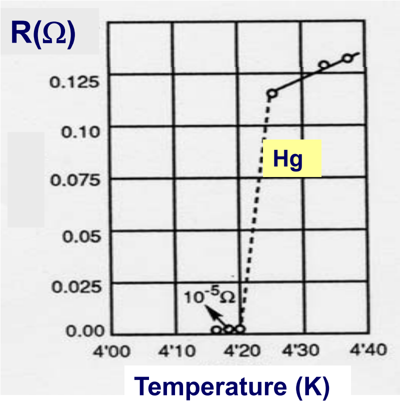
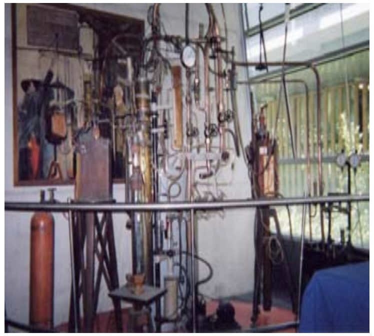
Superconductivity

“door meten tot weten”ー reaching a truth via the measurements ー



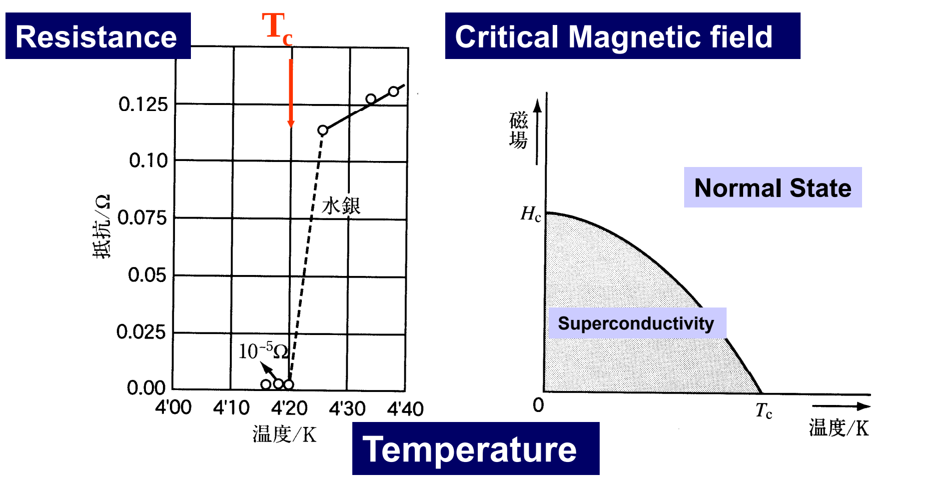
Kameringh Onnes (1911)



Zero resistance → no loss of energy
persistent current is forever

Discovery of Superconductivity in Hg

Small magnetic field suppresses Superconductivity



(a) Hg金属の電気抵抗の温度変化　(b) 超伝導臨界温度の磁場変化

図4

Electron Gas or Liquid in Metals

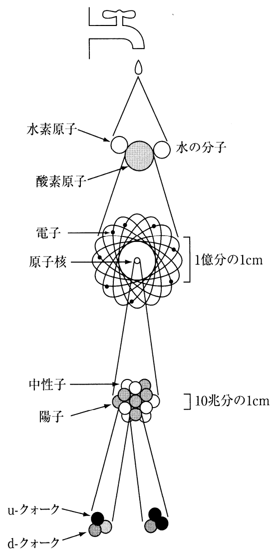
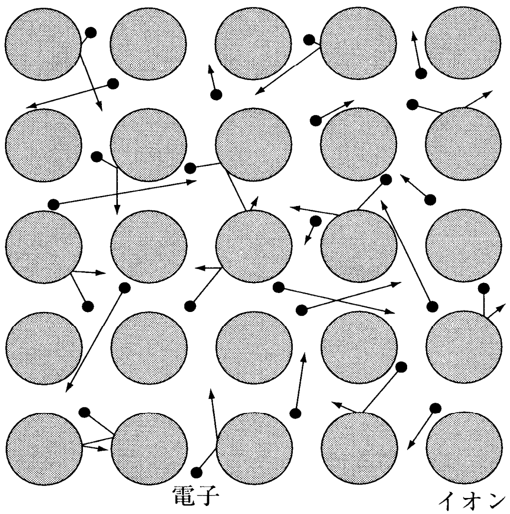
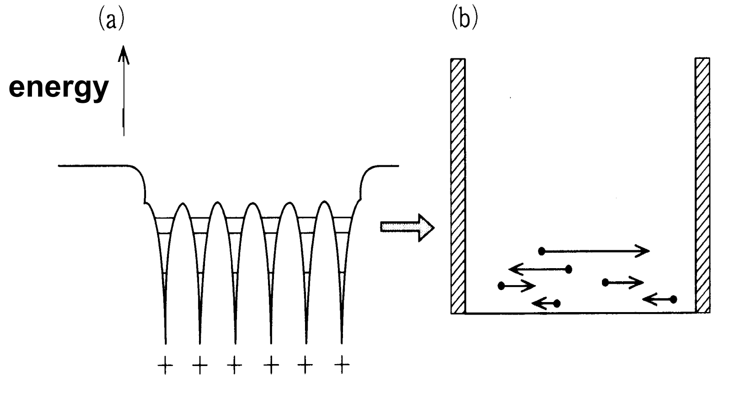


図8　水を構成するミクロな粒子



Ions form a lattice in metals

Free electrons model in metal



(a) potential energy in metal　(b) simple model

In model (b) where cubic box has a volume $V=L^3$, Schrödinger equation is given by

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

Here,

$$V(\mathbf{r}) = \begin{cases} 0 & 0<x,\ y,\ z<L \\ \infty & \text{otherwise} \end{cases}$$

Using a periodic boundary condition

$$\psi(x+L, y, z) = \psi(x, y+L, z) = \psi(x, y, z+L) = \psi(x, y, z)$$

We obtain a following plane-wave function :

