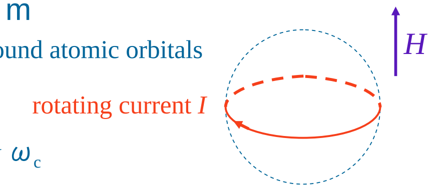
Diamagnetism of an atom

Unpaired electrons → rotation around atomic orbitals



$$I=(-Ze)\left(\frac{1}{2\pi}\frac{eB}{m}\right)\frac{1}{2}$$

charge　　cyclotron frequency ω_c

(magnetic moment)＝I×(area)

$$\mu=-\frac{Ze^2B}{4m}<x^2+y^2>=-\frac{Ze^2B}{6m}<r^2>$$

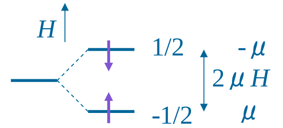
$$<x^2+y^2>=\frac{2}{3}<r^2>$$

よって

$$\chi=\frac{N\mu}{B}=-\frac{NZe^2}{6m}<r^2>$$ diamagnetism of an atom $\chi<0$

Given by the sum of the atomic Pascal diamagnetism.

Curie paramagnetism



Magnetic moment from an unpaired electron

$\mu=\gamma\hbar\boldsymbol{S}=-g\mu_B\boldsymbol{S}$

Zeemann splitting under the magnetic field, $\boldsymbol{H}$

$E=-g\mu_B\boldsymbol{HS}=-\mu\boldsymbol{H}$

Split to two at $S=1/2$. The thermal distribution is

$$\frac{N_\uparrow}{N}=\frac{e^{\mu H/k_BT}}{e^{\mu H/k_BT}+e^{-\mu H/k_BT}}\qquad\frac{N_\downarrow}{N}=\frac{e^{-\mu H/k_BT}}{e^{\mu H/k_BT}+e^{-\mu H/k_BT}}$$

gives

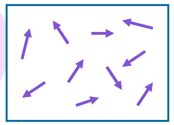
$$M=\mu_B(N_\uparrow-N_\downarrow)=N\mu\tanh\frac{\mu H}{k_BT}\approx N\mu\left(\frac{\mu H}{k_BT}\right)\leftarrow\frac{\mu H}{k_BT}<<1$$

$$\chi=\frac{M}{H}=\frac{N\mu^2}{k_BT}=\frac{C}{T}$$ ← Curie constant

For $S\neq1/2$　$C=\frac{NS(S+1)g^2\mu_B^2}{3k_B}$

comes only from S.

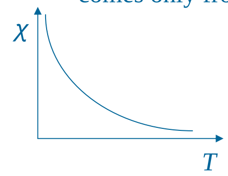
χ is inversely proportional to T.



Random spins

Aligned under magnetic field.

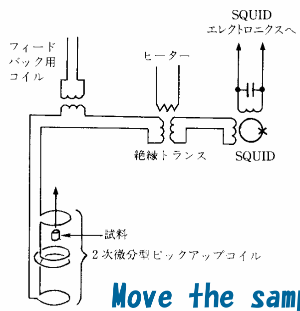
More easily aligned at low temperatures.



磁化測定:SQUID Superconductor Quantum Interference Device

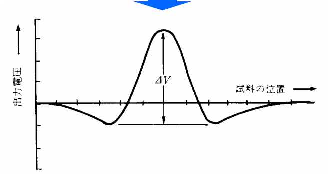
Measure magnetization M at rt～1.5 K

several ten μg sample



Move the sample by 10 cm up and down.

