

Magnetism of Metals (金属磁性)

HAMADA Noriaki (浜田典昭)

Tokyo U. of Science (東京理科大学 先端物理学科)

Osaka U. (大阪大学 エマージングサイエンスデザイン R³ センター)

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(参考文献)

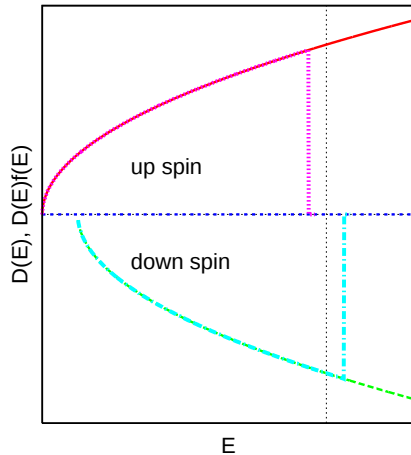
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- (2) 斯波弘行著「基礎の固体物理学」(培風館, 2007)
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- (6) 安藤陽一著「トポロジカル絶縁体入門」(講談社, 2014)
- (7) 齋藤英治, 村上修一著「スピン流とトポロジカル絶縁体入門」(共立出版, 2014)
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(S.I.)

$$\boldsymbol{B} = \mu_0(\boldsymbol{H} + \boldsymbol{M})$$

1 Paramagnetism in nonmagnetic metal (金属常磁性)

Zeeman splitting : $(\pm\mu_B B)$



$D_0(\epsilon)$: Density of states per spin

$$M = \mu_B B \times D_0(\epsilon_F) \times 2 \times \mu_B$$

Pauli susceptibility

in the noninteracting electrons : $(B = \mu_0 H)$

$$\chi_0 = \frac{M}{H} = \frac{\mu_0 M}{B} = 2\mu_0 \mu_B^2 D_0(\epsilon_F)$$

χ_0 can be obtained by the band structure calculation.

The susceptibility is enhanced, for example,

$$\chi_P = \frac{\chi_0}{1 - I\chi_0}$$

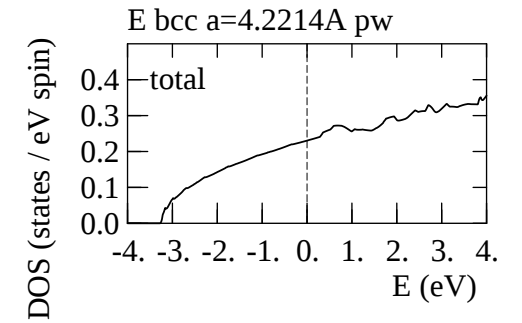
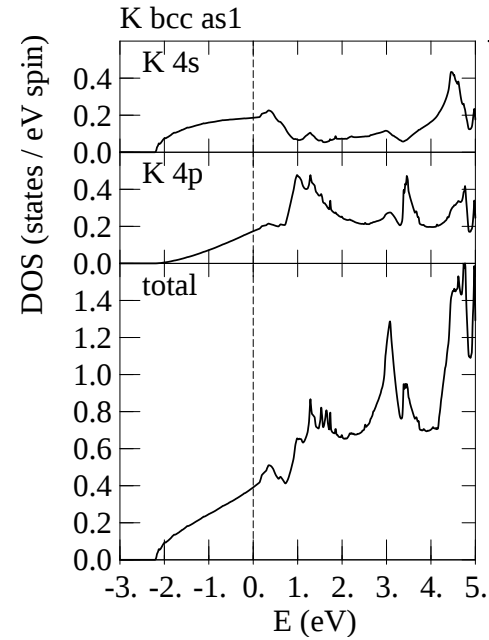
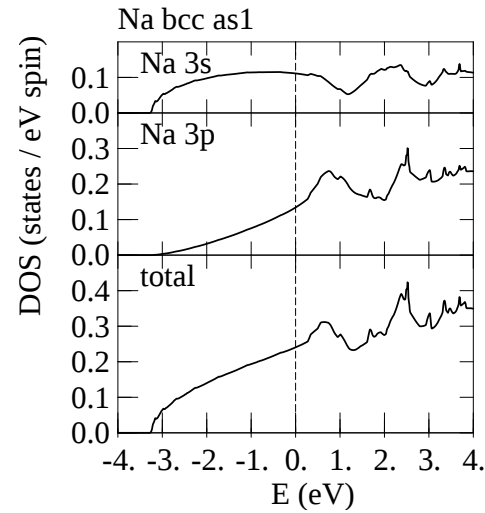
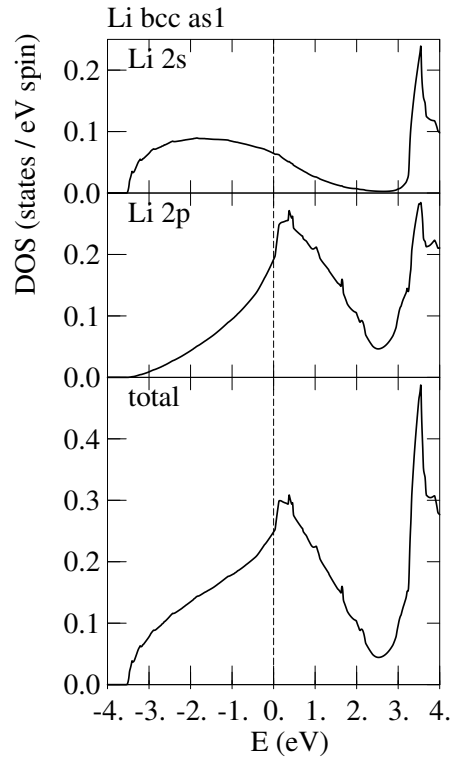
due to the electron-electron interaction.

Metal	$\chi/10^{-5}$		
	Free el. χ_0	Band cal. χ_0	exp. χ_P
Li	1.01	1.65	2.5
Na	0.83	0.86	1.4
K	0.67	0.72	1.1
Rb	0.63	0.70	1.0
Ti		3.8	18
V		9.8	35
Fe(NM)		22.0	

The temperature-independent susceptibility is often called as the Pauli susceptibility.

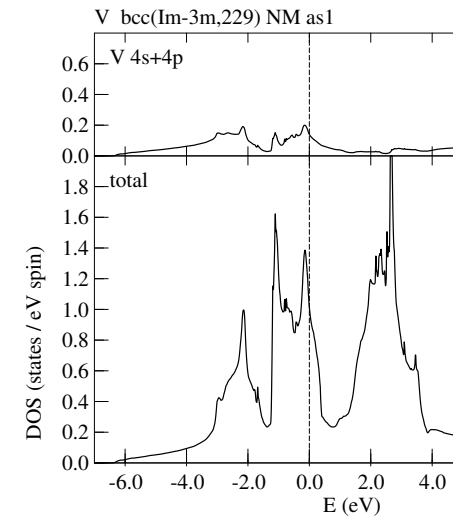
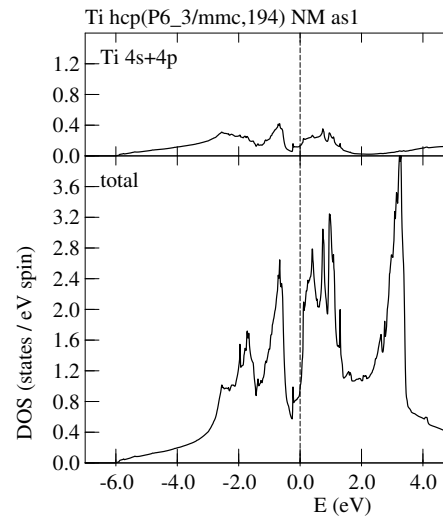
$\text{DOS}(\epsilon)$ [states/eV spin cell] ($= \Omega D_0(\epsilon)$; Ω =cell volume)

Alkali metals



3d-Transition metals (nonmag.)

- much higher $D_0(\epsilon)$
- still T-independent χ_P



2 Q-dependent susceptibility in crystals

$\mathbf{Q} = \mathbf{q} + \mathbf{G}$: wave vector

$\mathbf{q}$: inside the first Brillouin zone (Bloch wave v.)

$\mathbf{G}$: the reciprocal lattice vector

$H_{\mathbf{G}'}(\mathbf{q})e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}$: applied magnetic field

$M_{\mathbf{G}}(\mathbf{q})e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}$: induced magnetization

Q-dependent magnetic susceptibility $\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q})$

$$M_{\mathbf{G}}(\mathbf{q}) = \sum_{\mathbf{G}'} \chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) H_{\mathbf{G}'}(\mathbf{q}) . \quad (1)$$

Static polarization function $D_{\mathbf{G}\mathbf{G}'}(\mathbf{q})$

$$\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = 2\mu_0\mu_B^2 \frac{1}{\Omega} D_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) , \quad (2)$$

For the noninteracting electron system,

$$\chi_{00}(\mathbf{0}) \equiv \lim_{\mathbf{q} \rightarrow 0} \chi_{00}(\mathbf{q}) = \chi_0 \quad (3)$$

$$D_{00}(\mathbf{0}) \equiv \lim_{\mathbf{q} \rightarrow 0} D_{00}(\mathbf{q}) = \Omega D_0(\epsilon_F) \quad (4)$$