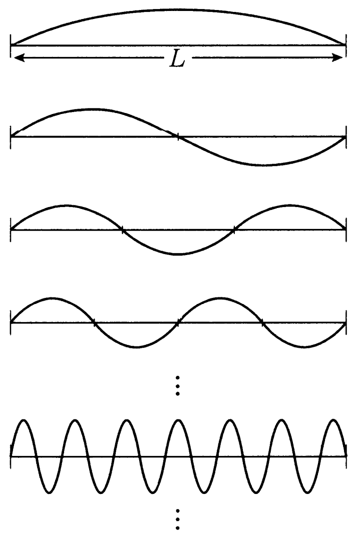
$$\psi(\mathbf{r}) = \frac{1}{\sqrt{L^3}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

With eigen energy : $\varepsilon(k) = \frac{\hbar k^2}{2m} = \frac{\hbar^2}{2m}(k_x{}^2 + k_y{}^2 + k_z{}^2)$

where wave numbers are quantized as follow: $k_x = \frac{2\pi}{L}n_x,\quad k_y = \frac{2\pi}{L}n_y,\quad k_z = \frac{2\pi}{L}n_z$

$$n_x,\ n_y,\ n_z = 0,\ \pm1,\ \pm2,\ \cdots$$

n-dependence of electron's wave length in cubic box



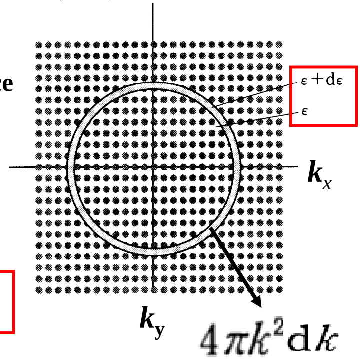
	Wave length	Momentum
	λ	$p=\frac{h}{\lambda}$
	$2L$	$\frac{1}{2L}h$
	$\frac{2L}{2}$	$\frac{2}{2L}h$
	$\frac{2L}{3}$	$\frac{3}{2L}h$
	$\frac{2L}{4}$	$\frac{4}{2L}h$
⋮	⋮	⋮
	$\frac{2L}{n}$	$\frac{n}{2L}h$
⋮		

(n : positive integer

Density of states, $D(\varepsilon)$ per unit volume(cm^3) is defined as number of states in between ε and $\varepsilon+d\varepsilon$.
Since two electrons with spin-up and-down exist in k-space volume $(2\pi/L)^3$, number of states per unit volume in k-space is $2\times(L/2\pi)^3$

$$k_x = \frac{2\pi}{L}n_x,\quad k_y = \frac{2\pi}{L}n_y,\quad k_z = \frac{2\pi}{L}n_z$$

$$n_x,\ n_y,\ n_z = 0,\ \pm1,\ \pm2,\ \cdots$$



$$D_{3D}(\varepsilon)d\varepsilon = \frac{1}{L^3}\times2\times\frac{L^3}{(2\pi)^3}\times4\pi k^2\frac{dk}{d\varepsilon}d\varepsilon$$

Using $\varepsilon = h^2k^2/2m$, the above equation is rewritten as the function of ε

$$D_{3D}(\varepsilon)d\varepsilon = \frac{2}{(2\pi)^3}4\pi k^2\frac{dk}{d\varepsilon}d\varepsilon = \frac{m}{\pi^2\hbar^2}k\,d\varepsilon = \frac{\sqrt{2}\,m^{3/2}}{\pi^2\hbar^3}\sqrt{\varepsilon}\,d\varepsilon$$

$$\frac{d\varepsilon}{dk} = \frac{\hbar^2 k}{m} \qquad k = \frac{\sqrt{2m\varepsilon}}{\hbar}$$

Mechanism of formation of electron pairs due to lattice vibration

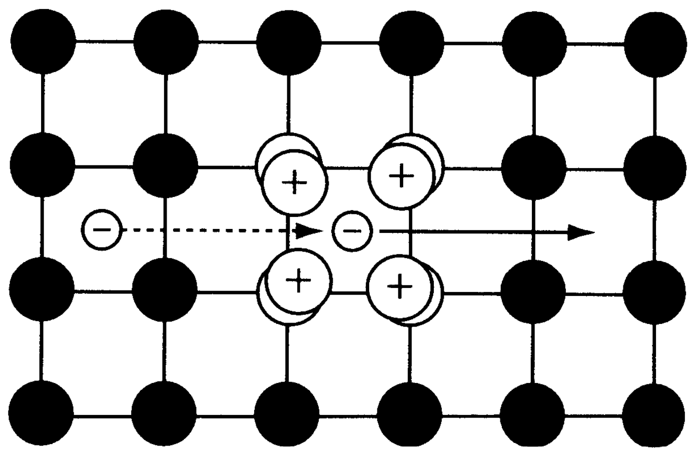


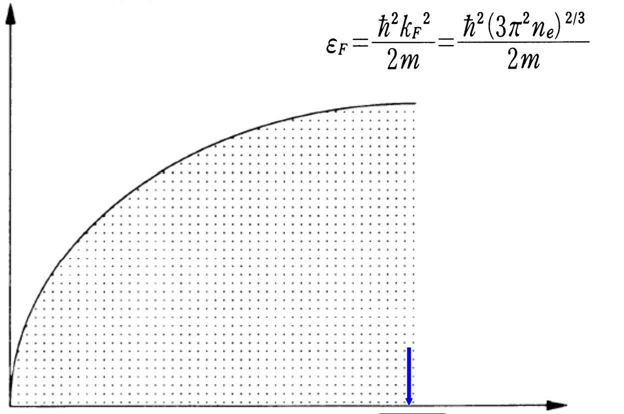
図12　電子間に引力が働く機構の模式図

$$D_{3D}(\varepsilon)=\frac{\sqrt{2}\,m^{3/2}}{\pi^2\hbar^3}\sqrt{\varepsilon}$$

$$n_e=\frac{2}{(2\pi)^3}\frac{4}{3}\pi k_F{}^3=\frac{k_F{}^3}{3\pi^2},\qquad k_F=(3\pi^2 n_e)^{1/3}$$