磁化 *M*



磁化測定:SQUID Superconductor Quantum Interference Device

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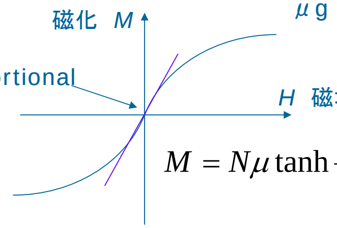
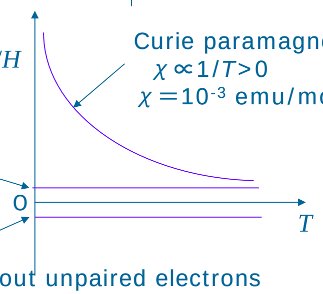


$$M=N\mu\tanh\frac{\mu H}{k_BT}$$

磁化率

$\chi=M/H$



Curie paramagnetism

$\chi\propto1/T>0$

$\chi=10^{-3}$ emu/mol

Metals

Pauli paramagnetism　$\chi>0$

$\chi=10^{-4}$ emu/mol

Diamagnetism　$\chi<0$

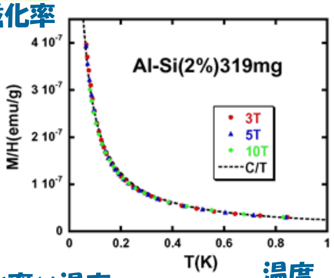
Organic compounds without unpaired electrons

Curie paramagnetism

$$\chi = \frac{M}{H} = \frac{N\mu^2}{k_B T} = \frac{C}{T}$$

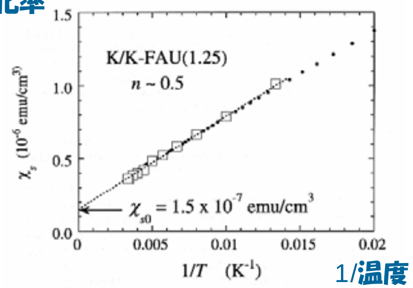
温度に反比例

磁化率



温度

磁化率

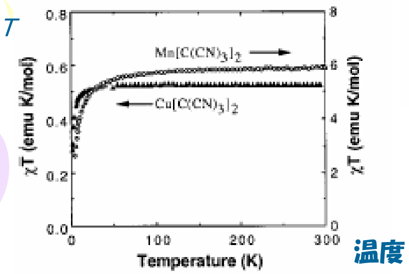


1/温度

図３ ゼオライトFAU中のカリウムクラスターのスピン磁化率の温度依存性．温度に依存しない成分が顕著に現れる．

磁化率×温度

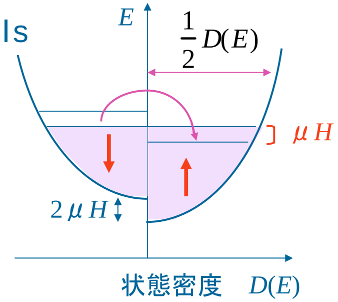
χT



温度

Pauli paramagnetism in Metals

磁場をかけると↓よりも↑の方が安定になる。



$$E_\uparrow = \frac{\hbar^2 k^2}{2m} - \mu H$$

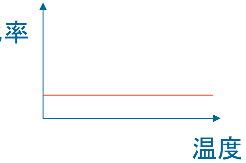
$$E_\downarrow = \frac{\hbar^2 k^2}{2m} + \mu H$$

磁化 $M = \mu(N_\uparrow - N_\downarrow)$

$$= \mu \frac{1}{2} D(E) \times 2\mu H$$

磁化率 $\chi = \frac{M}{H} = \mu^2 D(E_F)$

金属の常磁性 χ >0 は温度によらず一定 (パウリ常磁性)

