Chapter 14.

Diamagnetism and Pramagnetism

three source

- Spin
- orbital angular momentum] : paramagnetism

- charge of momentum : diamagnetism

수소 1S state

orbital momentum zero

spin 1/2

Helium

orbital $1s^2$ zero

spin zero

magnetic susceptibility per unit volume

$$\chi = \frac{M}{B}$$

per unit mass magnetic moment per gram

per one mole χ_M (molar susceptibility)

$\chi < 0$: diamagnetic

$\chi > 0$: paramagnetic

ordered arrays of magnetic moment :

ferromagnetic, ferrimagnetic, antiferromagnetic

helical

핵 : Nuclear paramagnetism

10^{-3} of electron

Langevin Diamagnetism Equation

- electron이 핵 주위를 도는데, 이곳에 B field를 가하면 전자가 한쪽 방향으로 더 돈다

B field가 없고 $\omega = \frac{eB}{2mc}$ 로 precession 하는 것과 같다.

Larmor Precession

$$I = (\text{Charge}) \cdot (\text{Revolution per unit time}) = (-Ze)\left(\frac{eB}{2mc}\right)\frac{1}{2\pi}$$

$$\text{Magnetic moment} = \frac{I}{C} \times A$$

$$= -(Ze)\frac{eB}{2mc}\frac{1}{2\pi}\pi\rho^2$$

$$= -\left(\frac{Ze^2B}{4mc}\right)\langle \rho^2 \rangle$$

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle$$

$$\langle r^2 \rangle = \frac{3}{2}\langle \rho^2 \rangle$$

$$\chi = N\frac{\mu}{B} = -\frac{NZe^2}{6mc^2}\langle r^2 \rangle$$ classical Langevin equation

Quantum theory of Diamagnetism of Mononuclear system

$$H = \frac{1}{2m}\left(\frac{\hbar}{i}\nabla - q\frac{\vec{A}}{c}\right)^2$$

$$= \frac{1}{2m}\left[-\hbar^2\nabla^2 - \frac{\hbar}{i}\frac{q}{c}(\nabla \cdot \vec{A} + \vec{A} \cdot \nabla) + \frac{q^2}{c^2}A^2\right]$$

$$= \frac{1}{2m}\left[-\hbar^2\nabla^2 - \frac{\hbar}{i}\frac{e}{c}(\nabla \cdot \vec{A} + \vec{A} \cdot \nabla) + \frac{e^2}{c^2}A^2\right]$$

$$A_x = -\frac{1}{2}yB, \quad A_y = +\frac{1}{2}xB, \quad A_z = 0$$ [Symmetry guage]

$$H^1 = \frac{\hbar e}{2mci} \cdot 2 \cdot \left(-\frac{1}{2}yB\frac{\partial}{\partial x} + \frac{1}{2}xB\frac{\partial}{\partial y}\right) + \frac{e^2}{emc}\left[\frac{1}{4}y^2B^2 + \frac{1}{4}x^2B^2\right]$$

$$\nabla \cdot \vec{A} = \frac{\partial}{\partial x}\left(-\frac{1}{2}yB\right) + \frac{\partial}{\partial y}\left(\frac{1}{2}xB\right)$$

$$= -\frac{1}{2}yB\frac{\partial}{\partial x} + \frac{1}{2}xB\frac{\partial}{\partial y}$$ 책이 틀림

$$= \frac{\hbar eB}{2mci}\left(-y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y}\right) + \frac{e^2B^2}{8mc}(x^2+y^2)$$

$$= \frac{ie\hbar B}{2mc}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) + \frac{e^2B^2}{8mc}(x^2+y^2)$$

=> $\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \sim \vec{L}$: orbital angular momentum과 같다.

Second term $E' = \frac{e^2B^2}{12mc^2}\langle r^2 \rangle$

$$\mu = -\frac{\partial E'}{\partial B} = -\frac{e^2\langle r^2 \rangle}{6mc^2}B$$ Magnetic moment로 Classical case와 같다.