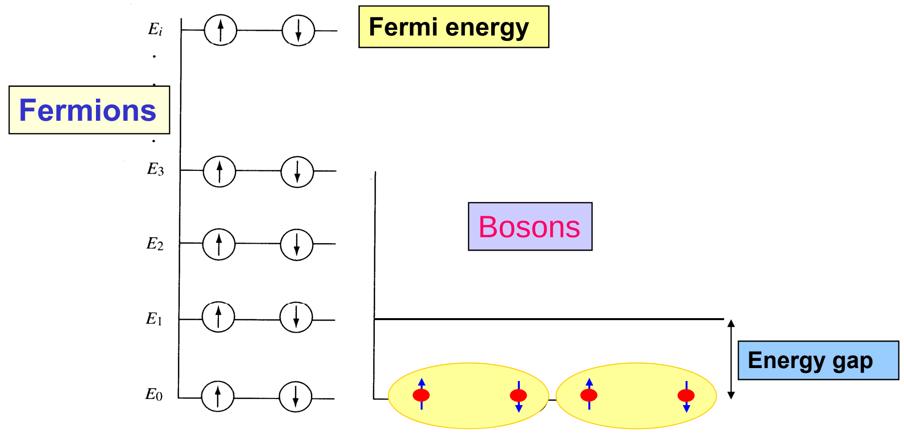
$$\varepsilon_F=\frac{\hbar^2 k_F{}^2}{2m}=\frac{\hbar^2(3\pi^2 n_e)^{2/3}}{2m}$$

5 ~ 10 eV

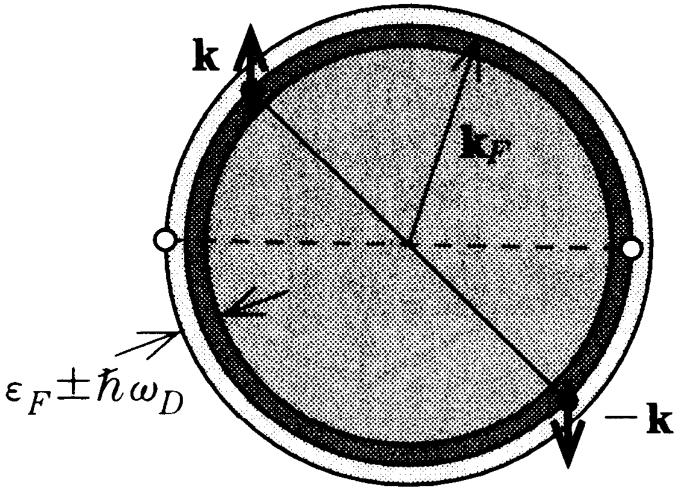


Electrons density : $n_e=\int_0^{\varepsilon_F} D_{3D}(\varepsilon)\,d\varepsilon=\int_0^{E_F}\frac{\sqrt{2}\,m^{3/2}}{\pi^2\hbar^3}\sqrt{\varepsilon}\,d\varepsilon=\frac{(2m\varepsilon_F)^{3/2}}{3\pi^2\hbar^3}$

Concept for Superconductivity



Provided that attractive interaction works between electrons near the Fermi level, electrons are always bounded making pairs - Cooper pairs -. In order to prove this theorem, we deal with a simple case where two electrons are added on the Fermi sea as illustrated below.



We deal with a following Schrödinger equation for two electrons with attractive potential $V(\mathbf{r}_1, \mathbf{r}_2)$;

$$\left[-\frac{\hbar^2}{2m}(\nabla_1{}^2+\nabla_2{}^2)+V(\mathbf{r}_1,\mathbf{r}_2)\right]\psi(\mathbf{r}_1,\mathbf{r}_2)=E\psi(\mathbf{r}_1,\mathbf{r}_2) \qquad (11.9)$$

In case of $V(\mathbf{r}_1, \mathbf{r}_2) = 0$, the wave function with a lowest energy at zero total momentum is described by the following formula;

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{L^{3/2}}e^{i\mathbf{k}\cdot\mathbf{r}_1}\frac{1}{L^{3/2}}e^{-i\mathbf{k}\cdot\mathbf{r}_2}=\frac{1}{L^3}e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)} \qquad (11.10)$$

Then, for $V(\mathbf{r}_1,\mathbf{r}_2)\neq 0$ a wave function is expressed as follow;

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{L^3}\sum_{|\mathbf{k}|>k_F}A_{\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)} \qquad (11.11)$$

Note that since this wave function is symmetric in orbital sector, the spin function is in anti-symmetric spin-singlet state.

Inserting (11.11) into (11.9) and using, $V_{\mathbf{k}}\equiv\int V(\mathbf{r})\,e^{-i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}$

$$(E-2\varepsilon_{\mathbf{k}})A_{\mathbf{k}}=\sum_{|\mathbf{k}'|>k_F}V_{\mathbf{k}-\mathbf{k}'}A_{\mathbf{k}} \qquad (11.12)$$

We can derive this eigen equation.

When the eigen energy in the eq. (11.12) has a solution for $E < 2\varepsilon_F$, two- electron bounded state (Cooper pair) is formed. Provided that $V(\mathbf{r}_1, \mathbf{r}_2)$ is approximated as follows;

$$V_{\mathbf{k}-\mathbf{k}'} = \begin{cases} \text{const} = V < 0 & |\varepsilon_{\mathbf{k}} - \varepsilon_F|,\ |\varepsilon_{\mathbf{k}'} - \varepsilon_F| < \hbar\omega_D \\ 0 & \textbf{otherwise} \end{cases} \quad (11.13)$$

Here, if the constant attractive interaction V is assumed to be effective only among electrons within energies in the range between the Fermi energy ε_F and the Debye energy $\hbar\omega_D$ which is the highest one of lattice vibration, we obtain the following equation;

$$(E - 2\varepsilon_{\mathbf{k}})A_{\mathbf{k}} = -|V| \sum_{|\mathbf{k}'|>k_F} A_{\mathbf{k}} \quad (11.14)$$