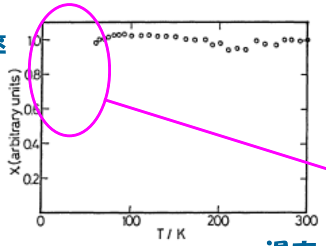


Pauli paramagnetism in Metals

$$\chi = \mu_B^2 D(E_F)$$

temperature independent

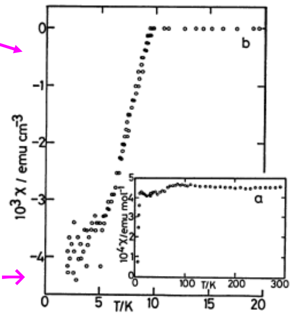
磁化率



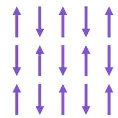
温度

κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

超伝導：完全反磁性　χ＝－４π

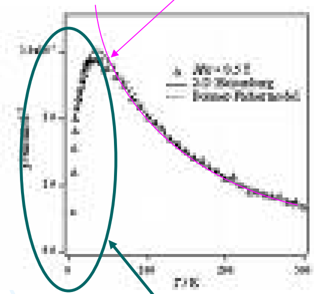


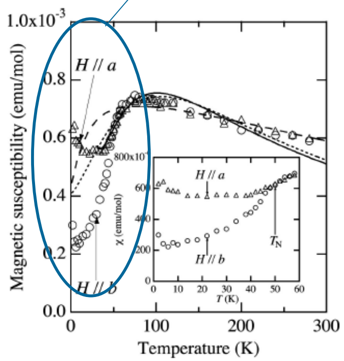
χ＝－４π →



antiferromagnetism

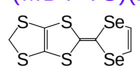
Curie paramagnetism





antiferromagnetism

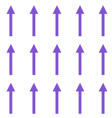
(MDT-TS)(AuI$_2$)$_{0.441}$



MDT-TS

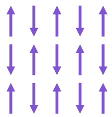
Magnetic order

Ferromagnetism: parallel spins
The material is a magnet.



$J>0$
$S_i // S_j$ parallel is stable

Antiferromagnetism:
alternately antiparallel spins
Not a bulk magnet.

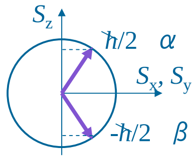


$J<0$
S_i と S_j antiparall is stable

Spin Hamiltonian

$$\hat{H} = -\sum_{i,j} 2J_{ij}\bar{S}_i\bar{S}_j - g\mu_B H\sum_i \bar{S}_i$$

Interaction   Zeemann splitting



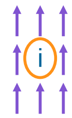
S_i is a vector like (S_x, S_y, S_z) (Heisenberg model).
Large magnetic anisotropy (the spin is always aligned in a particular direction (S_z) by the crystal field) → only S_z
(Ising model)

$S_i=1/2$, $S_j=1/2$ → $-J/2$
$S_i=1/2$, $S_j=-1/2$ → $J/2$
} energy difference J

(Old literatures define H $= -\sum_{i,j} J_{ij}\bar{S}_i\bar{S}_j$ make J duplicated.)

Molecular field approximation

We can sum up Σ j and use the average.



$$\hat{H} = \sum_i S_i\left(-\sum_j 2J_{ij}S_j - g\mu_B H\right) = -g\mu_B(H_{\mathrm{eff}} + H)\sum_i S_i$$

$$H_{\mathrm{eff}} = \frac{1}{g\mu_B}\sum_j 2J_{ij} < S_j >$$ average effective (internal) field on S_i, generated by the surrounding S_j

S_j should be time dependent, but we use the average value $<S_j>$.
(molecular-field or mean-field approximation)

Thermal distribution similarly obtained as Curie paramagnetism gives:

$$M = \frac{N\mu^2 H}{k_B T} \xrightarrow{H \to H_{\mathrm{eff}} + H} M = \chi_0(H_{\mathrm{eff}} + H)$$

using $M = Ng\mu_B<S>$

molecular field coefficient

$$H_{\mathrm{eff}} = \frac{\sum_j 2J_{ij}}{N(g\mu_B)^2}M = aM$$

put this to the above eq.

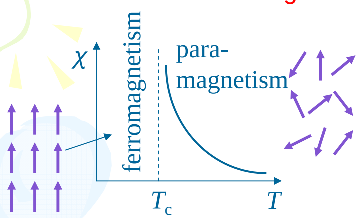
$M = \chi_0(aM+H)$
$M\{(1-\chi_0 a)\} = \chi_0 H$

$$\rightarrow \chi = \frac{M}{H} = \frac{\chi_0}{1-\chi_0 a} = \frac{C}{T-\theta}$$ Curie-Weiss role

$$\theta = \frac{1}{k_B}\sum_j 2J_{ij} = \frac{2zJ}{k_B}$$ ← Coordination number z for nearest neighbor J.