초전도연구단
단장 이 성 익

Paramagnetism

1. Atoms molecules, lattice defets로
   odd number of electrons
   free sodium atom, gaseous hitric oxide,
   organic free radicals
2. partly filled inner shell
3. even number electron 이지만
   산소분자 organic biradicals
4. Metal

Quantum theory of Paramagnetism

$$\vec{\mu} = \gamma \hbar \vec{J} = -g\mu_B \vec{J}$$

Bohr magnetom : $\mu_B = \dfrac{e\hbar}{2mc}$

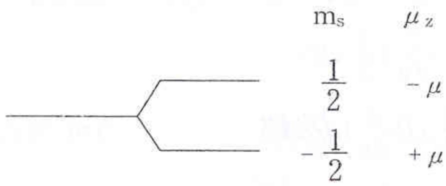
gyromagnetic ratio : g [for electron: g_{el} = 2.0023]

Free atom 인 경우

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Spin만 있는 경우 two level system을 생각하자

$m_j = \pm\dfrac{1}{2}$, g = 2



$$\therefore u = \vec{\mu}\cdot\vec{B} = +g\mu_B\vec{J}\cdot\vec{B}$$
$$= 2\mu_B\left(\pm\frac{1}{2}\right)B$$
$$= \pm\mu_B B$$

[⊕: $m_J = \dfrac{1}{2}$, ⊖: $m_J = -\dfrac{1}{2}$]

system이 two level이다.

$$\frac{N_1}{N} = \frac{\mathrm{Exp}(\mu B/T)}{\mathrm{Exp}(\mu_B/T) + \mathrm{Exp}(-\mu_B/T)} \qquad [\ \tau \equiv k_B T\ ]$$

$$\frac{N_2}{N} = \frac{\mathrm{Exp}(-\mu B/T)}{\mathrm{Exp}(\mu_B/T) + \mathrm{Exp}(-\mu_B/T)}$$

N_2 ———————— ⊕ $\mu_B B$ $m_s = \frac{1}{2}$

N_1 ———————— ⊖ $-\mu_B B$ $m_s = -\frac{1}{2}$

$$M = (N_1 - N_2)\mu = N\mu \cdot \frac{e^x - e^{-x}}{e^x + e^{-x}} = N\mu \tanh x$$

$$\text{for } \chi \ll 1 \text{ ; } \tanh x \cong x \qquad = N\mu\left(\frac{uB}{k_B T}\right)$$

$$= \frac{N\mu^2 B}{k_B T}$$

Angular momentum quantum number J has 2J+1 equally spaced energy level

$\vec{J}$	$\vec{\mu}$	$U = -\vec{\mu} \cdot \vec{B}$
J	$-g\mu_B J$	$g\mu_B JB$
J-1	$-g\mu_B(J-1)$	$g\mu_B(J-1)B$
0	0	0
-(J-1)	$g\mu_B(J-1)$	$-g\mu_B(J-1)B$
-(J)	$g\mu_B J$	$-g\mu_B JB$

Magnetization

$$M = N\frac{(-g\mu_B J)e^{-Jx} + (-g\mu_B(J-1))e^{-(J-1)x} + \cdots + (g\mu_B J)e^{Jx}}{e^{-Jx} + e^{-(J-1)x} + \cdots + e^{(J-1)x} + e^{Jx}}$$

$$= (-g\mu_B N)\frac{Je^{-Jx} + (J-1)e^{-(J-1)x} + \cdots (-J)e^{Jx}}{e^{-Jx} + e^{-(J-1)x} + \cdots + e^{(J-1)x} + e^{Jx}}$$

$$= -g\mu_B N \cdot \frac{-\frac{\partial}{\partial x}\left(\frac{e^{-Jx}(1-e^{(2J+1)x})}{1-e^x}\right)}{\frac{e^{-Jx}(1-e^{(2J+1)x})}{1-e^x}}$$