When taking $A \equiv \sum_{|\mathbf{k}'|>k_F} A_{\mathbf{k}}$, **form** (11.14) **we have** $A_{\mathbf{k}} = -\dfrac{|V|}{E - 2\varepsilon_{\mathbf{k}}} A$

Since $A = A|V| \sum_{0<(\varepsilon_{\mathbf{k}} - \varepsilon_F)<\hbar\omega_D} \dfrac{1}{2\varepsilon_{\mathbf{k}} - E}$ **, we obtain the following relation**

$$\frac{1}{|V|} = \sum_{\substack{\mathbf{k} \\ 0<(\varepsilon_{\mathbf{k}} - \varepsilon_F)<\hbar\omega_D}} \frac{1}{2\varepsilon_{\mathbf{k}} - E} \quad (11.15)$$

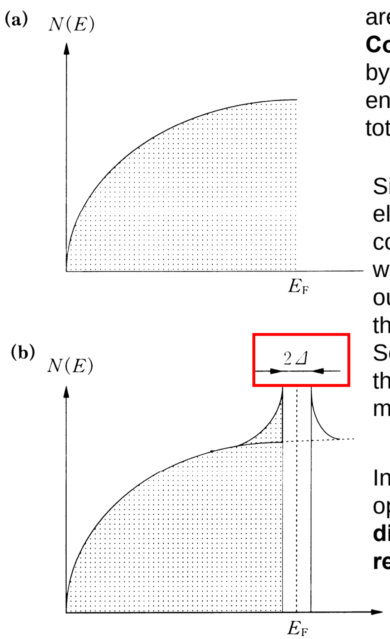
$$\frac{1}{|V|} = \int_{\varepsilon_F}^{\varepsilon_F + \hbar\omega_D} \frac{1}{2\varepsilon - E} N(\varepsilon)\, d\varepsilon$$

$$\approx N(\varepsilon_F) \int_{\varepsilon_F}^{\varepsilon_F + \hbar\omega_D} \frac{1}{2\varepsilon - E}\, d\varepsilon$$

$$= \frac{1}{2} N(\varepsilon_F) \ln\left(\frac{2\varepsilon_F - E + 2\hbar\omega_D}{2\varepsilon_F - E}\right)$$

$N(\varepsilon_F)|V| \ll 1$ **is considered and as a result**

we obtain the eigen energy as $E \approx 2\varepsilon_F - 2\hbar\omega_D e^{-2/N(\varepsilon_F)|V|}$



It was proved that electrons near the Fermi surface are bounded making pairs of (**k**, ↑) and (-**k**, ↓) - **Cooper pair-** via the attractive interaction mediated by lattice vibration with highest energy -Debye energy $\hbar\omega_D$ - . Here the Cooper pair is in the zero total momentum and the spin-singlet state.

Since Cooper pairs are formed by many body of electrons near the Fermi level, these are condensed into **a macroscopic quantum state** which is regarded as a Bose condensation. This outstanding aspect of superconductivity was theoretically clarified by Bardeen, Cooper and Schriefer, and hence this theory is called as BCS theory which is epoch-making event in condensed matter physics in the 20th century.

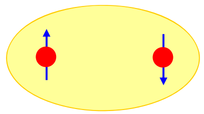
In this BCS state, **an isotropic energy gap Δ** opens on the Fermi level, yielding **a perfect diamagnetism called Meissner effect** and **zero-resistance effect.**

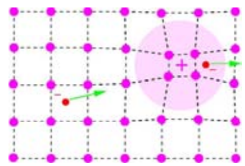
Superconductivity

Conventional superconductivity:

Cooper pair

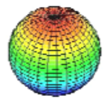
attractive interaction: electron-phonon coupling





s-wave spin singlet

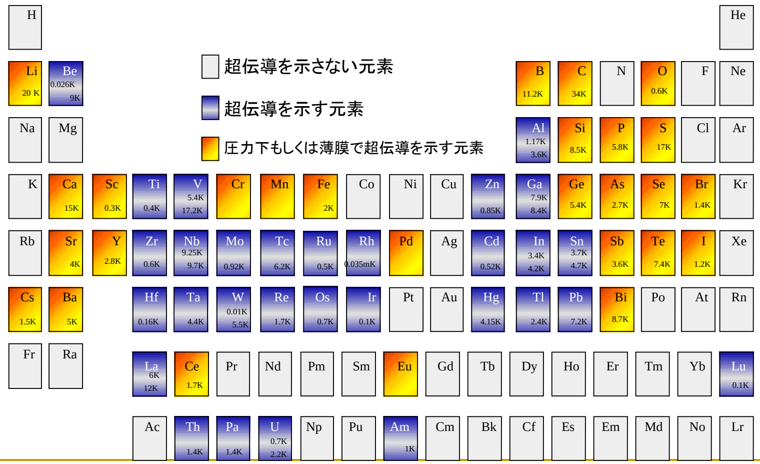
pairing channel: angular momentum l=0 and spin s=0



order parameter: $\Psi(\vec{r}) = |\Psi(\vec{r})| e^{i\phi(\vec{r})}$

broken symmetry: U(1) gauge →
- Meissner-Ochsenfeld-effect (Higgs)
- persistent currents
- flux quantization