Weiss temperature

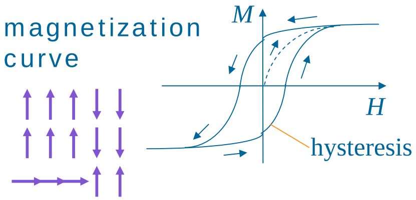
$J>0 \rightarrow \theta>0$ **Ferromagnetism**



Curie temperature

$\chi \rightarrow \infty$ at $T \rightarrow T_c$
$M \neq 0$ even at $H=0$ at $T < T_c$
→ spontaneous magnetism
T_c Fe 1043 K Ni 627 K

magnetization curve



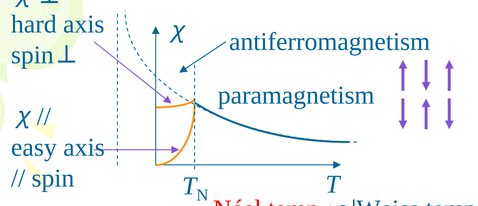
Usually small domains are randomly oriented.
Magnetic fields align the domain spins, to make the material a bulk magnet.

Ferrimagnetism

Cu^{2+} Mn^{2+}
$S=1/2$ $5/2$

Alternating antiparallel alignment of different spins makes net bulk magnetism.
e.g. Ferrite Fe_3O_4 has Fe^{3+} and Fe^{2+}.

$J<0 \rightarrow \theta<0$ **Antiferromagnetism**

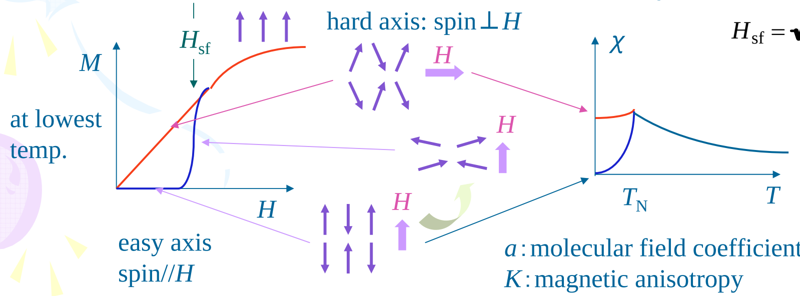


Néel temp. ∽ |Weiss temp.|

Easy axis in an antiferromagnet

Spin in an antiferromagnetism is restricted in a particular direction, due to 1) the dipole-dipole interaction, or 2) crystal field.
spin flop: increase H makes a spin ⊥ H state suddenly at H_{sf}.

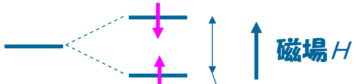
$$H_{sf} = \sqrt{2Ka}$$



a: molecular field coefficient
K: magnetic anisotropy

Electron Spin Resonance (ESR)

more sensitive than SQUID
one crystal



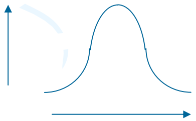
Zeeman splitting

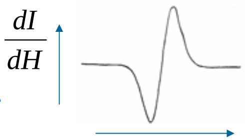
$$\hbar\omega = g\mu_B H$$

g = 2.0023
for free electron

9.5 GHz → H = 3400 gauss (X band)
35 GHz → H = 12500 gauss (Q band)

microwave absorption I

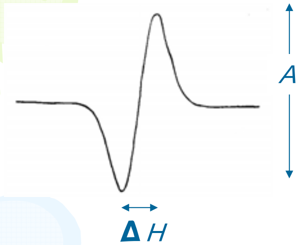




measure the derivative

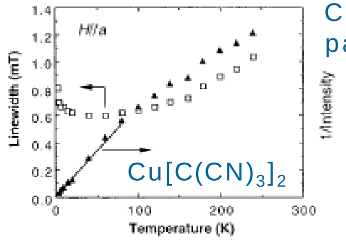
Electron Spin Resonance (ESR)

