

# SUPERCONDUCTIVITY WS 15-16

Monday 10:00-11:30

SR Exp. physics II

Prof. Paul H.M. van Loosdrecht

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[www.loosdrecht.net](http://www.loosdrecht.net)

# Materials

- Elemental
- Intermetallics (Alloys, A15 & other Xtals)
- Fullerene based
- Organic superconductors
- Heavy fermion compounds
- Cuprates & oxides

# Triplet superconductivity ?

VOLUME 88, NUMBER 1

PHYSICAL REVIEW LETTERS

7 JANUARY 2002

## Triplet Superconductivity in an Organic Superconductor Probed by NMR Knight Shift

I. J. Lee,<sup>1,\*</sup> S. E. Brown,<sup>2</sup> W. G. Clark,<sup>2</sup> M. J. Strouse,<sup>3</sup> M. J. Naughton,<sup>4</sup> W. Kang,<sup>5</sup> and P. M. Chaikin<sup>1</sup>

*Knight shift:* Shift of resonance frequency in NMR  
due to spin coupling of nuclei to conduction electrons

$$K = \alpha \chi_{\text{spin}}$$

Singlet superconductor:

$K = 0$ , change at  $T_c \sim$  pauli susceptibility

Triplet superconductor:

no change at  $T_c$

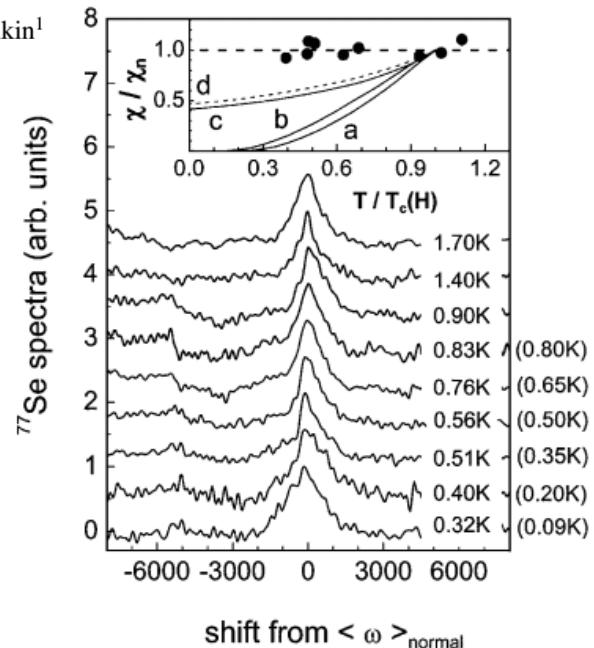
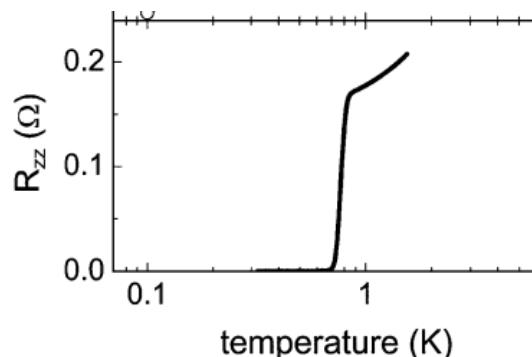
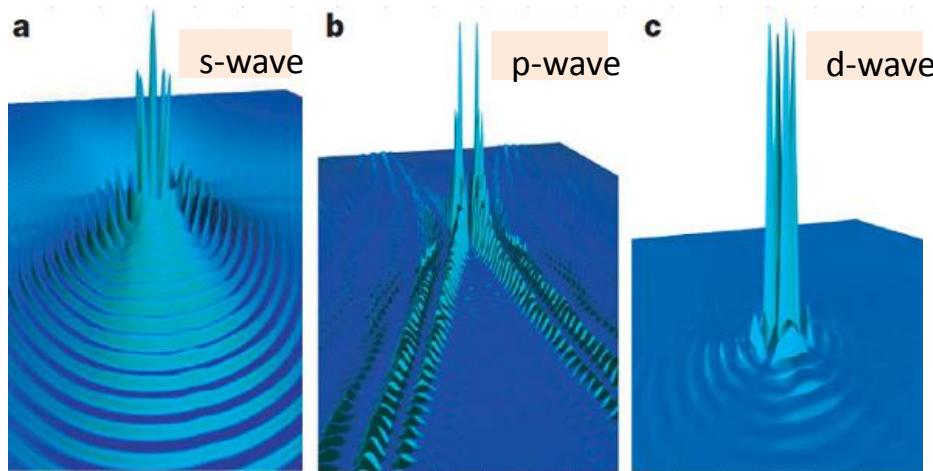


FIG. 3.  $^{77}\text{Se}$  NMR spectra collected above and below  $T_c$  (0.81 K at 1.43 T). Each trace is normalized and offset for clarity. The temperatures shown in parentheses are the measured equilibrium temperatures before the pulse. In the inset, the spin susceptibility normalized by the normal state  $\chi/\chi_n$  from measured first moments are compared with Fulde and Maki's calculation for  $H/H_{c2}(0) \sim 0$  (curve a) and 0.63 (curve b). Curves c and d are obtained from the ratio of applied field (1.43 T) to the measured upper critical field  $H_{c2}(T)$  at which the superconducting criteria "onset" and "50% transition" have been used, respectively, to determine  $H_{c2}(T)$ .

# Triplet superconductivity

- Cooper pair: bound state of 2 electrons
  - Singlet  $|\uparrow\downarrow - \downarrow\uparrow\rangle/\sqrt{2}$
  - Triplet  $|\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle, |\uparrow\downarrow + \downarrow\uparrow\rangle/\sqrt{2}$
- Total wavefunction anti-symmetric under exchange electrons
  - Singlet  $\otimes$  even orbital wavefunction  
 $L=0$  (s-wave), 2 (d-wave), ...
  - Triplet  $\otimes$  odd orbital wavefunction  
 $L=1$  (p-wave), 3 (f-wave), ...

# Real space wave functions (s,p,d superconductivity)



**Figure 1 | Cooper-pair states in real space in two dimensions.** a–c, The probability of finding one quasiparticle in a Cooper-pair state given that the other partner is at the origin. The symmetric form in **a** is characteristic of an *s*-wave spin-singlet state. The two-fold symmetry in **b** is characteristic of one of the possible *p*-wave spin-triplet states, whereas the four-fold symmetry in **c** is characteristic of a *d*-wave spin-singlet state. The Cooper-pair states

**s-wave:**

$$\psi(0) \neq 0$$

Suppressed by on-site coulomb  
Large spatial extend → weakly bound

**d-wave**

$$\psi(0) = 0$$

Avoids on-site coulomb  
Large amplitude nearest neighbors  
→ strong binding → high  $T_c$

# d-wave nature cuprates

FIG. 13. Three-dimensional rendering of a scanning SQUID microscope image of a thin-film YBCO tricrystal ring sample, cooled and imaged in nominally zero magnetic field. The outer control rings have no flux in them; the central three-junction ring has half of a superconducting quantum of flux spontaneously generated in it [Color].