§2　どんな超伝導体があるのだろう
どんな元素が超伝導になるのだろう？



Aoyama-Gakuin University

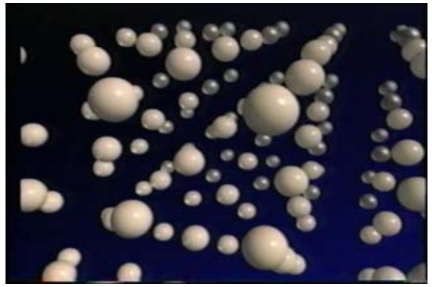
超伝導はどのようにしておこるか？
ーBCS理論による予測ー

左から、
John Bardeen、Leon N. Cooper、
J. Robert Schrieffer

$$T_c \simeq \theta_D \exp(-\frac{1}{\lambda})$$

格子の周波数が高い方が
高い T_c に有利

Pictures from Nobelprize.org



映像：日立サイエンスシリーズ, 超伝導　より

Aoyama-Gakuin University

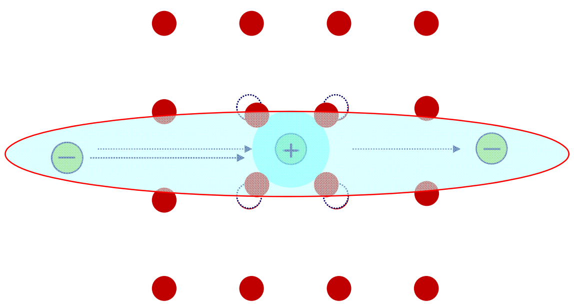
超伝導現象の解明-BCS理論

1957　Bardeen, Cooper, Schrieffer (BCS) 理論

Nobel Prize (1972)

電子2個が対をつくって運動（クーパー対を形成）

電子ー格子相互作用を媒介とした電子間引力



「BCSの壁」を越えた超伝導の発見

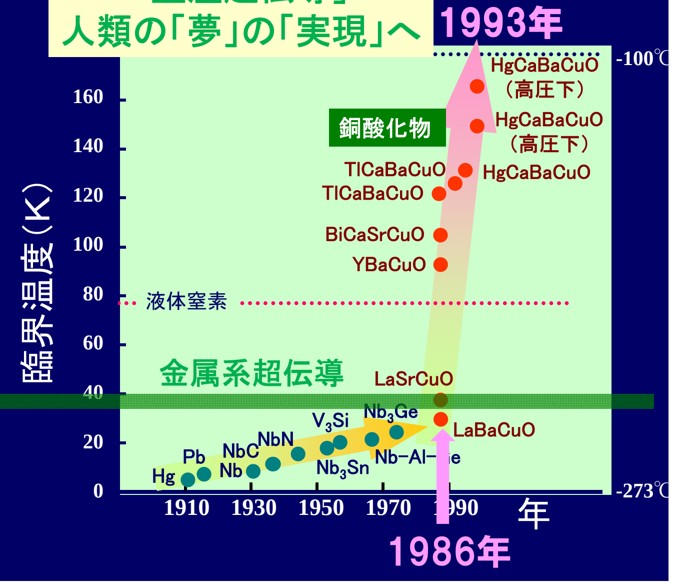
「室温超伝導」
人類の「夢」の「実現」へ

1986年以前の
超伝導転移温度
の最高記録
→ 24K（Nb_3Ge）

理論家は、、、、

超伝導転移温度
は高くても
30~40K程度まで

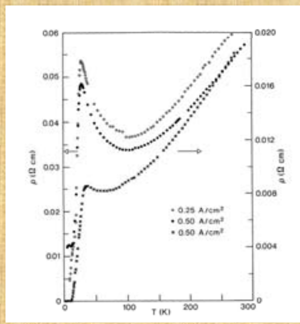
「BCSの壁」



高温超伝導の発見

物質科学における最大の発見のひとつ

“Possible High T_c Superconductivity in the Ba-La-Cu-O System”

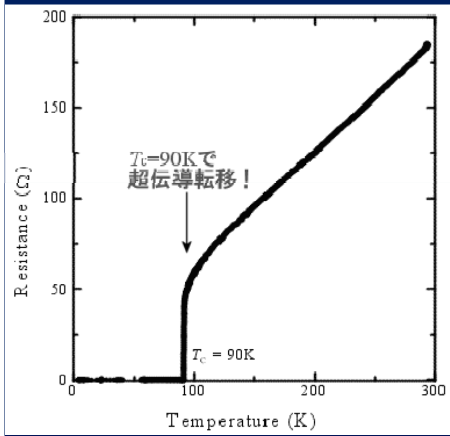


1987ノーベル物理科学賞

酸化物高温超伝導体の発見

J.G.Bednorz and K.A.Muller, Z.Physik B64,189 (1986)

