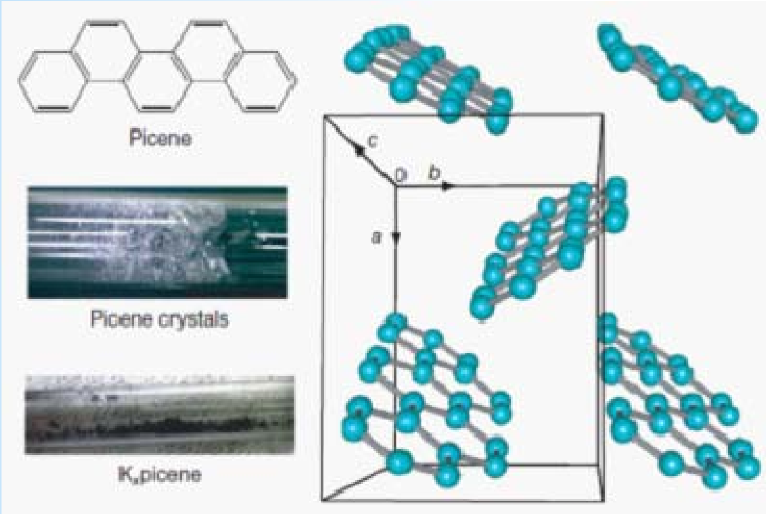


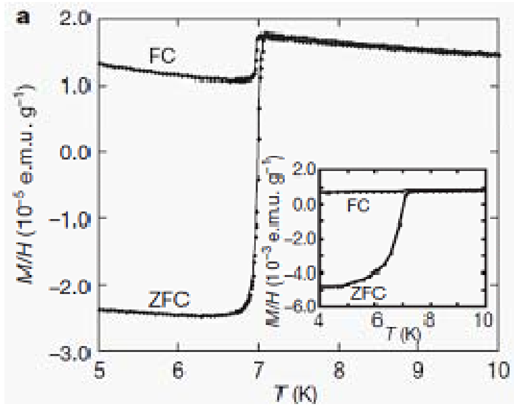
The intralayers (*ab*-planes) are stacked along *c*-direction.

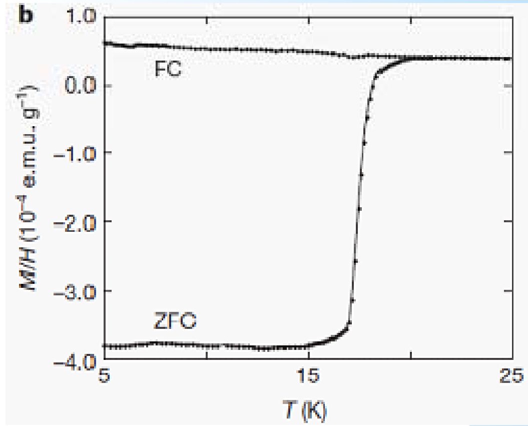
Pseudo-two dimensional (2D) crystal structure

Metal doping into picene crystals

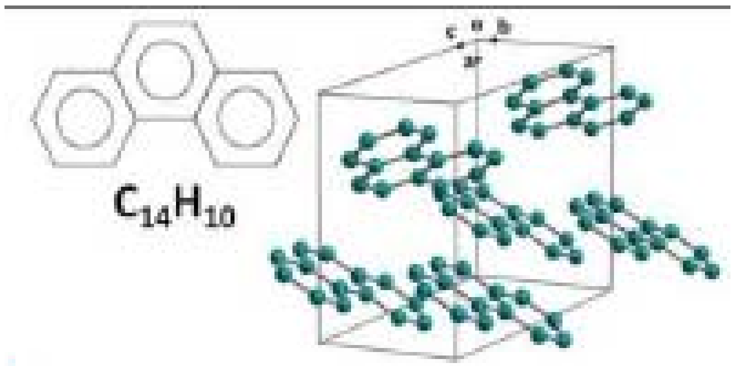
New Organic Superconductors

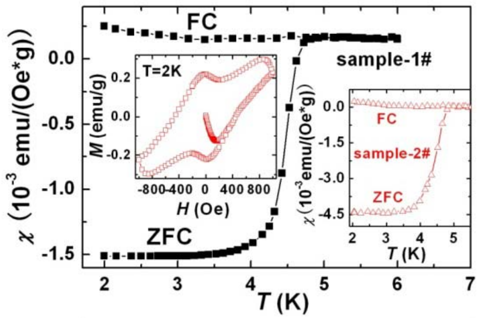


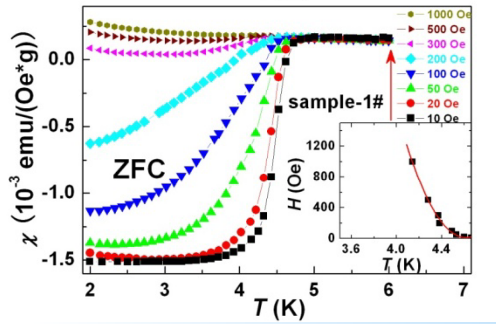




K_xPicene, Kobozono *Nature* 2010, Tc~18 K

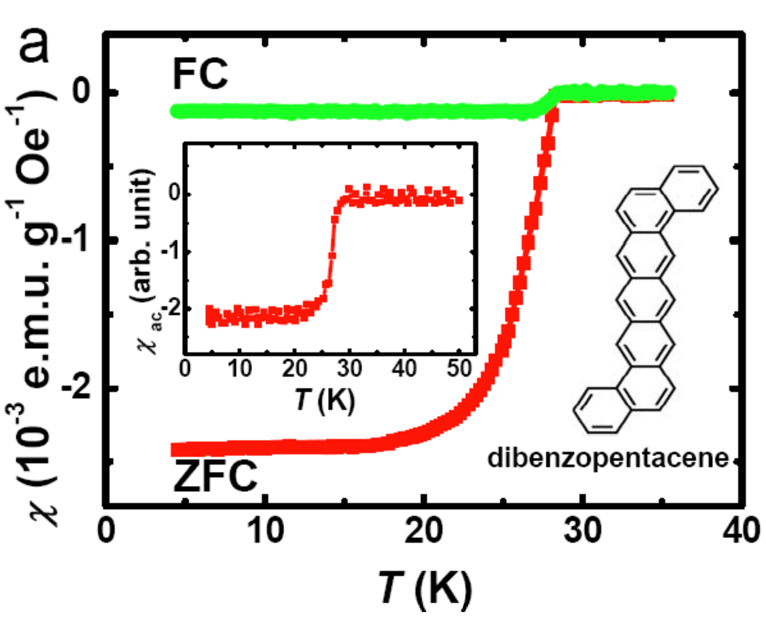




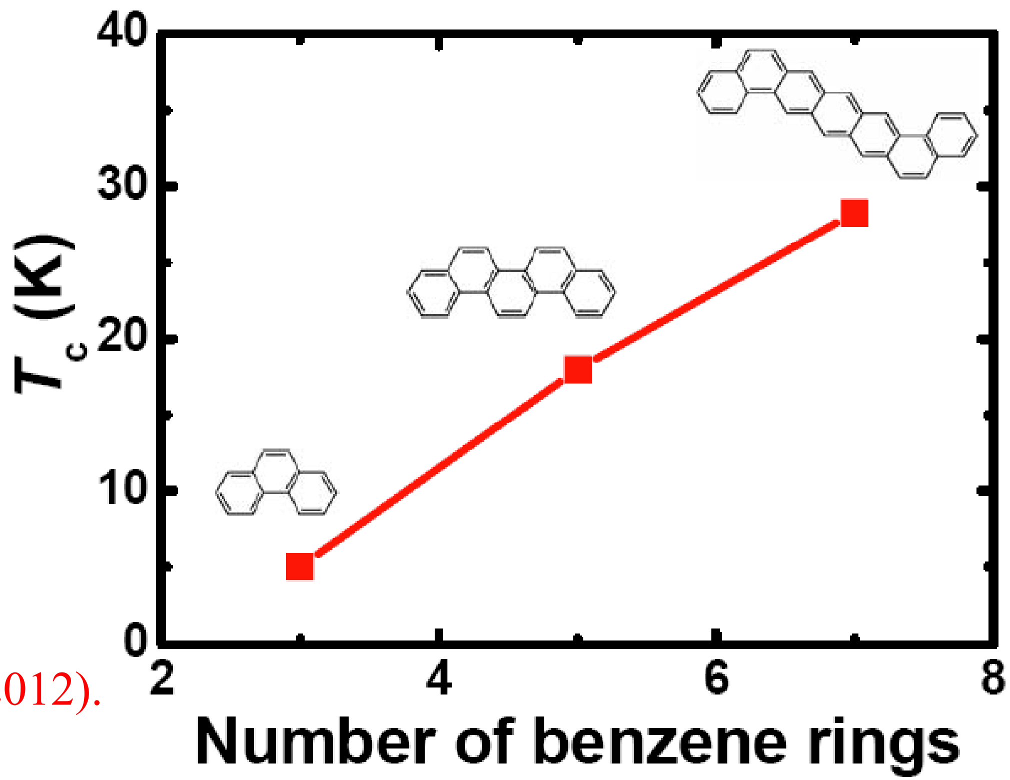


K_3Phenanthrene, X. H. Chen et al., *Nat. Commun.* (2011)

Superconductivity at 33 K in potassium-doped dibenzopentacene



Mianqi Xue et al., Scientific report 2, 389 (2012).



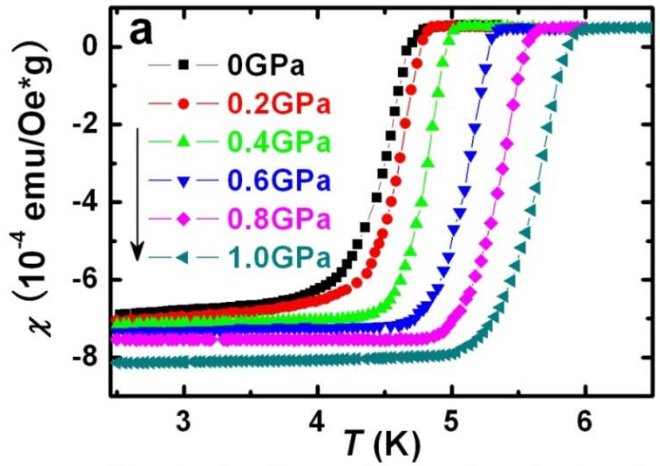
Question 1: Determination of superconducting phase and its crystal structure for hydrocarbon superconductors

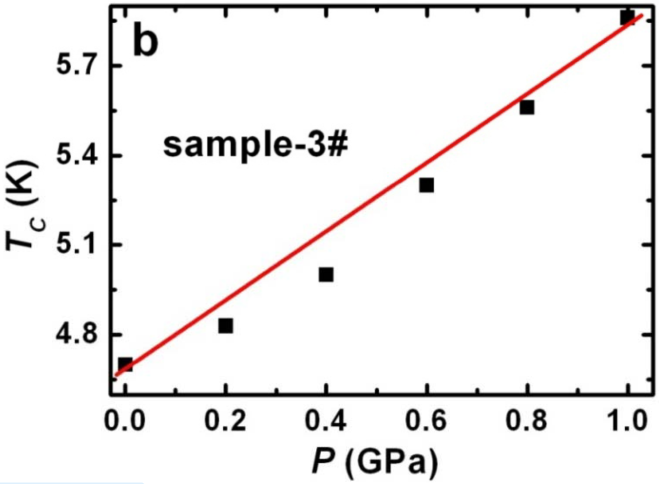
Question 2: Improve sample quality or growth of Single crystal suitable for physical property measurements

Question 3: It is not easy to reproduce the results **especially for picene and dibenzopentacene shielding fraction less than 5%, not reproducible for other group**

New organic superconductors

K_3Phenanthrene,

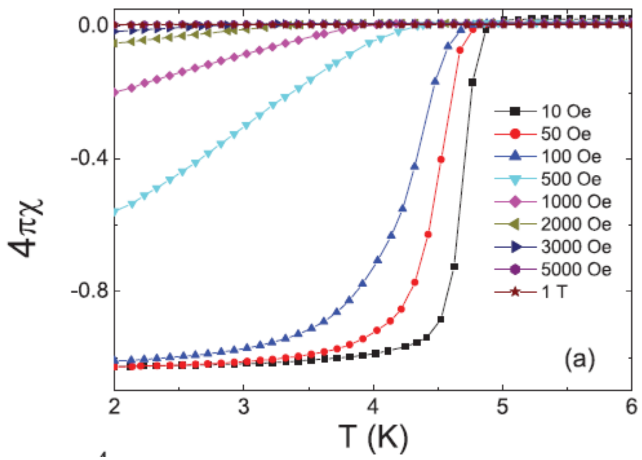




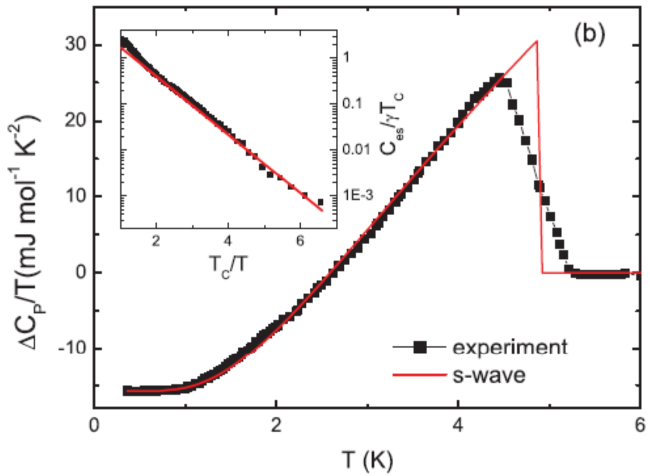
T_C is enhanced from 4.7 K at ambient pressure to 5.9 K at 1 GPa

X. H. Chen et al., *Nat. Commun.* (2011)

$Ba_{1.5}$Phenanthrene,



Full Meissner Effect



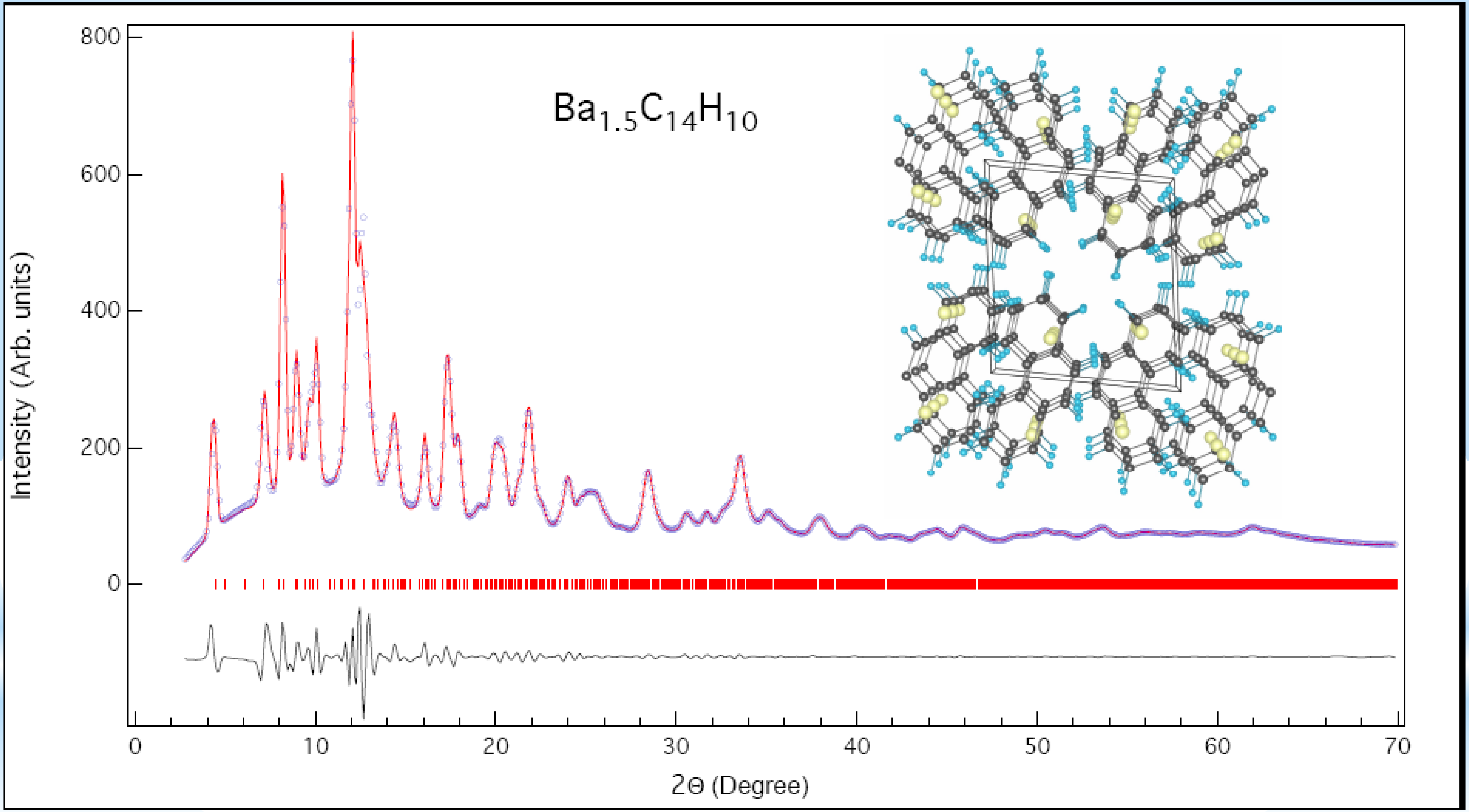
Superconducting Volume fraction>87%

Single-gap *s*-wave

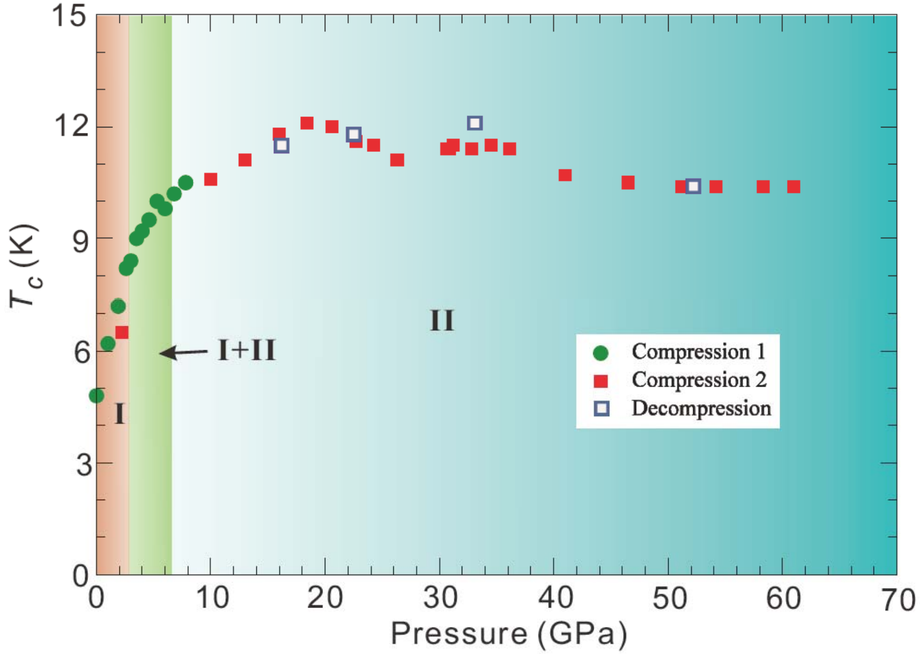
***J. J. Ying et al., PRB* 85, 180511(R) (2012).**