Diagonalize $D_{\mathbf{G}'\mathbf{G}}(\mathbf{q})$ in each $\mathbf{q}$,

$$\sum_{\mathbf{G}'} D_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) U_{\mathbf{G}'n}(\mathbf{q}) = U_{\mathbf{G}n}(\mathbf{q}) D_n(\mathbf{q}) \quad (5)$$

then, for a chosen n , eqn.(1) becomes

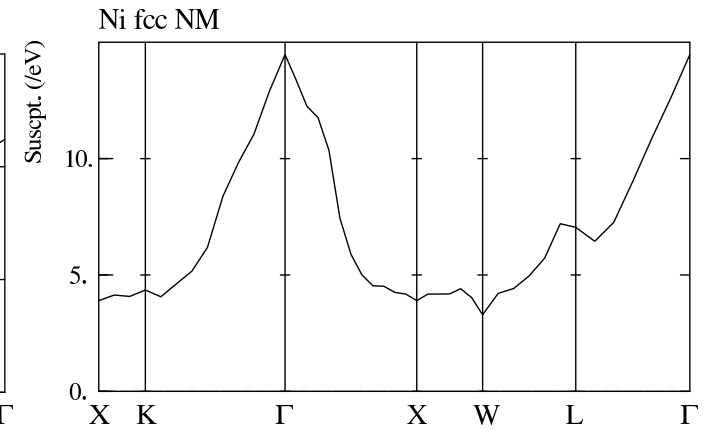
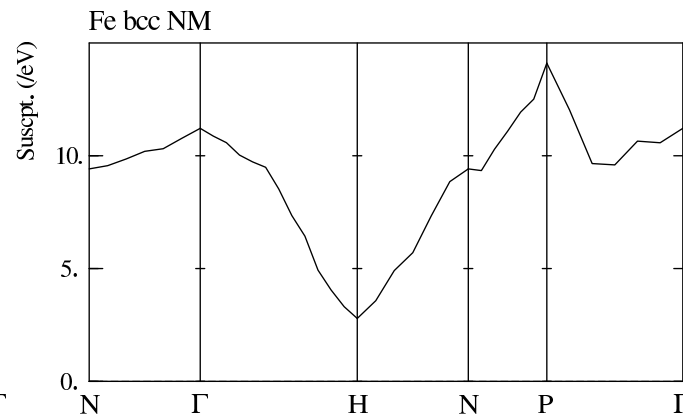
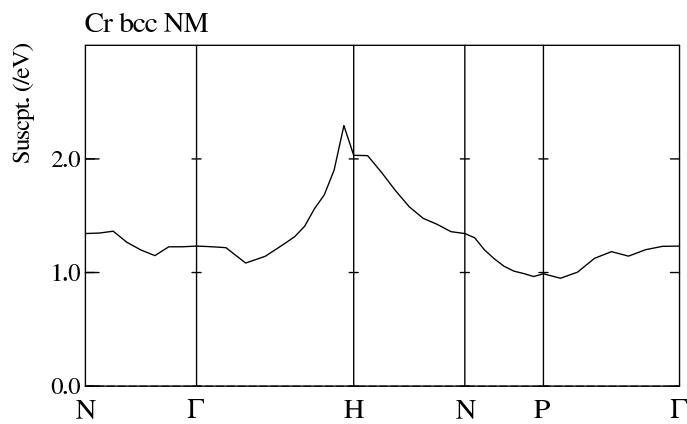
$$M_n(\mathbf{q}) = \chi_n(\mathbf{q}) H_n(\mathbf{q}) \quad (6)$$

$$\chi_n(\mathbf{q}) = 2\mu_0\mu_B^2 \frac{1}{\Omega} D_n(\mathbf{q}) \quad (7)$$

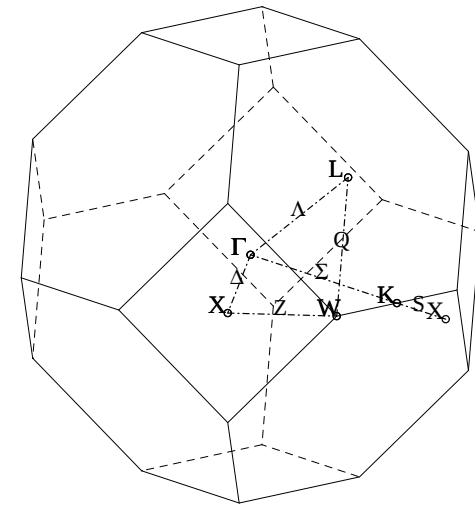
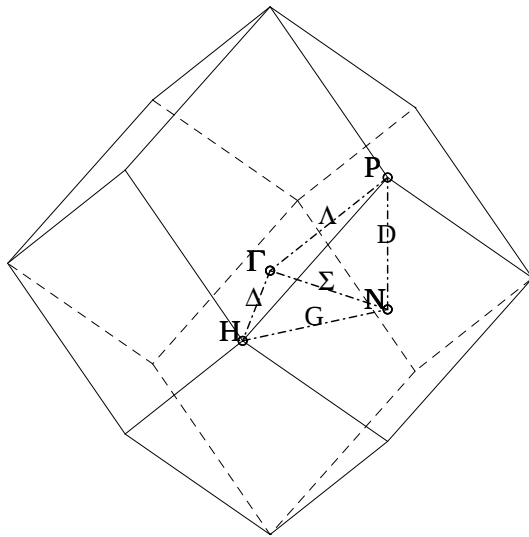
The largest eigenvalue: $D_1(\mathbf{q})$

$$D_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = \frac{-1}{N} \sum_{n'n\mathbf{k}} \frac{(f_{n'\mathbf{k}+\mathbf{q}} - f_{n\mathbf{k}}) \langle \psi_{n\mathbf{k}} | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{n'\mathbf{k}+\mathbf{q}} \rangle \langle \psi_{n'\mathbf{k}+\mathbf{q}} | e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} | \psi_{n\mathbf{k}} \rangle}{\epsilon_{n'\mathbf{k}+\mathbf{q}} - \epsilon_{n\mathbf{k}}} . \quad (8)$$

2.1 3d transition metals



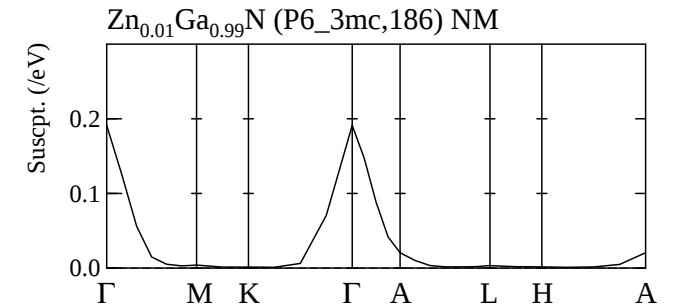
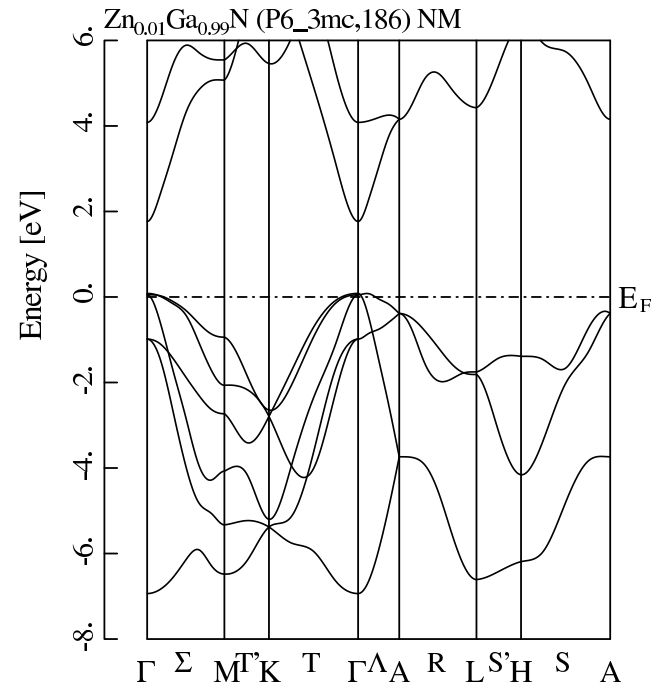
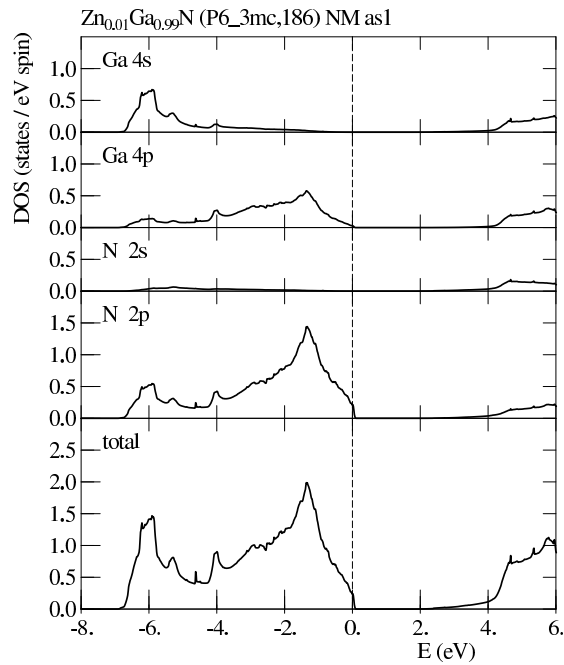
"Susceptibility" $D_1(\mathbf{q})$



Ferromagnetic susceptibility $\Leftrightarrow$ near-band-edge E_F

Antiferromagnetic susceptibility $\Leftrightarrow$ half-filled band

2.2 Doped GaN

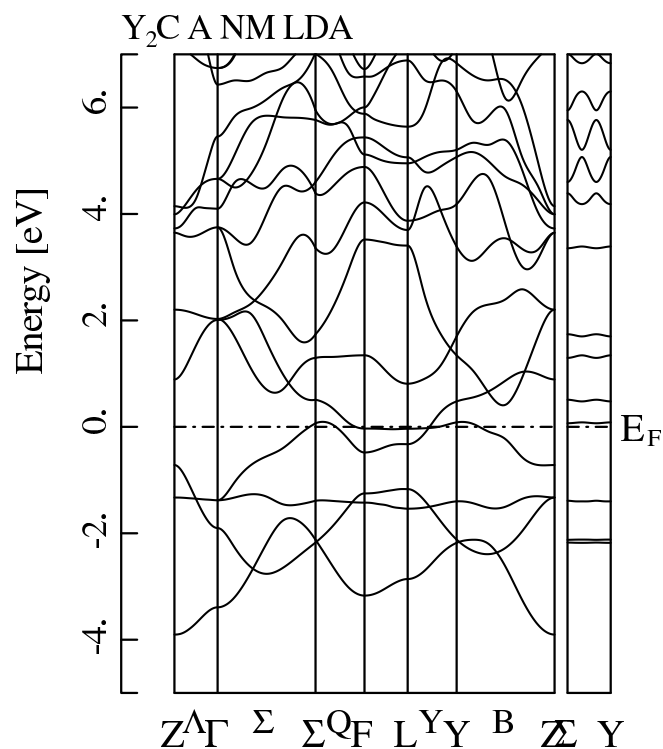
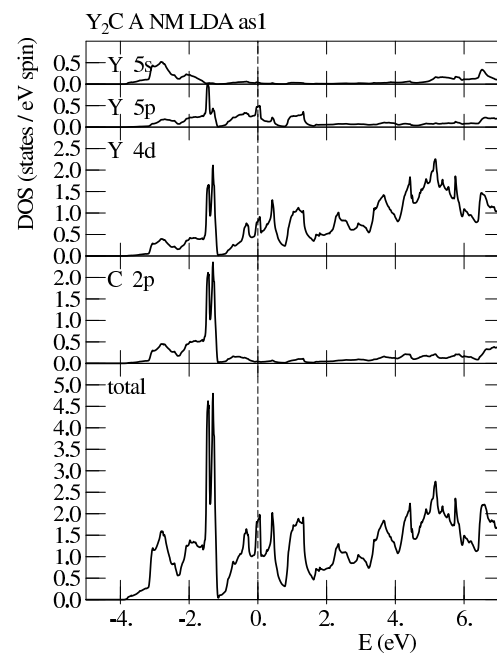
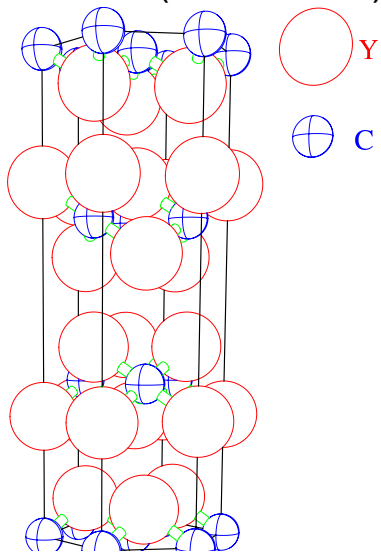


