# High T<sub>c</sub> Superconductivity



# Outline

- 1. Introduction to conventional superconductivity
- 2. Introduction to scanning tunneling microscopy (STM)
- 3. High T<sub>c</sub> Superconductor : Cuprates
- 4. High Tc Superconductor : Fe-based Compounds

# Outline

## 1. Introduction to conventional superconductivity

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Helium Liquefaction in 1908

July 10, 1908



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Heike Kamerlingh Onnes

Nobel Prize, 1913

"Door meten tot weten" (Knowledge through measurement)

## **Discovery of Superconductivity in 1911**







Heike Kamerlingh Onnes

Nobel Prize, 1913

"Door meten tot weten" (Knowledge through measurement)

H. Kamerlingh Onnes, Commun. Phys. Lab. Univ. Leiden. Suppl. 29 (Nov. 1911).

# The Meissner Effect in 1933

Perfect diamagnetism В В B=0  $T < T_C$ T>₽

### Walther Meißner



### Robert Ochsenfeld



©PTB Berlin Institute

## Perfect Conductor vs Superconductor



### **Basic Properties of Superconductors**

### Zero electrical resistance + Meissner effect



# Periodic Table of Superconductivity

Н		ambient pressure superconductor						high pressure superconductor									He
Li 0.0004 14 30 Na	Be 0.026 3.7 30 Mg	T <sub>c</sub> (K) T <sub>c</sub> <sup>max</sup> (K) P(GPa)					T <sub>c</sub> <sup>max</sup> (K) P(GPa)					<b>B</b> 11 250 <b>Al</b> 1.14	C Si	N P	<b>O</b> 0.6 100 <b>S</b>	F Cl	Ne
K	Са	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	8.2 15.2 Ge	13 30 As	17.3 190 Se	Br	Kr
	29 217	19.6 106	0.39 3.35 56.0	5.38 16.5 120			2.1 21				0.875	1.091 7 1.4	5.35 11.5	2.4 32	8 150	1.4 100	
Rb	Sr 7 50	<b>Y</b> 19.5 115	Zr 0.546 11 30	<b>Nb</b> 9.50 9.9 10	<b>Mo</b> 0.92	<b>Tc</b> 7.77	<b>Ru</b> 0.51	<b>Rh</b> .00033	Pd	Ag	Cd 0.56	<b>In</b> 3.404	<b>Sn</b> 3.722 5.3 11.3	<b>Sb</b> 3.9 25	<b>Te</b> 7.5 35	I 1.2 25	Xe
Cs 1.3 12	<b>Ba</b> 5 18	insert La-Lu	Hf 0.12 8.6 62	<b>Ta</b> 4.483 4.5 43	<b>W</b> 0.012	<b>Re</b> 1.4	<b>Os</b> 0.655	<b>Ir</b> 0.14	Pt	Au	<b>Hg-</b> α 4.153	<b>Tl</b> 2.39	<b>Pb</b> 7.193	<b>Bi</b> 8.5 9.1	Ро	At	Rn
Fr	Ra	insert Ac-Lr	Rf	На						1			1		•	<u></u>	
		La-fee 6.00 13 15	Ce 1.7 5	Pr	Nd	Pm	Sm	<b>Eu</b> 2.75 142	Gd	Tb	Dy	Но	Er	Tm	Yb	<b>Lu</b> 12.4 174	
		Ac	<b>Th</b> 1.368	<b>Pa</b> 1.4	U 0.8(β) 2.4(α) 1.2	Np	Pu	Am 0.79 2.2 6	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

M. Debessai et al., J. Phys.: Conf. Series 215, 012034 (2010).

## Type I & II Superconductors



J. N. Rjabinin, L.W. Schubnikow, Physikalische Zeitschrift der Sowjetunion 7, 122 (1935)

# **Superconducting Vortices**

### Decoration image of vortex lattice



U. Essmann and H. Trauble, Physics Letters 24A, 526 (1967)



### Alexei A. Abrikosov



Nobel Prize 2003



### **Vortex-Current Interaction**

• Lorentz force on *J<sub>S</sub>* due to the interaction between *J<sub>S</sub>* and *B*.

$$f = \int J_s \times B \ d^2r = J_{tr} \times \int B \ d^2r = J_{tr} \times (\phi_0 \widehat{B})$$

• Vortex motion implies that the vortex is subject to a power input per unit volume of vortex of characteristic radius  $r_B$ 

$$P = \frac{fv}{\pi r_B^2} = J_{tr} \frac{\phi_0}{\pi r_B^2} V = \underbrace{J_{tr} B V}_{\text{Lorentz force}}$$

- Vortex motion leads to dissipation! R≠0 !
- Vortex pinning is crucial for applications.