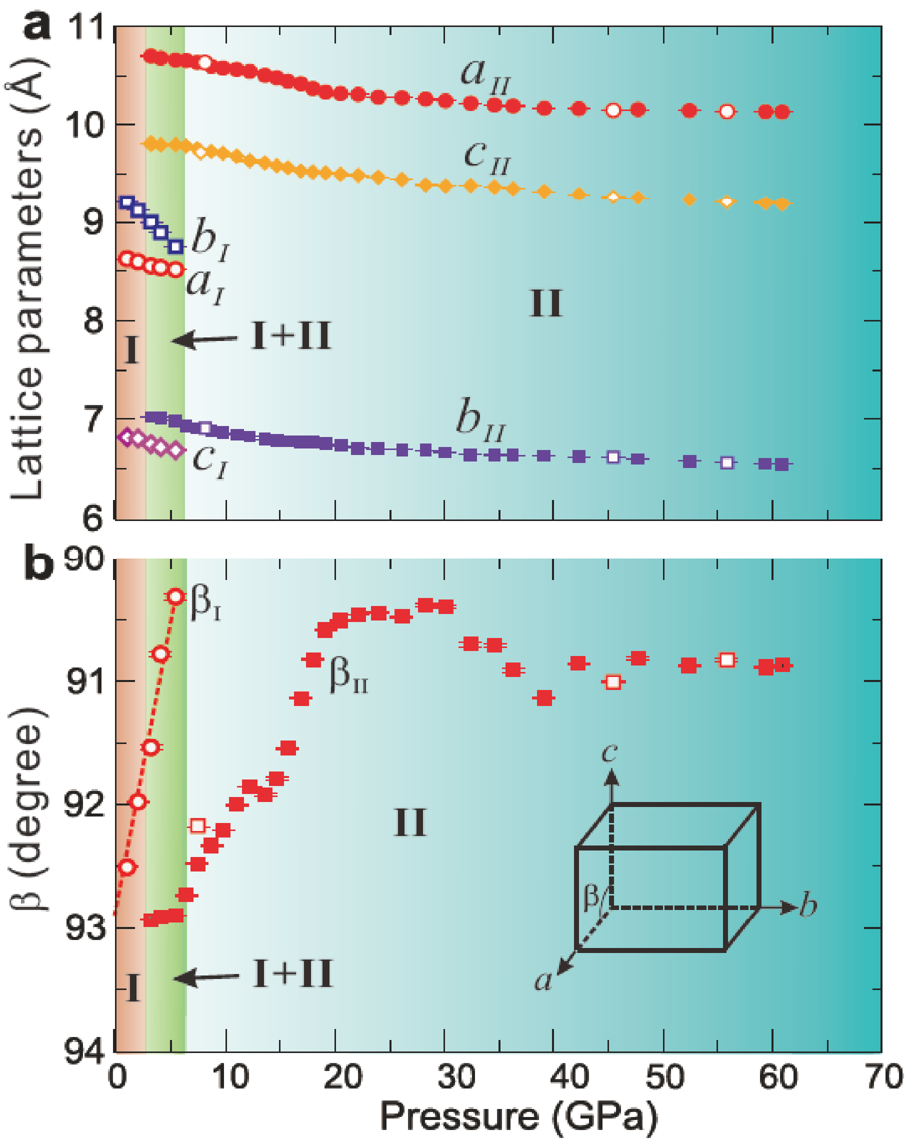
Kasahara and Iwasa PRB (2012) (reproducible)

X-ray diffraction patter and crystals structure



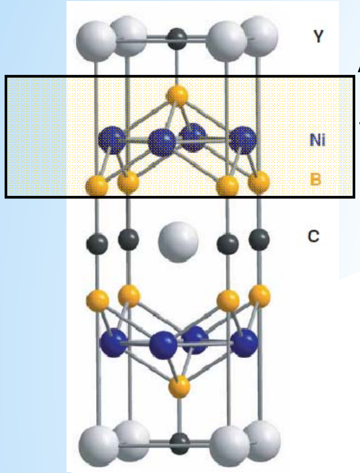
Evolution of Tc and lattice parameters with pressure





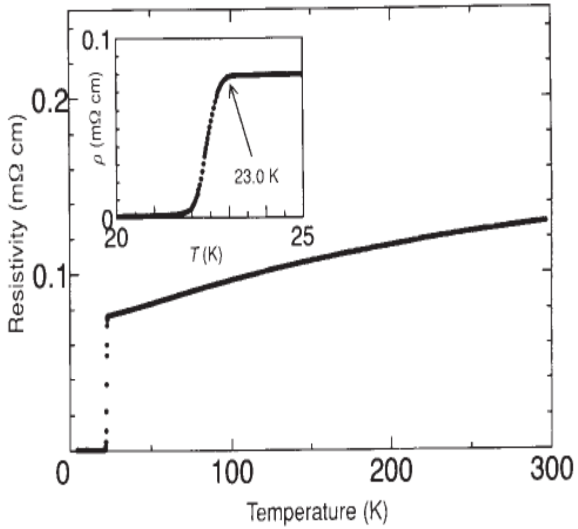
X. J. Chen, J. J. Ying, X. H.Chen et al.

Borocarbide superconductors

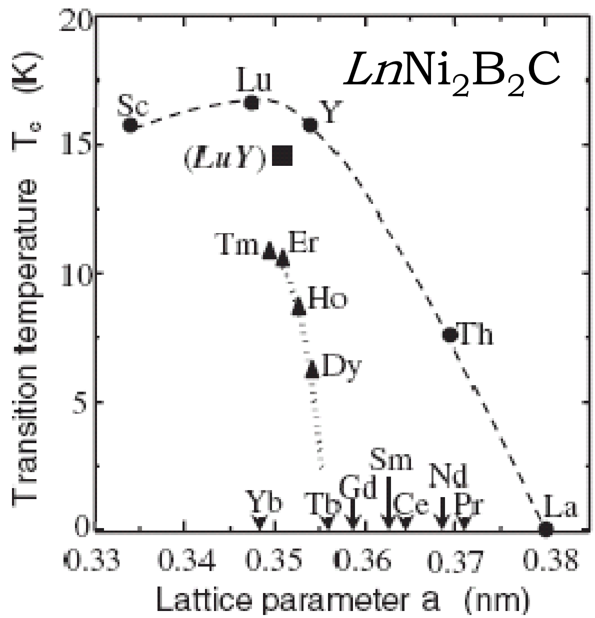


Anti-PbO structure

$LnNi_2B_2C$

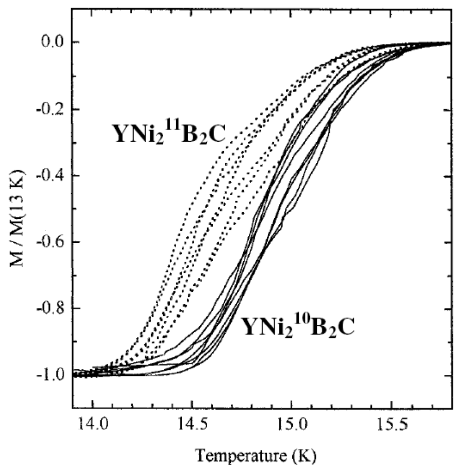


YPd_2B_2C, T_c~23K



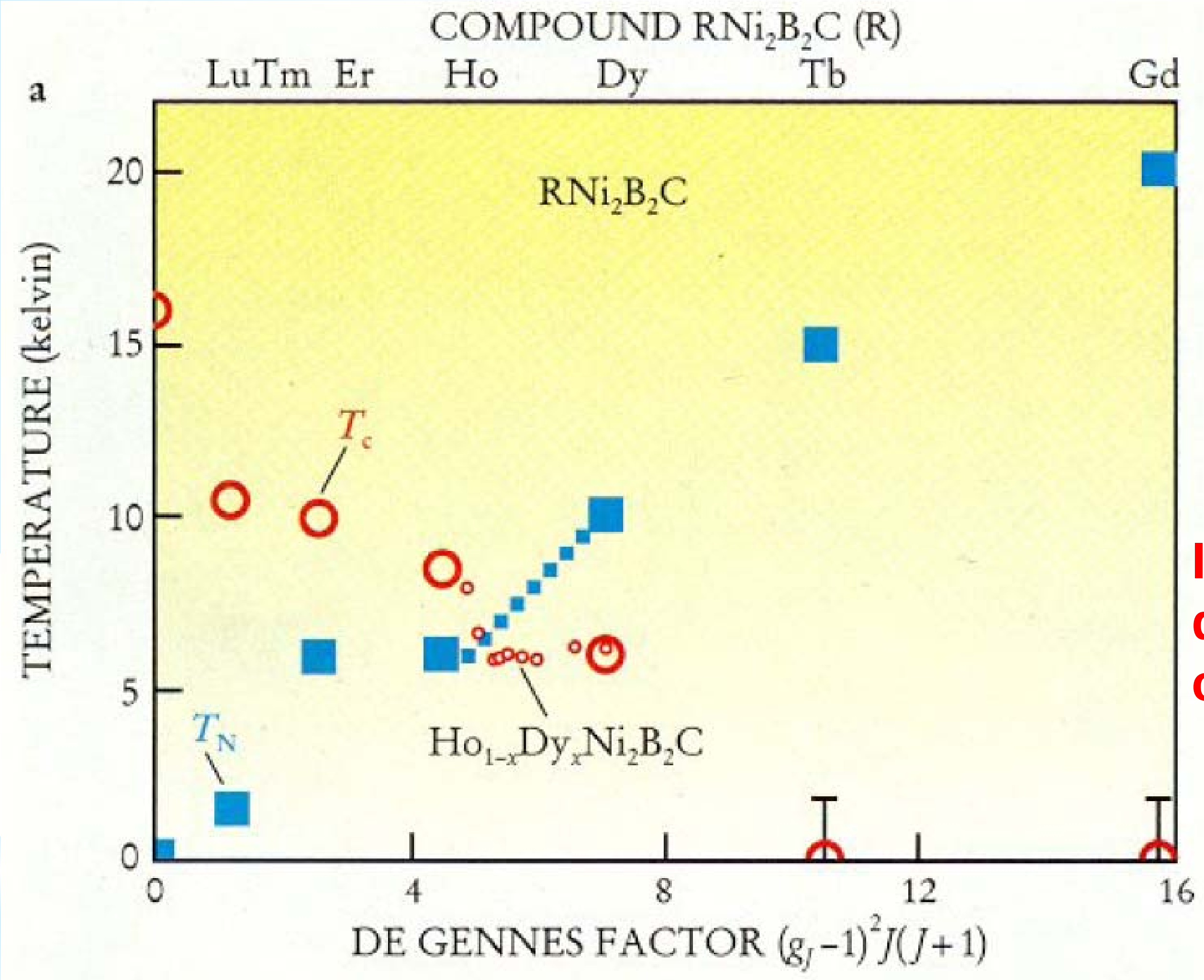
R.J. Cava *Nature* **367**,146 (1994); **367**, 252 (1994)

Compound	T_c (K)	T_N (K)	Compound	T_c (K)	T_N (K)
$CeNi_2B_2C$	0.1[a]	—	YRu_2B_2C	9.7[t]	—
$DyNi_2B_2C$	6.2[b], 6.4[c]	11[b,r]	$ThPd_2B_2C$	14.5[o]	—
$HoNi_2B_2C$	8[d], 7.5[e]	5 . . . 8[h,i,j]	YPd_2B_2C	23[p,s]	
$ErNi_2B_2C$	10.5[d,e]	6.8[k,l]			—
$TmNi_2B_2C$	11[d,e]	1.5[m,n]	$LaPt_2B_2C$	10[q]	—
$LuNi_2B_2C$	16.5[d,e]	—	$PrPt_2B_2C$	6[q]	—
YNi_2B_2C	15.5[d]	—	YPt_2B_2C	10[q]	—
$ScNi_2B_2C$	15[f]	—	$ThPt_2B_2C$	6.5[o]	
$ThNi_2B_2C$	8[g]	—			



No isotope effect on C site, but pronounced on B site.
Indication: e-p interaction

Does magnetic RE suppress superconductivity or not?



Conventional or Unconventional ?

Iron pnictides are totally different from the boride carbides

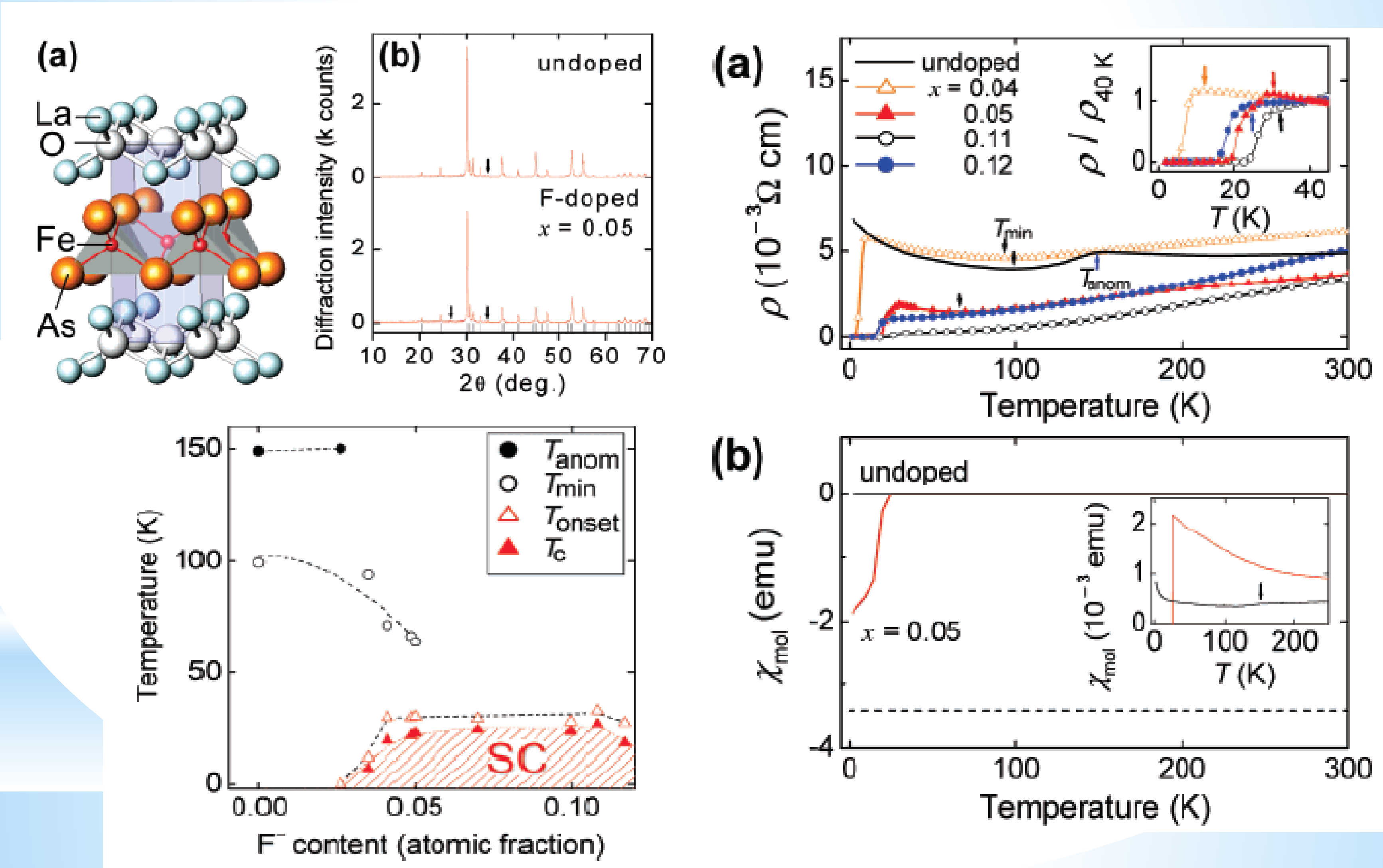
Substitution of magnetic ion Sm for non-magnetic ion La leads to an increase in Tc

- La(O,F)FeAs Tc=26 K, Sm(O,F)FeAs Tc=43 K and 55 K

It definitely indicates that iron pnictides are **unconventional superconductors**

Discovery of High-T_c iron-based superconductors

T_C= 26 K in $LaO_{1-x}F_xFeAs$

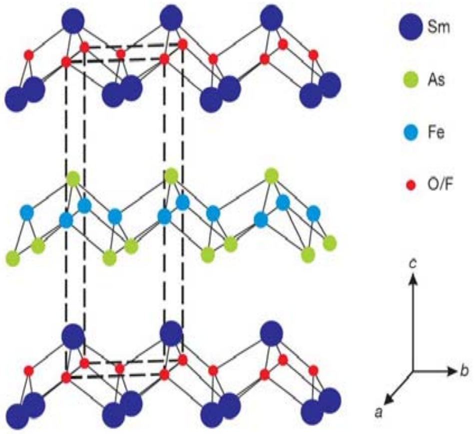


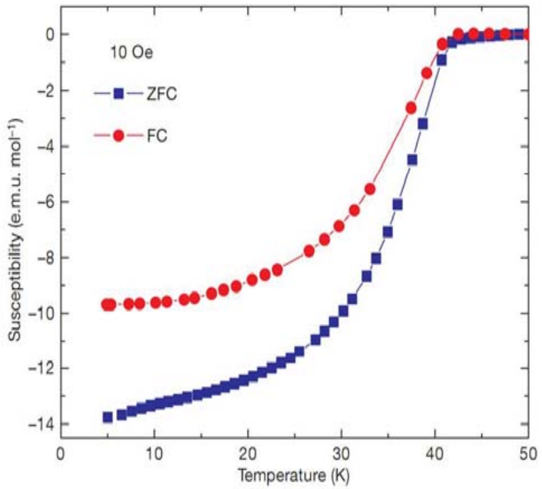
Y. Kamihara et al., *JACS* 130, 3296(2008).

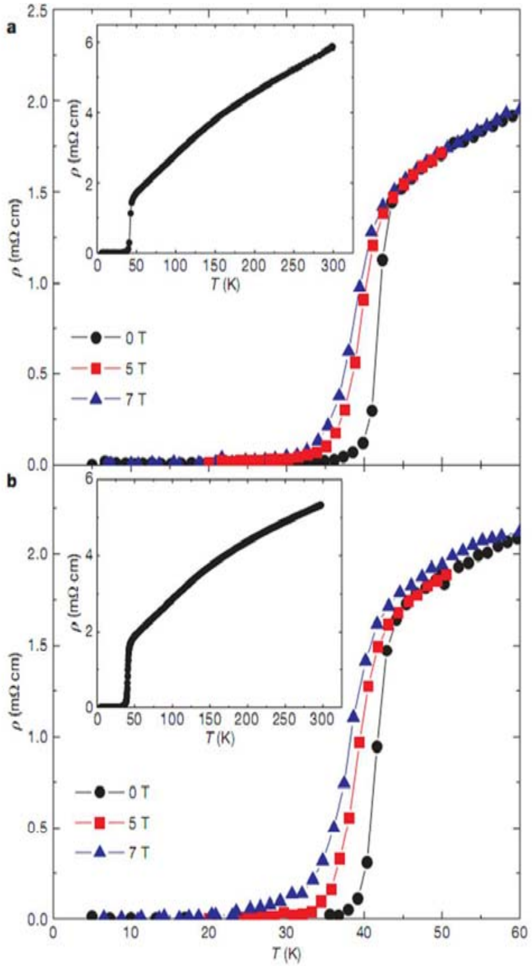
Discovery of High-T_C iron-based superconductors

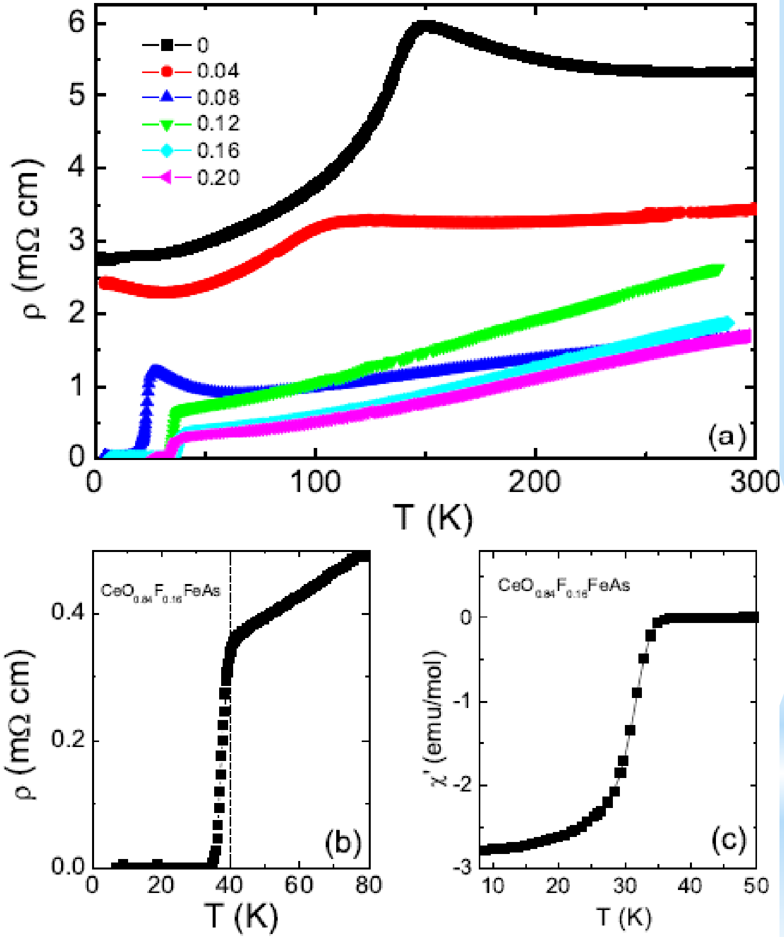
breakthrough in $SmFeAsO_{1-x}F_x$ x=0.15