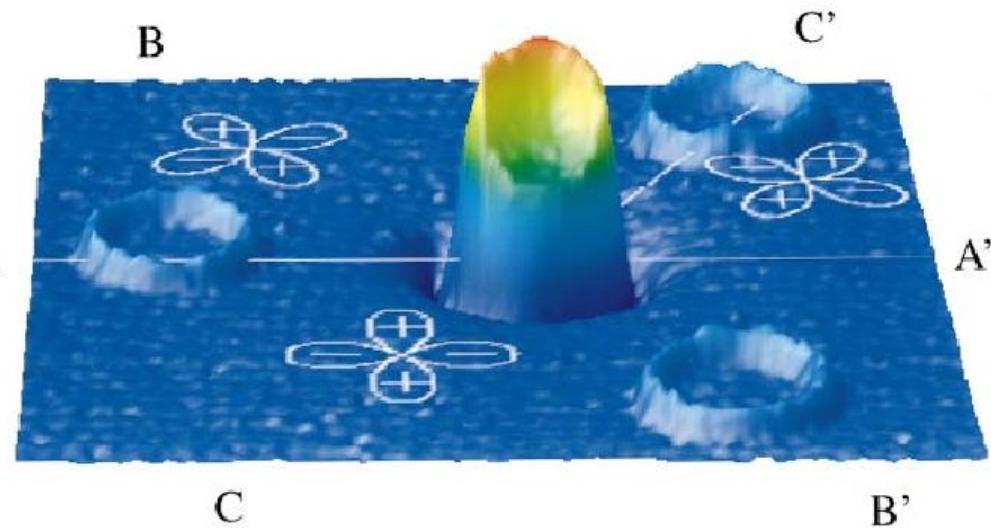
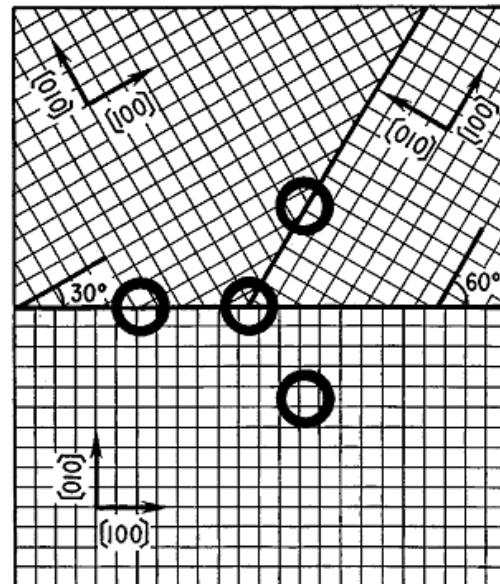
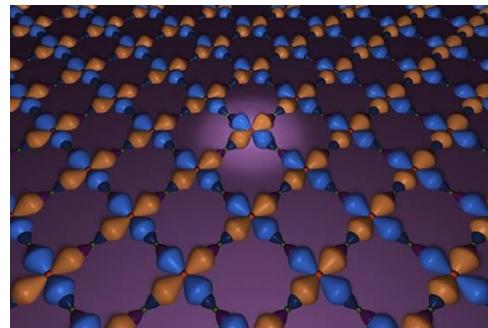
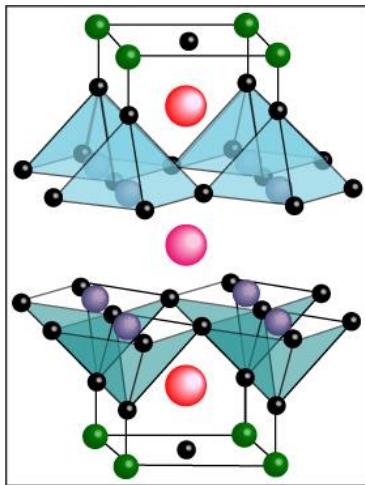


FIG. 11. Experimental configuration for the  $\pi$ -ring tricrystal experiment of Tsuei *et al.* (1994). The central, three-junction ring is a  $\pi$  ring, which should show half-integer flux quantization for a  $d_{x^2-y^2}$  superconductor, and the two-junction rings and zero-junction ring are zero rings, which should show integer flux quantization, independent of the pairing symmetry.

# Gap anisotropy, d-wave



Group-theoretic notation	$A_{1g}$	$A_{2g}$	$B_{1g}$	$B_{2g}$
Order parameter basis function	constant	$xy(x^2-y^2)$	$x^2-y^2$	$xy$
Wave function name	s-wave	g	$d_{x^2-y^2}$	$d_{xy}$
Schematic representation of $\Delta(\mathbf{k})$ in B.Z.				

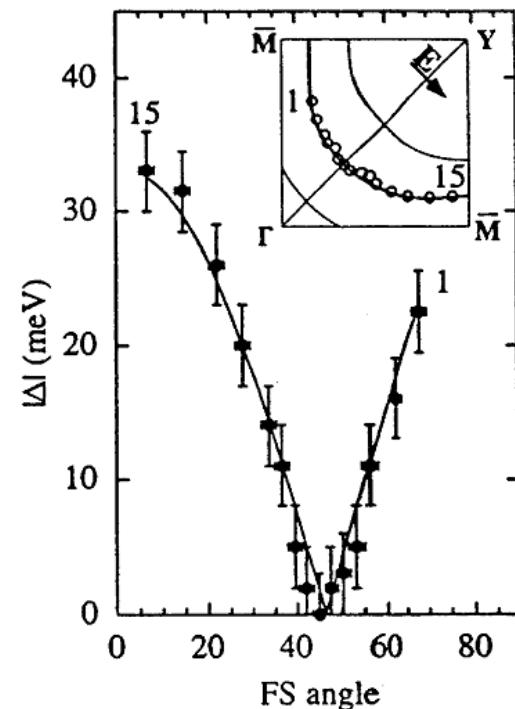
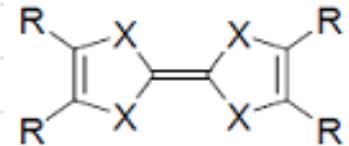


FIG. 4. Energy gap in Bi-2212: ●, measured with ARPES as a function of angle on the Fermi surface; solid curve, with fits to the data using a  $d$ -wave order parameter. Inset indicates the locations of the data points in the Brillouin zone. From Ding, Norman, *et al.* (1996).

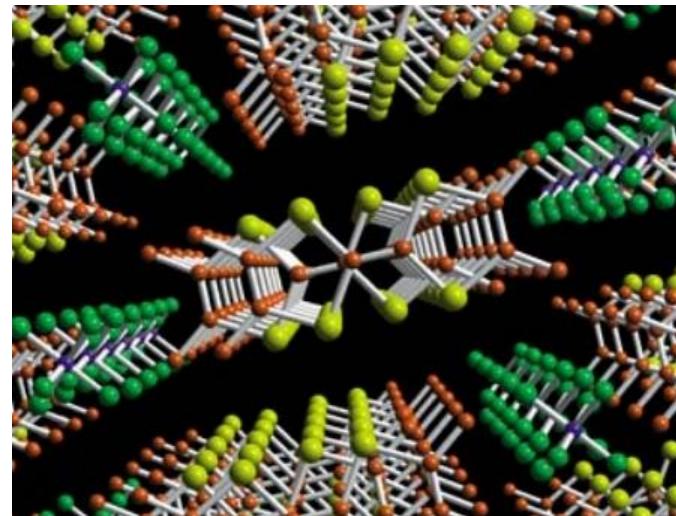
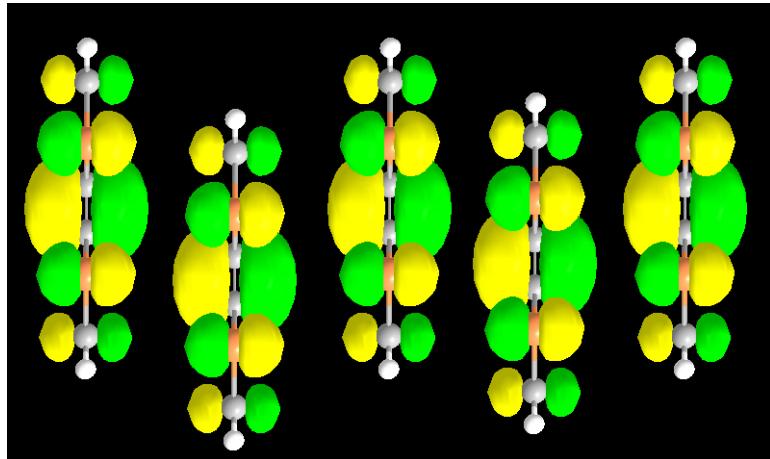
# Organic superconductors