### Magnus force



**Quantum Levitation** 

### Magnetic flux pinning is key. Unstable for type I superconductors.



© Quantum Experience ltd.



© NHMFL

# The Origin of Conventional Superconductivity

# Isotope Effect in 1950

- Lattice vibration is a part of the SC process.
- A crucial step to a microscopic theory.



#### Emanuel Maxwell, Phys. Rev. 78, 477 (1950) C.A. Reynolds et al., Phys. Rev. 78, 487 (1950)

### Emanuel Maxwell



© MIT

#### **Bernard Serin & Charles Reynolds**



© Rutgers University

# **Evidence for Energy Gap in 1953**

### Another motivation for the BCS theory of superconductivity.



A. Brown, M. W. Zemansky, and H. A. Boorse, Phys. Rev. 92, 52 (1953)B. B. Goodman, Proc. Phys. Soc. (London) A66, 217 (1953)

## **BCS Theory in 1957**

#### **Cooper Pairs**



Exchange boson: Lattice Vibration Mode



John Bardeen

### Microscopic theory for SC



Leon Cooper

Nobel Prize 1972



**Robert Schrieffer** 

J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957)

### **Bosons vs Fermions**





Pauli Exclusion Principle

### Wolfgang Pauli



Nobel Prize 1945

### **Bose-Einstein Condensation**



### Predicted in 1924 Satyendra Nath Bose Albert Einstein











Carl Wieman Wolfgang Ketterle



Nobel Prize 2001



## **Normal Metallic State**

Electrons in wave-like states in momentum-space (k-space)



 $p = \hbar k = h/\lambda$ 

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

# Superconducting Ground State



## Superconducting Ground States



$$\Psi_{BCS} = \prod_{k} \left( u_k + v_k c_{k\uparrow}^* c_{-k\downarrow}^* \right) | 0 >$$

 $u_k$  and  $v_k$ : coherence factor

BCS, Phys Rev 108, 1175 (1957)

### **Superconducting Excited States**



$$\gamma_{k\uparrow}^* = u_k c_{k\uparrow} + v_k c_{-k\downarrow}^*$$

Bogoliubov, Nuovo Cimento 7, 794 (1958)

BCS, Phys Rev 108, 1175 (1957)

 $u_k$  and  $v_k$ : coherence factor

### Superconducting Excited States





Bogoliubov, Nuovo Cimento 7, 794 (1958)

### Superconducting Excited States



Bogoliubov, Nuovo Cimento 7, 794 (1958)

### Superconducting Energy Gap in 1960

#### Ivar Giaever



Nobel Prize in 1973 ©Schenectady Museum

Tunneling junction

S I N



I. Giaever, Phys. Rev. Lett. 5, 147 (1960)I. Giaever, Phys. Rev. 126, 941 (1962)

### Superconducting Gap

Pair wave function :  $\Psi_{kss'} = \langle \Psi_{BCS} | c_{-ks'} c_{ks} | \Psi_{BCS} \rangle = g(k) \chi_{ss'}$ 

Spin part : 
$$\chi_{ss'}$$
  $(\uparrow \downarrow - \downarrow \uparrow)$   $S = 0$   
 $(\uparrow \uparrow, \uparrow \downarrow + \downarrow \uparrow, \downarrow \downarrow)$   $S = 1$   
Orbital part :  $g(k)$   $\psi(\mathbf{r}) \propto \sum_{k=1}^{k} \frac{\Delta(\mathbf{k})}{\sqrt{c(\mathbf{k})^2 + \Delta(\mathbf{k})^2}} \exp(-i\mathbf{kr})$ 

Spin	Orbital					
anti-symmetric ( <i>S</i> = 0)	symmetric ( <i>s</i> , <i>d</i> ,)					
symmetric ( <i>S</i> = 1)	anti-symmetric ( <i>p, f,</i> )					