$CeFeAsO_{1-x}F_x$









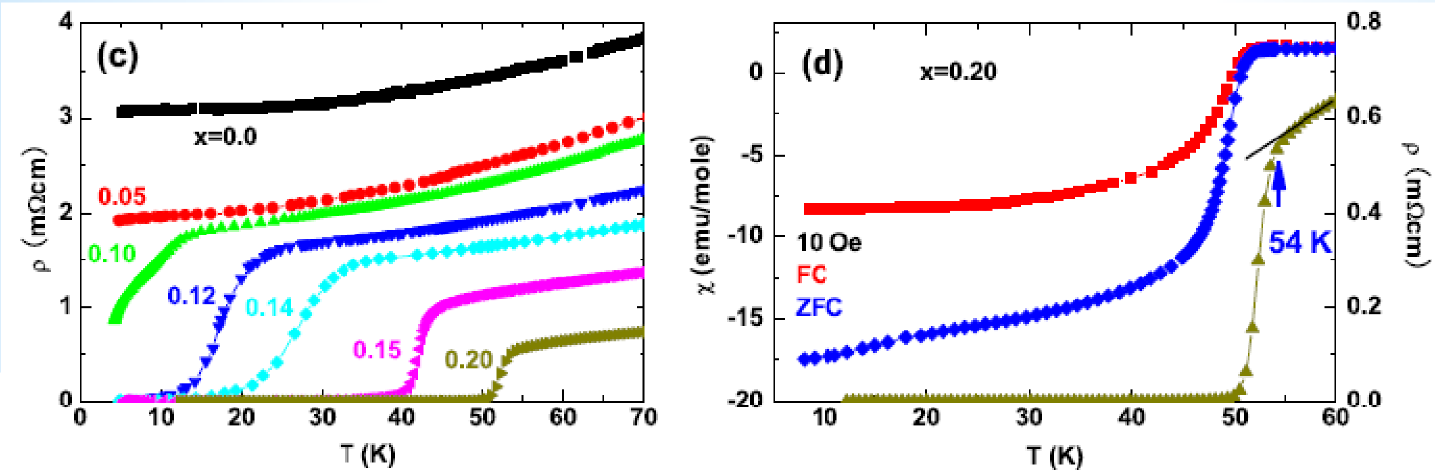
Tc=43 K higher than 39 K McMillan limit

It proves $LnFeAsO_{1-x}F_x$ as high-T_c superconductor

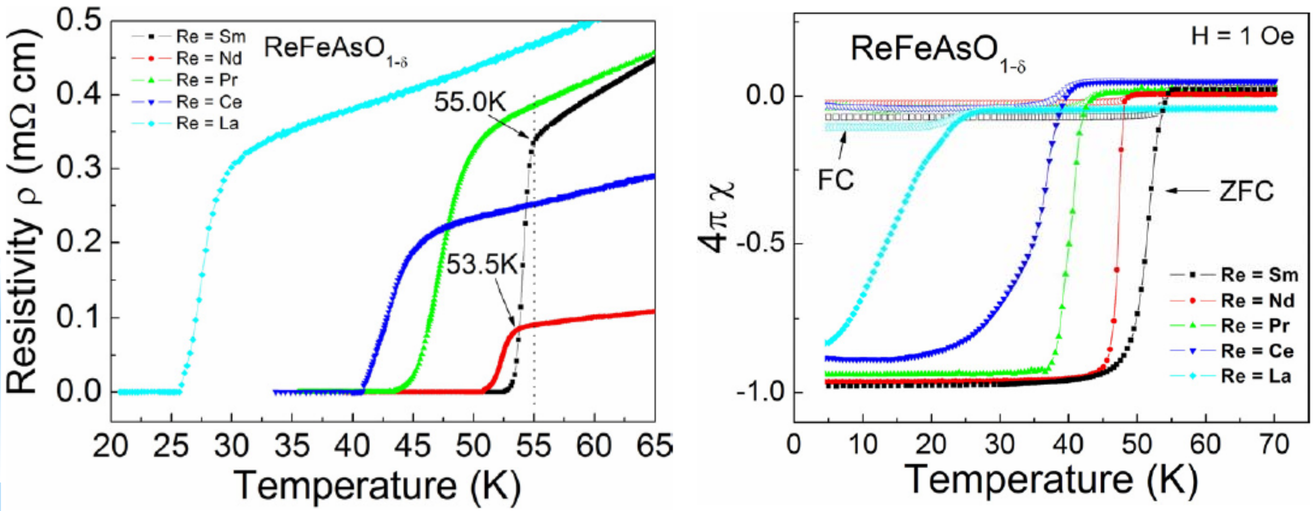
X. H. Chen et al., *Nature* **453**, 761(2008).

G.F. Chen and N.L. Wang et al., *PRL* (2008)

Evolution of Tc with x in $SmFeAsO_{1-x}F_x$



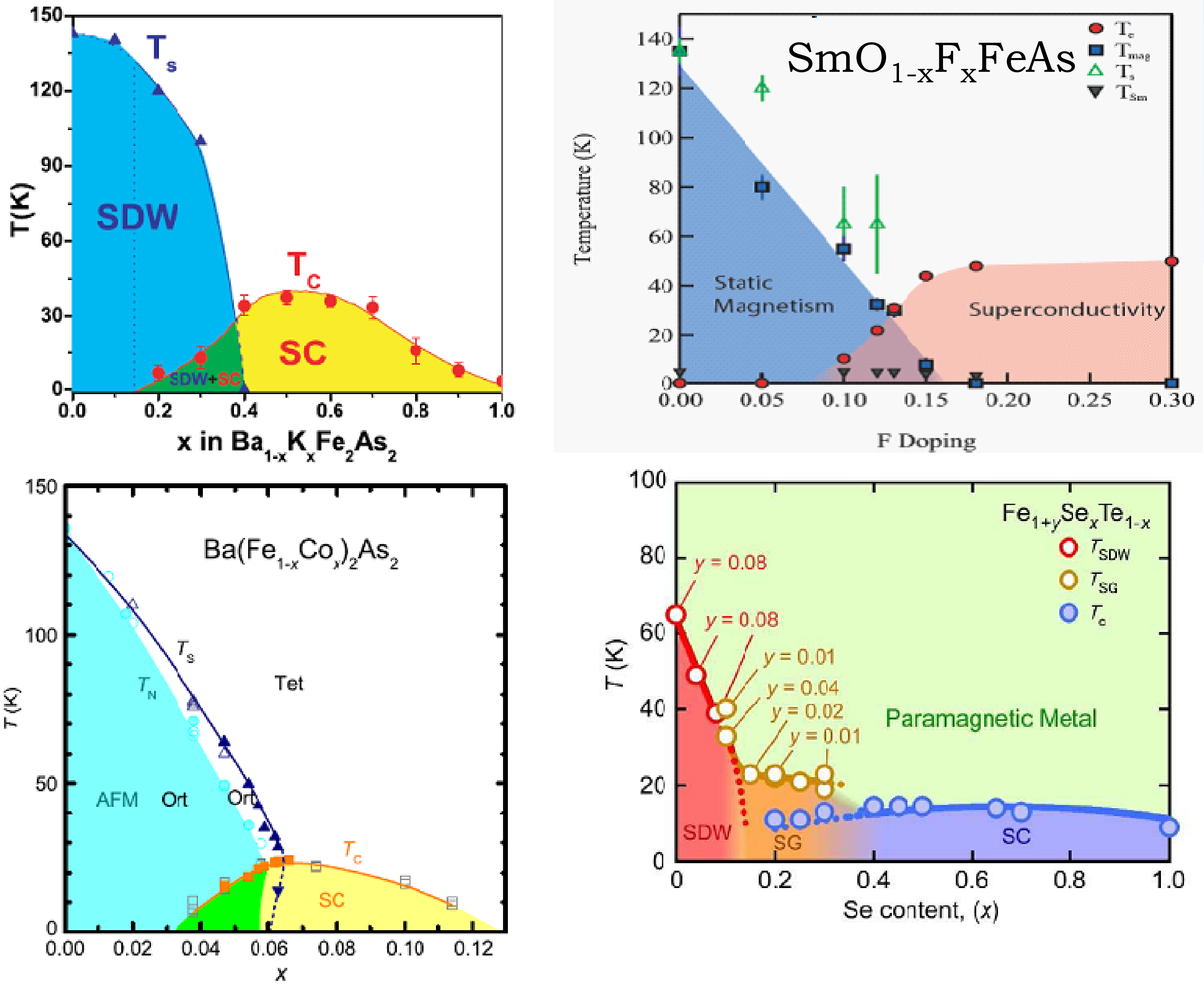
R. H. Liu, X. H. Chen et al., *Phys. Rev. Lett.* **101**, 087001(2008)



Highest T_C =55 K inIron-pnictides

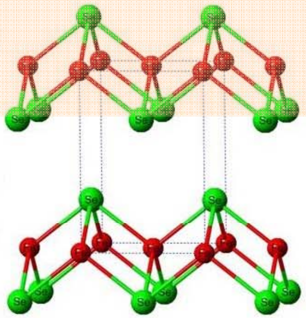
Z.A. Ren and Z.X. Zhao et al., *EPL* (2008)

Coexistence and competition between SC and magnetism

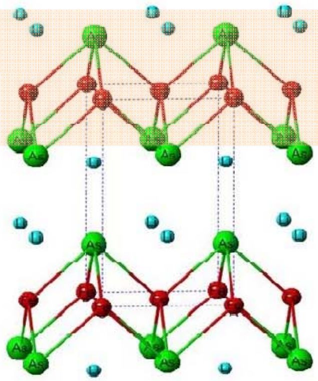


H Chen *et al.*, *EPL* (2009); Nandi *et al.*, *PRL* (2010);
Drew *et al.*, *Nat. Mater.* (2009); Katayama *et al.*,*JPSJ (2010)*

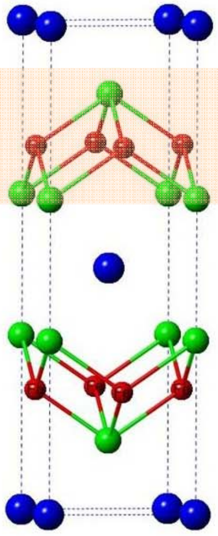
Iron-based high-T_c superconductors



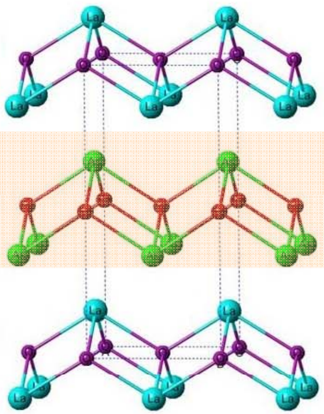
FeSe
(11)
T_c^{max} = 15 K



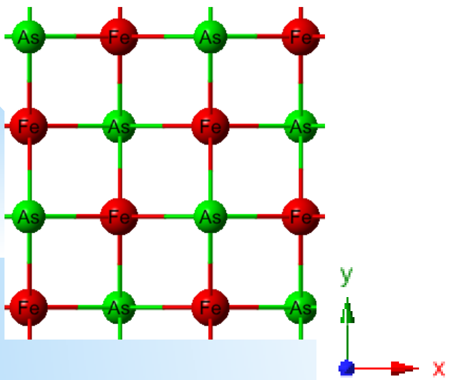
LiFeAs
(111)
T_c^{max} = 25 K

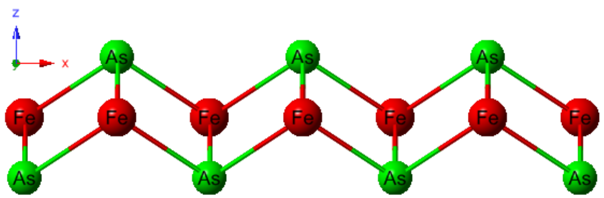


$BaFe_2As_2$
(122)
T_c^{max} = 38 K



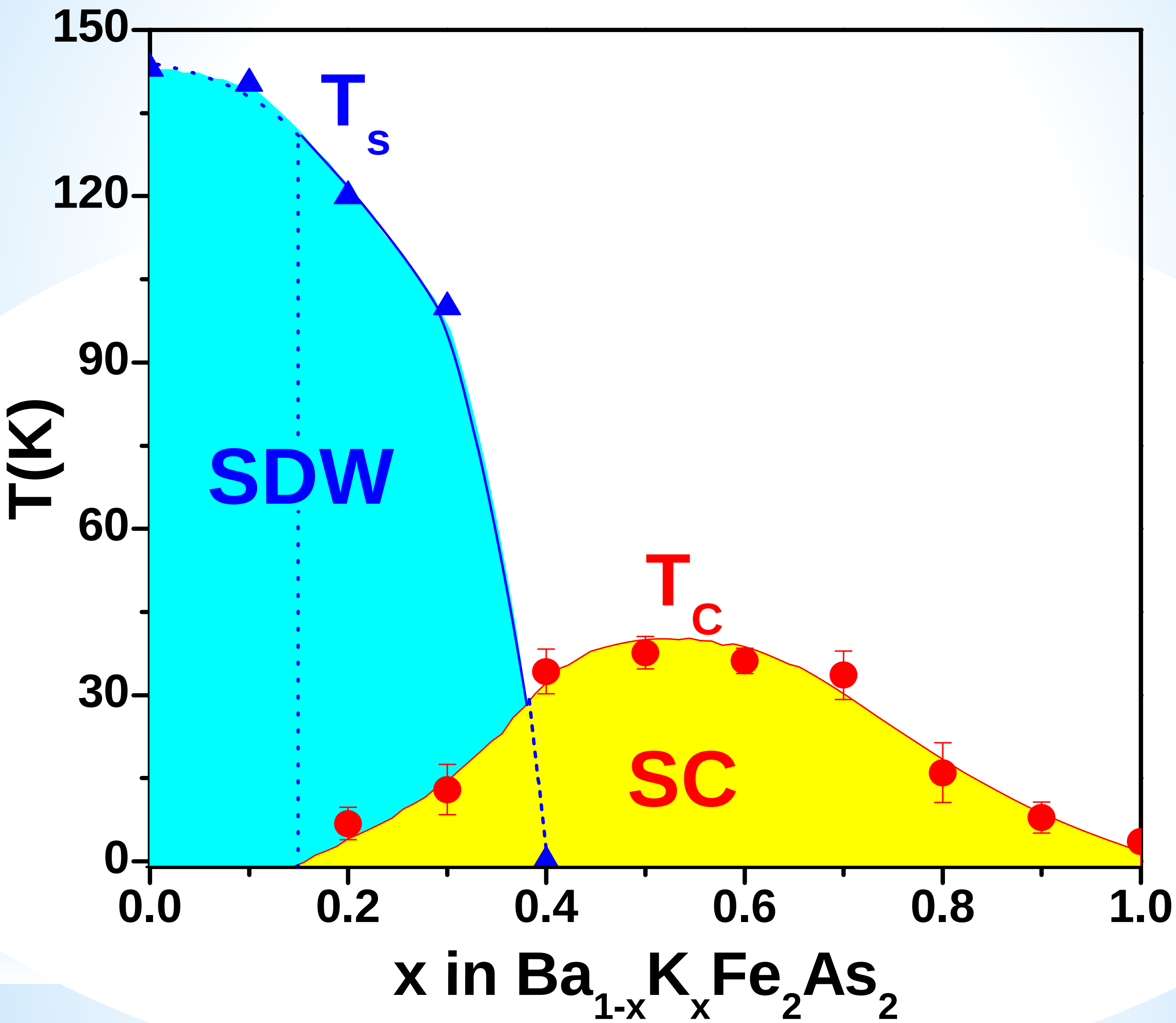
LaOFeAs
(1111)
T_c^{max} = 55 K





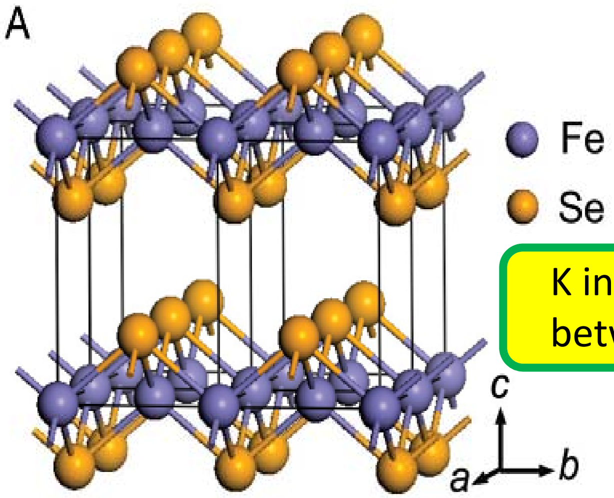
$(Sr_4V_2O_6)Fe_2As_2$
(42622)
T_c^{max} = 37 K

Phase diagram in $Ba_{1-x}K_xFe_2As_2$ System

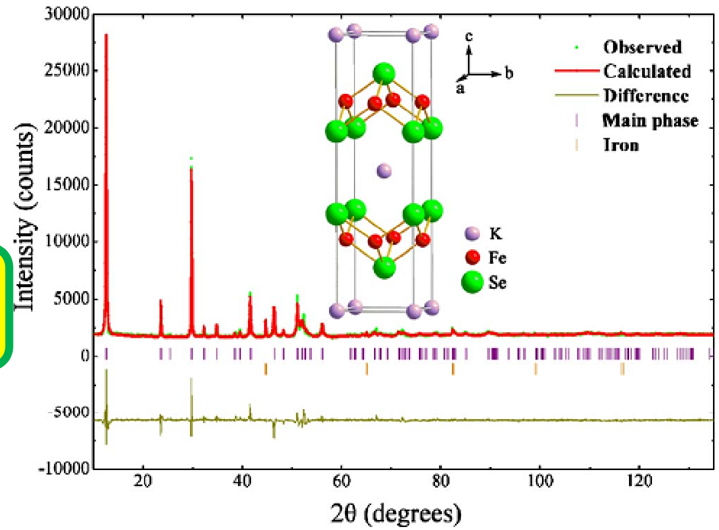


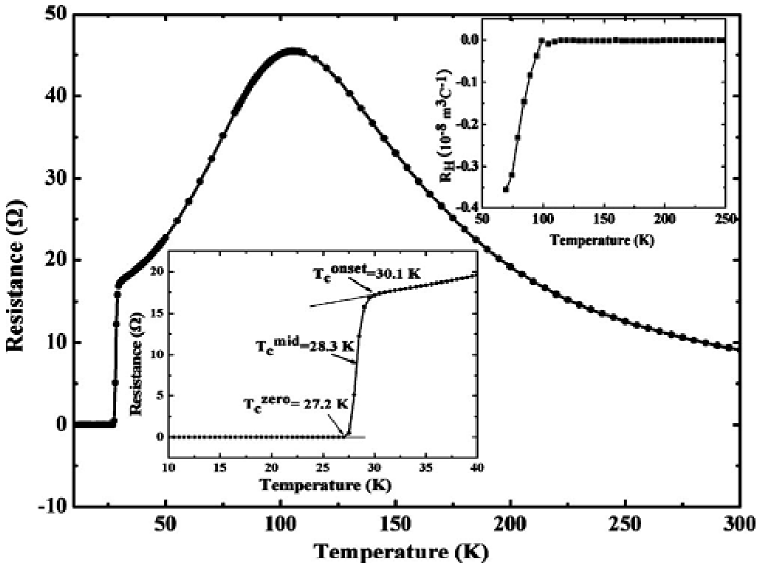
H. Chen, X. H. Chen et al., Europhys. Lett. 85, 17006 (2009).