$\text{Zn}_{0.01}\text{Ga}_{0.99}\text{N}$ (wz hP)

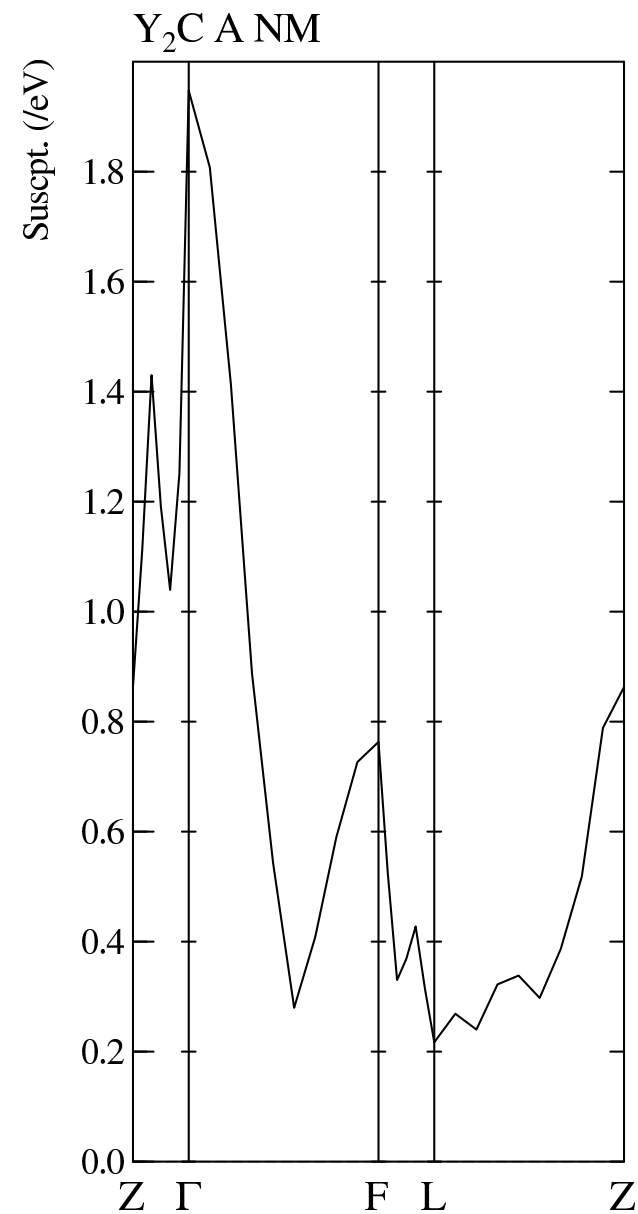
Ferromagnetic susceptibility $\Leftrightarrow$ Doped semiconductor (near-band-edge E_F)

2.3 Y_2C (Electride)

Y_2C hR(R-3m,166)



(2D semimetal)
large DOS
near-band-edge E_F



Large ferromag. suscept.

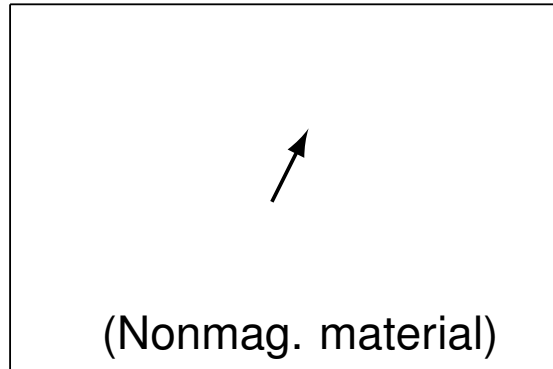
2.4 Conclusion

Q-dependent magnetic susceptibility may be useful to search magnetically ordered materials.

Doped semiconductor may be good for supporting ferromagnetic long range order,
by using the band edge property.

Two dimensional semimetal may provide a good ferromagnetic medium.

3 Magnetic Impurity in Nonmagnetic Material



(Example) Fe in Mo

3.1 Anderson Model

Anderson Hamiltonian: ($n_\sigma = d_\sigma^\dagger d_\sigma$)

$$H = H_0 + H_d + H_U + H_V$$

$$H_0 = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}$$

$$H_d = \sum_{\sigma} \epsilon_d n_{\sigma}, \quad H_U = U n_{\uparrow} n_{\downarrow}$$

$$H_V = \frac{1}{\sqrt{N_A}} \sum_{\mathbf{k}\sigma} \{ V_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger d_{\sigma} + V_{\mathbf{k}}^* d_{\sigma}^\dagger c_{\mathbf{k}\sigma} \}$$

(N_A : the number of unit cells in the crystal)

3.2 Hartree-Fock approximation

($\sigma = \uparrow, \downarrow$)

$$H_{\sigma} = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \epsilon_d n_{\sigma} + U \langle n_{-\sigma} \rangle n_{\sigma} \\ + \frac{1}{\sqrt{N_A}} \sum_{\mathbf{k}} \{ V_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger d_{\sigma} + V_{\mathbf{k}}^* d_{\sigma}^\dagger c_{\mathbf{k}\sigma} \}$$

Self-consistent calculation for $\langle n_{\uparrow} \rangle$ and $\langle n_{\downarrow} \rangle$

$$\text{Energy : } E = \sum_{\sigma} \langle H_{\sigma} \rangle - U \langle n_{\uparrow} \rangle \langle n_{\downarrow} \rangle$$

Partial DOS of d state (**Virtual bound state**):

$$D_{d\sigma}(\epsilon) = \frac{\Delta/\pi}{(\epsilon - \epsilon_{d\sigma})^2 + \Delta^2}$$

$$\epsilon_{d\sigma} = \epsilon_d + U \langle n_{-\sigma} \rangle$$

$$\Delta \approx \pi \langle |V_{\mathbf{k}}|^2 \rangle D_c(\epsilon_F)$$

3.3 Local magnetic moment μ

Susceptibility has a Curie term:

$$\chi(T) = \chi_P + \frac{B}{T}; \quad B = \frac{N\mu^2}{3k_B}$$

example) Fe impurity in various 4d metals,

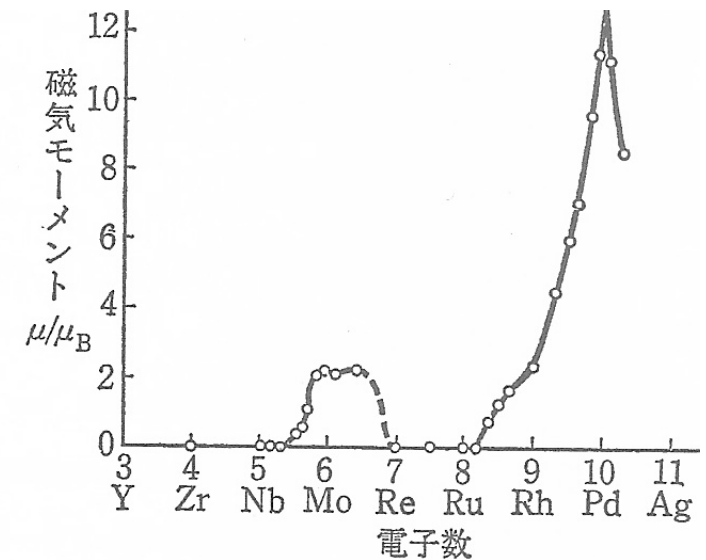
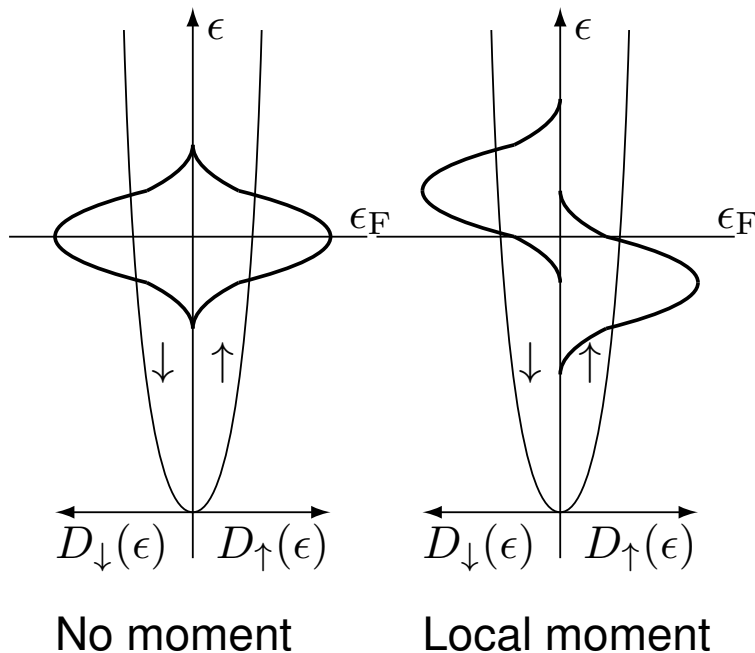


図 11-11 1% Fe を含む合金での Fe の磁気モーメント (Clogston et al)



Virtual bound state

(parameters: E_d , U , Δ)