$$= g\mu_B N \cdot \frac{\partial}{\partial x} \ln\left[\frac{e^{-Jx}(1-e^{(2J+1)x})}{1-e^x}\right]$$

$$M = g\mu_B N \cdot \frac{\partial}{\partial x} \ln\left[\frac{e^{x/2}(e^{-(2J+1)x/2} - e^{(2J+1)x/2})}{e^{x/2}(e^{-x/2} - e^{x/2})}\right]$$

$$= g\mu_B N \cdot \frac{\partial}{\partial x} \ln\left[\frac{\sinh\left(\frac{2J+1}{2}\right)x}{\sinh\left(\frac{1}{2}\right)x}\right]$$

$$= g\mu_B N \cdot \frac{\partial}{\partial x}\left[\ln\left\{\sinh\left(\frac{2J+1}{2}\right)x\right\} - \ln\left\{\sinh\left(\frac{1}{2}\right)x\right\}\right]$$

$$= g\mu_B N \cdot \left[\frac{(2J+1)}{2}\coth\left(\frac{2J+1}{2}\right)x - \frac{1}{2}\coth\left(\frac{1}{2}\right)x\right]$$

$$Let\ x' \equiv x \cdot J = \frac{g\mu_B BJ}{k_B T}$$

$$= g\mu_B NJ \cdot \left[\frac{(2J+1)}{2J}\coth\left(\frac{2J+1}{2J}\right)x' - \frac{1}{2}\coth\left(\frac{1}{2J}\right)x'\right]$$

x<<1 일때의 근사! : $\cosh x = \frac{1}{x} + \frac{x}{3}$, $x = gJ\mu_B B/k_B T$

$$M = NgJ\mu_B\left[\frac{2J+1}{2J}\coth\frac{(2J+1)x}{2J} - \frac{1}{2J}\coth\frac{x}{2J}\right]$$

$$= NgJ\mu_B\left[\frac{2J+1}{2J}\left(\frac{2J}{(2J+1)x} + \frac{(2J+1)x}{6J}\right) - \frac{1}{2J}\left(\frac{2J}{x} + \frac{x}{6J}\right)\right]$$

$$= NgJ\mu_B\left[\frac{(2J+1)^2 x}{12J^2} - \frac{x}{12J^2}\right]$$

$$= NgJ\mu_B\frac{(4J^2+4J)x}{12J^2}$$

$$= \frac{NgJ\mu_B \cdot 4 \cdot (J+1)x}{12}$$

$$= \frac{1}{3}Ng\mu_B(J+1)x = \frac{1}{3}Ng\mu_B(J+1)\frac{gJ\mu_B B}{K_B T}$$

$$\frac{M}{B} = \frac{Ng^2\mu_B^2(J+1)J}{3k_B T}$$

$$= \frac{N\mu_B^2 P^2}{3k_B T} = \frac{C}{T}$$

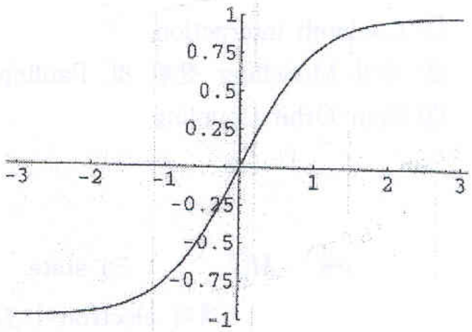
where $C = \frac{NP^2\mu_B^2}{3k_B}$ Curie constant