Iron chalcogenides



K intercalating between FeSe layers





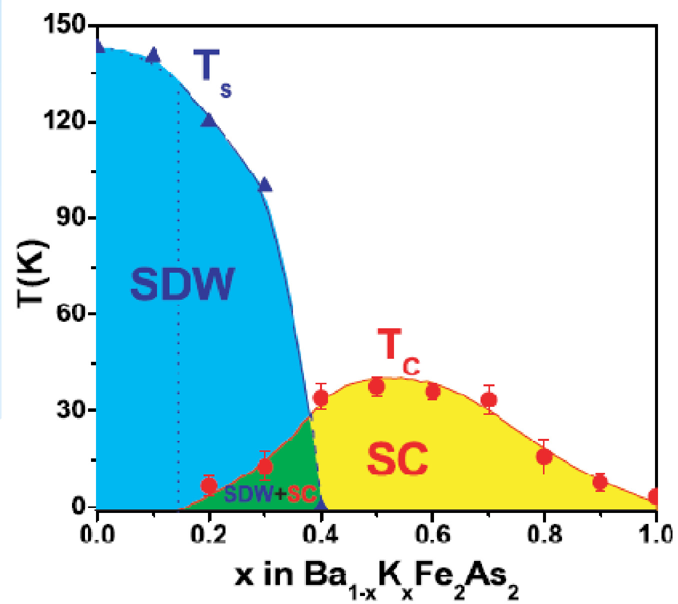
FeSe   Tc=8-15 K, 37 K under pressure

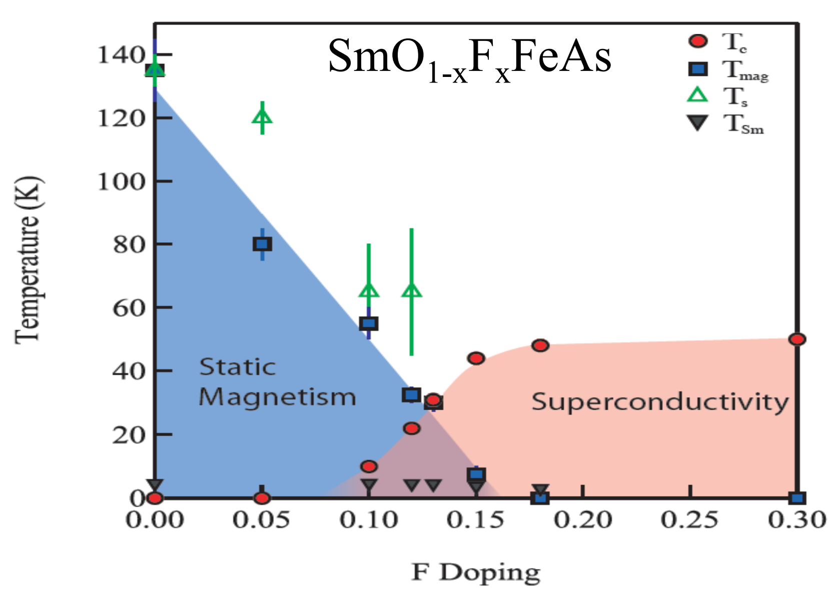
T_C rises to 31K without external pressure

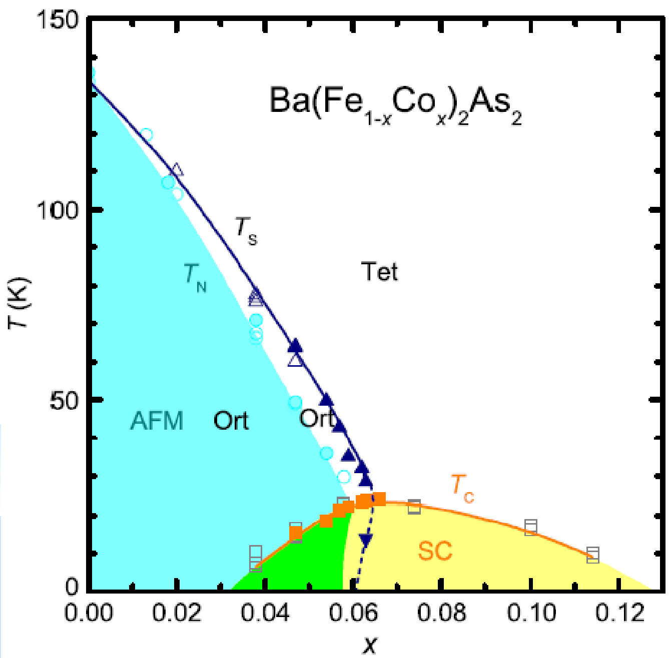
What is new in $K_xFe_{2-x}Se_2$ compared to pnictides ?

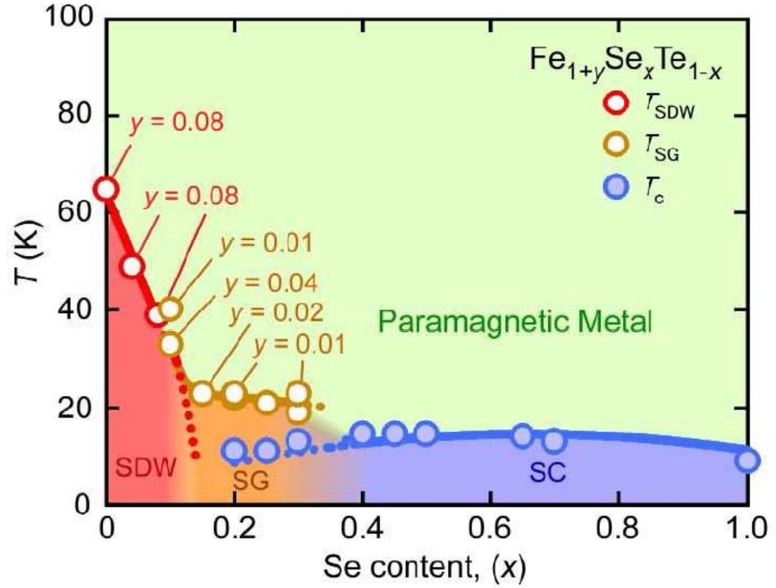
F. C. Hsu et al. *PNAS* (2008)
S. Medvedev et al. *Nat. Mater.* (2009)
J. G. Guo, et al. *PRB* (2010)

Phase diagram : coexistecne of SDW and SC in pnictides









H Chen *et al.*, *EPL* (2009); Nandi *et al.*, *PRL* (2010);
Drew *et al.*, *Nat. Mater.* (2009); Katayama *et al.*,*JPSJ (2010)*

Phase diagram of $Fe_xFe_{2-y}Se_2$:

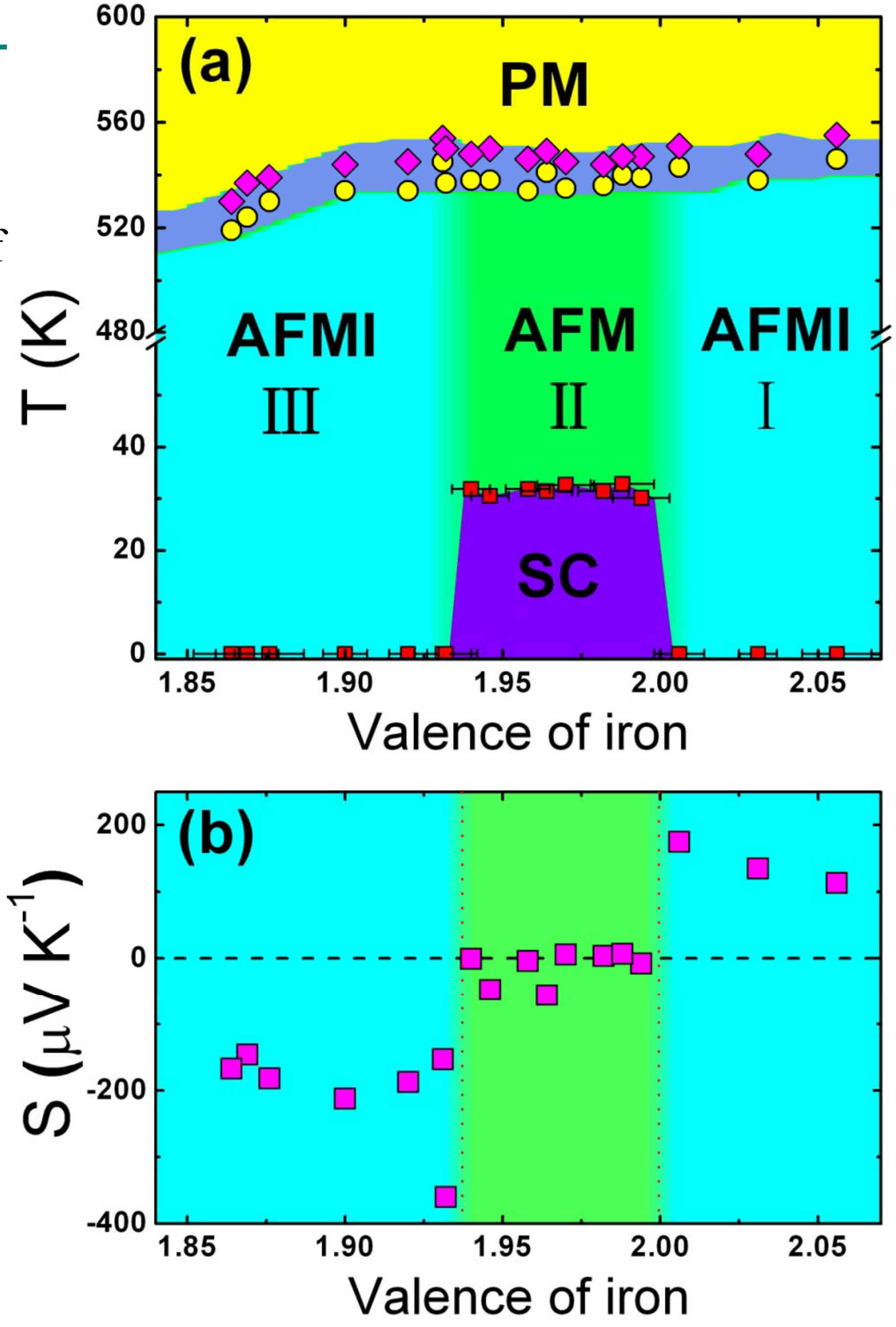
More than twenty single crystals

Phase I

Fe vacancy orders with modulation wave vector of q_1=(1/5, 3/5, 0) with larger positive TEP ;

Phase III

q_2=(1/4, 3/4, 0) with larger negative TEP.



Phase II

Coxexistence of SC and AFM ?
Phase separation
mesoscopic or macroscopic?

Yan et al. Scientific Reports (2011)
arXiv:1104.4941

Two phases in the superconducting regime of phase diagram

Superconductivity with Tc=32 K without Fe vacancy

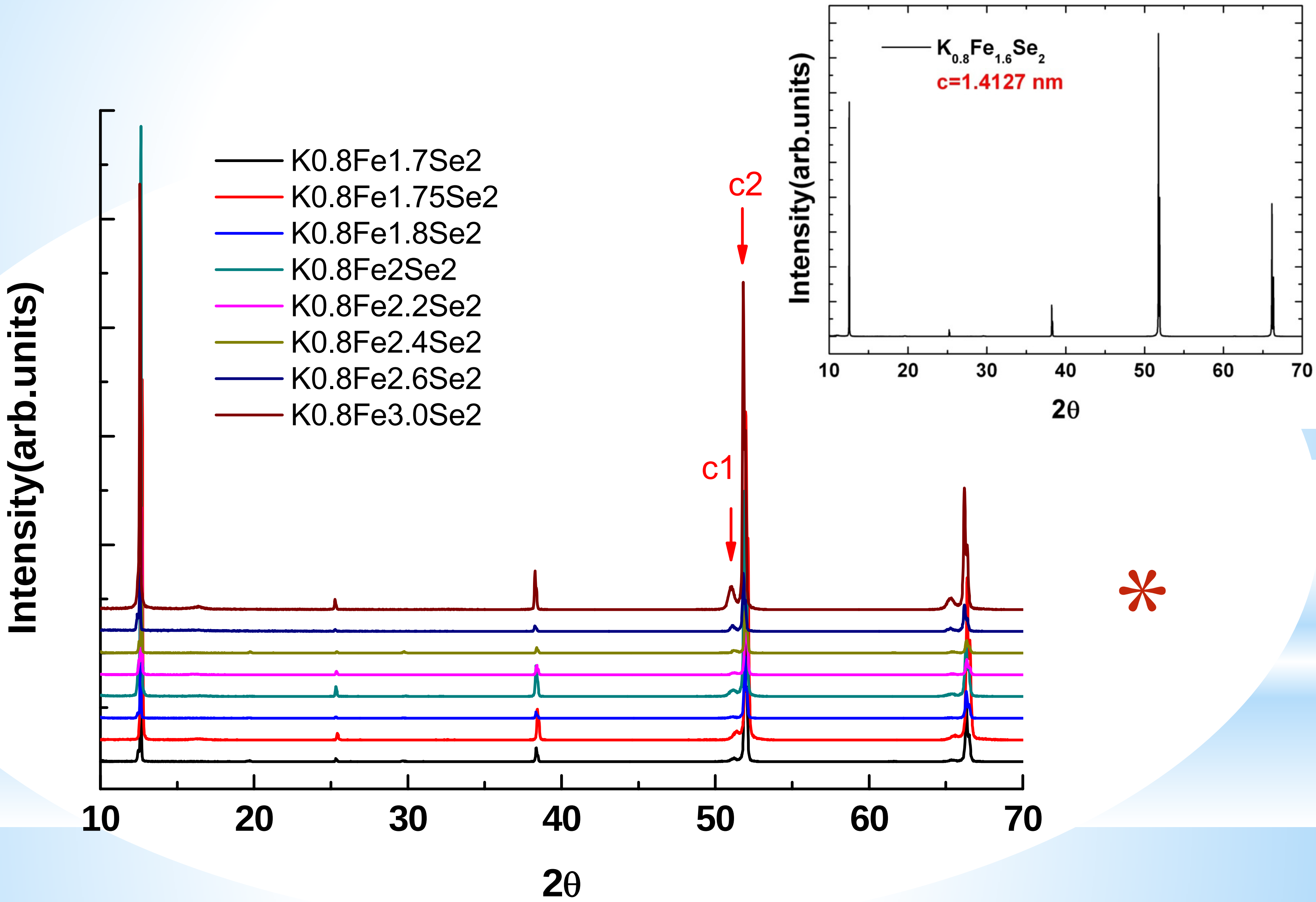
Insulating AFM with T_N =550 K and Fe vacancy order √5x√5 or 2x2

How do the two phases stay in the superconducting regime?

Coexistence or phase separation

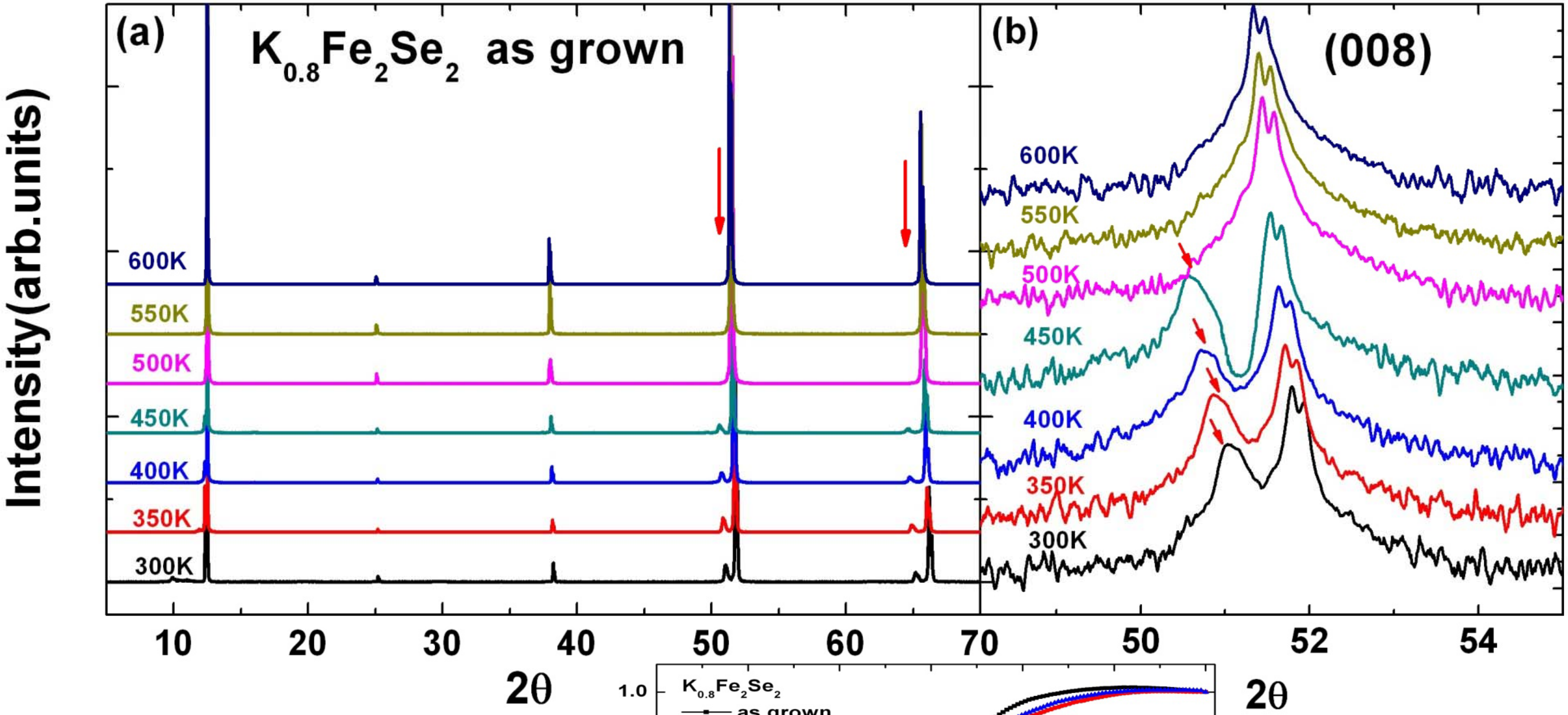
Correlation between the two phases or not ?

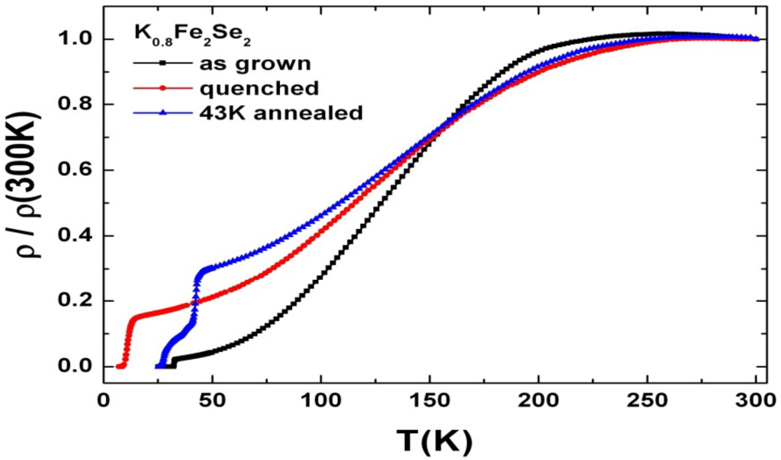
Only one phase is observed for the sample $K_{0.8}Fe_{1.6}Se_2$ ($K_2Fe_4Se_5$)



*

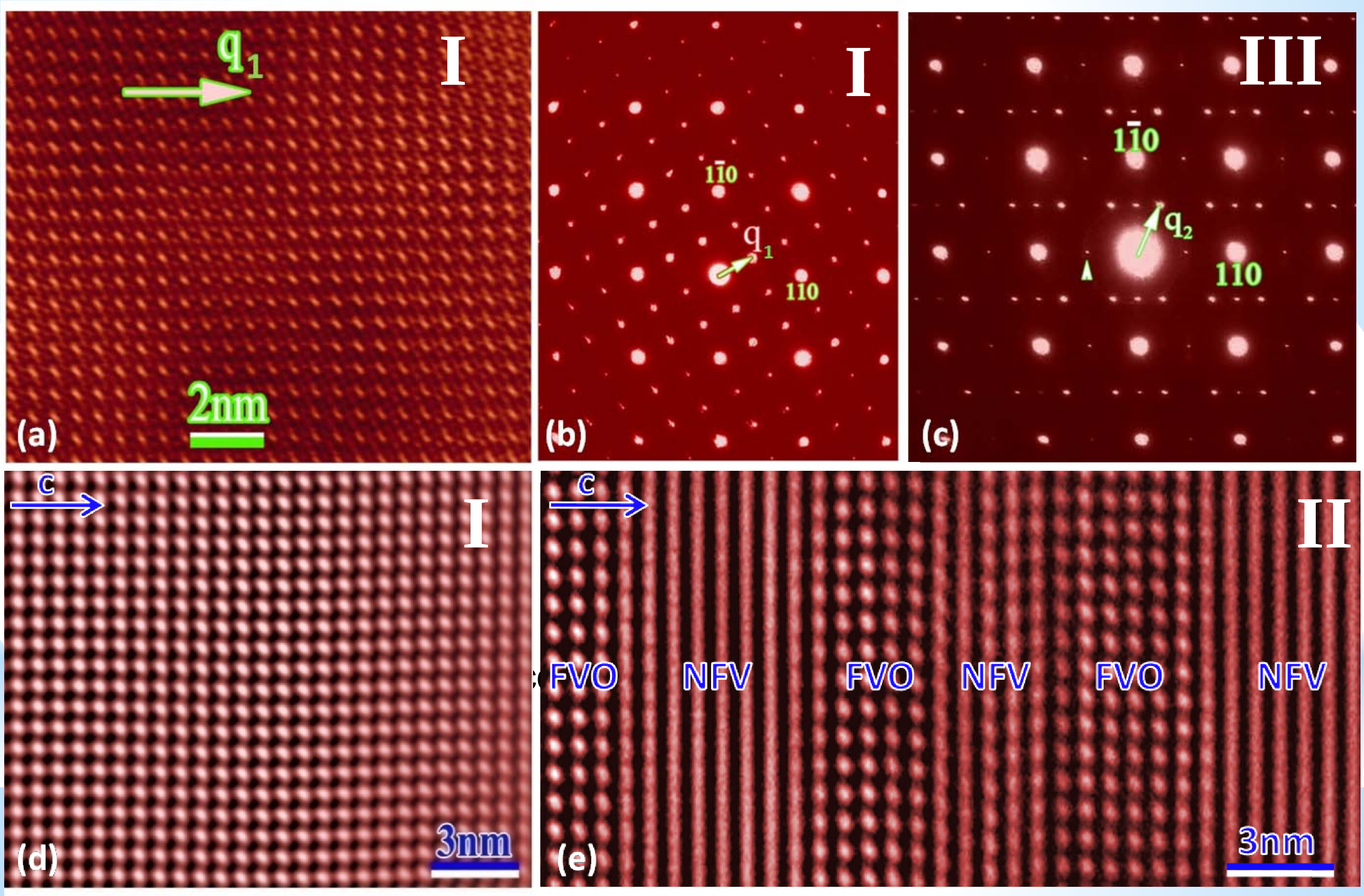
Evolution of the superconducting phase and insulating phase with temperature up to 600 K for $K_{0.8}Fe_2Se_2$