Starting with no magnetic moment,

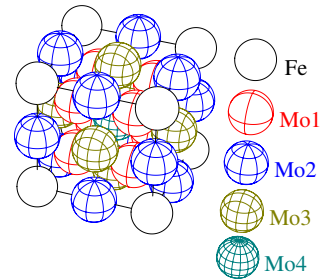
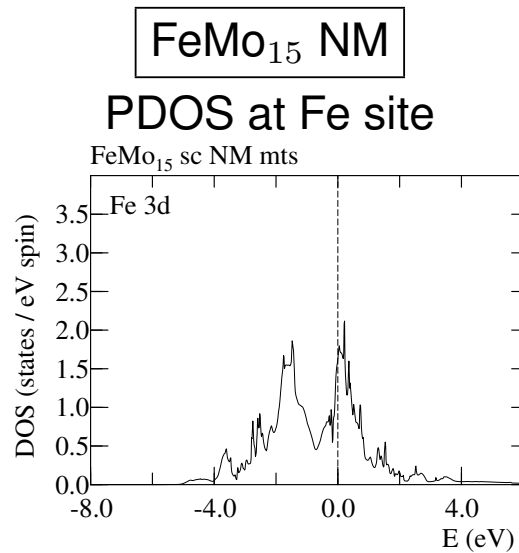
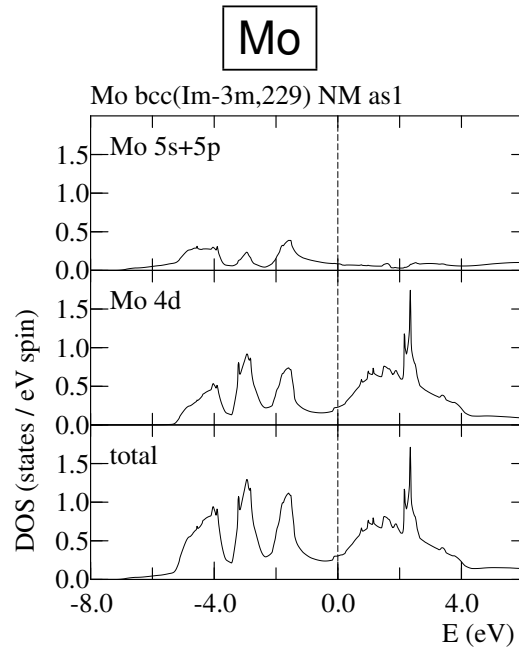
$$D_d(\epsilon_F) \equiv D_{d\uparrow}(\epsilon_F) = D_{d\downarrow}(\epsilon_F)$$

Appearance of local moment:

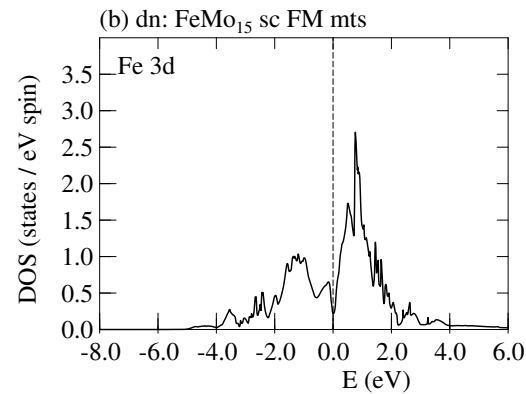
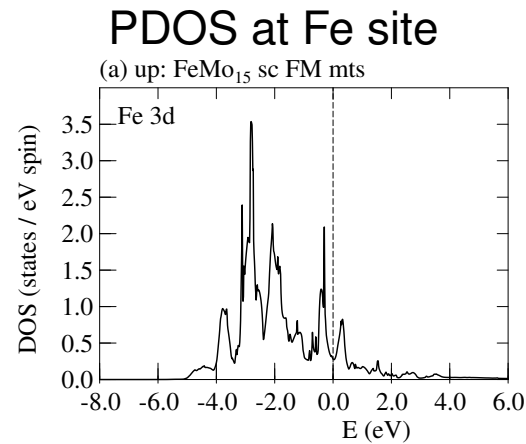
$$UD_d(\epsilon_F) > 1$$

The Fe magnetic moment induces large moment at surrounding Pd atoms.

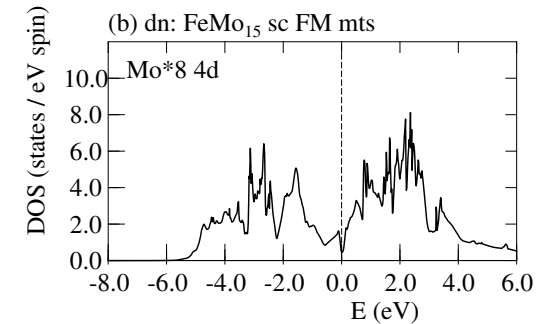
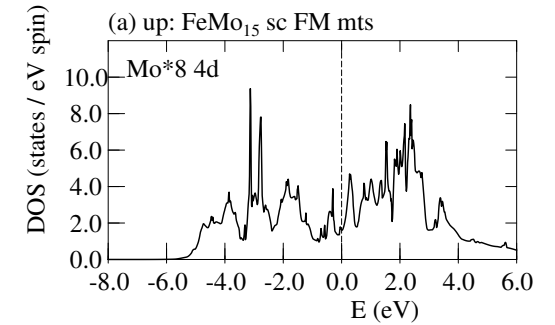
3.3.1 Band structure calculation: Fe in Mo (bcc*8-sc supercell)



FeMo₁₅ FM



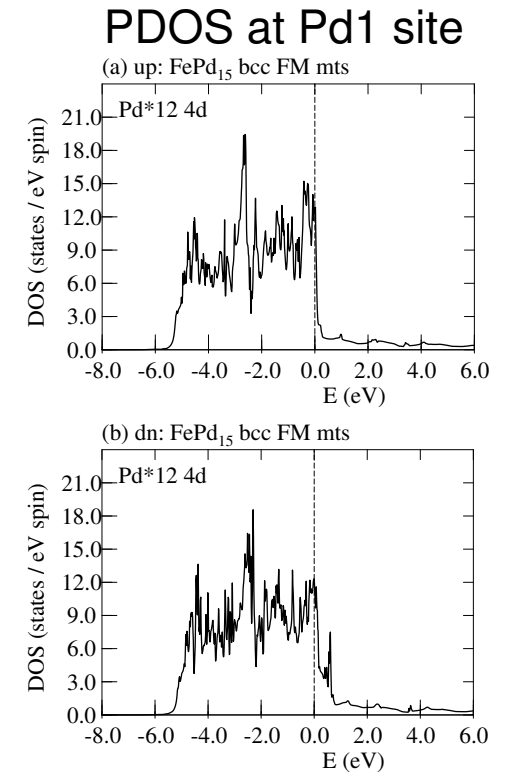
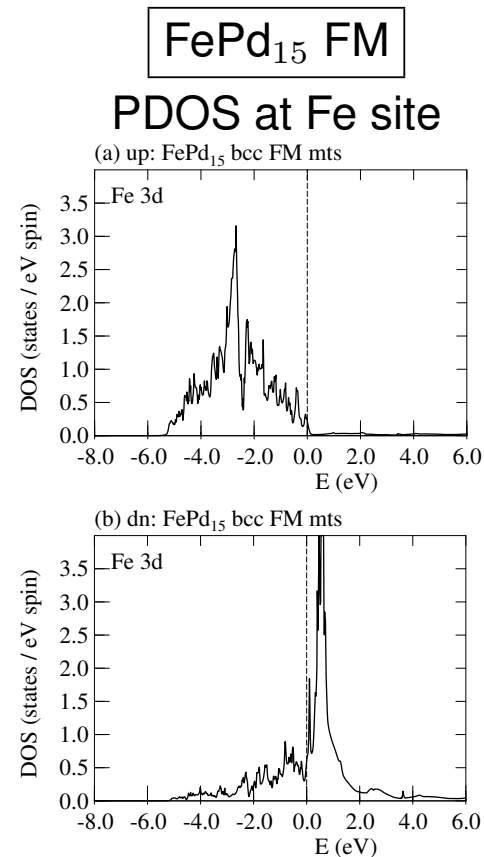
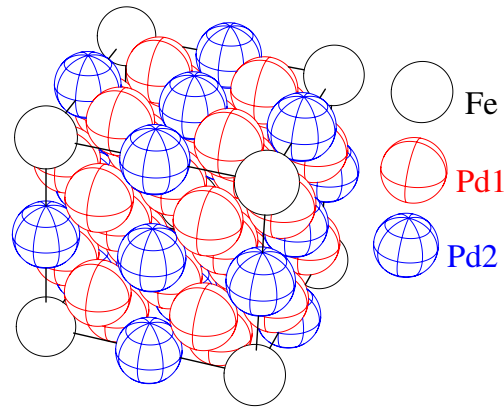
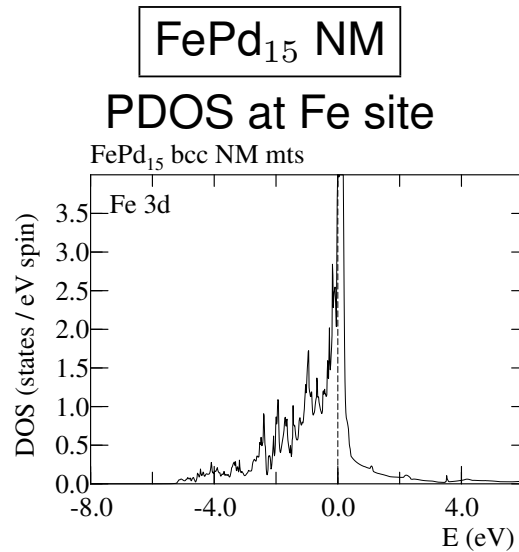
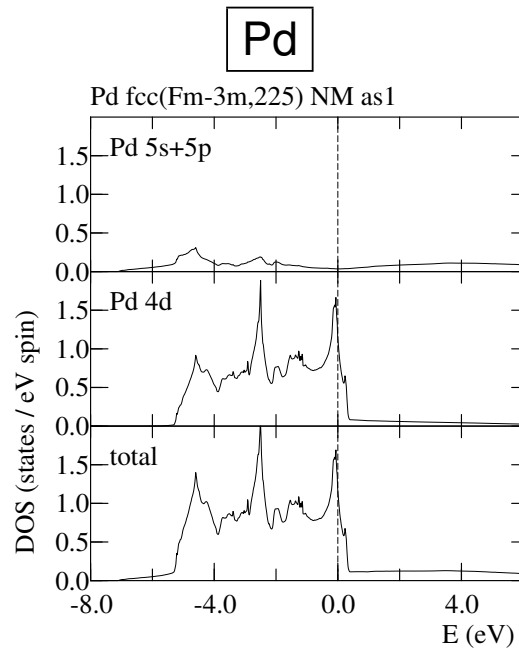
PDOS at Mo1 site



Magnetic moment [μ_B]