- l = 0 : s wave (conventional SC) l = 1 : p wave (superfluid <sup>3</sup>He)
- l = 2 : d wave (cuprate SC)

If l > 0,  $\psi(0) = 0$ 

repulsive interaction  $\begin{cases}
\Delta(k) \text{ must change its sign}
\end{cases}$ 

### **Gap Equation**

$$\Delta(\mathbf{k}) = -\frac{1}{2} \sum_{\mathbf{q}} V(\mathbf{q}) \frac{\Delta(\mathbf{k})}{\sqrt{\epsilon(\mathbf{k} + \mathbf{q})^2 + \Delta(\mathbf{k} + \mathbf{q})^2}} \tanh \frac{\sqrt{\epsilon(\mathbf{k} + \mathbf{q})^2 + \Delta(\mathbf{k} + \mathbf{q})^2}}{2k_B T}$$
Pairing interaction
In conventional BCS,  $V(\mathbf{q}) = -|V| < 0 : \Delta$  is always positive.
If  $V(\mathbf{q} = \mathbf{Q}) > 0$  plays a role,  $\Delta(\mathbf{k})$  and  $\Delta(\mathbf{k} + \mathbf{Q})$  have a different sign.



# Flux Quantization Theory in 1950

\* We note that in order for  $\Psi$  to be a single-valued function, as required by quantum mechanics, it is necessary that the moduli of  $\chi$  fulfill a kind of quantum condition:

$$<\chi>=\oint \overline{\mathbf{p}}_{s}\cdot \mathbf{ds}=Kh$$

where K must be an integer. This means that there exists a <u>universal unit for the fluxoid</u>:

$$\Phi_1 = hc/e \simeq 4 \cdot 10^{-7} \text{ gauss} \cdot \text{cm}^2$$

### Fritz London



### Superconducting ring



©Duke Univ.

Superfluids, Macroscopic Theory of Superconductivity, Structure of Matter Vol. 1 (Wiley, New York, 1950)

# Flux Quantization Experiments in 1961

#### **Bascom Deaver**





©APS

©Duke Univ.

**Robert Doll** 





©Walther-Meißner-Institute

 $|\Phi| = n^{hc}/_{2e} = n\Phi_0,$ where  $\Phi_0 = 2.0 \times 10^{-15} Tesla - m^2$ Each vortex carries one flux quanta SC carriers are 2e! Confirmation of Cooper pairs!



B. D. Deaver and W. M. Fairbank, PRL **7**, 43 (1961) R. Doll and M. Näbauer, PRL **7**, 51 (1961)

### History of Conventional SC

![](_page_30_Figure_1.jpeg)

### History of Conventional SC

![](_page_31_Figure_1.jpeg)

# Matthias's Rules for Searching High TC SC

#### **Bernd Matthias**

![](_page_32_Picture_2.jpeg)

By Joel Broida©

- 1. Stay away from insulators; transition metals are better.
- 2. There are favorable electron/atom ratios.
- 3. High symmetry is good; cubic symmetry is best.
- 4. Stay away from Oxygen
- 5. Stay away from magnetism
- 6. Stay away from theorists.
  - W. E. Pickett , Physica B 296, 112 (2001)I. I. Mazin, Nature 464, 183 (2010)

# The Beginning of Unconventional SC: Heavy Fermion SC

Enormous effective mass of their charge carriers. This is achieved by a sharp spike in the DOS at the Fermi surface, to as much as 1000 times the density of states in Cu.

![](_page_33_Picture_2.jpeg)

**Frank Steglich** ©Max Planck Institute

### The Woodstock of Physics : Discovery of Cuprates

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

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

Received April 17, 1986

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

### J. Georg Bednorz

![](_page_34_Picture_6.jpeg)

Nobel Prize 1987

### K. Alex Müller

![](_page_34_Picture_9.jpeg)

### $La_{2-x}Ba_{x}CuO_{4}$ , Tc=30K

![](_page_34_Picture_11.jpeg)

# The Woodstock of Physics : Discovery of Cuprates

![](_page_35_Picture_1.jpeg)