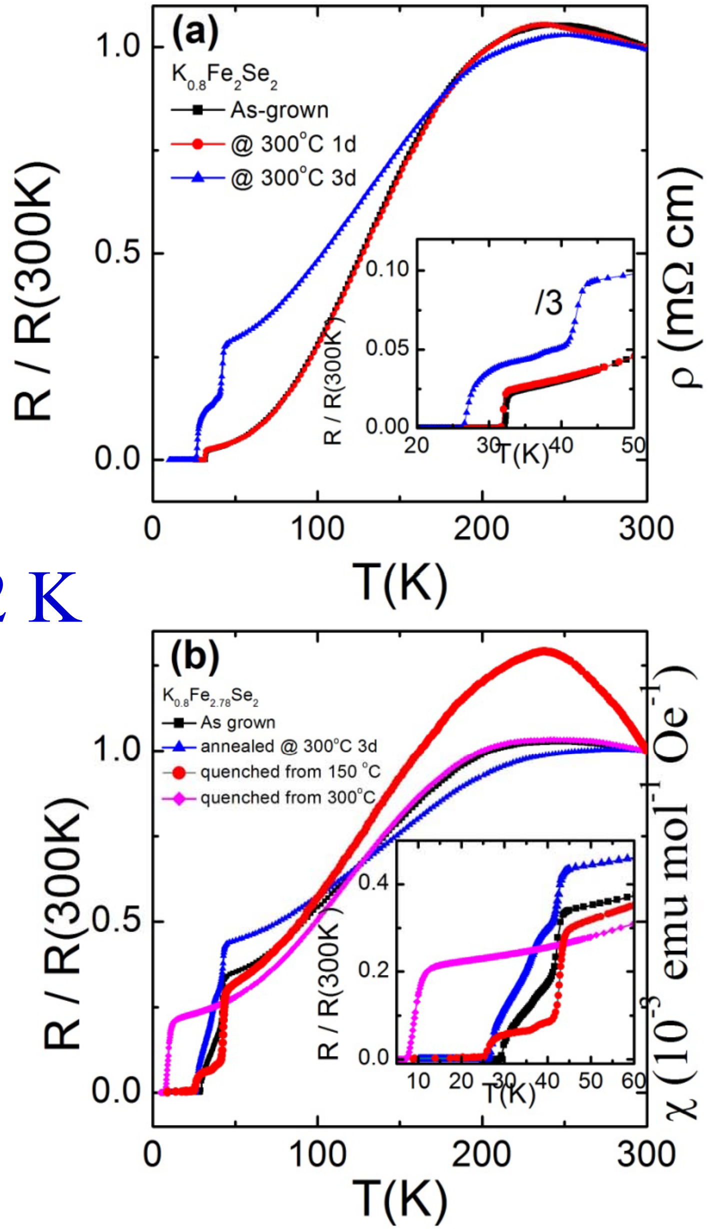
TEM observations in th… in the phase diagram

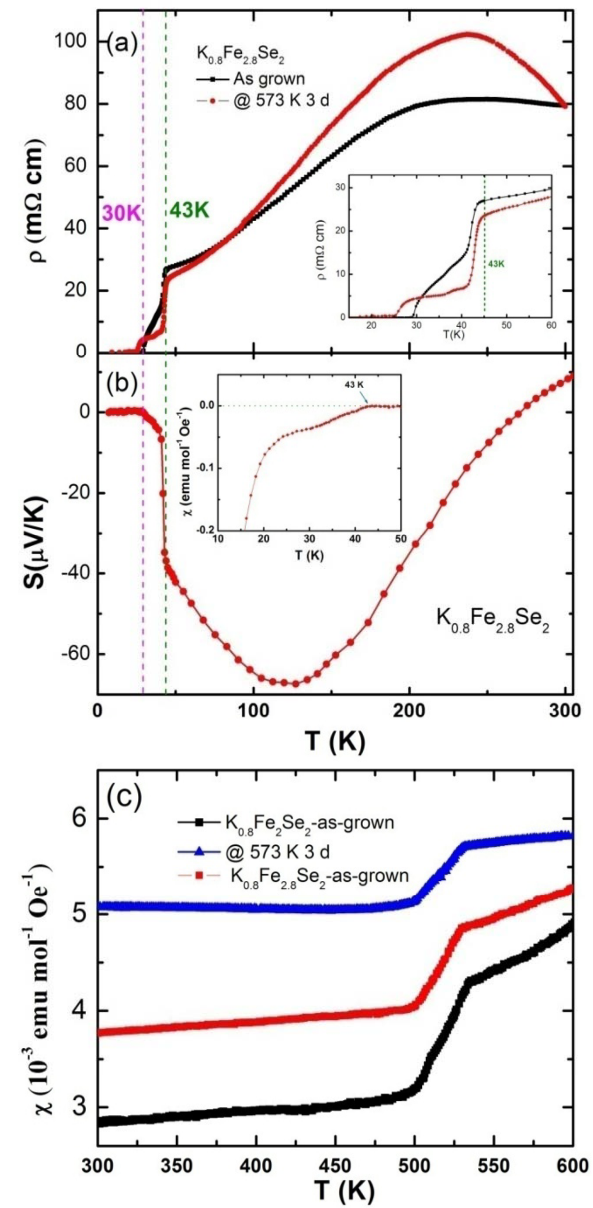
q_1=(1/5, 3/5, 0) q_2=(1/4, 3/4, 0)



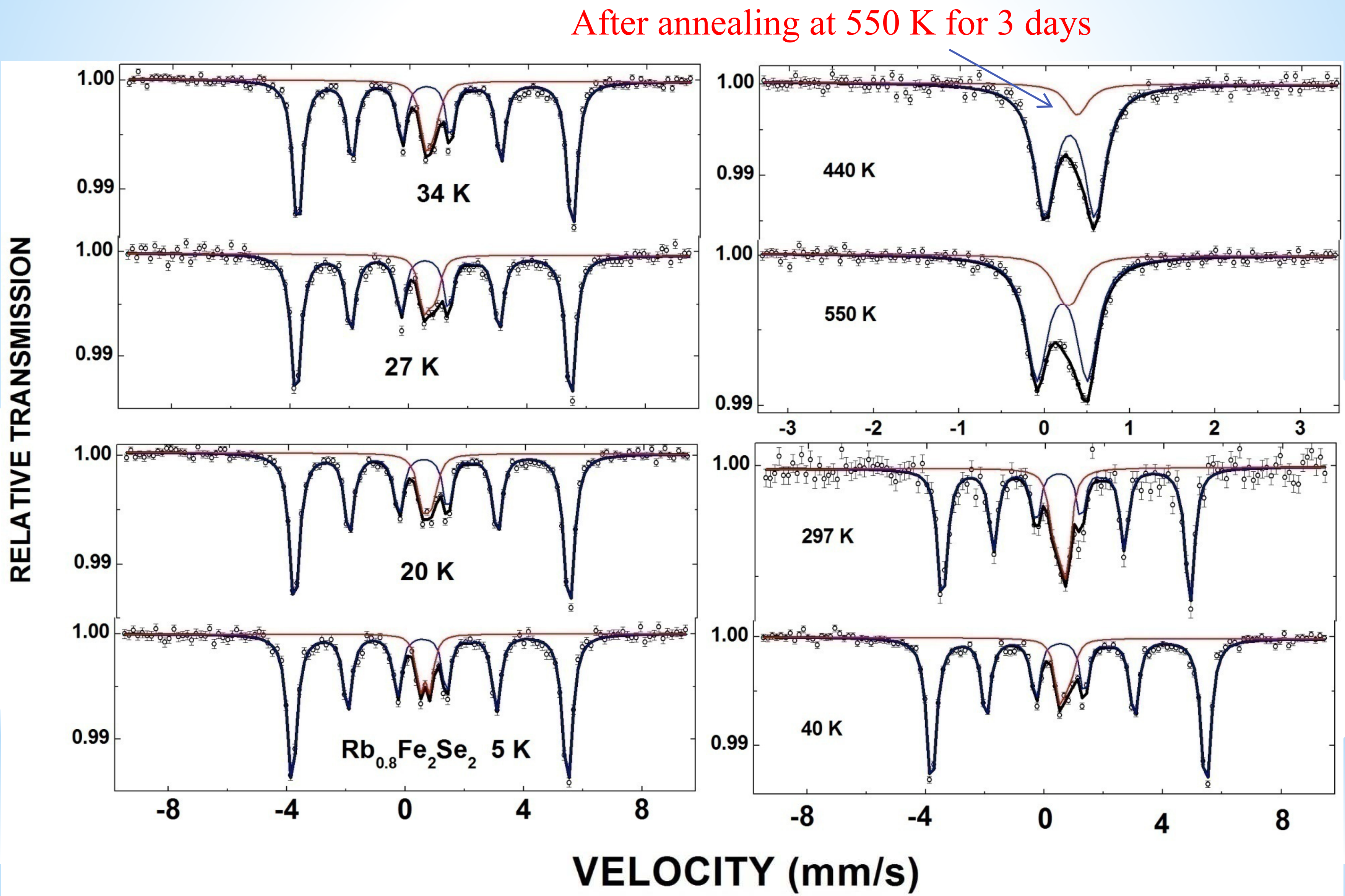
Effect of post-annealing on Tc, 44 K phase develops

Tc=44 K phase develops from 32 K phase by post-annealing





Temperatutre dependence of Mossbauer spectra



I. Felner and X. H. Chen et al., Supercond. Sci. Technol. (2011)

Tc=44 K phase is intrinsic in $K_xFe_{2-y}Se_2$, Tc=32 K is observed due to mesoscopic phase separation

of AFM and SC. AFM order is competing with SC.

Suppression of AFM order leads to enhancement

of Tc from 32 K to 44 K. These results suggest that there exists correlation between AFM and SC

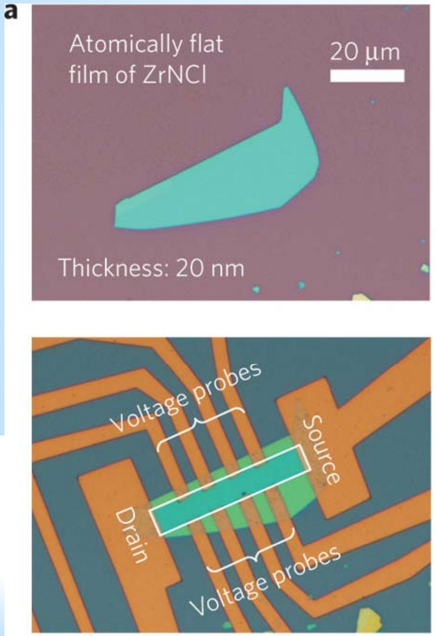
- **Superconductors discovered after Cuprate Superconductors**

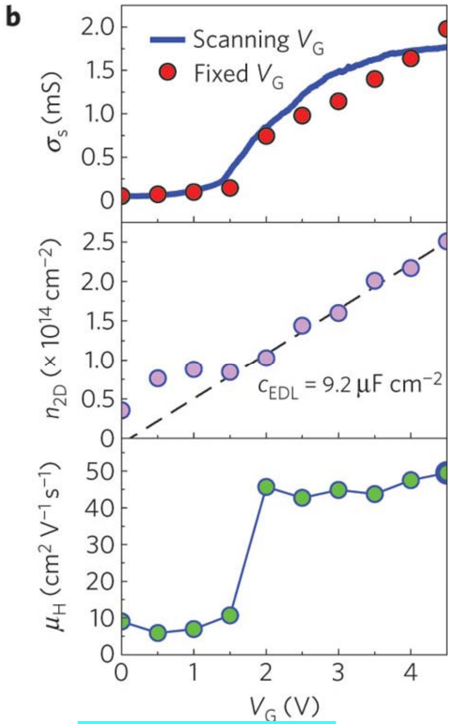
*** Others and superconductivity induced by different ways**

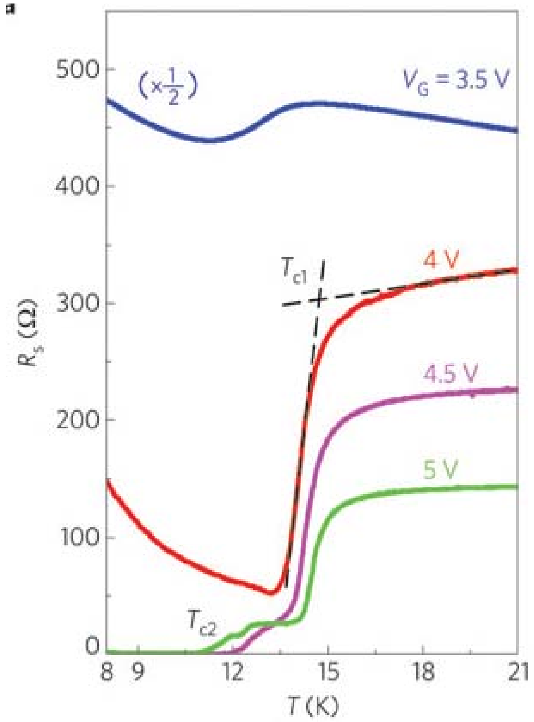
Liquid gating, pressure, topological superconductor etc.

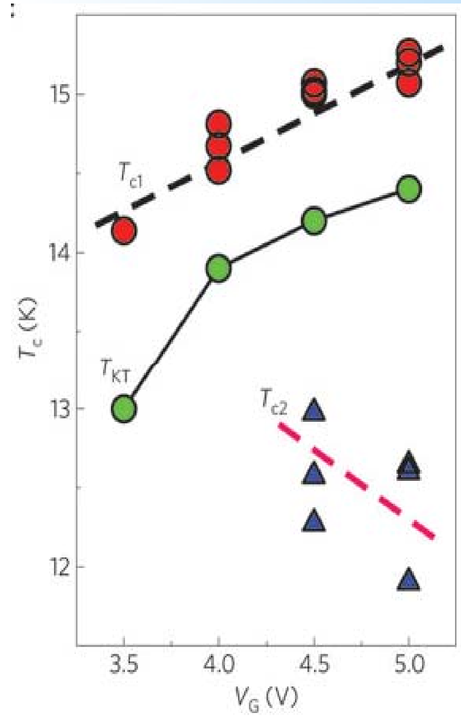
SC in Liquid gated ZrNCl,HfNCl

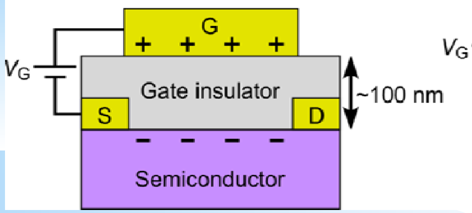
Electric-field-driven SC

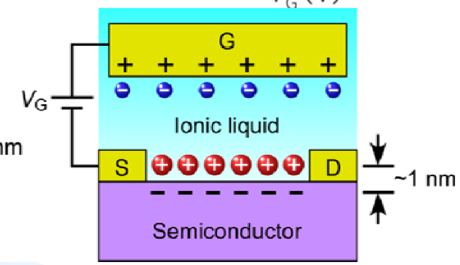






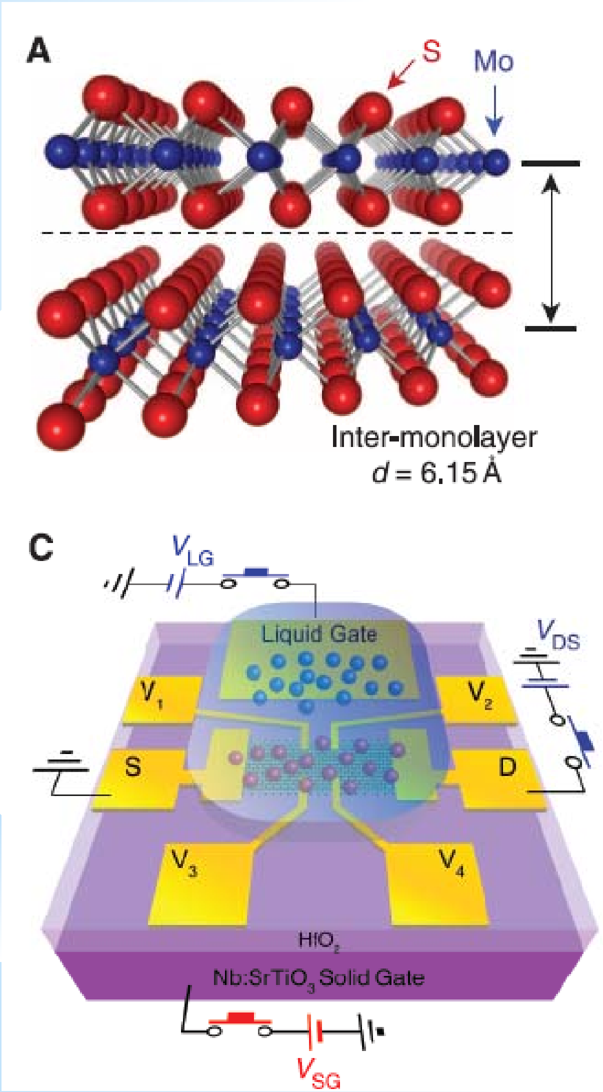


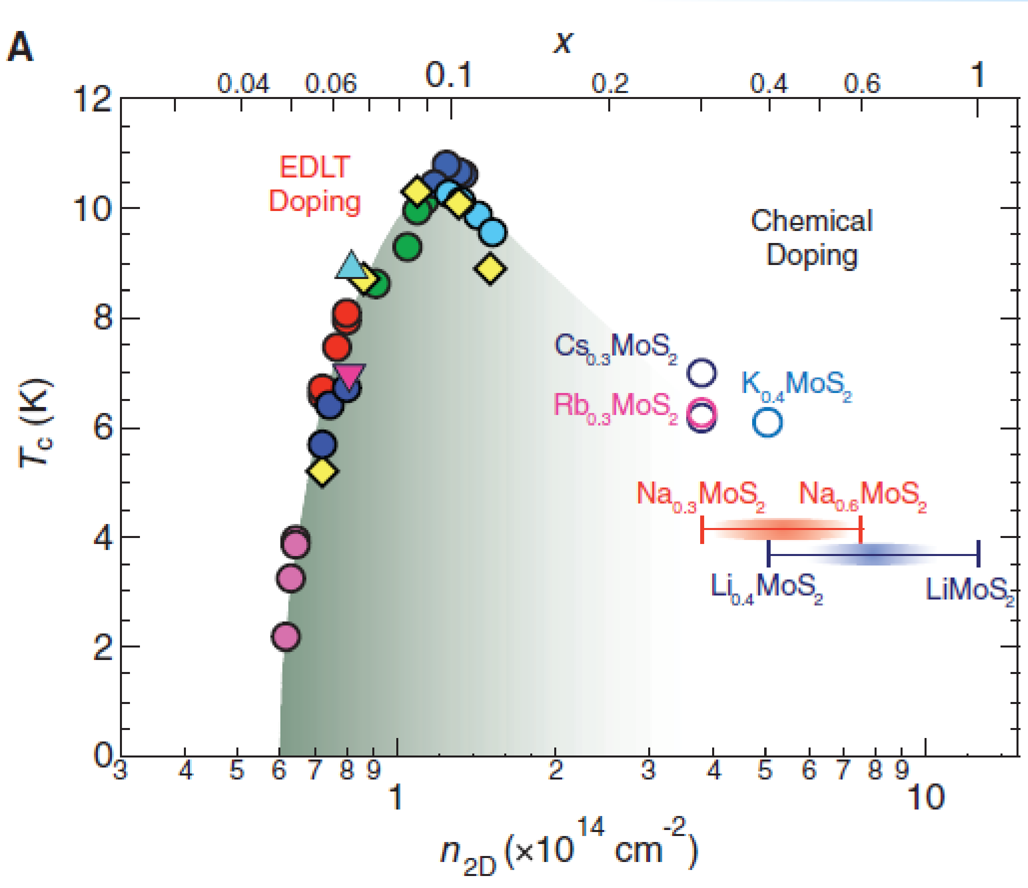




J.T. Ye et al., *Nat. Mater.* **9**, 125 (2010)