Total	Fe	Mo1	Mo2
2.08	2.12	-0.01	0.02

3.3.2 Band structure calculation: Fe in Pd (fcc*8-bcc supercell)



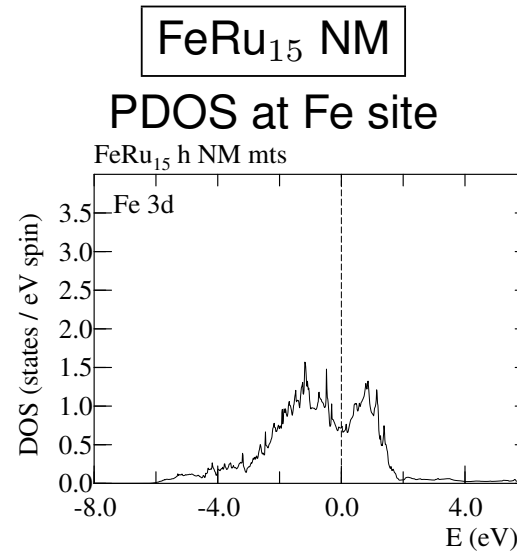
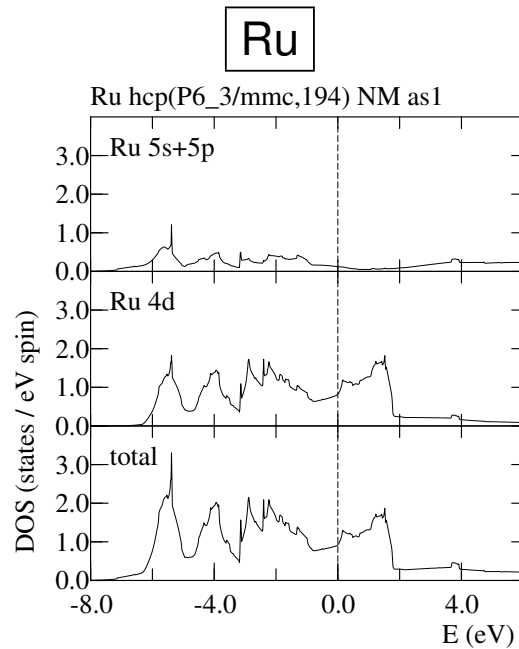
Magnetic moment [μ_B]

Total	Fe	Pd1	Pd2
6.69	3.19	0.22	0.24

Large moments are induced at many Pd sites.

The supercell is too small.

3.3.3 Band structure calculation: Fe in Ru (hcp*8-h supercell)



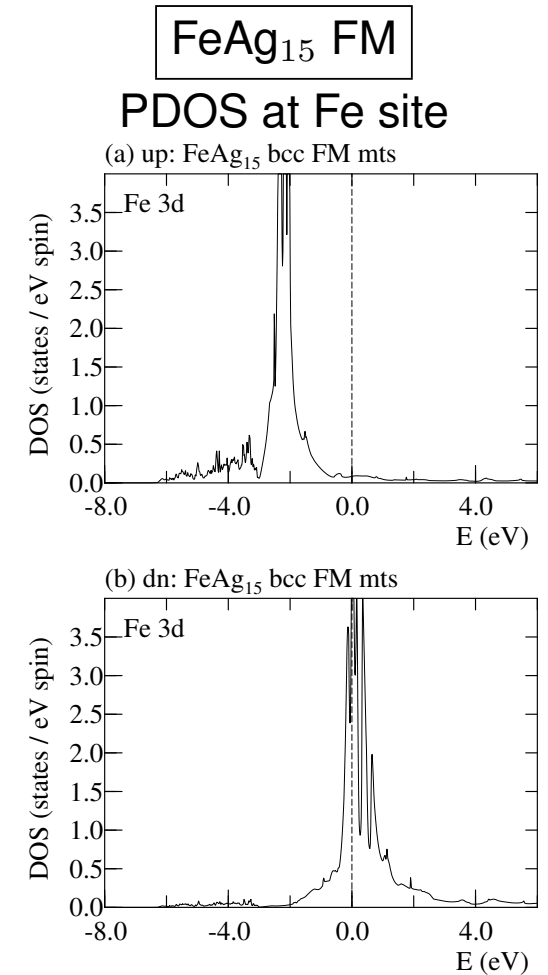
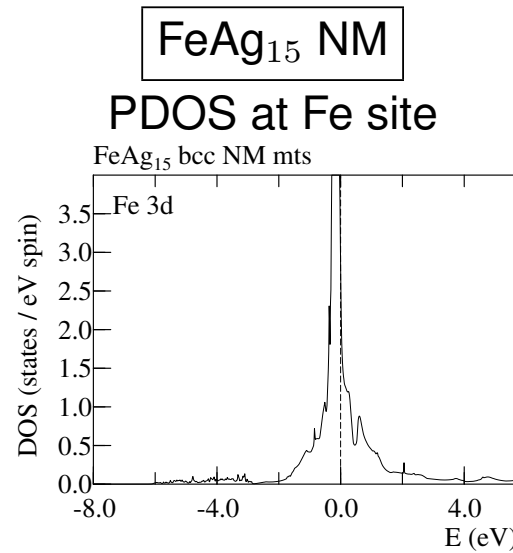
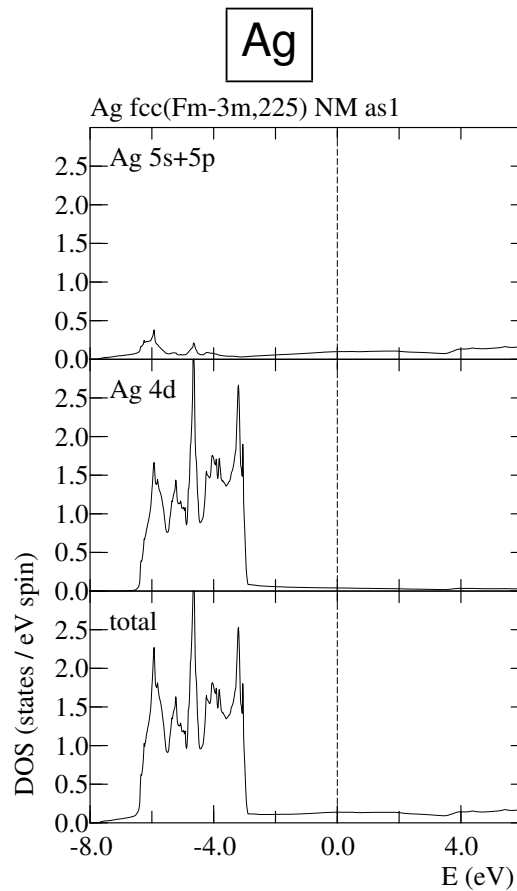
FeRu₁₅ FM

No magnetic solution

The Fe impurity in Ru is really nonmagnetic.

The LDA/GGA calculation works well.

3.3.4 Band structure calculation: Fe in Ag (fcc*8-bcc supercell)



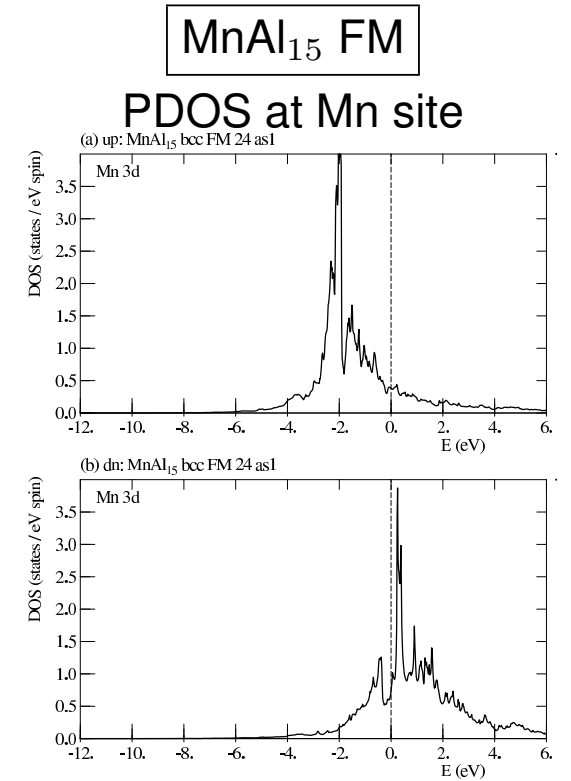
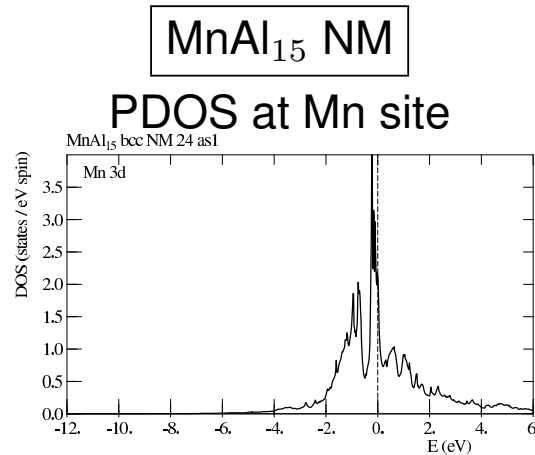
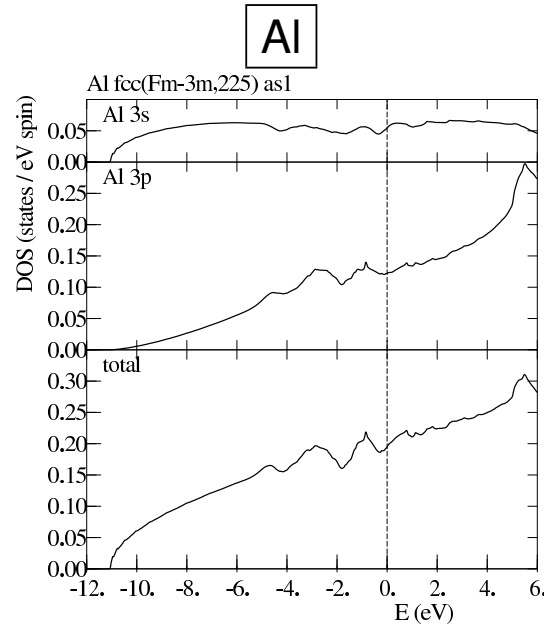
The LDA/GGA calculation has a magnetic solution.

The LDA/GGA calculation fails to predict the ground state.

At low temperatures $T \lesssim T_K$, the local moment disappears.

Kondo effect

3.3.5 Band structure calculation: Mn in Al (fcc*8-bcc supercell)



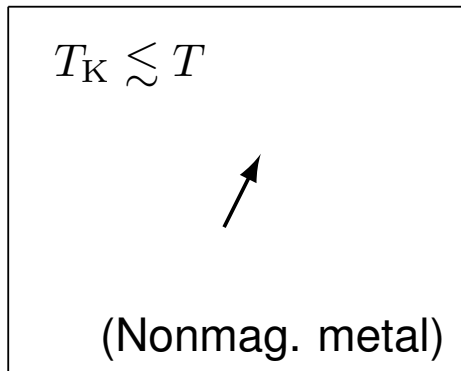
The LDA/GGA calculation has a magnetic solution.

Experimentally, the magnetic moment is not observed at the room temperature.