Bechaard salts (D. Jérôme, A. Mazaud, M. Ribault et K. Bechgaard, J. Physique Lett. 41, 95-98 (1980))

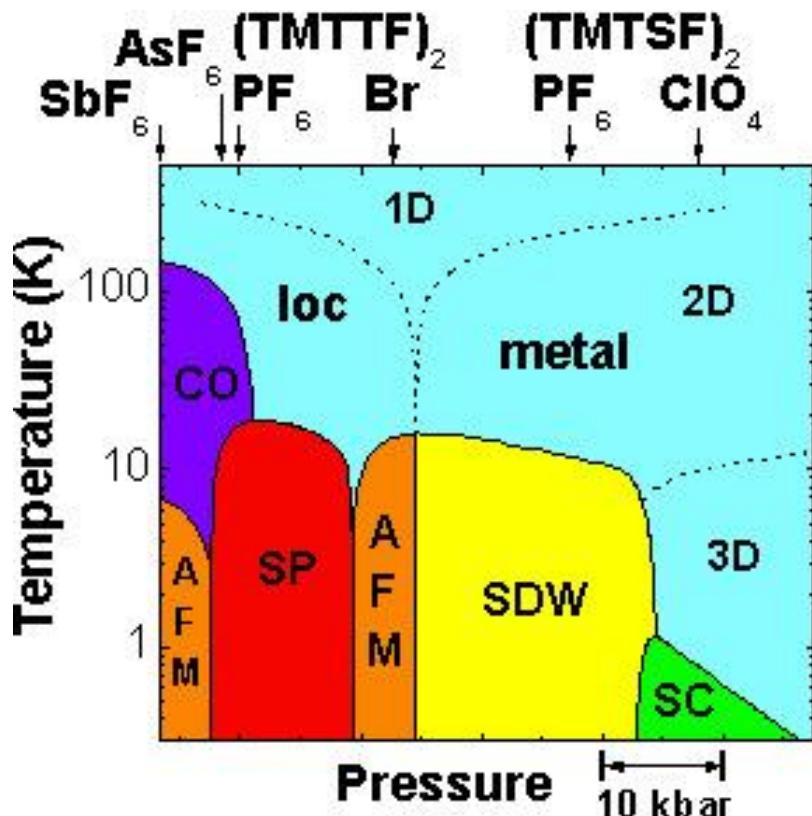
- Charge transfer salts
  - Cation (donor) TMTSF  
(tetramethyltetraseleniafulvalene)
  - Anion (acceptor)  $\text{PF}_6^-$ ,  $\text{ClO}_4^-$ ,  $\text{AsF}_6^-$ , ....
- Quasi one-dimensional



TTF : X=S, R=H  
TSF : X=Se, R=H  
TTeF : X=Te, R=H  
TMTSF : X=Se, R=Me  
TMTTF : X=S, R=Me



# Organic superconductors



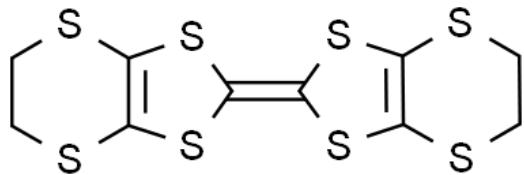
Material	TC (K)	pext (kbar)
(TMTSF) <sub>2</sub> ClO <sub>4</sub>	1.4	0
(TMTSF) <sub>2</sub> SbF <sub>6</sub>	0.36	10.5
(TMTSF) <sub>2</sub> PF <sub>4</sub>	1.1	6.5
(TMTSF) <sub>2</sub> AsF <sub>6</sub>	1.1	9.5
(TMTSF) <sub>2</sub> ReO <sub>4</sub>	1.2	9.5
(TMTSF) <sub>2</sub> TaF <sub>6</sub>	1.35	11
(TMTTF) <sub>2</sub> Br	0.8	26

Complex electronic phase diagram  
Pressure enhances dimensionality  
when  $t_{\text{perp}} \gg kT$

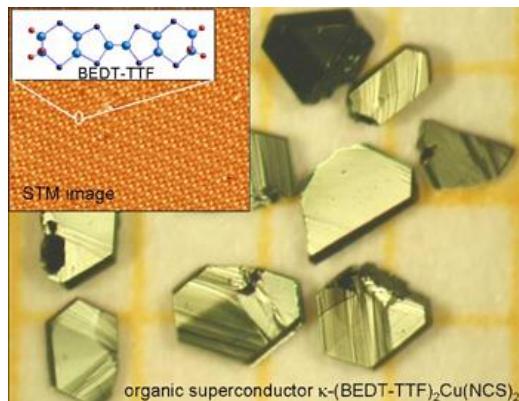
# Organic superconductors

## BEDT-TTF Salts (ET-salts)

- Charge transfer salts
  - Donor BEDT-TTF
  - Acceptor I<sub>3</sub>, KHg(SCN)<sub>4</sub>, ...
- Two dimensional
  - Many different patterns:  $\beta$ ,  $\kappa$ ,  $\theta$ , ...
- Possibly d-wave pairing