液体窒素温度を超える高温超伝導体

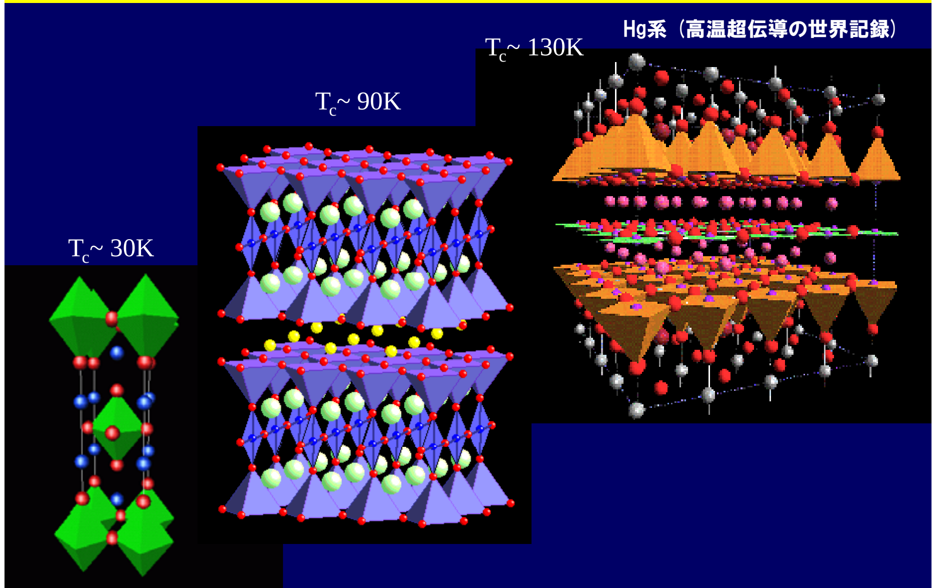


金属の超伝導を解明したBCS理論では、高温超伝導を説明できない。

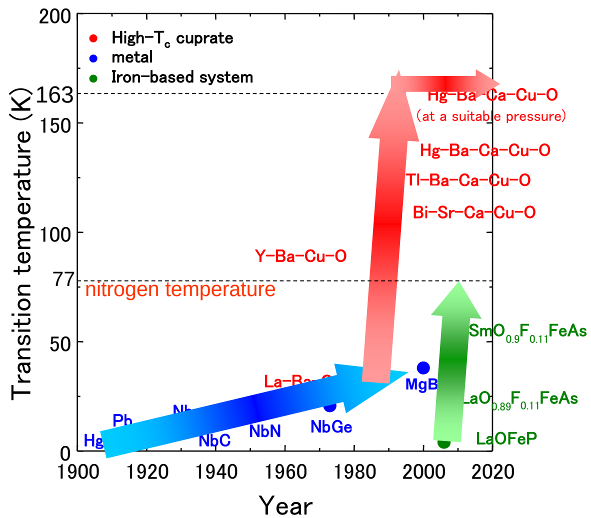
それに代わる理論も、発見後、25年経った現在も、決定的なものは現れていなかった。

銅酸化物　$YBa_2Cu_3O_{7-y}$

高温超伝導物質の構造と物性



Why T_c is so high？



1911

Superconductivity was discovered

1986

High-T_c cuprate was discovered

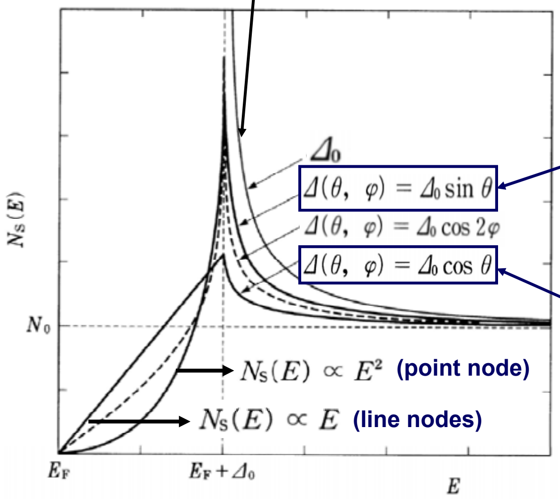
2006

Iron-based system was discovered

Quasi-particle DOS in SC state

s-wave with isotropic gap

$N_s(E)=N_0E/(E^2-\Delta^2)^{1/2}$



p-wave with point–node gap

$$N_s(E)=\frac{N_0E}{4\pi}\int_0^{2\pi}\int_0^{\pi}\frac{\sin\theta\,d\theta\,d\varphi}{\sqrt{E^2-\Delta_0^2\sin^2\theta}}=\frac{N_0E}{2\Delta_0}\ln\left|\frac{E+\Delta_0}{E-\Delta_0}\right|$$

p-wave with line–node gap

$$N_s(E)=\frac{N_0E}{4\pi}\int_0^{2\pi}\int_0^{\pi}\frac{\sin\theta\,d\theta\,d\varphi}{\sqrt{E^2-\Delta_0^2\cos^2\theta}}=\frac{\pi}{2}\frac{N_0E}{\Delta_0}\quad(E<\Delta_0)$$

Spin susceptibility

Spin polarization in superconducting phase

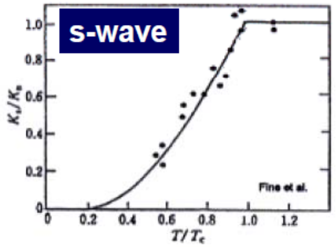
Spin singlet pairing:

- breaking up of Cooper pairs
- decrease of spin susceptibility
- vanishing susceptibility at T=0

$$\chi_s=2\mu_B^2N_0Y(T),$$

where $Y(T)$ is the *Yosida function* defined by[38]

$$Y(T)=-\frac{2}{N_0}\int_0^{\infty}N_{BCS}(\varepsilon)\frac{df(\varepsilon)}{d\varepsilon}d\varepsilon,$$

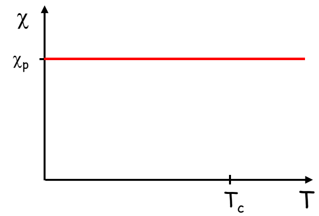


^{27}Al Knight shift

Spin triplet pairing:

- polarization without pair breaking
- no reduction of spin susceptibility for equal-spin pairing

$\chi=$ const. for $\vec{d}(\vec{k})\cdot\vec{H}=0$



Spin susceptibility

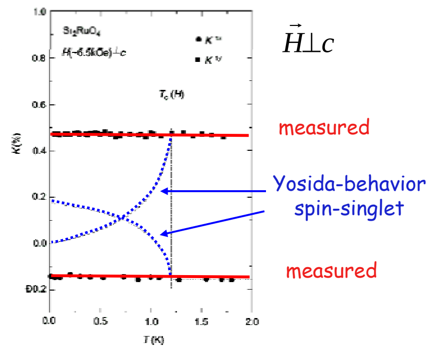
Spin polarization in superconducting phase

Spin triplet pairing:

- polarization without pair breaking
- no reduction of spin susceptibility for equal-spin pairing

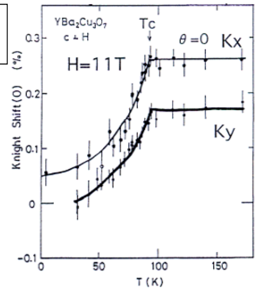
$\chi=$ const. for $\vec{d}(\vec{k})\cdot\vec{H}=0$

^{17}O-Knight shift In Sr_2RuO_4



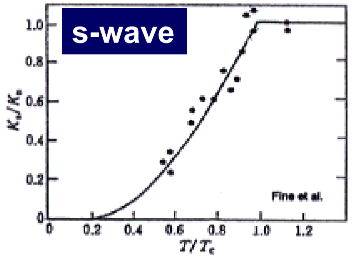
Ishida et al., Nature 396, 242 (1998)

^{17}O-Knight shift (High-T_c oxides)