T_K may be much higher than the room temperature.

Kondo effect may be very popular.

4 Magnetic Impurity in nonmagnetic metal — Kondo effect —



(Example) Fe in Cu

At high temperatures

Susceptibility : Curie law

Local magnetic moment



At low temperatures

Susceptibility : → a constant

No local magnetic moment

Kondo effect

4.1 Anderson Model

Anderson Hamiltonian: ($n_\sigma = d_\sigma^\dagger d_\sigma$)

$$H = H_0 + H_d + H_U + H_V$$

$$H_0 = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}$$

$$H_d = \sum_{\sigma} \epsilon_d n_{\sigma}, \quad H_U = U n_{\uparrow} n_{\downarrow}$$

$$H_V = \frac{1}{\sqrt{N_A}} \sum_{\mathbf{k}\sigma} \{ V_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger d_{\sigma} + V_{\mathbf{k}}^* d_{\sigma}^\dagger c_{\mathbf{k}\sigma} \}$$

'Magnetic' impurity: $V_{\mathbf{k}} \ll U$

- Large U perturbation theory explains the Kondo effect (but, breaks down at $T \lesssim T_K$.)
- Perturbation theory from $U = 0$ is also needed.

4.2 Large-U perturbation theory

In the Anderson Hamiltonian,

- Unperturbed Hamiltonian: $H_0 + H_d + H_U$
Free electron ground state ('Fermi sea'): $|F\rangle$
Unperturbed ground states: $d_{\downarrow}^{\dagger} |F\rangle$, $d_{\uparrow}^{\dagger} |F\rangle$
- Perturbation Hamiltonian: H_V

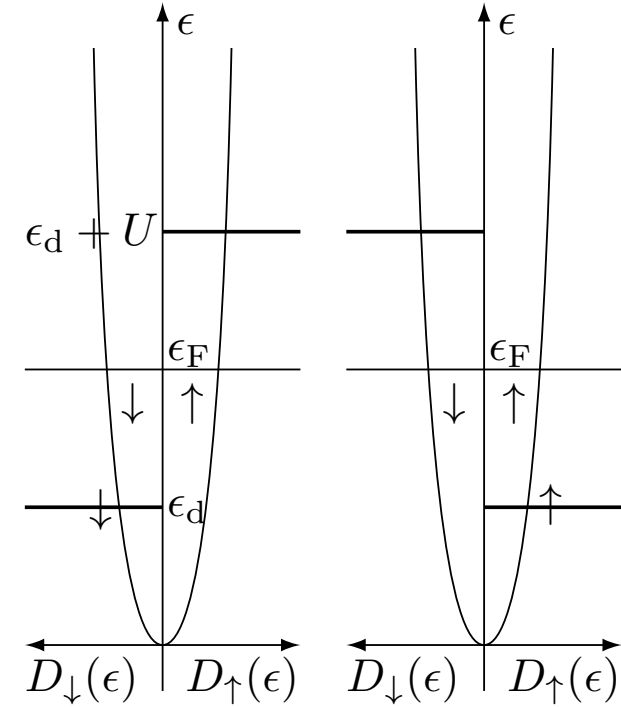
Assumption: $V_{k\sigma} = V \ll U$ or $\Delta = \pi V^2 D_c(\epsilon_F) \ll U$

$\Downarrow$ (2-nd order perturbation)

Effective Hamiltonian: $(\epsilon_d \sim -U/2)$

$$H_{\text{eff}} = H_0 + \frac{1}{N_A} \sum_{\mathbf{k}\mathbf{k}'\sigma} \frac{V^2}{2} \left(\frac{1}{-\epsilon_d} - \frac{1}{\epsilon_d + U} \right) c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}'\sigma} \\ + \frac{1}{N_A} \sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'} \frac{V^2}{2} \left(\frac{1}{-\epsilon_d} + \frac{1}{\epsilon_d + U} \right) c_{\mathbf{k}\sigma}^{\dagger} \boldsymbol{\sigma}_{\sigma\sigma'} c_{\mathbf{k}'\sigma'} \cdot \mathbf{S}$$

σ : conduction electron spin (Pauli matrix), $\mathbf{S}$: localized (d electron) spin



Unperturbed ground states

The first term = 0, when $\epsilon_d = -U/2$ (sym.A.M.)
(simple potential scattering = 0)

The second term:

(spin-flip scattering due to sd exchange)

⇓

Kondo (sd exchange) Hamiltonian

$$H_K = H_0 - \frac{J}{2N_A} \sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'} c_{\mathbf{k}\sigma}^\dagger \boldsymbol{\sigma}_{\sigma\sigma'} c_{\mathbf{k}'\sigma'} \cdot \mathbf{S}$$

$$J = -2V^2 \left(\frac{1}{-\epsilon_d} + \frac{1}{\epsilon_d + U} \right) = -\frac{8V^2}{U} < 0$$

Antiferromagnetic exchange interaction!

Due to spin-flip scattering, $R_i \rightarrow$ larger ($T \rightarrow +T_K$)

$|J_{\text{eff}}| \rightarrow$ larger (Creation of Kondo singlet)

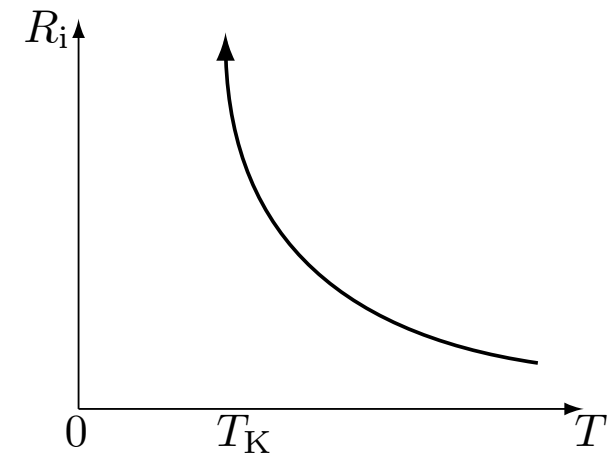
The large U perturbation expansion breaks down in $T \lesssim T_K$.

$$k_B T_K = W \exp \frac{1}{JD_c(\epsilon_F)} = W \exp \frac{-\pi U}{8\Delta} \quad (11)$$

Resistivity by magnetic impurities
(sum of the most divergent terms):

$$R_i(T) = \frac{R_B}{\left(1 - JD_c(\epsilon_F) \ln \frac{k_B T}{W}\right)^2} \quad (9)$$

$2W =$ conduction band width (10)



4.3 Perturbation theory from $U = 0$

Unperturbed system: $U = 0$

No local magnetic moment

"Fermi liquid"

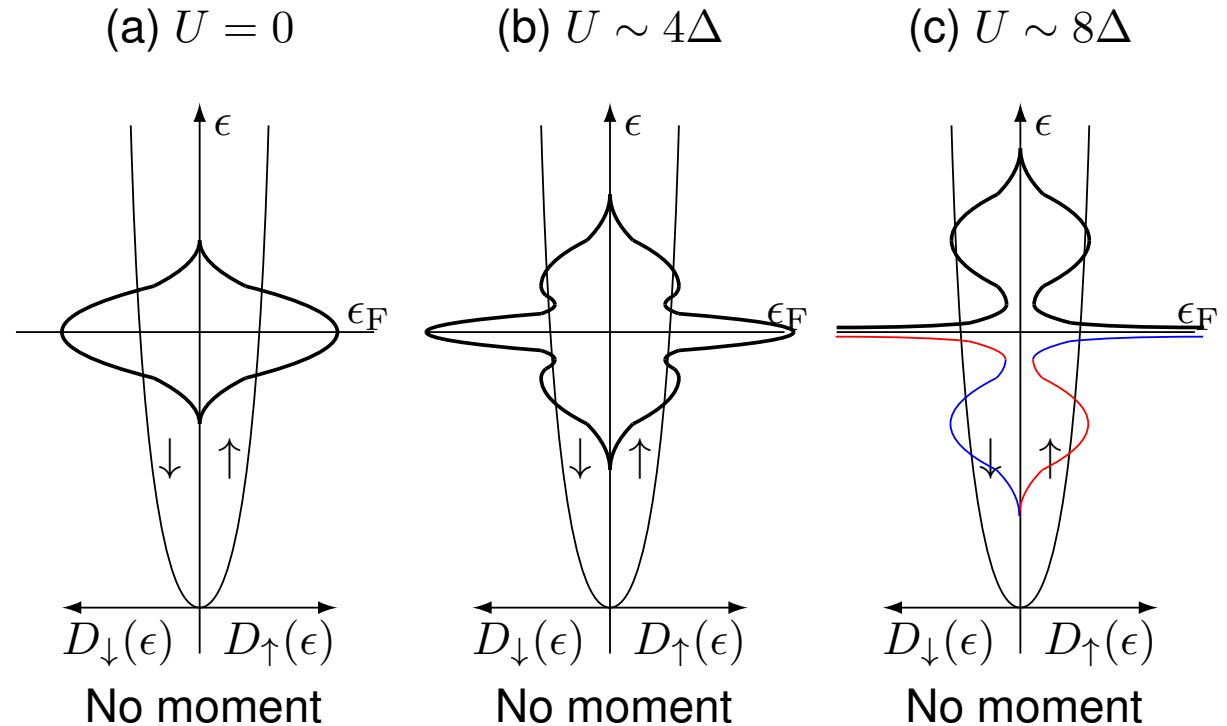
Perturbation: $H' = U n_{\uparrow} n_{\downarrow}$

↓ (even if $U \rightarrow \infty$)

No local moment state is kept.

"Kondo singlet"

This has the property of the "Fermi liquid".

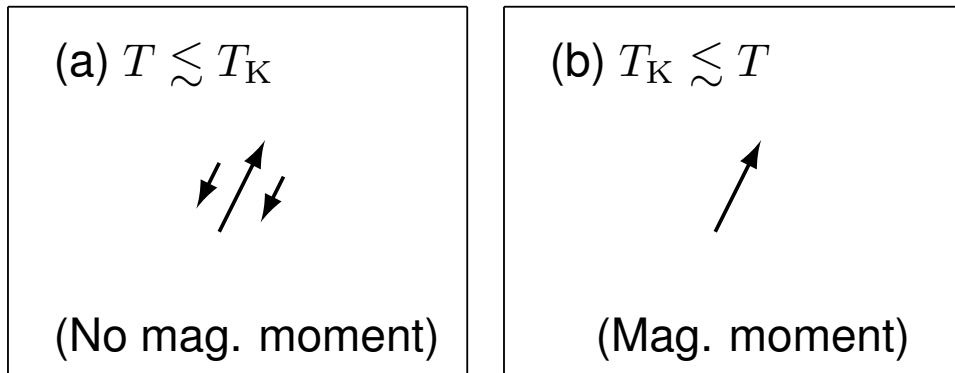


DFT must describe this "Fermi liquid" state (ground state).