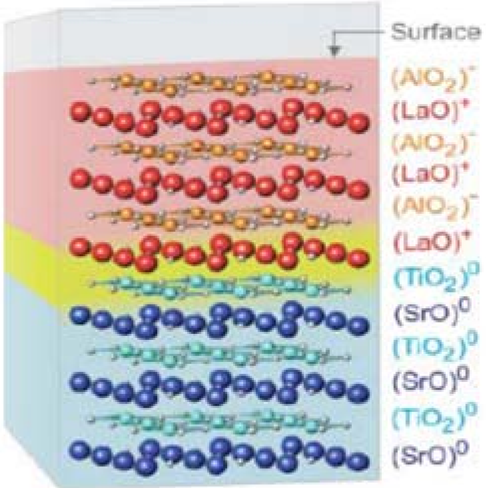
Gate-Tuned Band Insulator MoS_2

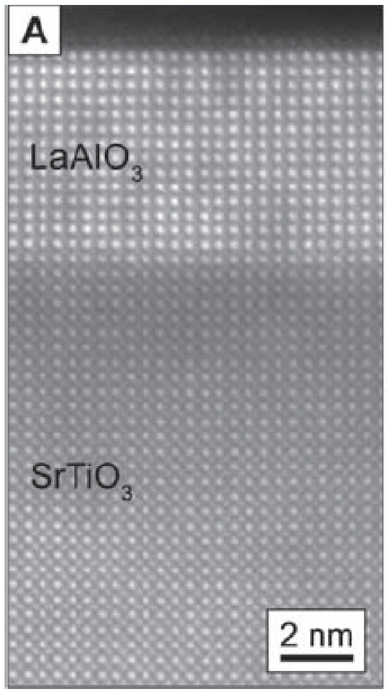


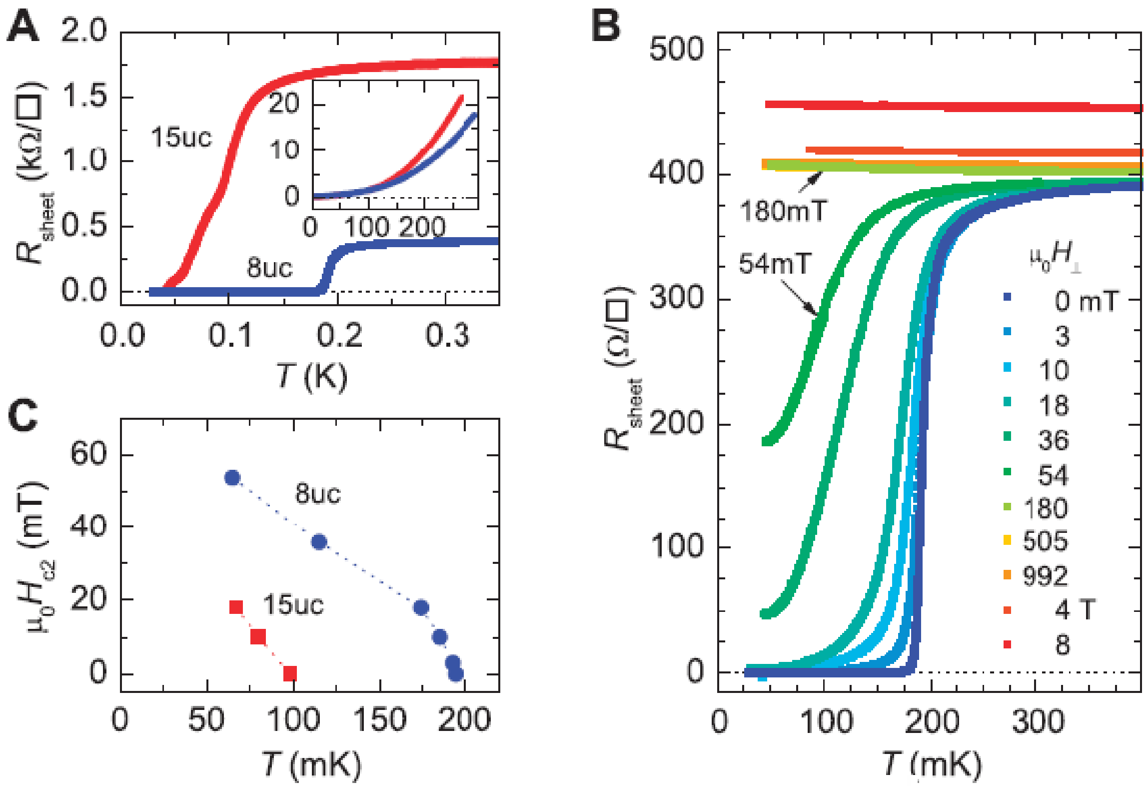


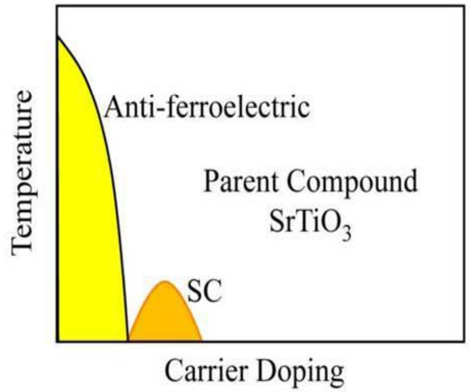
J.T. Ye et al., *Science* **338**, 1193 (2012)

Interface SC between Mott insulator and Band Insulator



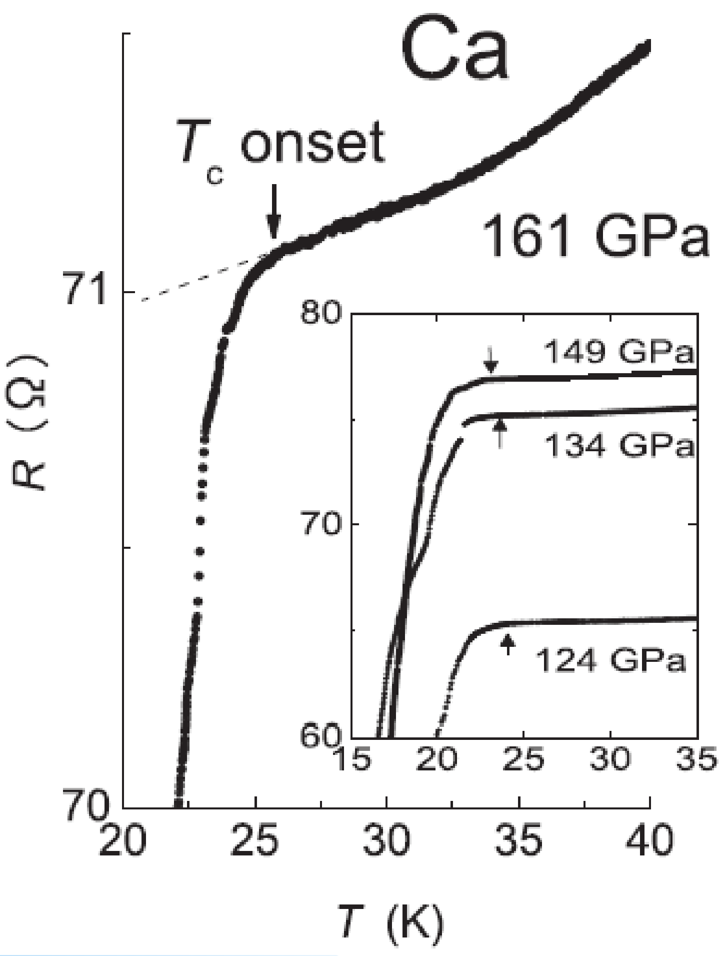


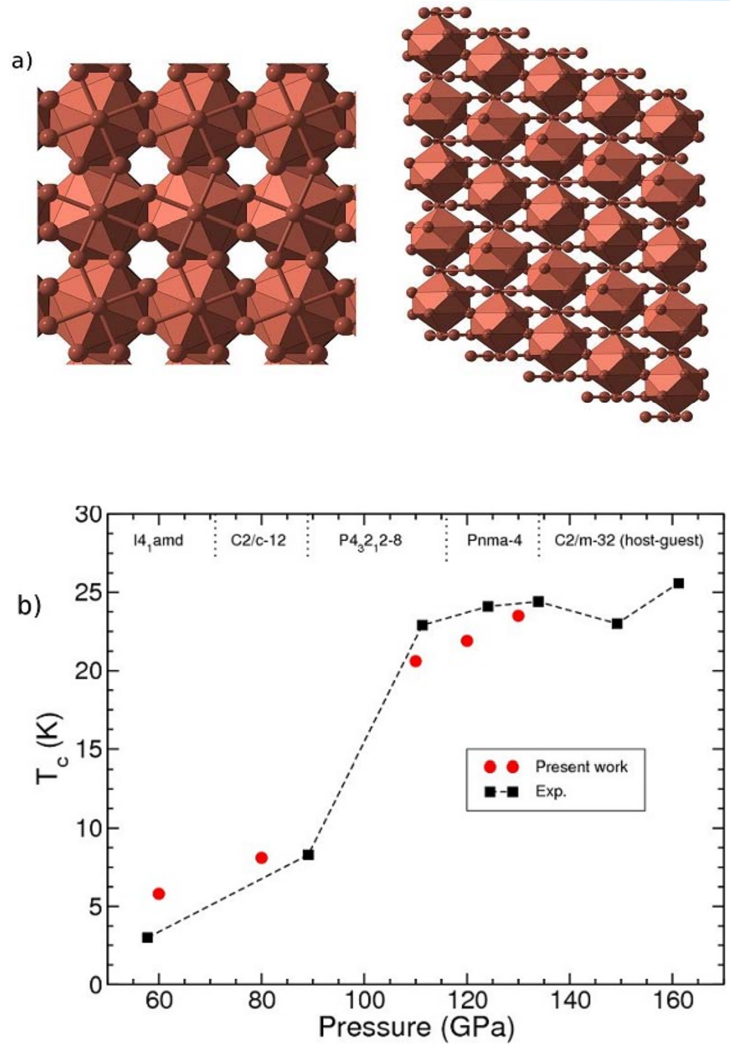




Oxygen defects and Nb,La-doping···

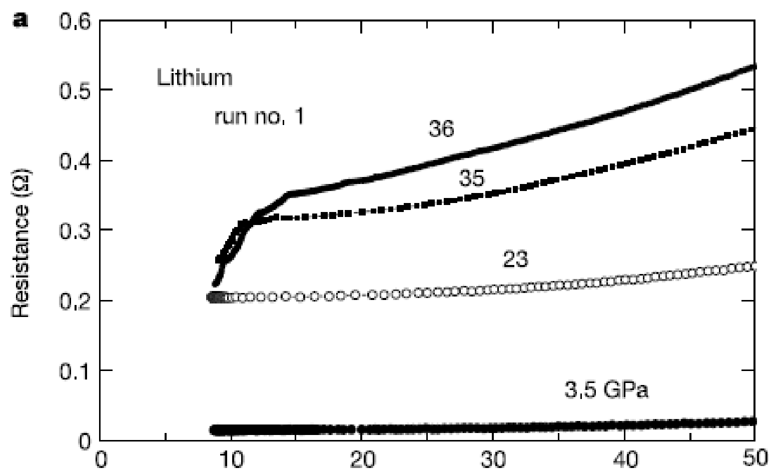
Superconductivity at 25 K in the elemental calcium under ultra-high pressure