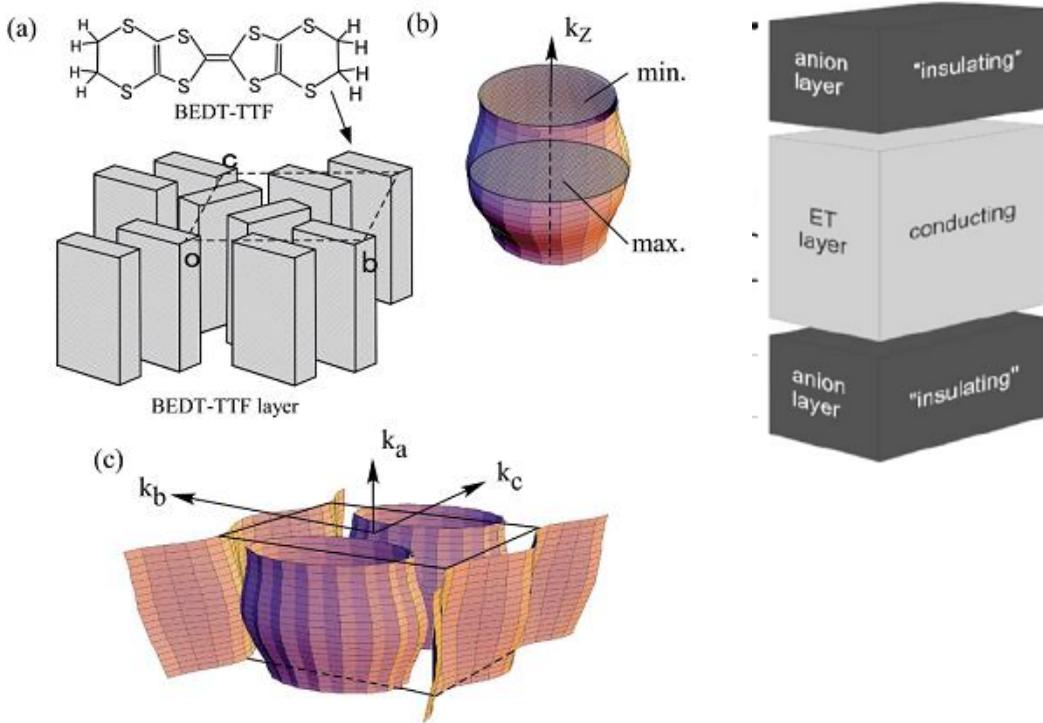


bisethylenedithio-tetrathiafulvalene



Material	T <sub>C</sub> (K)	p <sub>ext</sub> (kbar)
$\beta_H$ -(ET) <sub>2</sub> I <sub>3</sub>	1.5	0
$\theta$ -(ET) <sub>2</sub> I <sub>3</sub>	3.6	0
$\kappa$ -(ET) <sub>2</sub> I <sub>3</sub>	3.6	0
$\alpha$ -(ET) <sub>2</sub> KHg(SCN) <sub>4</sub>	0.3	0
$\alpha$ -(ET) <sub>2</sub> KHg(SCN) <sub>4</sub>	1.2	1.2
$\beta''$ -(ET) <sub>2</sub> SF <sub>5</sub> CH <sub>2</sub> CF <sub>2</sub> SO <sub>3</sub>	5.3	0
$\kappa$ -(ET) <sub>2</sub> Cu[N(CN) <sub>2</sub> ]Cl	12.8	0.3
$\kappa$ -(ET) <sub>2</sub> Cu[N(CN) <sub>2</sub> ]Cl deuterated	13.1	0.3
$\kappa$ -(ET) <sub>2</sub> Cu[N(CN) <sub>2</sub> ]Br deuterated	11.2	0
$\kappa$ -(ET) <sub>2</sub> Cu(NCS) <sub>2</sub>	10.4	0
$\kappa$ -(ET) <sub>4</sub> Hg <sub>2.89</sub> Cl <sub>8</sub>	1.8	12
$\kappa_H$ -(ET) <sub>2</sub> Cu(CF <sub>3</sub> ) <sub>4</sub> ·TCE	9.2	0
$\kappa_H$ -(ET) <sub>2</sub> Ag(CF <sub>3</sub> ) <sub>4</sub> ·TCE	11.1	0

wikipedia



**Fig. 6.1.** (a) BEDT-TTF (ET) molecule and the ET packing arrangement (conducting layer) of an organic superconductor  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>. The ET molecule (conducting) and Cu(NCS)<sub>2</sub> anion (insulating) layers stack alternately along the  $a$  axis. (b) A quasi-two-dimensional Fermi surface. When the field is applied along the cylindrical ( $k_z$ ) axis, two extremal (minimum and maximum) cross sections are well defined, indicated by shaded areas. (c) The calculated Fermi surface of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>. The solid lines show the first Brillouin zone boundaries. There exist two open sheets of 1D Fermi surface and a closed 2D Fermi surface

# FFLO state

PHYSICAL REVIEW

VOLUME 135, NUMBER 3A

3 AUGUST 1964

## Superconductivity in a Strong Spin-Exchange Field\*

PETER FULDE AND RICHARD A. FERRELL

Fulde-Ferrel-Larkin-Ovchinnikov

PRL 99, 187002 (2007)

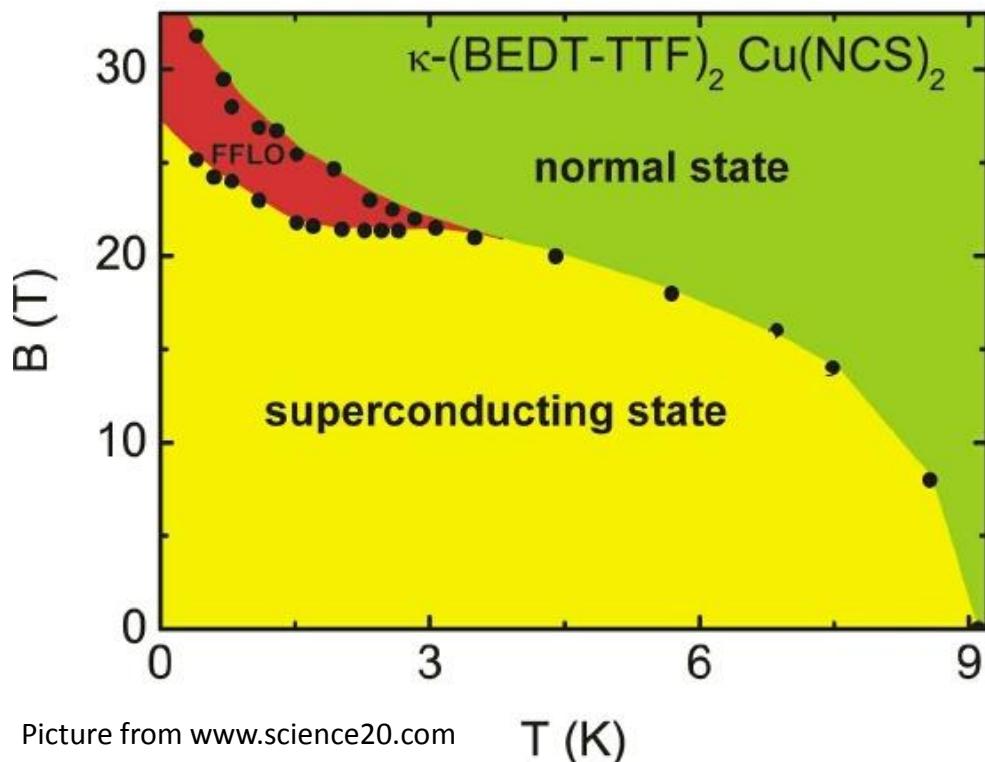
PHYSICAL REVIEW LETTERS

week ending  
2 NOVEMBER 2007



### Calorimetric Evidence for a Fulde-Ferrell-Larkin-Ovchinnikov Superconducting State in the Layered Organic Superconductor $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>

R. Lortz,<sup>1</sup> Y. Wang,<sup>2</sup> A. Demuer,<sup>2</sup> P. H. M. Böttger,<sup>3</sup> B. Bergk,<sup>3</sup> G. Zwicknagl,<sup>4</sup> Y. Nakazawa,<sup>5</sup> and J. Wosnitza<sup>3</sup>



Normally SC state stable until  
zeeman E can break pairs  
Competing phase: SC formed from  
spin-split normal state  
→ FFLO state

- Finite  $q$  cooper pairs
- Spatially modulated order parameter

# Heavy fermion systems

## Heavy fermion materials

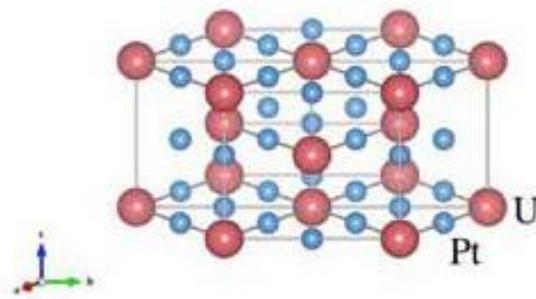
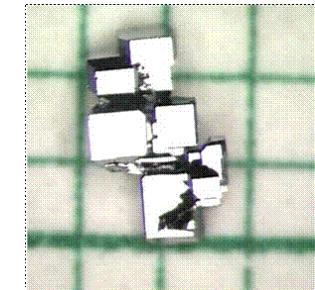
- partially filled f-shell compounds
- Strong on-site repulsion favoring localized spins
- hybridization with conduction electrons
- narrow bandwidth peak near Fermi level
- high effective mass
- Kondo physics