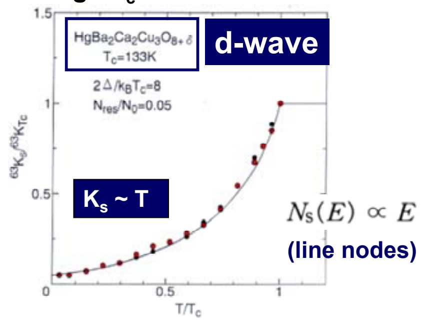
inplane equal-spin pairing $\vec{d}\parallel\hat{z}$

Summary1 : Knight shift



^{27}Al Knight shift

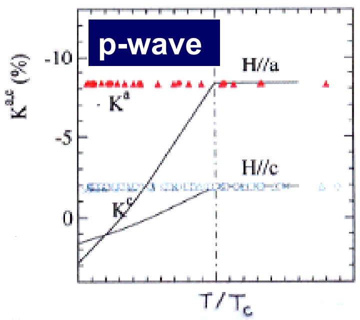
High-T_c SC : ^{63}Cu-NMR



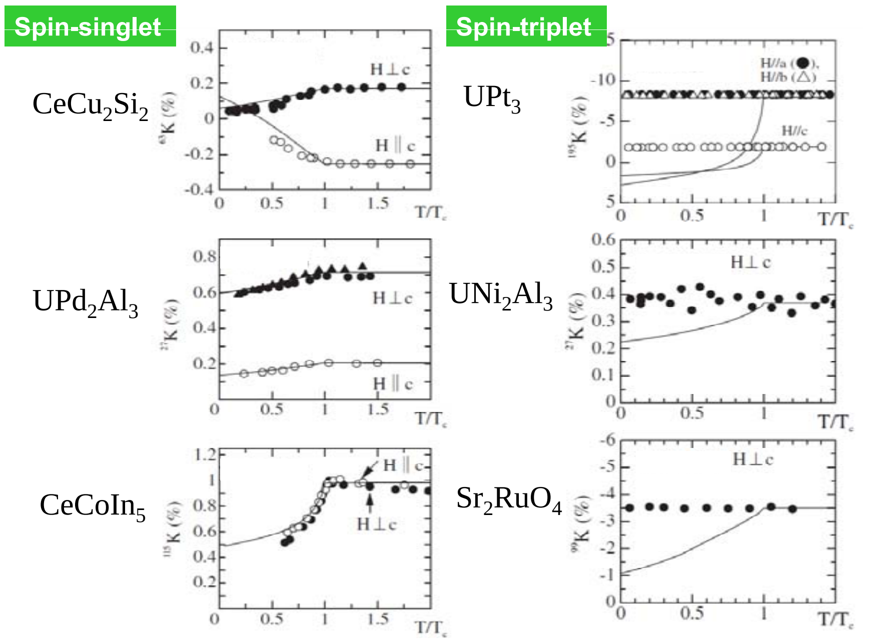
$N_s(E)\propto E$ (line nodes)

Heavy-Fermion SC

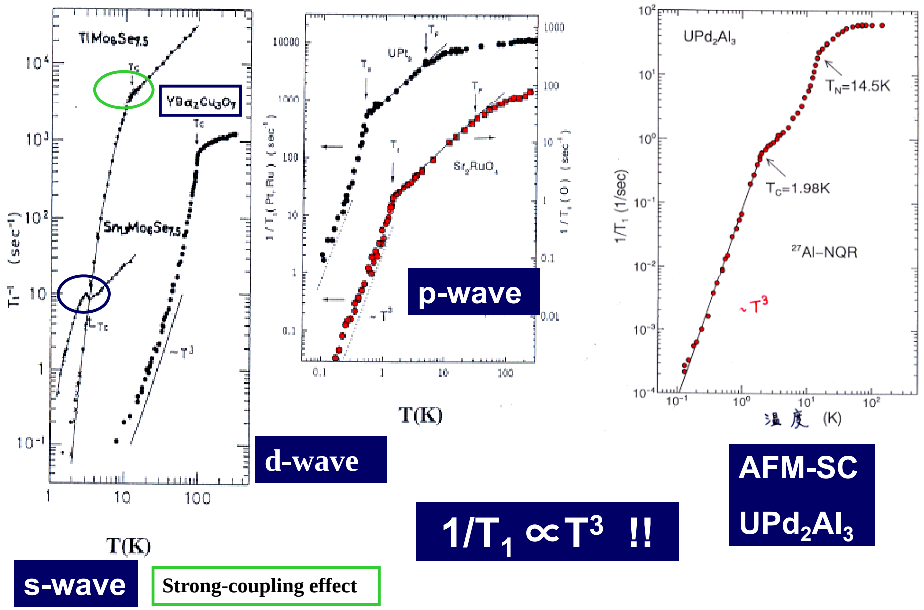
UPt_3 : ^{195}Pt-NMR



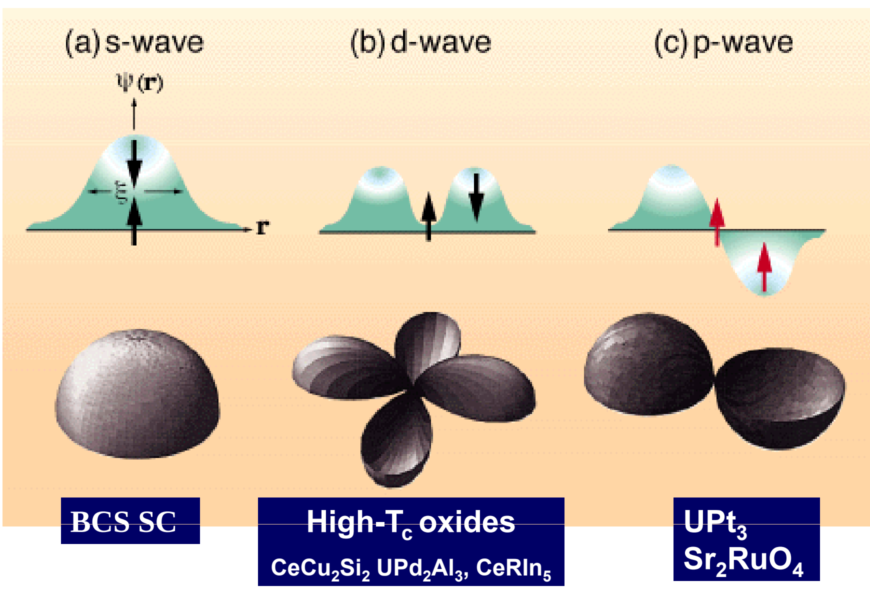
Summary2 : pairing state in unconventional superconductors