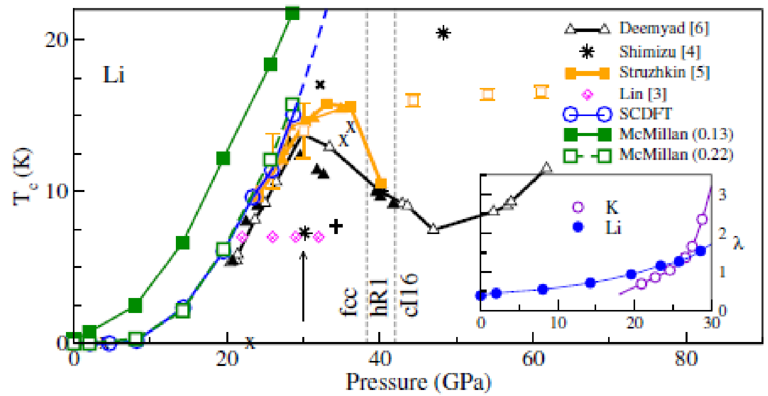


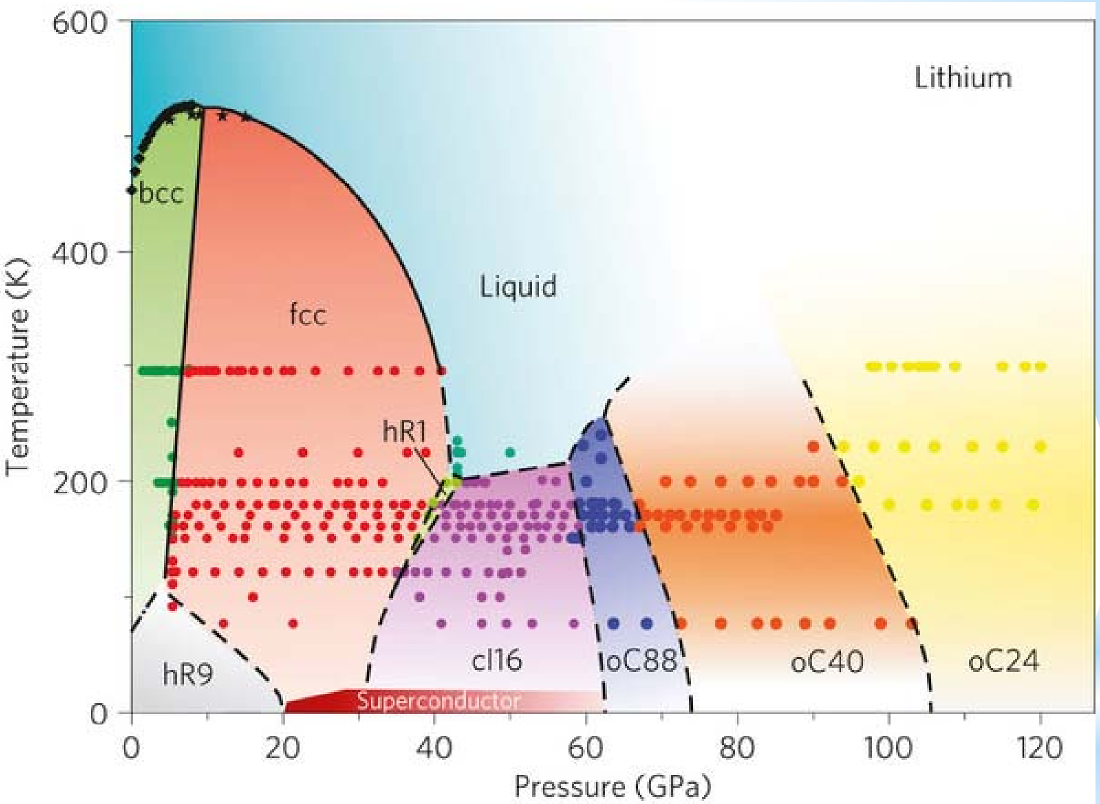


K. Yabuuchi et al. *J. Phys. Soc. Jpn. 75*, 083703 (2006)

Superconductivity at Tc>10 K in the elemental Lithium under ultra-high pressure

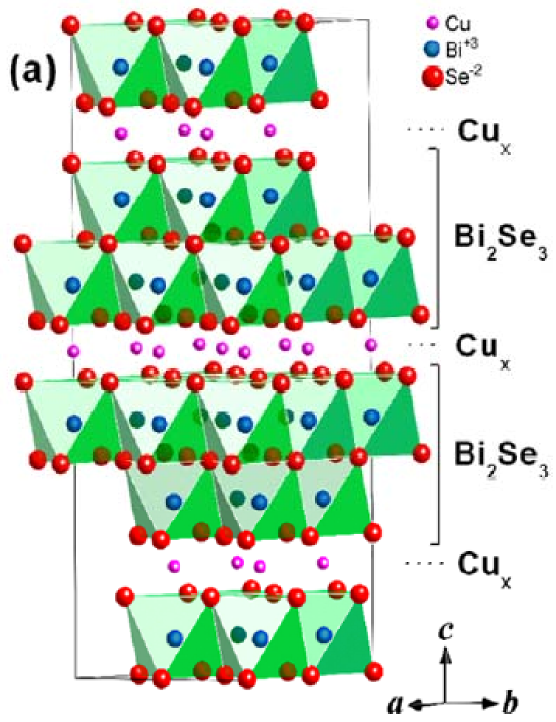


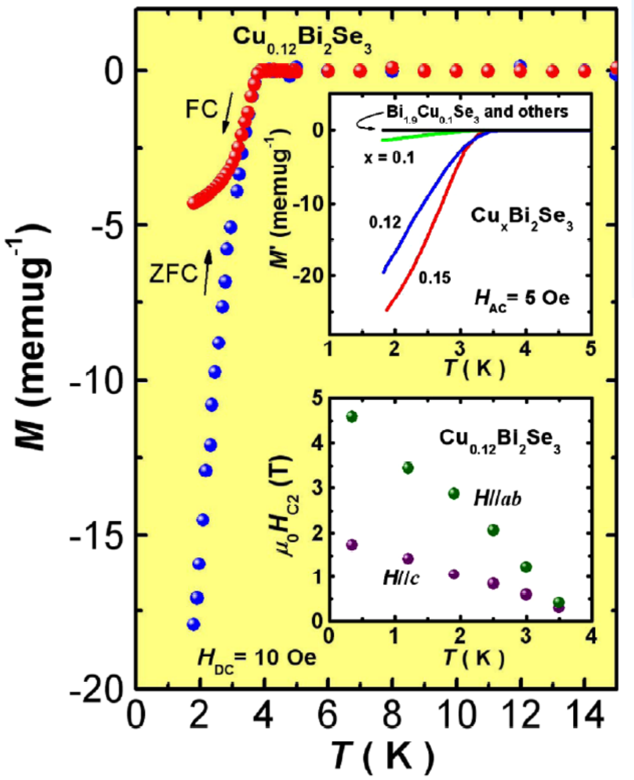


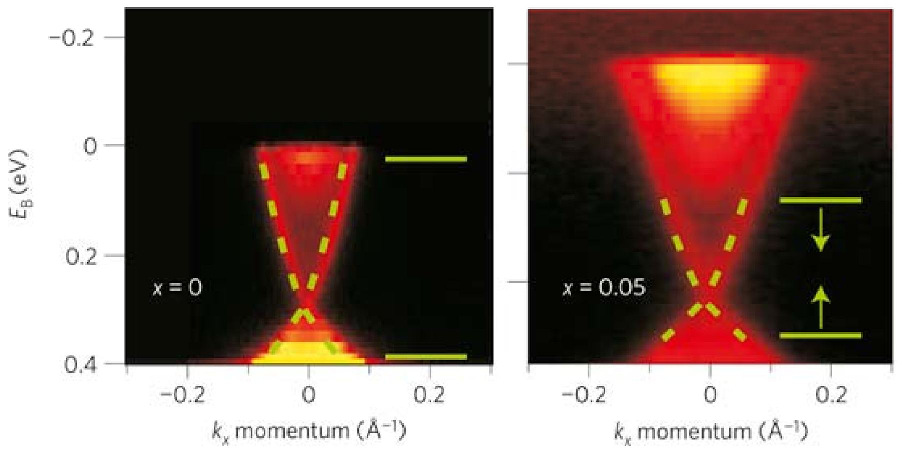


K. Shimizu et al. *Nature* **419**, 597 (2002); V.V. Struzhkin et al. *Science* **298**, 1213 (2002)

Topological superconductor

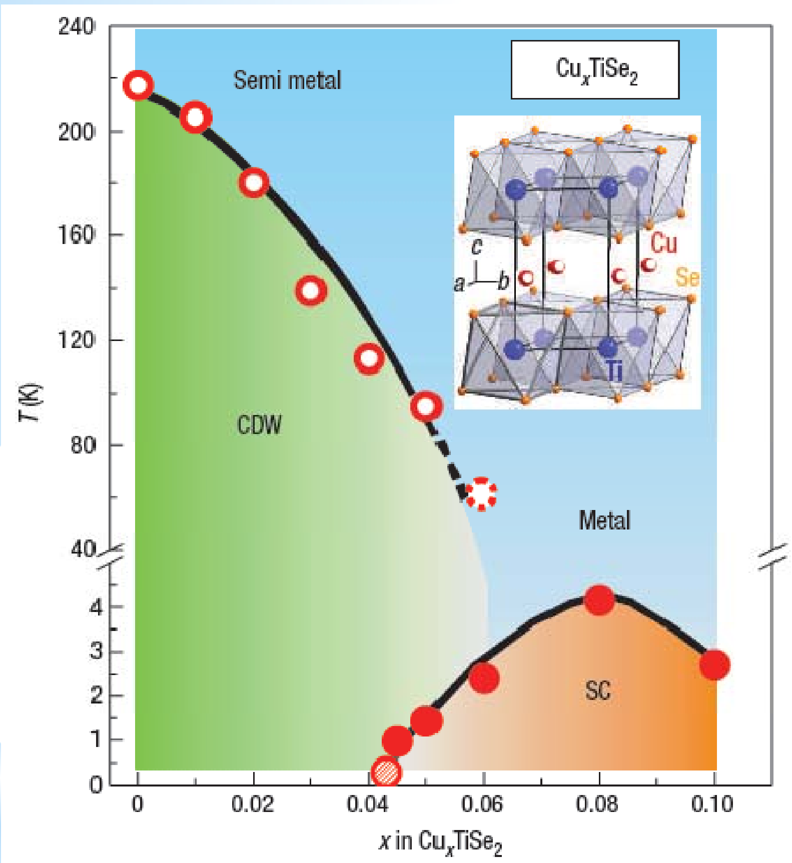


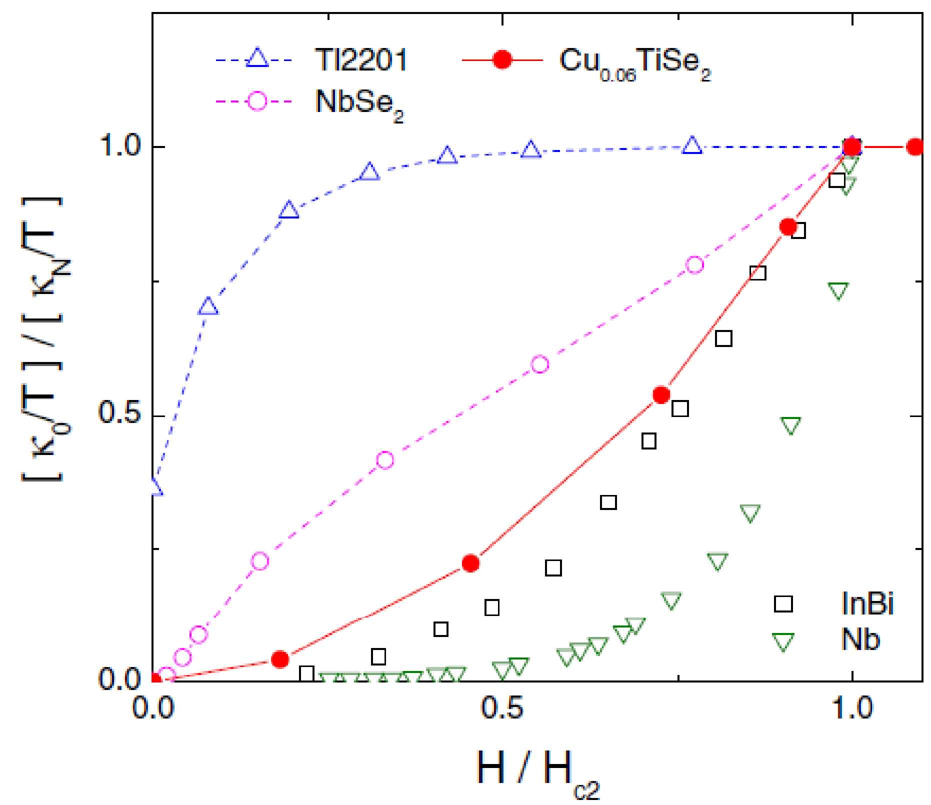




Y. S. Hor et al., *PRL* **104**, 057001 (2010)

Cu_xTiSe_2: SC develops from CDW

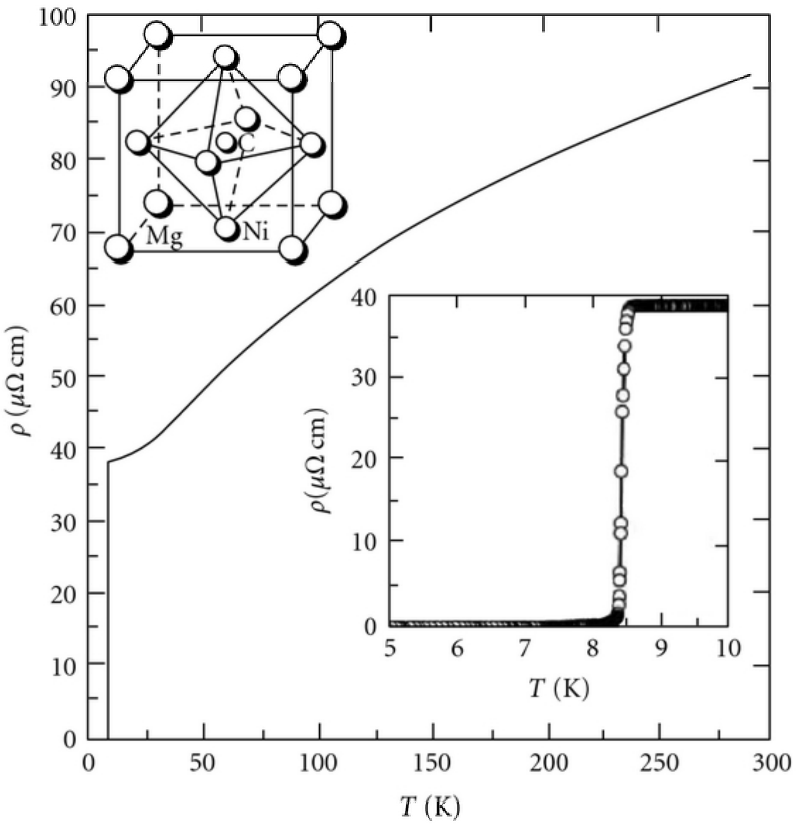


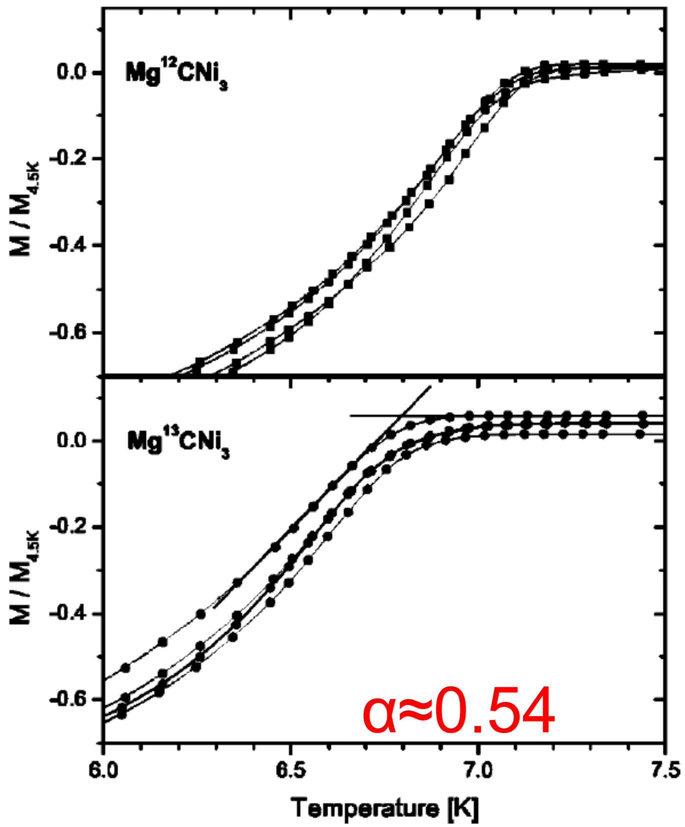


Isotropic *s*-wave

E. Morosan et al., *Nat. Phys.* **2**, 544 (2006)

Anti-provskite superconductor: $MgCNi_3$



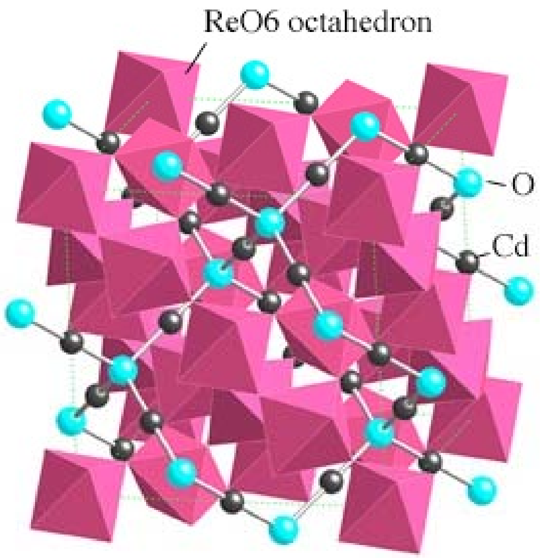


T_c~8 K

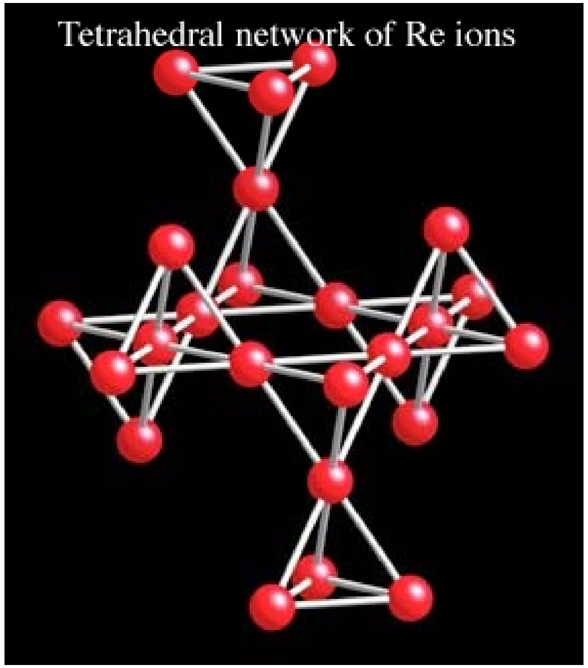
T. He et al., *Nature* **41**, 54 (2001)

Though theoretical calculations indicate $MgCNi_3$ is near the FM instability, isotope effect coefficient of C was found to be consistent with phonon-mediated SC

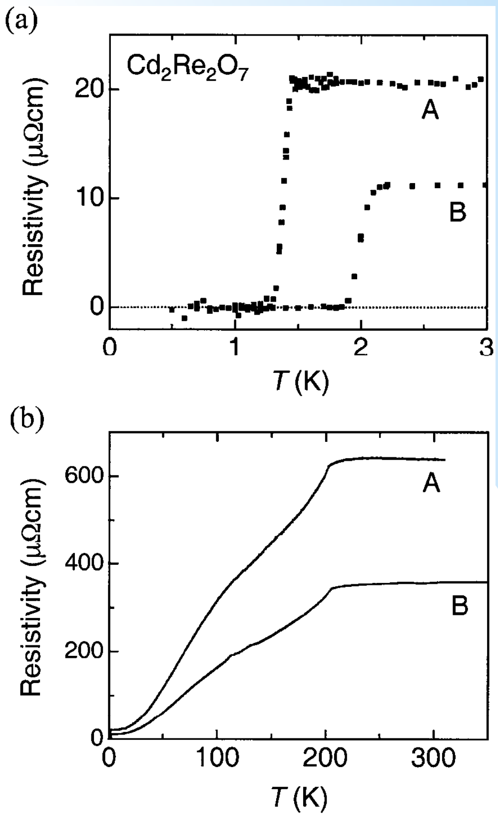
First pyrochlore superconductor



$Cd_2Re_2O_7$

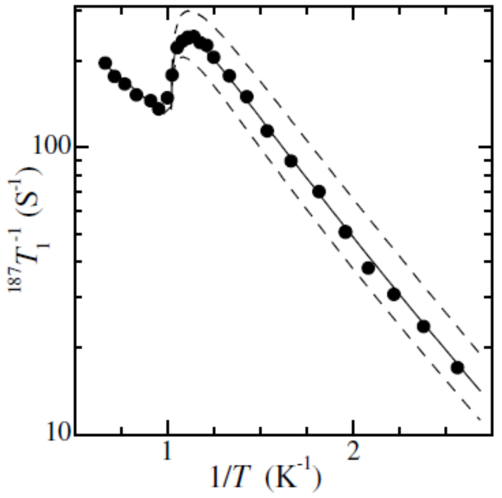


Geometrically frustration



T_c~1-2K

M. Hanawa et al., *PRL* (2001)

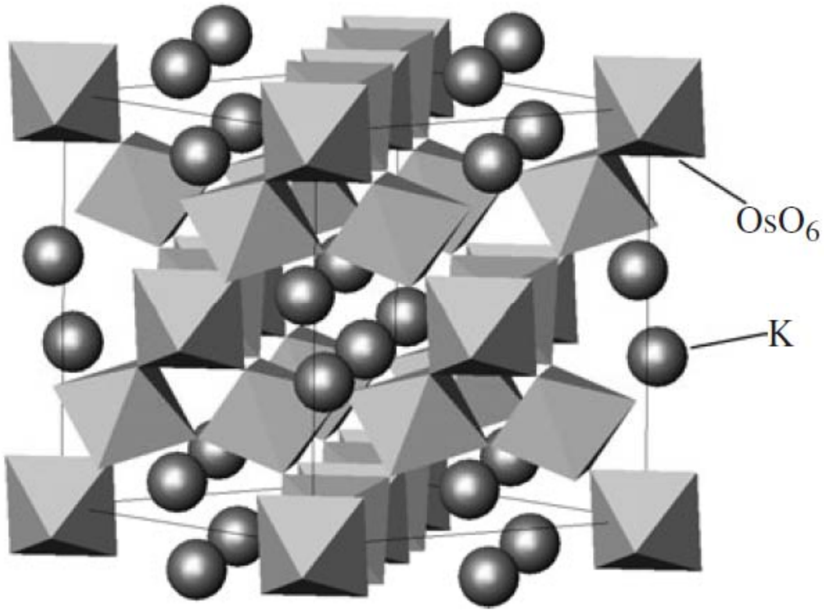


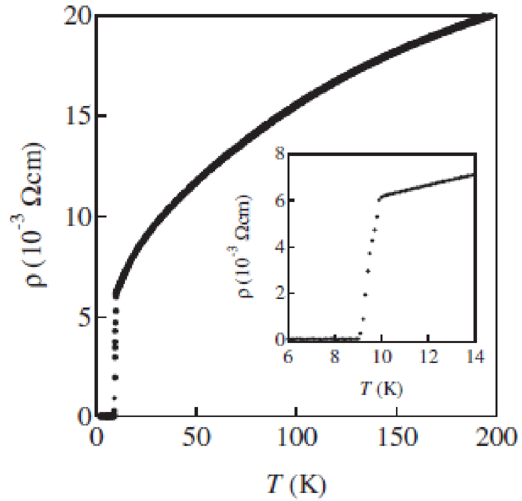
Good fit to the week-coupling BCS theory

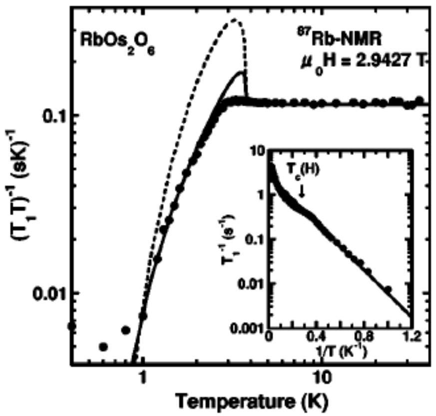
O. Vyaselev et al., *PRL* (2002)

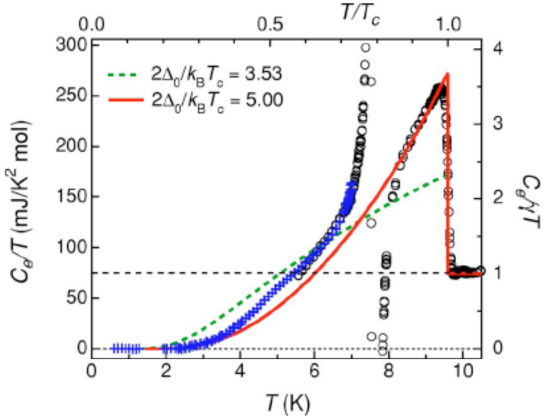
Pyrochlore-related superconductor

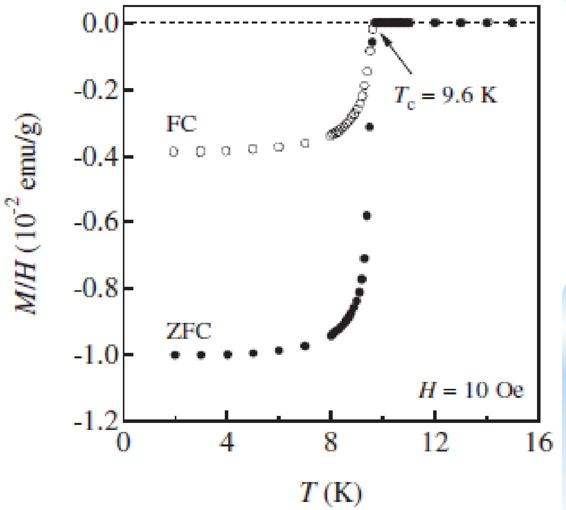
KOs_2O_6











T_c~9.6K

Strong-coupling *s*-wave superconductor

S. Yonezawa et al., *JPCM* (2004)

Unconventional SC in strongly correlated system

i) Typical Examples: Ruthenates (only superconductor, Sr_2RuO_4)
Heavy Fermion
Cuprates
Organic superconductors
Iron-pnictides and –chalcogenides

ii) Unconventional SC also exists in C60-derived superconductors

Why "unconventional"

a) Non isotropic *s*-wave SC gap;
b) Maybe not e-p mediated;
c) Multiband effect may be important;
d) Isotope effect disappears or not conventional;
e) Coherent factor is different from prediction of BCS theory;
f) Coherence length is small;
g) Dimension is reduced;
h) Metallic properties are weak or bad;
i) SC emerges in proximity to magnetically ordered state;
j) SC pairing order shows symmetric and time-inverse breaking

All above tell us that we must reconsider and the simple BCS theory should be amended.

Thank you for your attention!