$p \equiv g[J(J+1)]^{1/2}$:

effective number of Bohr magneton

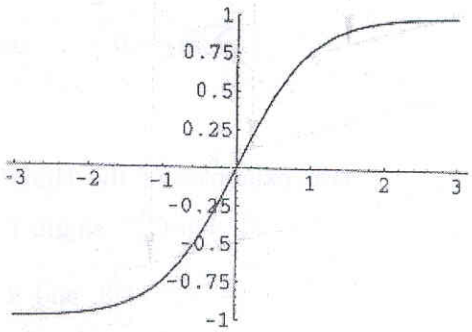
[참고]" $2\coth(2x) - \coth(x) = \tanh(x)$"임을 이용하면, $J=\frac{1}{2}$일 때 위의 일반식이 two level system의 specific case와 동일함을 알 수 있다. [그림 참고]

Plot[{2 Coth[2 x] - Coth[x]}, {x, -3, 3}, P



- Graphics -

Plot[{Tanh[x]}, {x, -3, 3}, PlotRange → {-



Rare Earth Ions

Rare earth : chemical properties similar
Magnetic properties are fascinating

최근에서나 분리가능

Outermost electron shell
$5s^2\ 5p^6$

$5s^2\ 6p^6\ 4f$

4f shall 이 매우 다름

Lanthanum	4f	empty
Cerium	4f	one
Ytterbium	$4f^{13}$	
Lutecium	$4f^{14}$	

이온의 radii

1.11Å - 0.94Å

4f 또는 대개 0.3 Å이다.

(2J+1) fold degenerate ground state

이것은 magnetic field에 의해 lifted

Effective magneton number : 실험, 이론 거의 같다.

S_m^{3+} : 틀린다.

Hund의 법칙 [Pauli Exclusion Principle(P.E.P)에 의해]

1. S를 maximum으로
2. 1이 만족되며 L을 maximum으로
3. 반보다 못 차면 $J=|L-S|$
   반보다 더 차면 $J=L+S$

① Coulomb interaction
② 가장 Modelling 잘된 것. Pauling, Wilson 1935
③ Spin-Orbit Coupling

예 : M_n^{2+} 3d state

5개의 electron이 있다.

m_L = 2, 1, 0, -1, -2

$\therefore S_{state} = \frac{5}{2}$

$\sum m_L = 0$ only possible value of L=0

two examples of the Hund's rule

① ion C_e^{3+} single f electron

l=3, and s = $\frac{1}{2}$

$J = |L-S| = L - \frac{1}{2} = \frac{5}{2}$

② P_r^{3+} 2개의 f electron

S=1, m_l = 3, 2

$\therefore$ L = 5, S = 1

$J = |L-S| = 5 - 1 = 4$

Iron group Irons

P= g $[J(J+1)]^{1/2}$ 이 아니라 2 $[S(S+1)]^{1/2}$ 에 더 잘 맞는다.

꼭 orbital moment가 없는 것처럼 보인다.

orbital moment are quenched

Crystal field splitting

Paramagnetism Rare earth 4f : 맨 아래에 있다.

Iron 3d : outer shell에 있다.

$\therefore$intensive inhomogeneous electric field called Crystal field라 한다.

(1) L과 Sd,; Coupling이 깨진다.
(2) 2L+1 sublevel이 degenerate 되어있지 않고
Crystal field에 의해 split 된다.
orbital motion의 magnetic moment 기여를 줄인다.

Quenching of orbital Angular moment

Central field 내에서는 L^2, L_Z가 constant

noncentral field : orbit의 plane은 move about

angular moment는 Const 아님

만약 $\langle L_Z \rangle = 0$ 이면, angular momentum이 "quenched"

orbital magnetic moment가 quench 이면 L_Z도 quenching 된다.