But usual approximation (LDA, GGA, ...) may not describe the state appropriately.

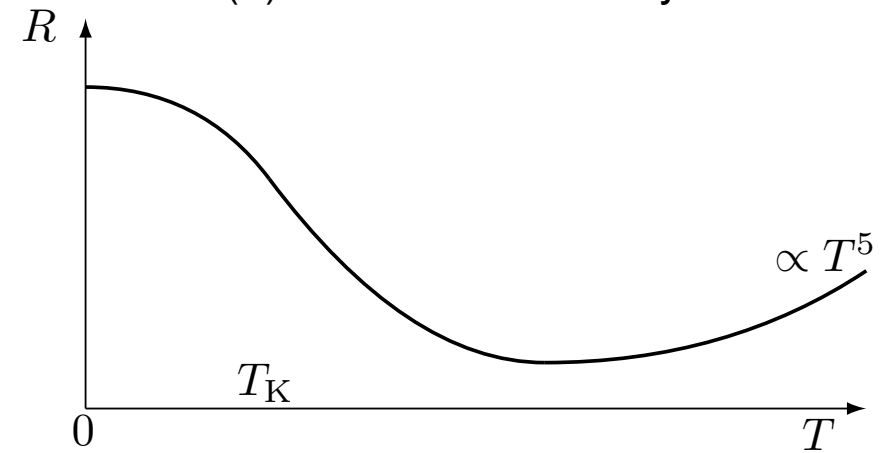
$$E(\text{Kondo}) < E(\text{M}) \ll E(\text{NM}); \quad E(\text{Kondo}) - E(\text{M}) \approx -k_B T_K$$

4.4 Summary

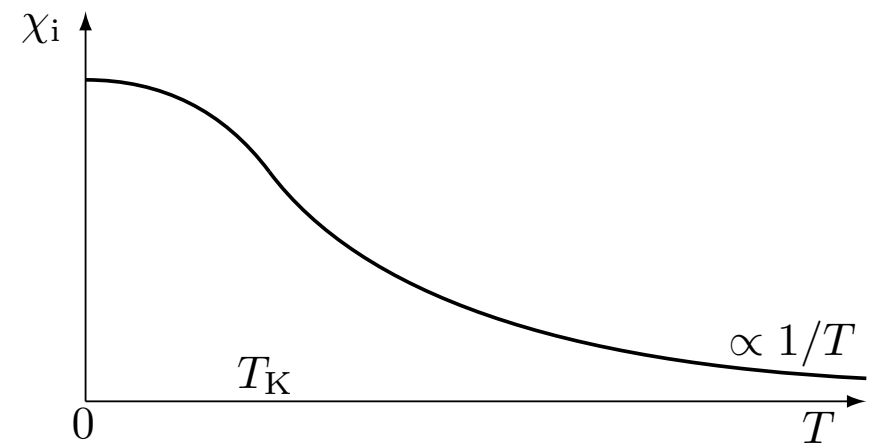


Kondo singlet

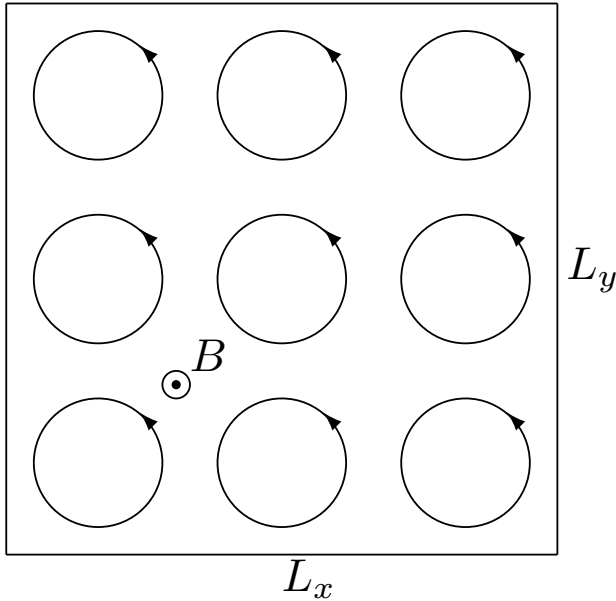
(a) Electrical resistivity



(b) Magnetic susceptibility by the impurity



5 Free electron under the uniform magnetic field



(Classical picture)

Eq. of motion: $m \frac{v^2}{r} = evB$

$\omega_c = \frac{v}{r} = \frac{eB}{m}$

 : cyclotron frequency

v, r : arbitrary

When $B = 1 \text{ T}$,

$$\omega_c \approx 1.8 \times 10^{11} \text{ rad} \cdot \text{s}^{-1}, \quad \hbar \omega_c \approx 1.2 \text{ meV}$$

5.1 Landau level

(Quantum mechanical treatment)

Magnetic field: $\mathbf{B} = (0, 0, B) = \text{rot} \mathbf{A}$

Vector potential: $\mathbf{A} = \left(-\frac{By}{2}, \frac{Bx}{2}, 0 \right)$

Free electron system:

$$H = \frac{1}{2m} \left[\left(p_x - \frac{eBy}{2} \right)^2 + \left(p_y + \frac{eBx}{2} \right)^2 + p_z^2 \right]$$

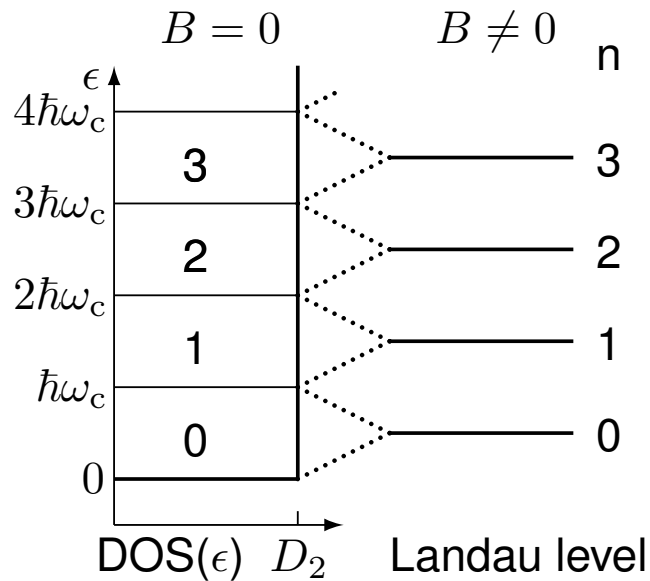
Eigenenergy:

$$\epsilon_n(k_z) = \hbar \omega_c \left(n + \frac{1}{2} \right) + \frac{\hbar^2 k_z^2}{2m}$$

$$n = 0, 1, 2, \dots, \quad k_z = \frac{2\pi}{L_z} n_z \quad (n_z = \text{integer})$$

n : Landau level index

2-D free-electron system



Density of states (per unit area) : $D_2 = \frac{m}{2\pi\hbar^2}$

The **degeneracy of Landau level (per unit area)**:

$$N(B) = \hbar\omega_c D_2 = \frac{eB}{h} = \frac{B}{\phi_0} = \frac{1}{2\pi l^2} \quad (12)$$

(macroscopic number!)

$\phi_0 = \frac{h}{e}$: magnetic flux quantum

$l = \sqrt{\frac{\hbar}{eB}}$: cyclotron radius

- The spin of electron is ignored, here.

"**Spinless fermion**"

- N_e : the electron density [/ unit area]

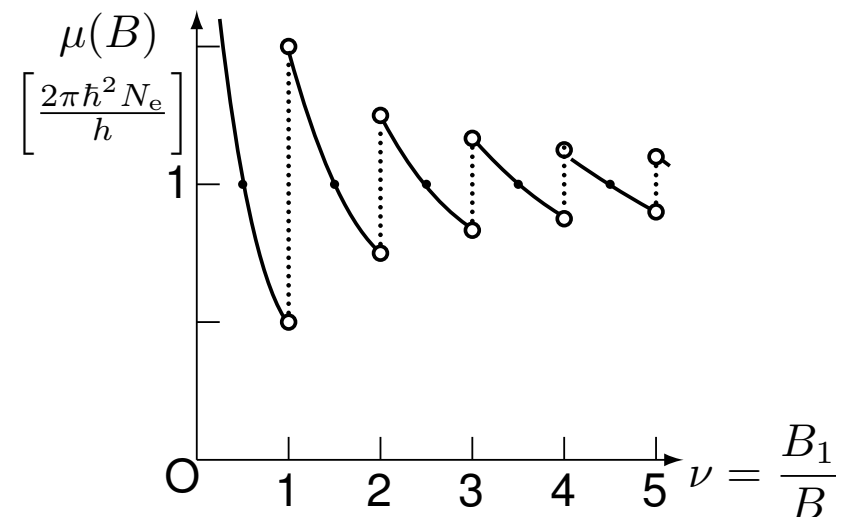
" $N_e = \text{constant}$ " is assumed, here.

- Filling factor** of Landau level:

$$\nu = \frac{N_e}{N(B)} = \frac{B_1}{B}$$

- B_1 (def.): $N(B_1) = N_e \rightarrow B_1 = N_e \phi_0$

Chemical potential:



5.2 The electron motion in the k and the r spaces – Semiclassical description –

Band electron in $B = 0$: (Bloch state) $|\psi_{\mathbf{k}}\rangle$

$$\langle \mathbf{r} | \psi_{\mathbf{k}} \rangle = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \quad (= e^{i\mathbf{k} \cdot \mathbf{r}}) \quad (13)$$

$$\varepsilon = \varepsilon(\mathbf{k}) \quad \left(= \frac{\hbar^2}{2m} \mathbf{k}^2 \right) \quad (14)$$

[1] Velocity in the real space:

$$\mathbf{v} \equiv \dot{\mathbf{r}} = \langle \psi_{\mathbf{k}} | \frac{d\mathbf{r}}{dt} | \psi_{\mathbf{k}} \rangle = \frac{1}{\hbar} \nabla_{\mathbf{k}} \varepsilon(\mathbf{k}) \quad (15)$$

[2] Equation of motion in the k space

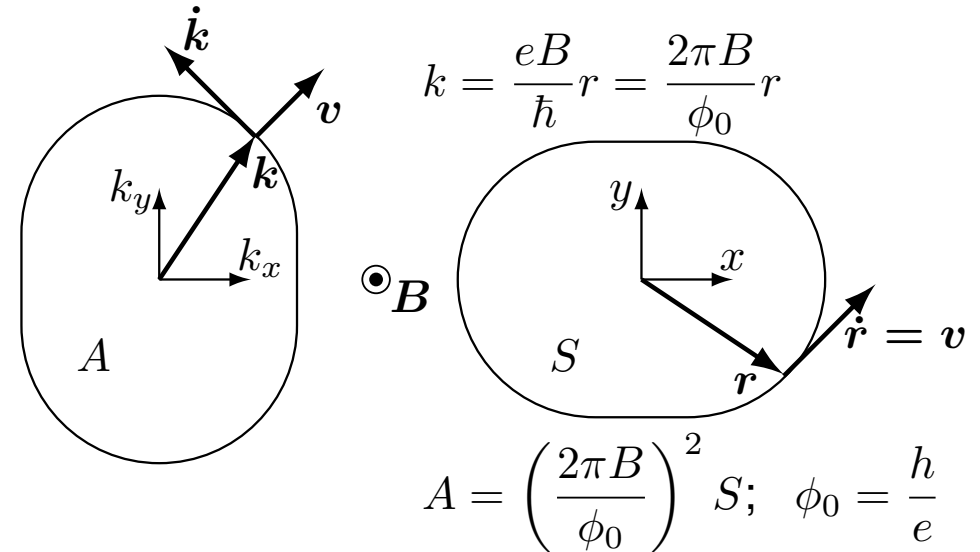
$$\hbar \dot{\mathbf{k}} \equiv \hbar \frac{d\mathbf{k}}{dt} = -e\mathbf{v} \times \mathbf{B} \quad (16)$$

B : no work to the electron

k moves on the equienergy surface.