At high T:

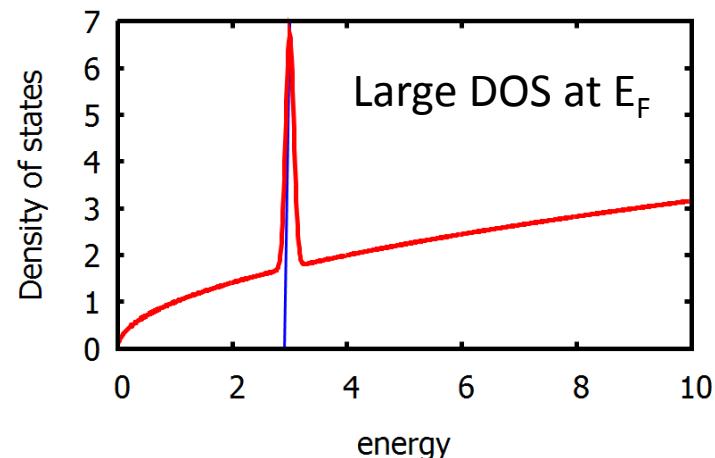
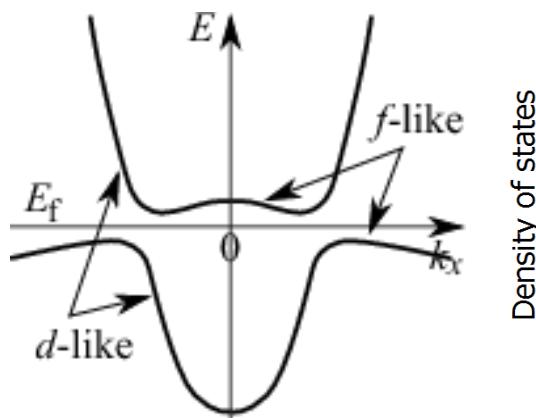
conduction electrons scatter on local spins

At low T ( $<<10K$ ):

local spins screened by conduction electron spins



UPt<sub>3</sub>



- High temperature phase often non-fermi liquid  
 $\rho \sim T$  instead of  $T^2$  (*FL*)

- Competition (& coexistence?) of SC and magnetism

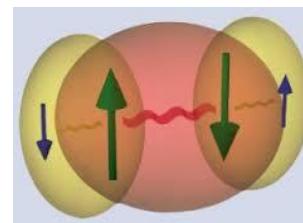
- Strong on-site correlations not in favor of s-wave pairing

- Pairing of electronic origin?

- UPt<sub>3</sub> (and others) triplet superconductor

- Often SC in vicinity quantum critical point

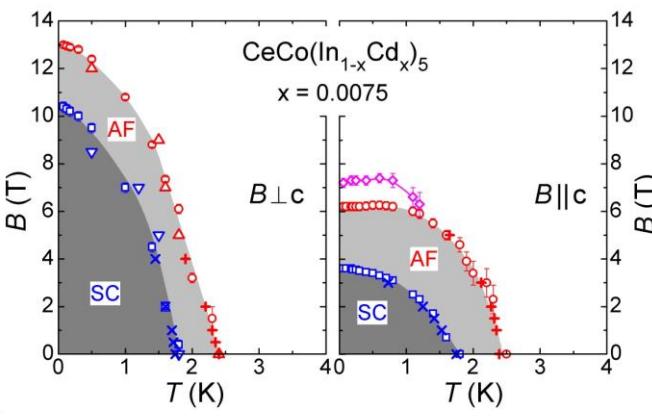
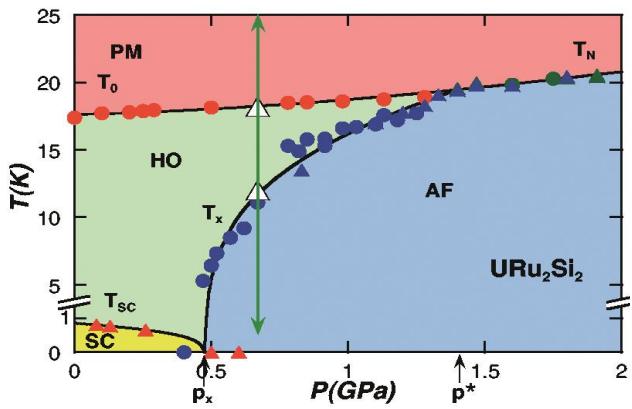
- Record  $T_c = 18.5$  K for PuCoGa<sub>5</sub> (Sarrao et al., Nature 2002)



Electronic (Magnon)  
glue?

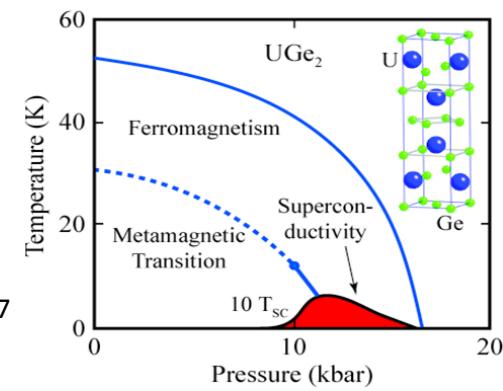
Material	$T_c$ (K)
CeCu <sub>2</sub> Si <sub>2</sub>	0.7
<a href="#">CeCoIn<sub>5</sub></a>	2.3
CeIn <sub>3</sub>	0.2
UPt <sub>3</sub>	0.48
URu <sub>2</sub> Si <sub>2</sub>	1.3
UPd <sub>2</sub> Al <sub>3</sub>	2.0
UNi <sub>2</sub> Al <sub>3</sub>	1.1

wikipedia



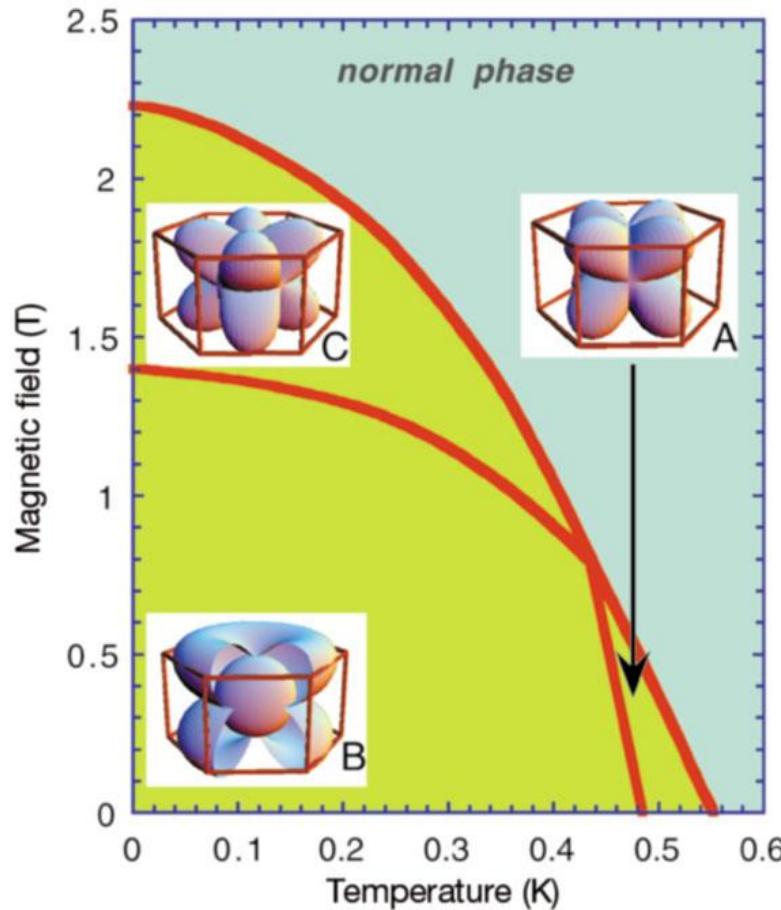
Sunil Nair et al., Proc. Natl. Acad. Sci. USA **107** (2010) 9537