Lorentzian



Intensity /∝ $A(\Delta H)^2$

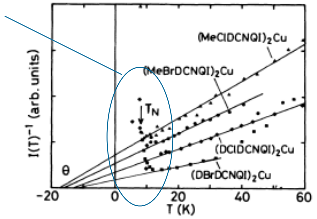
➡ /∝ spin susceptibility χ

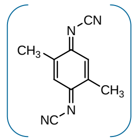


Curie paramagnetism

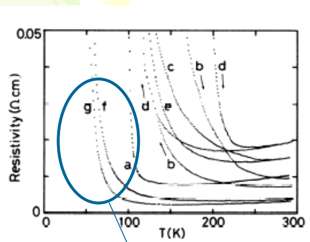
$$\chi = \frac{C}{T}$$

antiferromagnetism





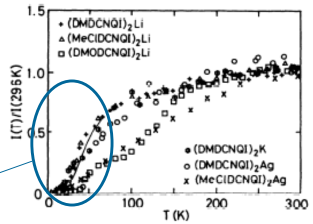
Electron Spin Resonance (ESR)



metal-insulator transition

ESR Intensity

linewidth



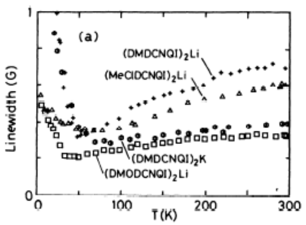
Pauli paramagnetism
χ = const. (metal)

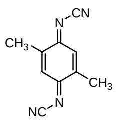
Linewidth：relaxation time of the electron spin
large in heavy atoms

narrow for mobile electrons
motional narrowing

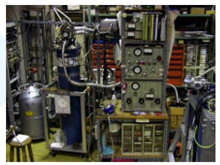
very large for magnetic order

linewidth





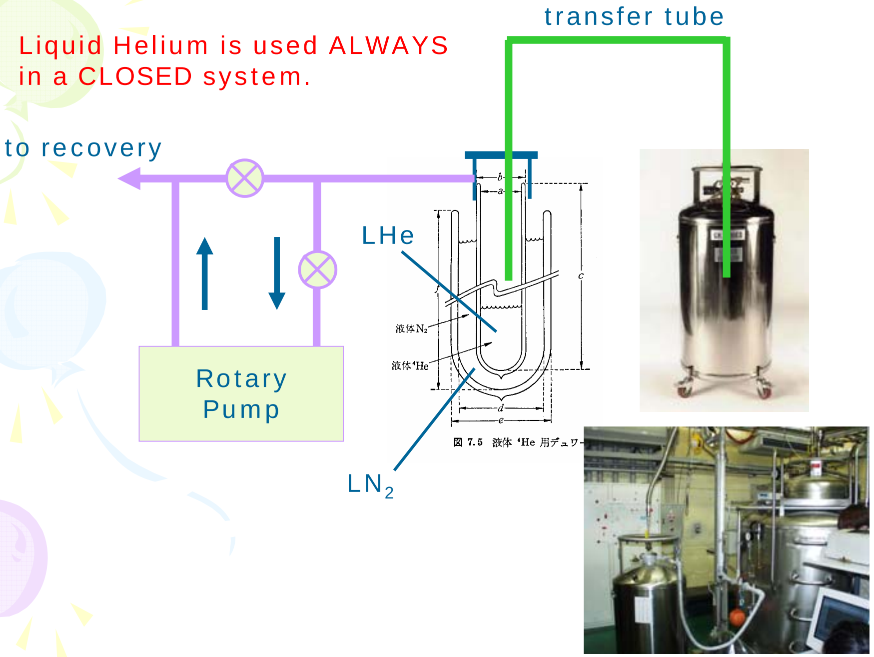
Generating Low Temperatures



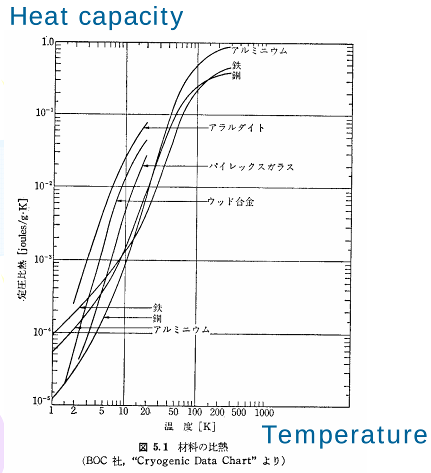
195 K	dry ice
77 K	liquid N_2
1.5 K – 4.2 K	pumping, ^4He
0.3 K	^3He pumping
	$^3He/^4He$ dilution refrigerator