Line-nodes gap SC in correlated electrons SC



Possible SC order parameters and their spin-state



Spin-fluctuations mediated d-wave superconductivity

When the eigen energy in the eq. (11.12) has a solution for E < $2\varepsilon_F$, two- electron bounded state (Cooper pair) is formed. Provided that $V(\mathbf{r}_1, \mathbf{r}_2)$ is approximated as follows;

$$V_{\mathbf{k}-\mathbf{k}'} = \begin{cases} \text{const} = V < 0 & |\varepsilon_{\mathbf{k}} - \varepsilon_F|,\ |\varepsilon_{\mathbf{k}'} - \varepsilon_F| < \hbar\omega_D \\ 0 & \text{otherwise} \end{cases} \quad (11.13)$$

Here, if the constant attractive interaction V is assumed to be effective only among electrons within energies in the range between the Fermi energy ε_F and the Debye energy $\hbar\omega_D$ which is the highest one of lattice vibration, we obtain the following equation;

$$(E - 2\varepsilon_{\mathbf{k}}) A_{\mathbf{k}} = -|V| \sum_{|\mathbf{k}'| > k_F} A_{\mathbf{k}} \quad (11.14)$$

When taking $A \equiv \sum_{|\mathbf{k}'| > k_F} A_{\mathbf{k}}$, form (11.14) we have $A_{\mathbf{k}} = -\frac{|V|}{E - 2\varepsilon_{\mathbf{k}}} A$

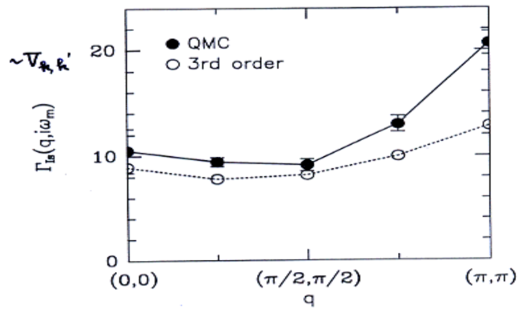
Since $A = A|V| \sum_{0 < (\varepsilon_{\mathbf{k}} - \varepsilon_F) < \hbar\omega_D} \frac{1}{2\varepsilon_{\mathbf{k}} - E}$, we obtain the following relation

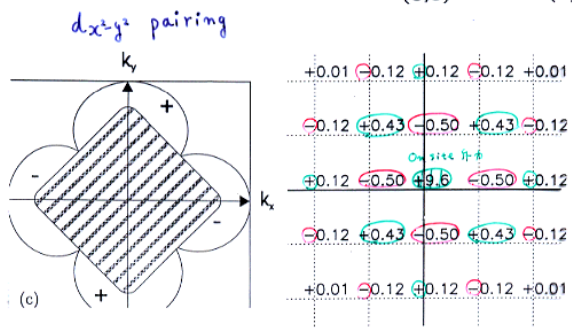
$$\frac{1}{|V|} = \sum_{\substack{\mathbf{k} \\ 0 < (\varepsilon_{\mathbf{k}} - \varepsilon_F) < \hbar\omega_D}} \frac{1}{2\varepsilon_{\mathbf{k}} - E} \quad (11.15)$$

A general SC gap equation

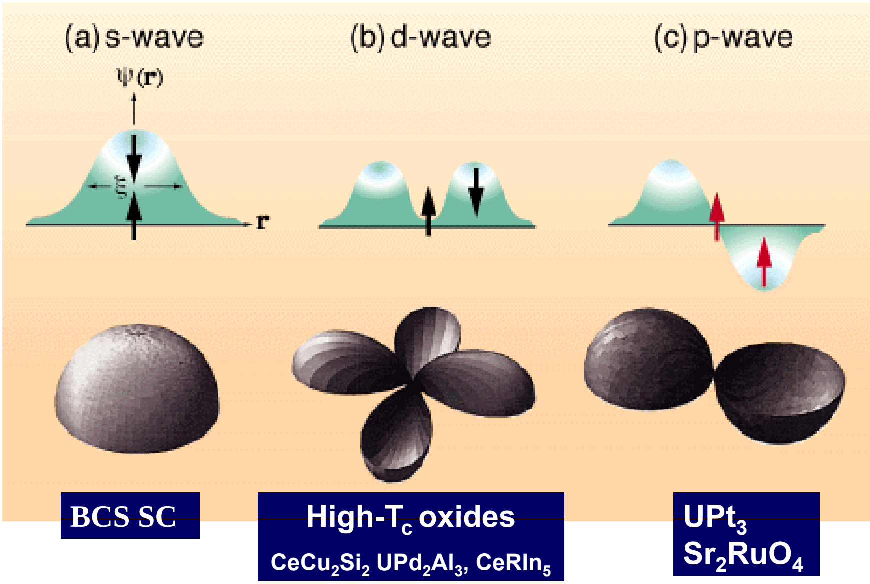
$$\Delta_{\mathbf{k}} = -\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \frac{\Delta_{\mathbf{k}'}}{E_{\mathbf{k}'}}$$

d-wave superconductivity due to the on-site Coulomb repulsive interaction





Possible SC order parameters and their spin-state



NMR/NQR probes of emergent properties in correlated-electron superconductors

- Symmetry of the Cooper pair of either spin-singlet or spin-triplet
- SC gap with either isotropic or nodal structure
- Characters of spin fluctuations