A. Villaume, et al., Physical Review B 78 (2008) 012504



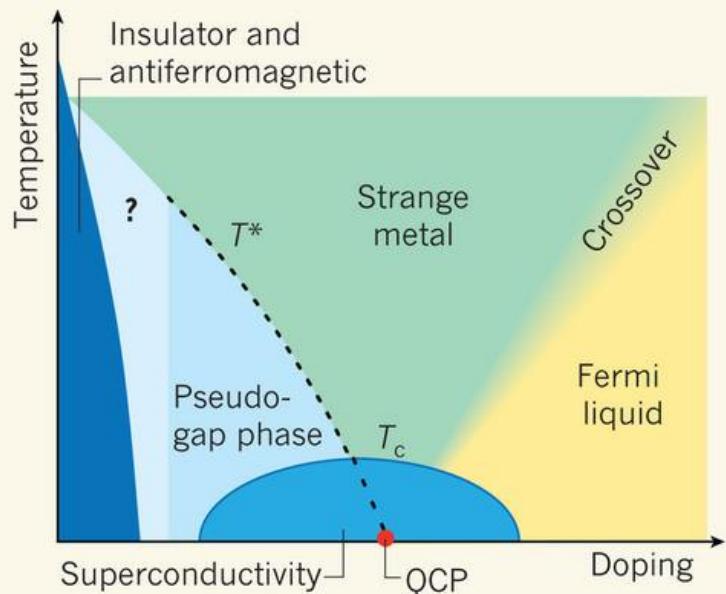
Dept. Physics, cambridge univ.

3 superconducting phases in  $\text{UPt}_3$  (3 different gap symmetries)  
derived from flux-lattice symmetry



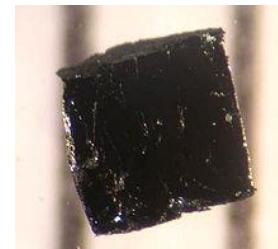
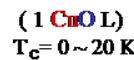
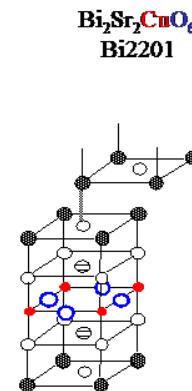
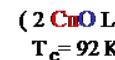
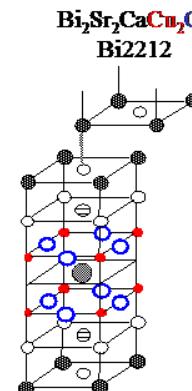
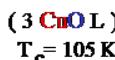
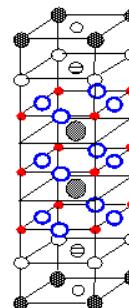
Huxley et al., Nature 406, 160 (2000)

# Cuprates & other oxides



Chandra Varma, Nature 468, 184 (2010)

CuO planes are the key components of high  $T_c$  superconductors



Bi2223, wikipedia

# High Tc cuprates

Bednorz & Mueller, Z.Physik B 64, 189 (1986):

Ba-La-Cu-O ~30 K

Current record:

135 K in Hg-1223 (Chu et al, Nature 1993)

166 K in Hg-1223 (fluorinated)

@ 23 Gpa (Monteverde, EPL 2005)

2D planes → low dimensionality

Strong electron correlations (Mott-Hubbard physics)

Undoped materials are anti-ferromagnetic Mott insulators

Doping → competition S.C. and antiferromagnetism

spin fluctuations are important (glue??)

d-wave superconductors

Formula	Notation	T <sub>c</sub> (K)	#Cu-O planes	Crystal structure
Bi <sub>2</sub> Sr <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>6</sub>	Bi-2223	110	3	Tetragonal
Bi <sub>2</sub> Sr <sub>2</sub> CaCu <sub>2</sub> O <sub>8</sub>	Bi-2212	85	2	Tetragonal
Bi <sub>2</sub> Sr <sub>2</sub> CuO <sub>6</sub>	Bi-2201	20	1	<a href="#">Tetragonal</a>
HgBa <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>8</sub>	Hg-1223	134	3	Tetragonal
HgBa <sub>2</sub> CaCu <sub>2</sub> O <sub>6</sub>	Hg-1212	128	2	Tetragonal
HgBa <sub>2</sub> CuO <sub>4</sub>	Hg-1201	94	1	Tetragonal
Tl <sub>2</sub> Ba <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>10</sub>	Tl-2223	125	3	Tetragonal
Tl <sub>2</sub> Ba <sub>2</sub> CaCu <sub>2</sub> O <sub>8</sub>	Tl-2212	108	2	Tetragonal
Tl <sub>2</sub> Ba <sub>2</sub> CuO <sub>6</sub>	Tl-2201	80	1	Tetragonal
TlBa <sub>2</sub> Ca <sub>3</sub> Cu <sub>4</sub> O <sub>11</sub>	Tl-1234	122	4	Tetragonal
YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>		123	2	<a href="#">Orthorhombic</a>

wikipedia

conductivity and superconductivity. On this basis I was able to explain most of the experimental data about layered cuprates without dividing them into “good” ones, which should be mentioned on every possible occasion, and “bad” ones, which should be forgotten. As a result I can state that the so called “mystery” of high- $T_c$  superconductivity does not exist.



Abrikosov, NP 2003

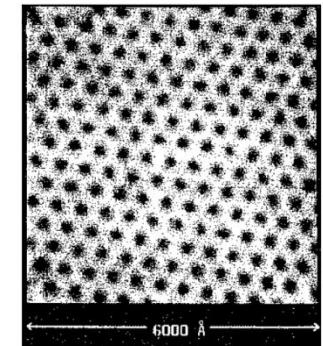
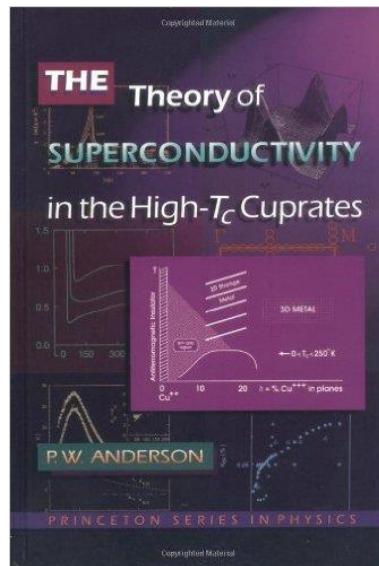
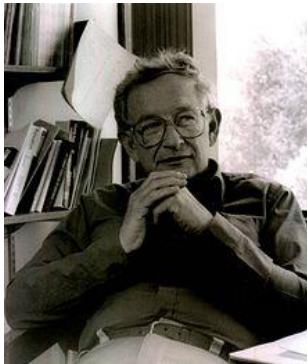
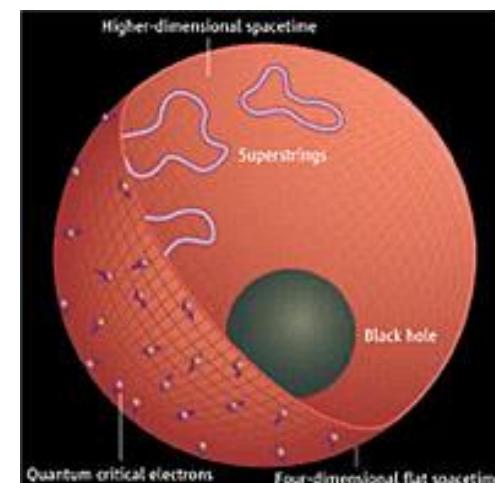