L=1 인 경우

L=1 인 전자가 핵 주위를 도는데 inhomogeneous Crystalline

$$e\phi = Ax^2 + By^2 - (A+B)Z^2$$ electrostatic potential

with [A, B const, $\nabla^2\phi = 0$]

Free space

three wave functions

$$u_X = xf(r), \quad u_Y = yf(r), \quad u_Z = zf(r)$$

세 개는 orthogonal하다.

$$L^2 u_i = L(L+1)u_i = 2u_i$$

Perturbation 시작하자 $\langle u_x | e\phi | u_y \rangle = \langle u_x | e\phi | u_z \rangle = \langle u_y | e\phi | u_z \rangle = 0$

$$\langle u_x | e\phi | u_y \rangle = \int xy |f(r)|^2 \{Ax^2 + By^2 - (A+B)z^2x^2\} dxdydz = 0$$

$$\langle u_x | e\phi | u_x \rangle = \int |f(r)|^2 \{Ax^4 + Bx^2y^2 - (A+B)z^2x^2\} dxdydz = 0$$
$$= A(I_1 - I_2)$$

$$with\ I_1 = \int |f(r)|^2 x^4 dxdydz \quad / \quad I_2 = \int |f(r)|^2 x^2y^2 dxdydz$$

같은 방법으로

$$\langle u_y | e\phi | u_y \rangle = B(I_1 - I_2)$$

$$\langle u_z | e\phi | u_z \rangle = -(A+B)(I_1 - I_2)$$

Orbital moment of each levels[u_x, u_y, u_z]

$$\langle u_x | L_z | u_x \rangle = \langle u_y | L_z | u_y \rangle = \langle u_z | L_z | u_z \rangle = 0$$

이 effect는 quenching이라 불리 운다.

Van Vleck Temperature-dependent Paramagnetism

Atomic molecular system : no magnetic moment in G.S

어떤 것은 $\langle S \mid \mu_z \mid 0 \rangle \neq 0$인 놈도 있다.

$\triangle = E_s - E_0$ by standard Perturbation

$$\Phi' = \Phi_0 + \frac{B}{\triangle} \langle S \mid \mu_z \mid 0 \rangle \mu_s$$

$$\Phi_s{}' = \Phi_s + \frac{B}{-\triangle} \langle 0 \mid \mu_z \mid S \rangle \mu_0$$

perturbed ground state

$$\langle 0' \mid \mu_z \mid 0' \rangle \cong 2B \mid \langle S \mid \mu_z \mid 0 \rangle \mid^2 / \triangle$$

upper state $\langle s' \mid \mu_z \mid s' \rangle \simeq -\frac{2B \mid \langle s \mid \mu_z \mid 0 \rangle \mid^2}{\triangle}$

(case 1) $\triangle \ll k_B T$

Surplus population $\cong \frac{N\Delta}{2k_BT}$

$$M = \frac{2B \mid \langle s \mid \mu_z \mid 0 \rangle \mid^2}{\triangle} \cdot \frac{N\triangle}{2k_BT}$$

ground state에 이만큼 더 있다

$$\therefore \chi = N \mid \langle s \mid \mu_z \mid 0 \rangle \mid^2 / k_BT$$

(case 2) $\triangle \gg k_B T$

모든것이 ground state에 있다

$$M = \frac{2NB \mid \langle s \mid \mu_z \mid 0 \rangle \mid^2}{\triangle}$$

Magnetic suscptibility

$$\therefore \chi = \frac{2N \mid \langle s \mid \mu_z \mid 0 \rangle \mid^2}{\triangle}$$

Cooling by Isentropic Demagnetization

1K 아래로 온도 내린다.

: Isentropic(adiabatic) demagnetization

10^{-3} K : magnetic field를 가해서 partly line up

entropy : disorder Tc ↔온도 大

①온도를 내리고 magnetic걸고

→ ② 같은 온도에서 align

→ ③열 차단 [단열: $\Delta S = 0$]

→ ④magnetic field 제거

∴온도가 내려간다.

lattice vibration의 entropy가 줄면서,

이것이 spin-system의 entropy를 증가시킨다.