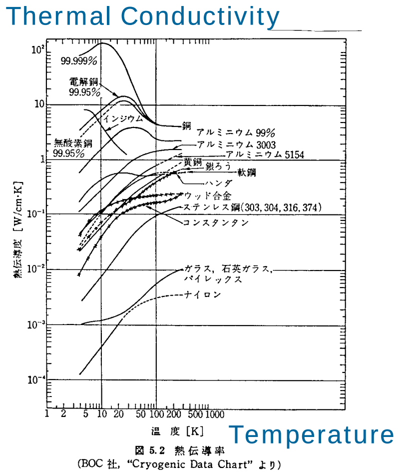
1 mK — 10 mK — 0.1 K — 1 K — 10 K — 100 K
Temperature

Liquid Helium is used ALWAYS in a CLOSED system.

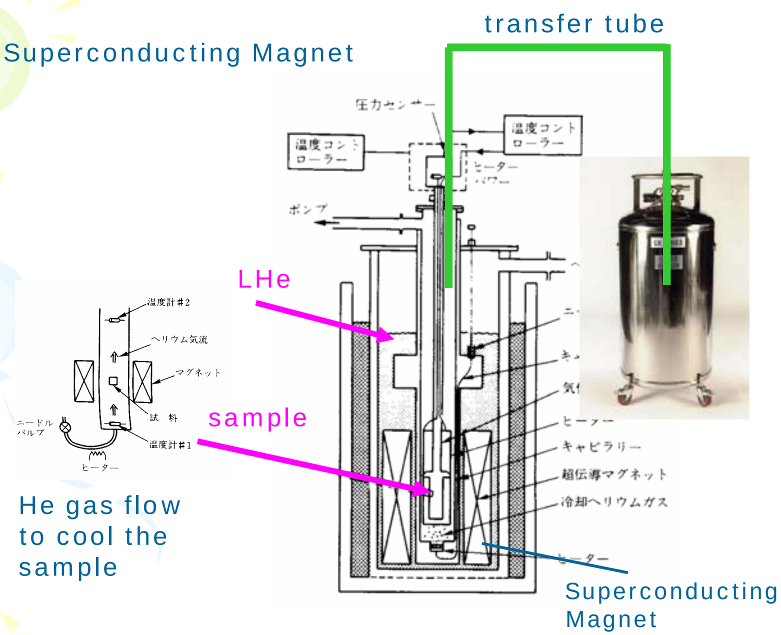


Both heat capacity and thermal conductivity decrease at low temperatures.