Figure 6. Vortices in  $\text{NbSe}_2$  defined by scanning tunneling microscopy (STM)



ADS/CFT theories for HTc's (image: P. Huey, Science 2008)

## Theory of High- $T_c$ Superconductivity: Transition Temperature

Dale R. Harshman<sup>1,2,3,6</sup>, Anthony T. Fiory<sup>4</sup> and John D. Dow<sup>3,5</sup>

# $\text{Sr}_2\text{RuO}_4$

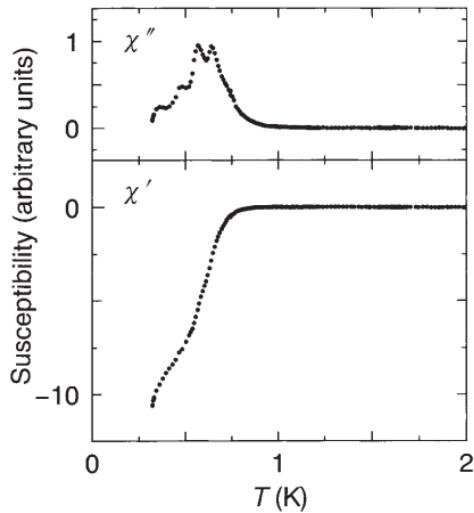


FIG. 2 The a.c. susceptibility of a single crystal of  $\text{Sr}_2\text{RuO}_4$  measured by a mutual-inductance method at a magnetic field of  $H=0.67$  Oe (root-mean-squares value) parallel to the  $c$ -axis, and at a frequency of 1,000 Hz. Top,  $\chi''$  (imaginary part); bottom,  $\chi'$  (real part).

Maeno et al., Nature 1994

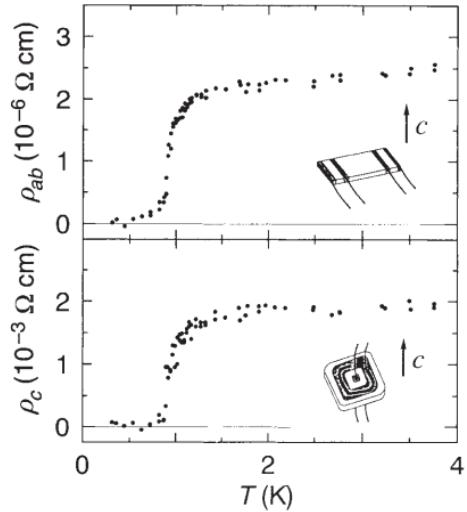
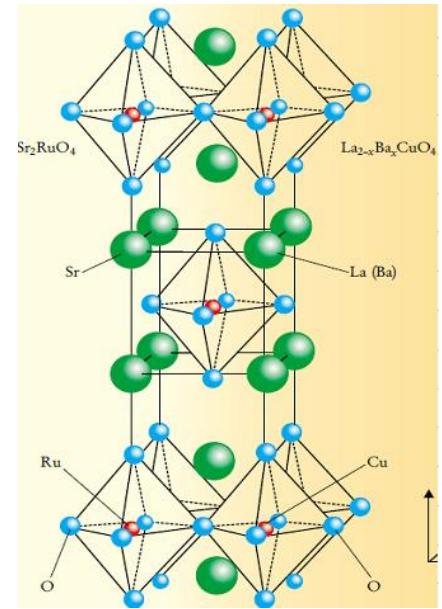


FIG. 3 Anisotropy in the resistivity  $\rho$  of  $\text{Sr}_2\text{RuO}_4$  below 4 K. The superconducting transition is at  $T_c=0.93$  K. Insets, attachment of the electrodes.



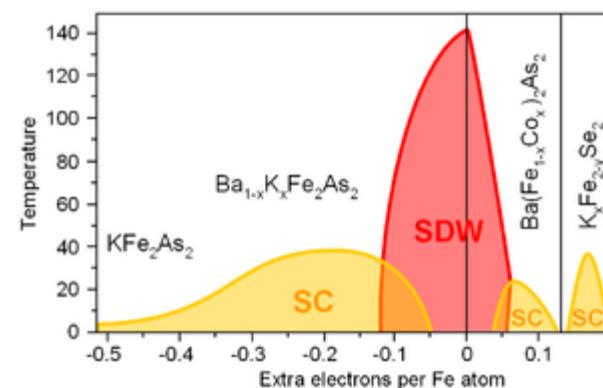
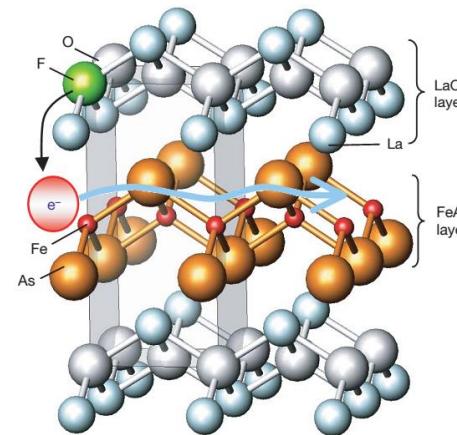
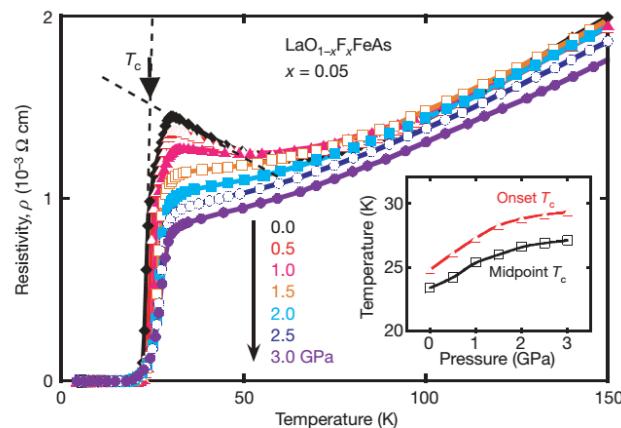
$T_c = 1.5$  K  
p-wave superconductor

For review see e.g. Maeno, Rice, Sigrist, Phys. Today, Jan. 2001

## LETTERS

# Superconductivity at 43 K in an iron-based layered compound $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$

Hiroki Takahashi<sup>1</sup>, Kazumi Igawa<sup>1</sup>, Kazunobu Arii<sup>1</sup>, Yoichi Kamihara<sup>2</sup>, Masahiro Hirano<sup>2,3</sup> & Hideo Hosono<sup>2,3</sup>