M. K. Wu et al., PRL 58, 908 (1987)
### Woodstock of Physics - March Meeting 1987

"The stores and the bars were all 'Physicists welcome,' " said Paul M. Grant, who headed the superconductivity research at I.B.M.'s Almaden Research Center in San Jose. He recalled a discotheque in Chelsea with a long line of people waiting to get in. "The bouncers took anybody that had a physical society badge on to the front," Dr. Grant recalled, "and we got in gratis. Can you imagine what a culture shift? We had a hell of a good time." – NY Times



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### **History of Superconductors**



## The Discovery of Fe-based Superconductors (FeSC)

2006 : LaFeP( $O_{1-x}F_x$ ),  $T_C \sim 5K$ 2007 : LaNiPO,  $T_C \sim 3K$ Feb 23, 2008 : LaFeAs( $O_{1-x}F_x$ ),  $T_C \sim 26K$ 

### Hideo Hosono





- Y. Kamihara et al., JACS. 128, 10012 (2006)
- T. Watanabe et al., JACS. 46, 7719 (2007)
- Y. Kamihara et al., JACS. 130, 3296 (2008)

## History of Conventional and High T<sub>c</sub> Superconductors



# Honorable Mention : MgB<sub>2</sub> in 2001

Tc=39K

Two superconducting gaps Strong  $sp^2$  bonding and hybridization  $E_{2g}$  phonon and  $\sigma$  bond coupling leads to high Tc







J. Nagamatsu *et al.*, Nature 410, 63 (2001) Amy Liu *et al.*, PRL 87, 087005 (2001) H.J. Choi *et al.*, Nature 418, 758 (2002)

# Honorable Mention : H<sub>3</sub>S in 2015

T<sub>c</sub>=203K under High Pressure Likely H-rich H<sub>3</sub>S Conventional superconductor?



### **Mikhail Eremets**

© Max-Planck-Institut für Chemie

A. P. Drozdov et al., Nature 525, 73 (2015)

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# Scanning Tunneling Microscope (STM)

### Heinrich Rohrer & Gerd Binnig



Nobel Prize in 1986 ©IBM



©Wikipedia

# **Quantum Tunneling**

### Erwin Schrödinger



Nobel Prize in 1933



B. Bleaney, Contemp. Phys. 25, 315 (1984)

# Tunneling current

$$I(\vec{r}, z, V) \propto \exp(-2\kappa(\vec{r})z) \int_{0}^{E=eV} LDOS_{sample}(\vec{r}, E) dE$$
  
where  $\kappa(\vec{r}) = \frac{\sqrt{2m\phi(\vec{r})}}{\hbar} \sim 1 \text{\AA}^{-1}$ 





# Constant Current Topography

$$I(\vec{r}, z, V) \propto \exp(-2\kappa(\vec{r})z) \int_{0}^{E=eV} LDOS_{sample}(\vec{r}, E) dE$$
  
where  $\kappa(\vec{r}) = \frac{\sqrt{2m\phi(\vec{r})}}{\hbar} \sim 1 \text{\AA}^{-1}$ 





### Si(111) 7x7 © Omicron Nanotechnology GmbH

# Si(111) 7x7 Structure



G. Binning et al., Phys. Rev. Lett. 50, 120 (1983)



© Omicron Nanotechnology GmbH



# **Tunneling Spectroscopy**

Local Density of States :  $\frac{dI}{dV}(\vec{r}, V) \propto LDOS_{sample}(\vec{r}, E = eV)$ 

 $I(V + \Delta V \sin \omega t) = I(V) + \frac{dI}{dV} \Delta V \sin \omega t + \dots$ 



### Superconducting Energy Gap in 1960

### Ivar Giaever



Nobel Prize in 1973 ©Schenectady Museum

**Tunneling junction** 

S I N



Ivar Giaever, Phys. Rev. Lett. 5, 147 (1960) I. Giaever, Phys. Rev. 126, 941 (1962)

# Superconducting Energy Gap by STM

Energy resolution is thermally limited.