그러나 이온도 에서는 lattice vibration은 거의 무시

∴entropy는 demagnetization에 되는 동안 실질적으로 불변

Magnetic cooling is a one shot operation, not cyclic

온도:T, N ions, each of spin: S

△ : interaction을 characterize해서

spin이 제멋대로 향하도록 하는데 필요한 에너지

$E_{int} \equiv k_B \triangle$

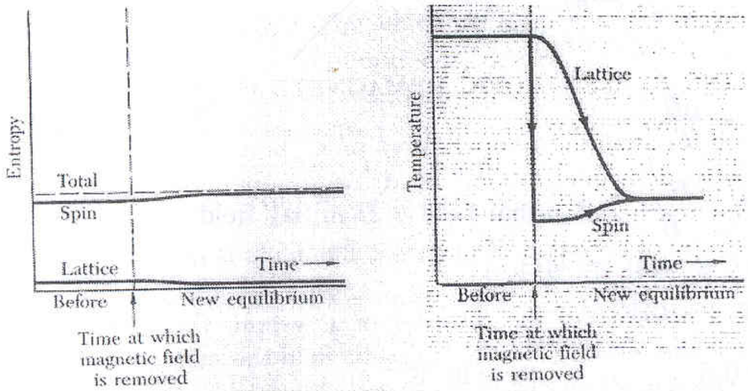
가능한 상태수가 G인 system의 entropy: $\sigma = k_B \ln G$

온도가 높으면 2S+1 state가 모든 ion에 있다.

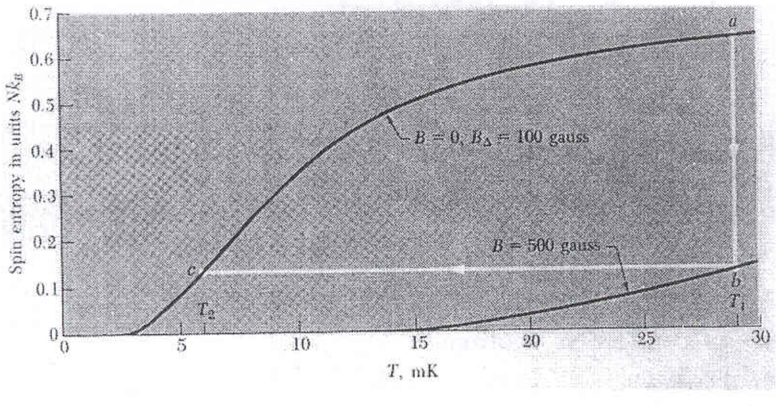
$G=(2S+1)^N$, 여기서 spin entropy σ_s는

$\sigma_s = k_B \ln (2S+1)^N$

$= Nk_B \ln (2S+1)$



└magnetic field를 없앤다



Nuclear Demagnetization

Magnetic sublevel의 population은 μB / $k_B T$의 함수 ∴ $\frac{B}{T}$의 함수

spin entropy도 $\frac{B}{T}$의 함수이다.

위 graph에서

$\frac{\mu B}{T}$ 가 일정 $\therefore \frac{\mu B_{\triangle}}{T_2} = \frac{\mu B}{T_1}$

$$T_2 = T_1 \cdot \frac{B_{\triangle}}{B}$$ $B_{\triangle}$:final field , B: initial field

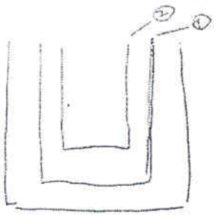
이렇게 온도를 줄일 수 있다.

start B=50kG T_1 = 0.01K

$\frac{\mu B}{k_B T_1} = 0.5$ $T_2 \approx 10^{-7}$K

Cu: 처음으로 electric cooling 0.02K 얻은 후

nuclear cooling 1.2×10^{-6}K 얻는다.



①을 cooling 하여 0.01K를 얻고

다시 ①,②에 magnetic field를 가한 후

②를 cooling한다. magnetic cooling

Paramagnetic Susceptibility of conduction electrons

전자가 금속 내에 있으면

classically magnetic moment of one Bohr magneton μ_B

exp $M = N\mu_B B / k_B T$

그러나 실험결과 M은 온도에 무관한 것이 밝혀진다.