# Heterostructure oxide interfaces

$T_c \sim 200$  mK

Heterostructure of wide bandgap materials

$\text{LaAlO}_3$ : 5.6 eV;  $\text{SrTiO}_3$  3.2 eV

2D electron gas at interface

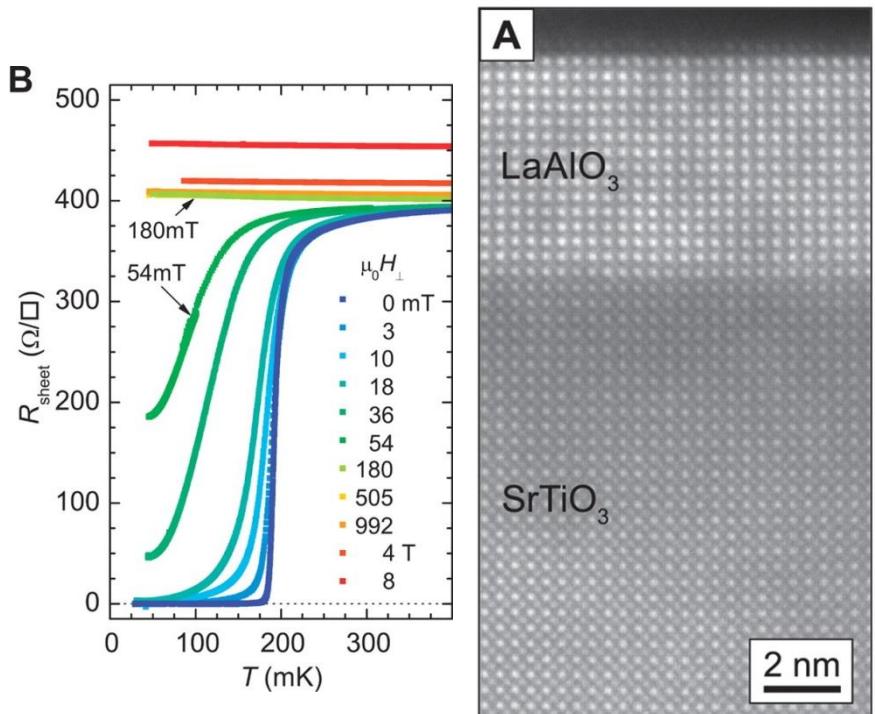
- Oxygen stoichiometry?
- Polar catastrophe?

$\text{SrTiO}_3$ : Stack of neutral layers ( $\text{SrO}/\text{TiO}_2/\dots$ )

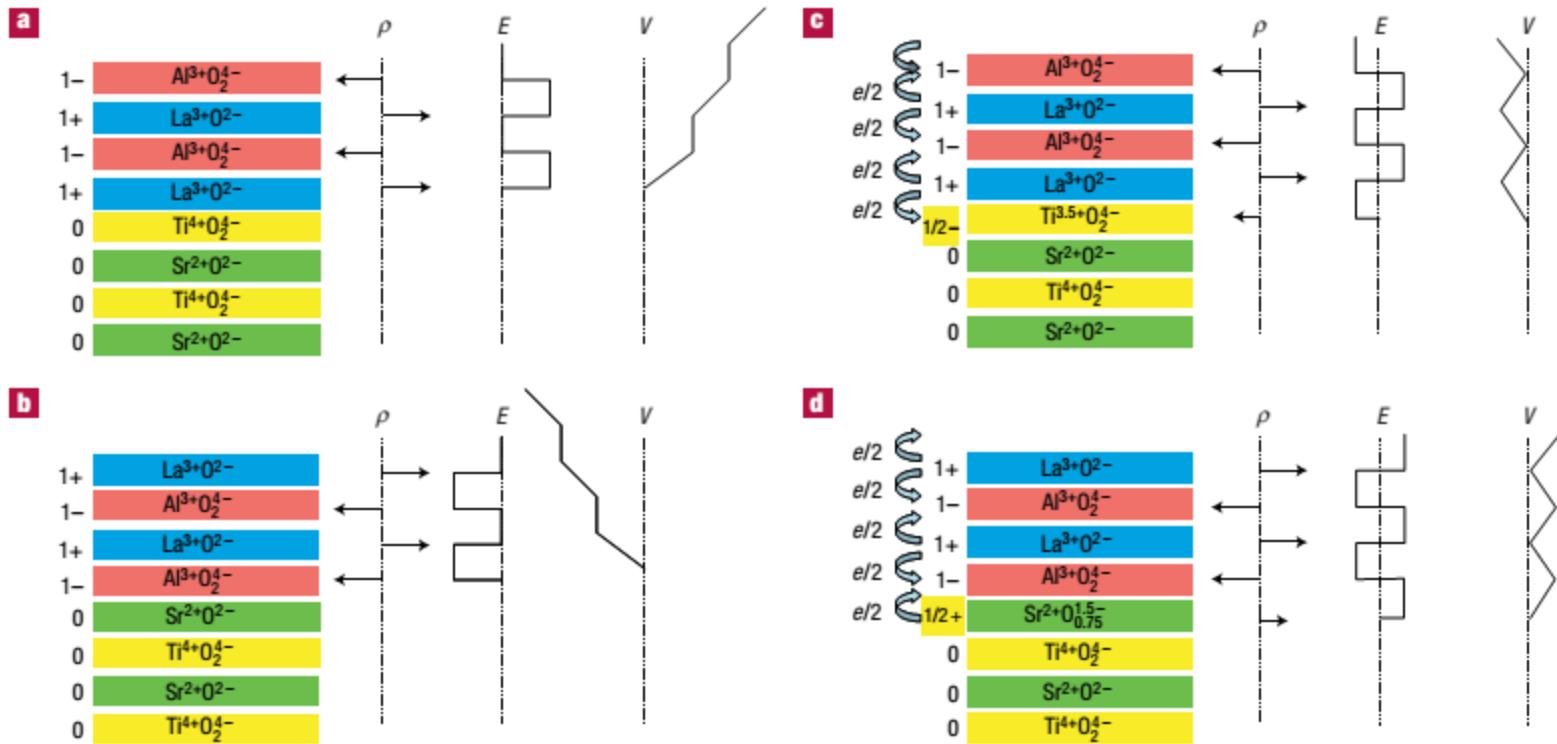
$\text{LaAlO}_3$ : Charged layers ( $\text{LaO}^+/\text{AlO}_2^-/\dots$ )

$\text{LaAlO}_3$  Polar surface? : leads to divergent potential

→ electronic reconstruction



Reyren et al., Science 317, 1196 (2007)



**Figure 1** The polar catastrophe illustrated for atomically abrupt (001) interfaces between LaAlO<sub>3</sub> and SrTiO<sub>3</sub>. **a**, The unreconstructed interface has neutral (001) planes in SrTiO<sub>3</sub>, but the (001) planes in LaAlO<sub>3</sub> have alternating net charges ( $\rho$ ). If the interface plane is AlO<sub>2</sub>/LaO/TiO<sub>2</sub>, this produces a non-negative electric field ( $E$ ), leading in turn to an electric potential ( $V$ ) that diverges with thickness. **b**, If the interface is instead placed at the AlO<sub>2</sub>/SrO/TiO<sub>2</sub> plane, the potential diverges negatively. **c**, The divergence catastrophe at the AlO<sub>2</sub>/LaO/TiO<sub>2</sub> interface can be avoided if half an electron is added to the last Ti layer. This produces an interface dipole that causes the electric field to oscillate about 0 and the potential remains finite. The upper free surface is not shown, but in this simple model the uppermost AlO<sub>2</sub> layer would be missing half an electron, which would bring the electric field and potential back to zero at the upper surface. The actual surface reconstruction is more complicated<sup>21</sup>. **d**, The divergence for the AlO<sub>2</sub>/SrO/TiO<sub>2</sub> interface can also be avoided by removing half an electron from the SrO plane in the form of oxygen vacancies.

# Superconducting materials

- Many, many superconducting materials
- High Debye frequency (conventional SC)
- High DOS at Fermi level
- Low dimensionality favorable
- Competing interactions,  
vicinity other phase transitions
- On-site Coulomb suppresses s-wave
- Electronic mechanisms (charge, spin)
- No theoretical limit for  $T_c$  (at this point in time)