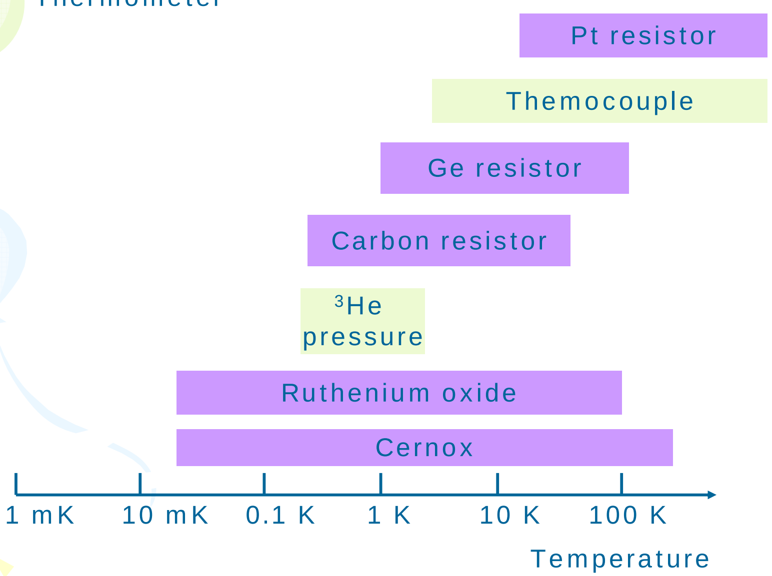




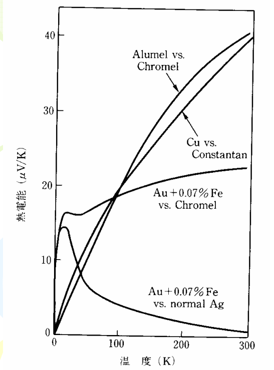
Superconducting Magnet



Thermometer

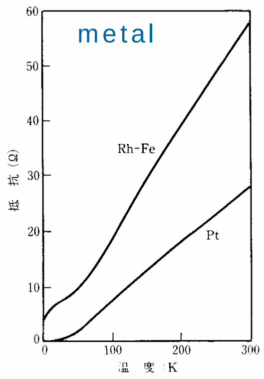


Themocouple



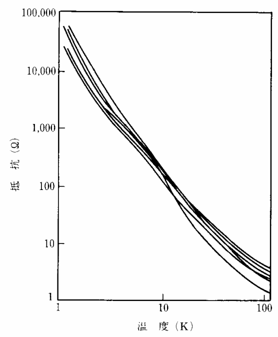
Alumel・chromel 60～400 K
Cu・contantan 60～400 K
Au/Fe・chromel 4～400 K

metal



Pt resistor

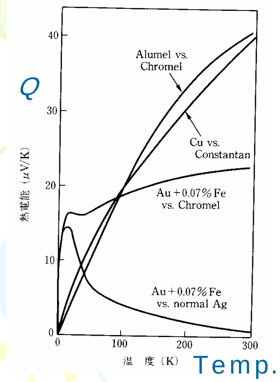
semiconductor



Carbon resistor

Themocouple 熱電対

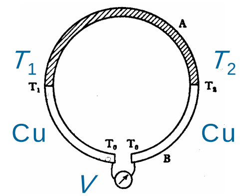
Q



Temp.

Alumel・chromel 60～400 K
Cu・contantan 60～400 K
Au/Fe・chromel 4～400 K

contantan



Connect two kinds of metals, apply temp. diff. between T_1, and T_2.

Standard T_2
0℃(ice)、LN_2、rt
T_1 is measured.

Themopower Seebeck effect

$$Q = \frac{\Delta V}{\Delta T} \qquad Q = \frac{\pi^2 k_B^2 T}{3e}\left[\frac{\partial \ln \sigma(E)}{\partial E}\right] = \frac{\pi^2 k_B^2 T}{6eE_F} \propto T$$

metal

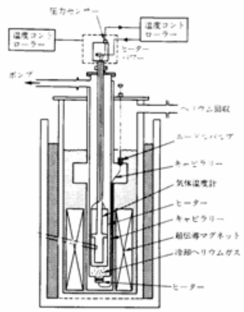
insensitive at LT

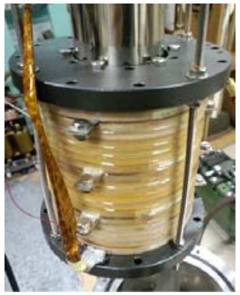
$$Q = \frac{\pi^2 k_B^2 T}{3e}\frac{E_g}{T}$$

semiconductor

Q：entropy of electron＝curvature of energy band

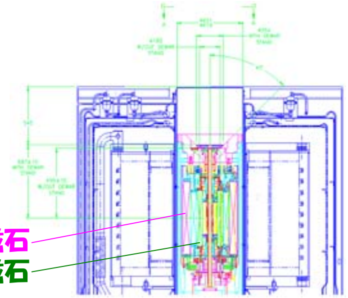
強磁場：超伝導マグネット ～ 15 T





強磁場

物材機構：35 T ハイブリッド磁石



外側 超伝導磁石
内側 常伝導磁石

フロリダ 国立強磁場施設：
45 T ハイブリッド磁石