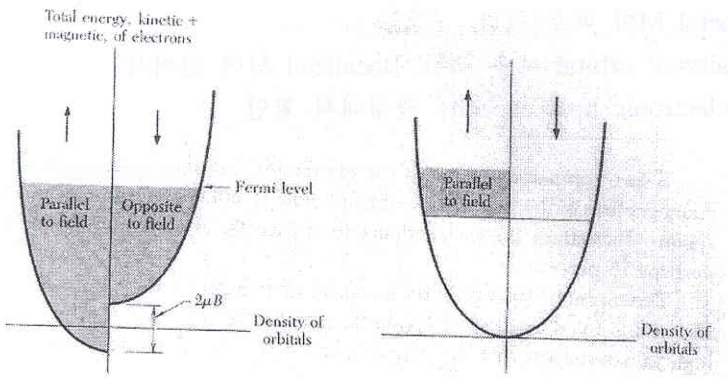
Pauli Fermi-Dirac distribution

위 식 $M = N \cdot \frac{\mu_B}{k_B T} \cdot \mu_B$

antiparallel할 확률

단지 $\frac{T}{T_F}$ 만이 contribute 한다.

$$M \simeq \frac{N\mu_B B}{k_B T} \cdot \frac{T}{T_F} = \frac{N\mu^2}{kT_F} \cdot B$$



$\vec{J}$가 parallel하면 에너지 높고

$\vec{\mu}$가 parallel하면 에너지 낮고

parallel한 것이 에너지가 낮다.

$$U = -\vec{\mu} \cdot \vec{B}$$
$$= +g\mu_B \vec{J} \cdot \vec{B}$$

$\vec{\mu} = -g\mu_B J$, g=2.0 for electron

$\vec{\mu}$ // $\vec{B}$ 에너지 낮다. [$k_B T \ll \varepsilon_F$]

$$N_+ = \frac{1}{2}\int_{-\mu}^{\varepsilon_F} d\varepsilon f(\varepsilon) D(\varepsilon + \mu B) \simeq \frac{1}{2}\int_0^{\varepsilon_F} d\varepsilon f(\varepsilon) D(\varepsilon) + \frac{1}{2} 2\mu B \cdot \frac{1}{2} D(\varepsilon_F)$$

$$N_- = \frac{1}{2}\int_{\mu B}^{\varepsilon_F} d\varepsilon f(\varepsilon) D(\varepsilon - \mu B) \simeq \frac{1}{2}\int_0^{\varepsilon_F} d\varepsilon f(\varepsilon) D(\varepsilon) - \frac{1}{2} 2\mu B \cdot \frac{1}{2} D(\varepsilon_F)$$

Magnetization

$$M = \mu(N_+ - N_-)$$
$$= \mu \cdot \left[\frac{1}{2}\int + \frac{1}{2}\mu B D(\varepsilon_F) - \frac{1}{2}\int + \frac{1}{2}\mu B D(\varepsilon_F)\right]$$
$$= \mu \cdot \mu B D(\varepsilon_F)$$

$$D(\varepsilon_F) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{\frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{\frac{1}{3}}}$$

$$= \mu^2 B \cdot \frac{3N}{2k_B T_F}$$

or $D(\varepsilon_F) = \frac{3N}{2\varepsilon_F} = \frac{3N}{2k_B T_F}$

$$= \frac{3N\mu^2}{2k_B T_F} B$$

Pauli spin magnetization

가정 : electron의 움직임이 magnetic field의 영향을 받지 않음

***> Diamagnetism(Landau)가 total의 $-\frac{1}{3}$ 기여

$$\therefore M = \frac{N\mu_B^2}{k_B T_F} B$$ [for free electron gas nearly same as in metal]

Transition metal M이 매우 크다

Density of orbital 매우 크다. [localized 되어 있어서]

=>electronic heat capacity 측정에서 확인