Some features of Heavy fermion superconductors

Low Tc, heavy electron or hole involve in SC

Pairing mechanism: (1) BCS-type; (2) *p*-wave;

(3) low-energy spin-fluctuation mediated SC, intimately related to magnetic order

Some common HF superconductors:

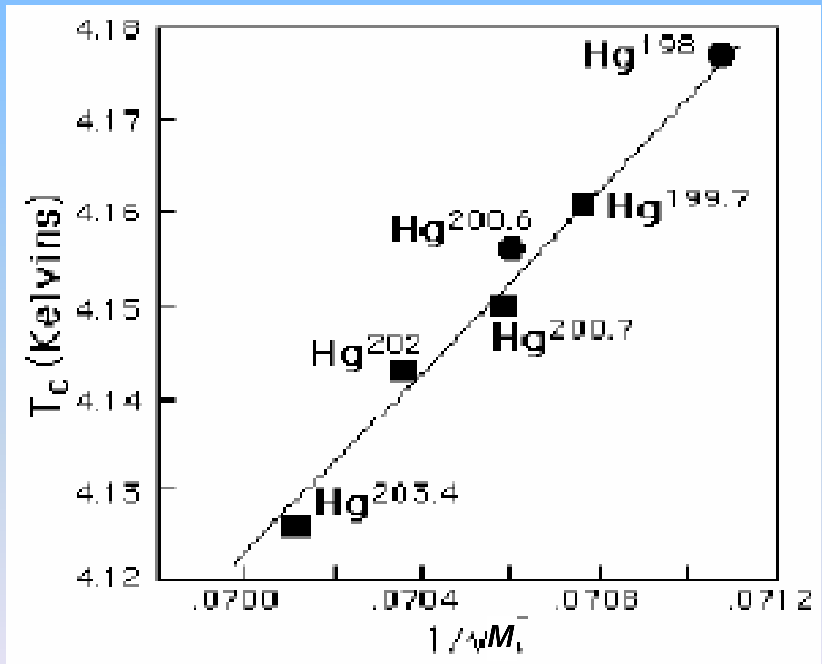
* $CeMIn_5$ (M=Co,Ir,Rh,⋯.) (2000)
* CeM_2X_2 (M=Cu,Ni,Ru,Rh,Pd,Au,⋯ X=Si,Ge,⋯.)
* UPt_3, UBe_{13}, UGe_2, UPd_2Al_3

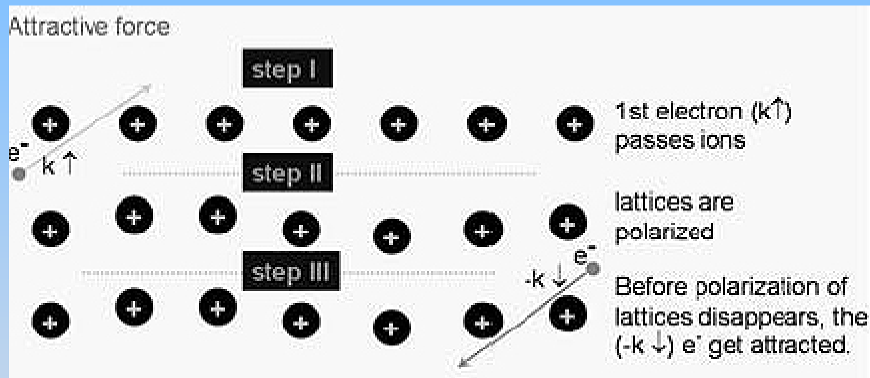
Compound	g (mJ/mol K^2)
$CeCu_2Si_2$	1000
$CeRhIn_5$	400
$PrInAg_2$	6000
YbBiPt	8000
UBe_{13}	1000
URu_2Si_2	200
Na	1

Isotope effect in pnictide superconductors

Remarkable sensitivity of superconductivity and magnetism to the lattice

Indicating unconventional electron-phonon coupling

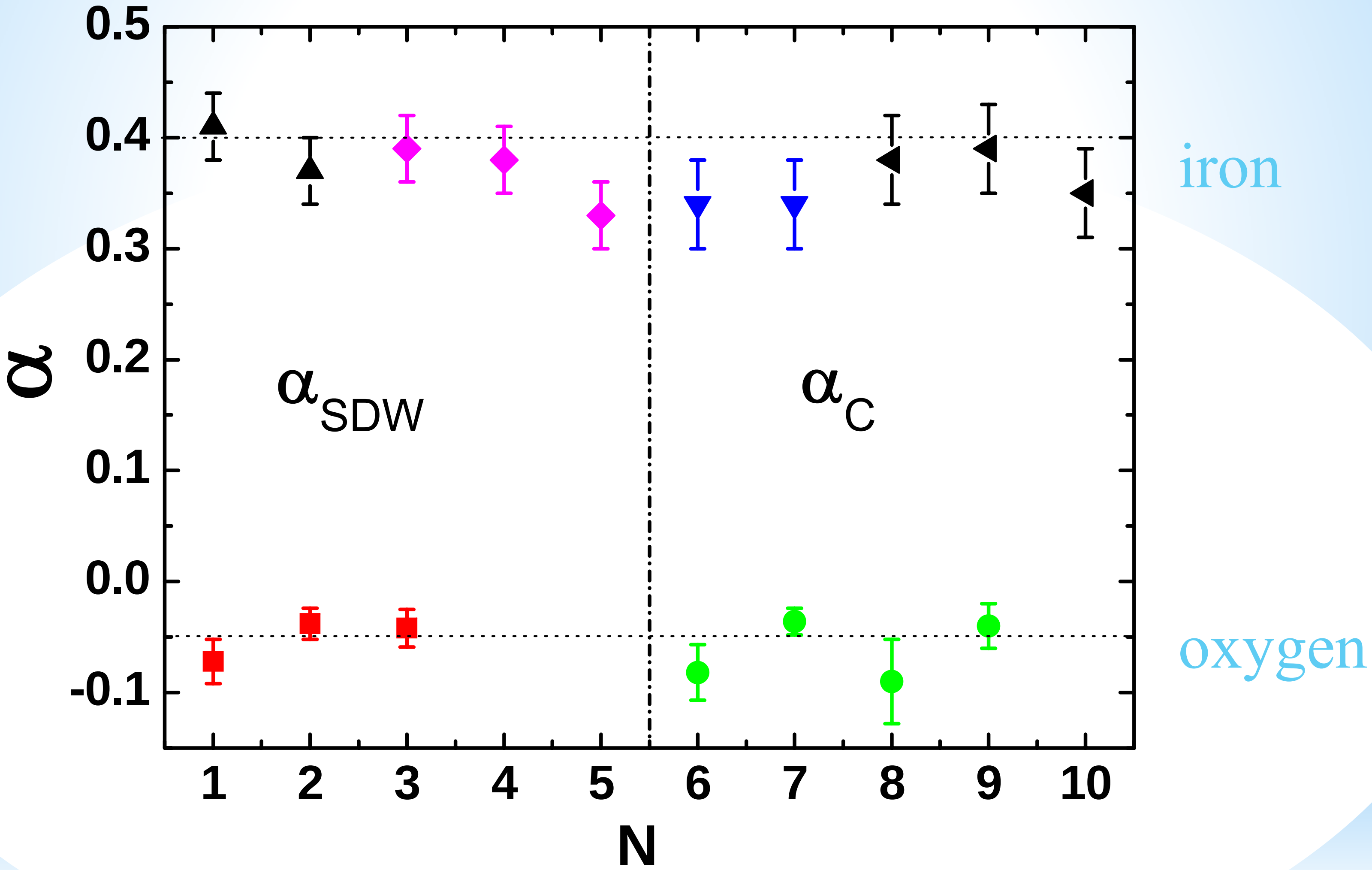




同位素效应（1950）：超导电性的发生不仅仅包含电子，还应该考虑晶格的作用

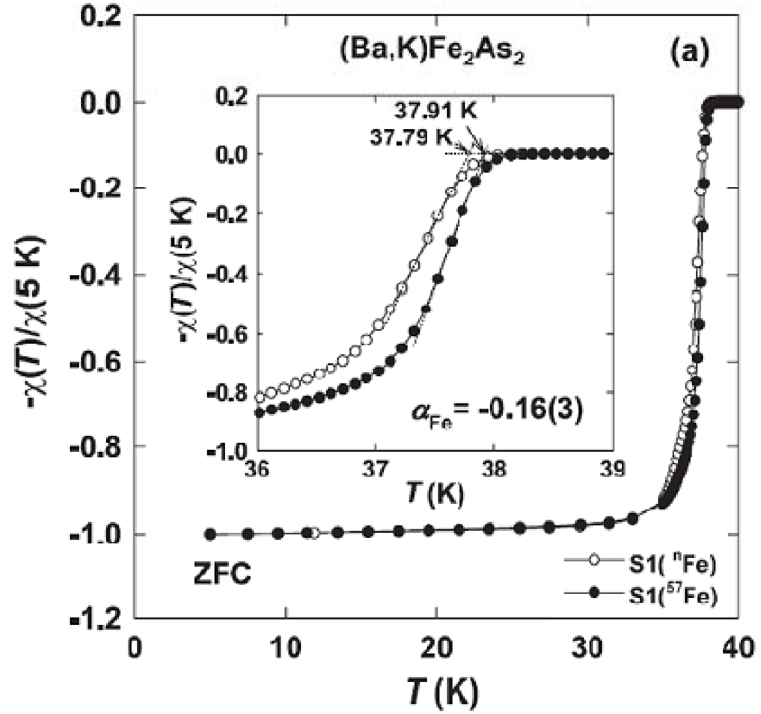
同位素效应对**BCS**理论的建立是至关重要的

* Oxygen and Iron Isotope component α_C and α_{SDW}



R. H. Liu, X. H. Chen et al., Nature **459**, 64-67(2009).

Inverse iron isotope effect in $Ba_{1-x}K_xFe_2As_2$



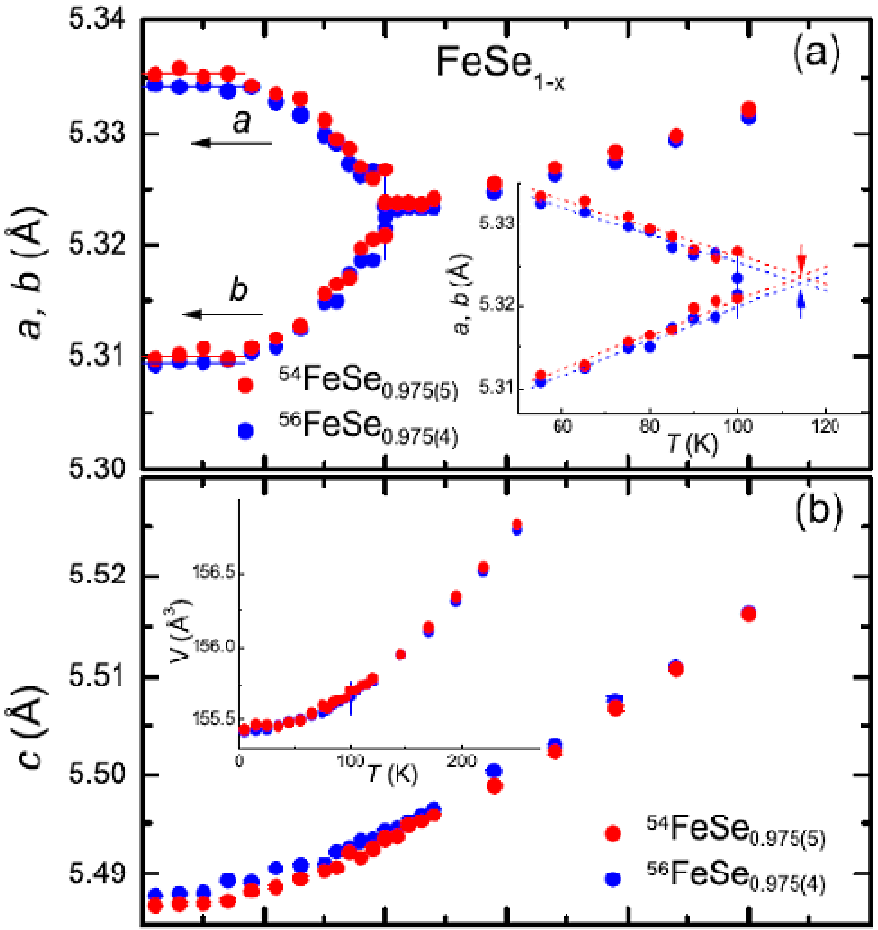
a=3.914(1) A, c=13.310(1)A for ^{57}Fe
a=3.914(1) A, c=13.313(1)A for ^{54}Fe

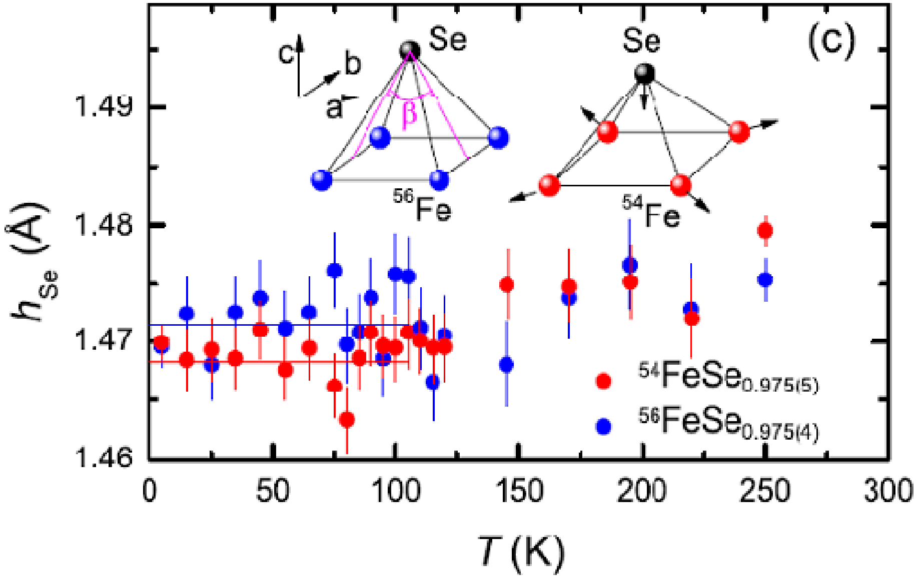
	$T_{c(\chi)}$ (K) ^{54}Fe	^{n}Fe	^{57}Fe	$\Delta T_{c(\chi)}$	α_{Fe}
*S*1		37.79(1)	37.91(1)	−0.12(2)	−0.16(3)
*S*2	37.56(1)		37.82(2)	−0.26(3)	−0.13(1)
*S*3	37.51(1)	37.76(1)		−0.25(2)	−0.20(1)
*S*4	37.54(1)	37.79(2)		−0.25(2)	−0.20(2)
*S*5	37.32(1)		37.75(1)	−0.43(2)	−0.21(1)
*S*6	37.42(1)		37.77(1)	−0.35(2)	−0.17(1)
*S*7	37.39(1)		37.76(1)	−0.37(2)	−0.18(1)

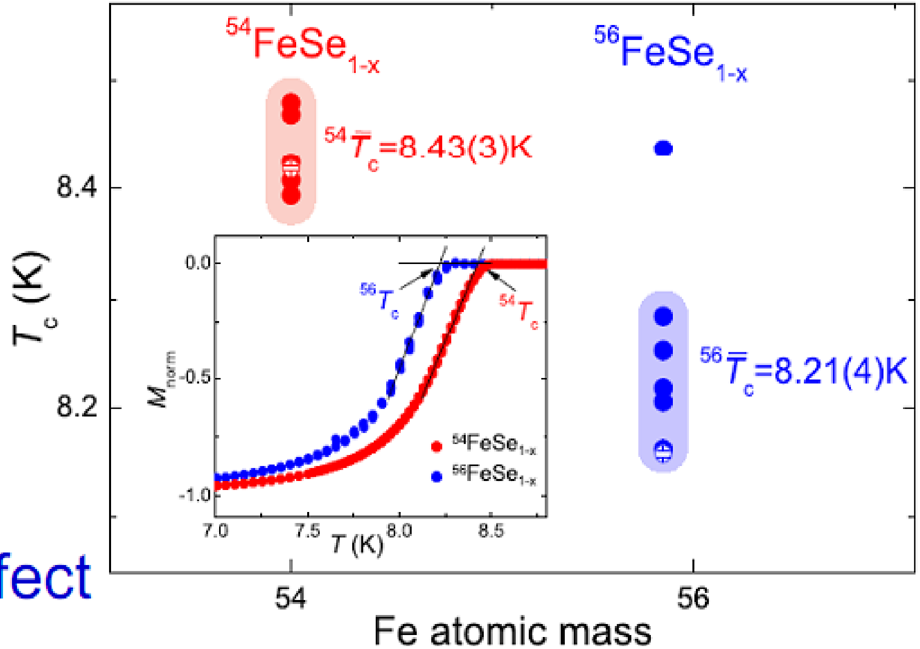
High pressure synthesis, 50% extra K

Shirage et al., PRL103, 257003(2009).

Iron isotope effect in $FeSe_{1-x}$







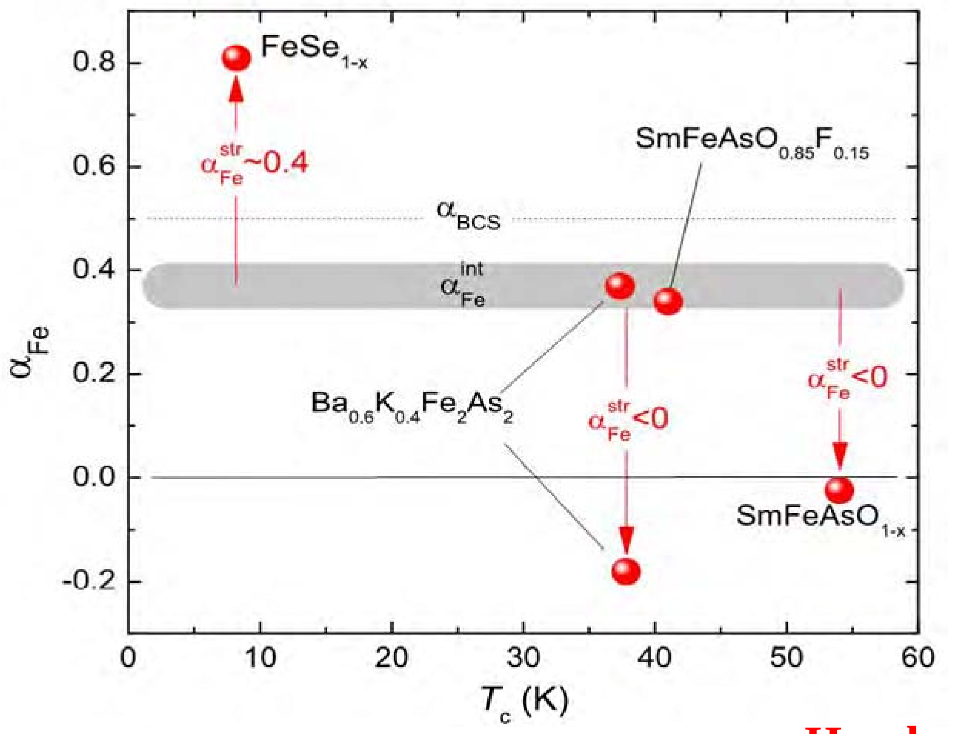
ΔT_c=0.22 K, α_{Fe}=0.81

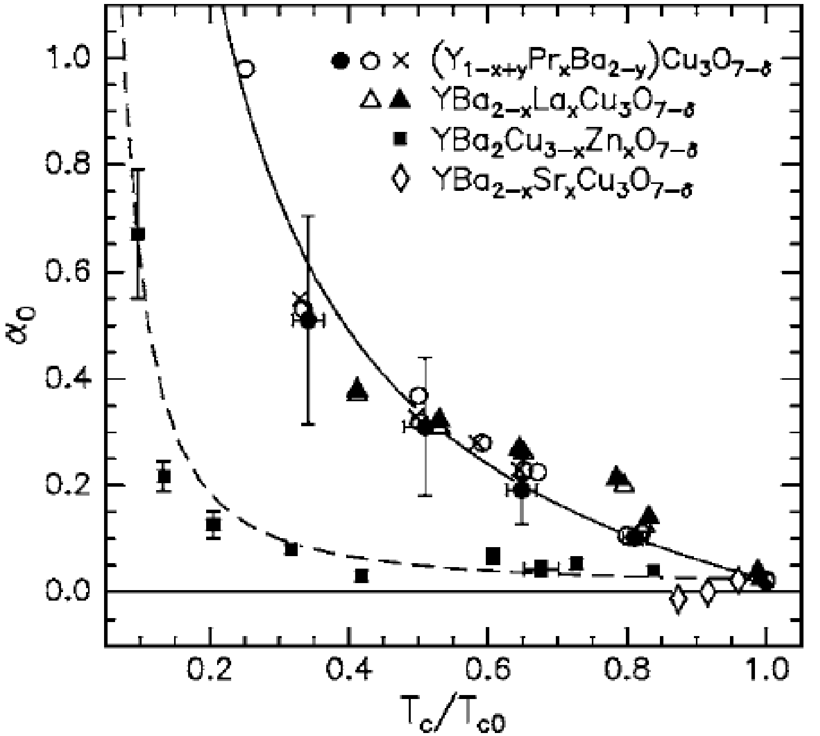
ΔT_c=0.13 K, α_{Fe}=0.48 structure distortion

ΔTc=0.09 K, α_{Fe}=0.33 Intrinsic effect

R. Khasanov et al., arXiv:1002.2510v1

Consistent isotopic effect in iron-pnictide superconductors





Harshman et al., PRB 77, 024523(2008).

Sample	($^{nature}Fe$) $T_C(K)$	α_{Fe}	($^{light}Fe$) $c(\AA)$	($^{heavy}Fe$) $c(\AA)$	$\Delta c/c$	α_{Fe}^{str}	α_{Fe}^{int}
$FeSe_{1-x}$ [85]	8.21(4)	0.81(15)	5.48683(9)	5.48787(9)	> 0	$\simeq 0.4$	$\simeq 0.4$
$Ba_{0.6}K_{0.4}Fe_2As_2$ [82]	37.30(2)	0.37(3)	13.289(7)	13.288(7)	~ 0	~ 0	~ 0.35
$Ba_{0.6}K_{0.4}Fe_2As_2$ [83]	37.78(2)	-0.18(3)	13.313(1)	13.310(1)	< 0	~ -0.5	~ 0.35
$SmFeAsO_{0.85}F_{0.15}$ [82]	41.40(2)	0.34(3)	8.490(2)	8.491(2)	~ 0	~ 0	~ 0.35
$SmFeAsO_{1-y}$ [84]	54.02(13)	-0.024(15)	8.4428(8)	8.4440(8)	≥ 0	< 0	

YBCO: the first material with T_c higher than 77 K

In Spring of 1987, Paul Ching-Wu Chu (U. Houston) and Zhong-Xian Zhao (IOP) independently to each other, discovered that YBCO has a T_C of 92 K. Their work inspired a rapid succession of new high temperature superconducting materials, ushering in a new era in material science.