2H-NbSe<sub>2</sub> ,  $T_c$  = 7.1 K, measured at  $T \sim 0.4$ K







**©RIKEN** 

# Scanning Tunneling Spectroscopy (STS) Mapping

Atomic resolution energy resolved conductance images, g(r,E)  $\propto$  LDOS(r,E)









# Atomic Resolution Energy Resolved Images, LDOS(r,E)



## **Our Resolution and Stability**



STM Tip on Piezo Scanner

@Wikipedia

 $0.5pm/6mm \rightarrow 42nm/509m!$ 

#### Ivar Giaever



Nobel Prize 1973

The best way to do science is not to buy a big piece of expensive equipment and use it to do research. There are lots of other people who have the same big expensive equipment. The best way to do science is if you can make your own equipment, make your own thing.

- Ivar Giaever, BCS@50 Conference, 2007

# 1.6K-9Tesla Cryogenic UHV STM @ Academia Sinica

### 100% Homemade!



http://www.phys.sinica.edu.tw/~chuangtm/

# Vortex Imaging of NbSe<sub>2</sub> by STM

### Harald F. Hess

### 2H-NbSe<sub>2</sub> : T<sub>c</sub> = 7.1 K, T<sub>CDW</sub> = 29 K



© www.janelia.org



H. F. Hess *et al.*, PRL 62, 214 (1989). H. F. Hess *et al.*, PRL 64, 2711 (1990).

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H. F. Hess *et al.*, PRL 62, 214 (1989). H. F. Hess *et al.*, PRL 64, 2711 (1990).

# **Quasiparticle Scattering Interference (QPI)**

A path to determining momentum space structure by STM

## Quasiparticle Scattering Interference (QPI)



# Inferring Band Structure from QPI



### **QPI on Simple Metals**

Landau quasiparticle standing waves at the surface of a 2D electron gas system. Scattering off impurities and edges.



#### **Dispersion relation of Bloch electrons**

Y. Hasegawa and Ph. Avouris, PRL 71, 1071 (1993).
M.F. Crommie *et al.*, Nature **363**, 524 (1993)

### Atomic Scale Visualization of Novel Materials by STM

Advantages:

- Both occupied and empty states can be explored.
- Both real and momentum spaces can be explored.
- Magnetic-field compatible.
- Excellent energy resolution at low temperature

Disadvantages:

- Quasi-particle scatterers are necessary.
- Measurement takes VERY long time.

- 1. Introduction to conventional superconductivity
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# High Tc Cuprate Superconductors (CuSC)







Antiferromagnetic Mott Insulator

Z. Phys. Rev. B 64 189 (1986)





Each Ba atom substituted for Sr captures and electron from  $CuO_2$  plane leaving p holes per unit cell

Ba

Z. Phys. Rev. B 64 189 (1986)

# CuO<sub>2</sub>: Charge transfer yields a Cu-3d<sup>9</sup> $d_{x^2-y^2}$ band



# Half filling: Antiferromagnetic Mott Insulator



### Mott Insulator: Repulsive Coulomb U~3eV



No double occupancy allowed..

N.F. Mott, Proc. Phys. Soc A62, 416 (1949)

## Antiferromagnetic: Superexchange J~0.14eV







P. W. Anderson, *Phys. Rev.* 115, 2 (1959)

### Holes introduced $\Longrightarrow$ carriers become mobile



Dopant density p = number of holes per CuO<sub>2</sub> plaquette

$$H = -t \sum_{\langle i,j \rangle} (c_{i\sigma}^{\dagger} c_{j\sigma} + h.c.) + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

J. Hubbard, Proc. Roy. Soc A276, 238 (1963)
## How could this state become superconducting?



## How could this state become superconducting?



### Schematic Phase Diagram of Hole-doped Cuprates



### Normal State Band Structure



CEC (E): The location in kspace of states with energy E

> Fermi Surface CCE(0)

# Superconducting State : $d_{\chi^2 - \gamma^2}$ Pairing Symmetry

The SC energy gap,  $\Delta(\mathbf{k})$  has four nodes.



# Superconducting State : $d_{\chi^2 - \gamma^2}$ Pairing Symmetry

(b)

1000

### **DC SQUID**



# Superconducting State : $d_{x^2-v^2}$ Pairing Symmetry

### **DC SQUID**



D. A. Wollman *et al.*, PRL 71, 2134 (1993)D. A. Wollman *et al.*, PRL 74, 797 (1995)

### ARPES



H. Ding *et al.*, PRB 54, 9678 (1996) J. Mesot *et al.*, PRL 83, 840 (1999)