For 2D system, Eq. (16) :

$$\dot{k} = -\frac{eB}{\hbar}\dot{r} \quad (17)$$



The energy surface is quantized in $B \neq 0$:

$$\varepsilon_n = \hbar\omega_c (n + \lambda) \quad (n = 0, 1, 2, \dots) \quad (18)$$

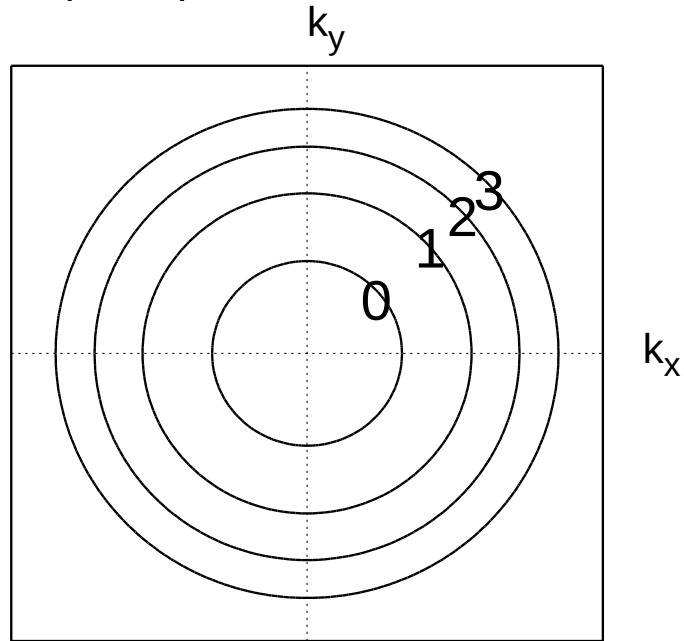
$$A_n = \frac{4\pi^2 B}{\phi_0} (n + \lambda) \quad (19)$$

$$S_n = \frac{\phi_0}{B} (n + \lambda) \quad (20)$$

where λ depends on the band structure.

2-D free-electron system ($B \neq 0$)

k-space picture

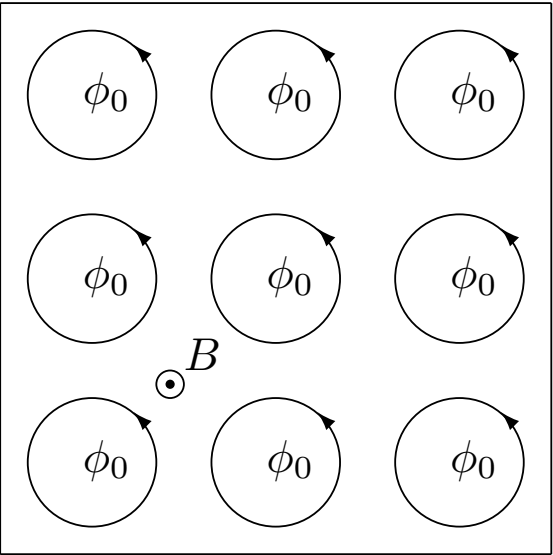


Landau loop (tube)

degeneracy: $N(B)$

r-space picture

for each Landau level



$$B = N(B)\phi_0$$

5.3 Quantum Hall effect (2D)

For the electric field $E_x \neq 0$ and $E_y = 0$, the center of the cyclotron motion moves in the $-y$ direction with the velocity $u_y = -\frac{E_x}{B}$, which causes the Hall current density

$$j_y = -eu_y N_e = \frac{eN_e}{B} E_x ,$$

where N_e is the total electron number per unit area.

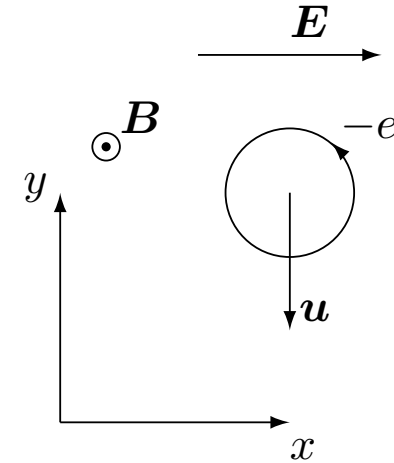
The Hall conductivity is

$$\sigma_{yx} = \frac{j_y}{E_x} = \frac{eN_e}{B} = \frac{eB_1}{\phi_0 B} = \frac{e^2}{h} \frac{B_1}{B} , \quad (21)$$

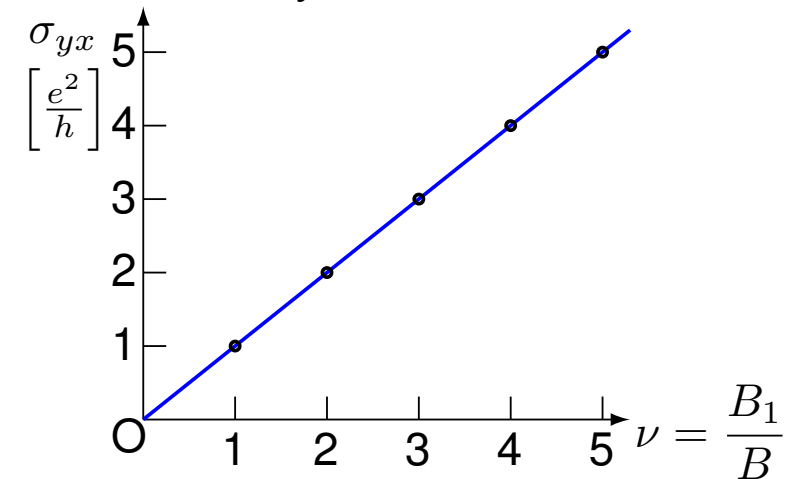
where $\frac{B_1}{B}$ is the filling factor of Landau level, ν :

$$\sigma_{yx} = \frac{e^2}{h} \nu . \quad (22)$$

The system is insulating, when $\nu = \text{integer}$.

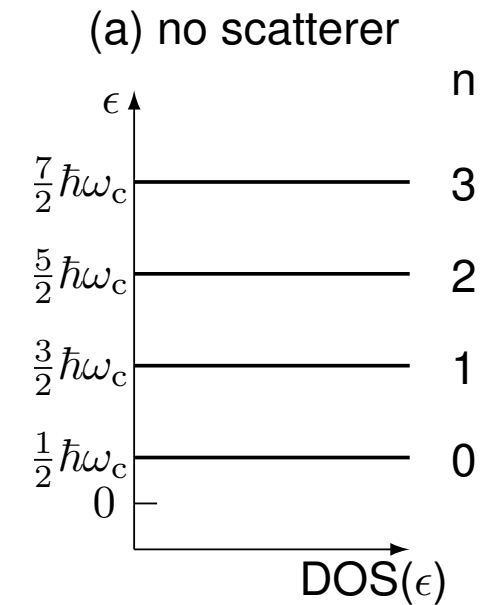


Hall conductivity with **no scatterer**



5.3.1 Effect of random scatterers

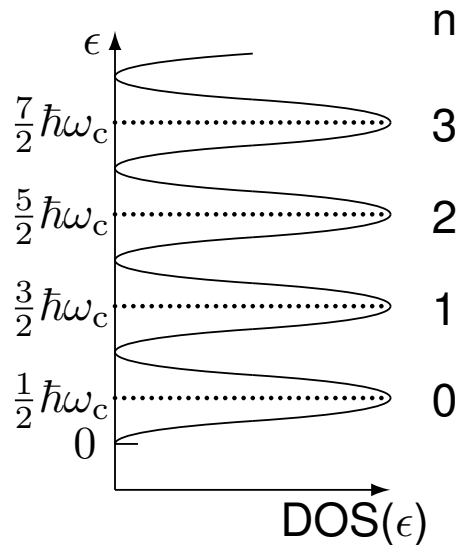
$$\sigma_{yx} = \frac{e^2}{h} \nu \quad (\nu : \text{filling factor of extended state})$$



All states are extended.

$$\nu = \frac{B_1}{B}$$

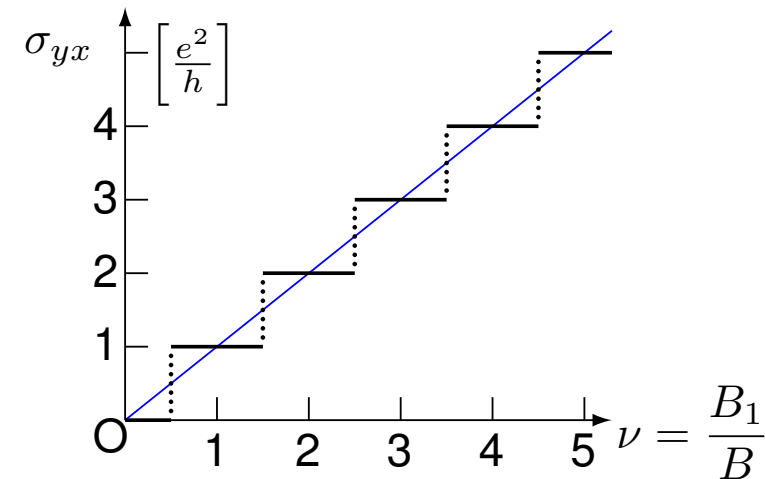
(b) strong random scatterers



The most states are localized.
Only central states are extended.

$$\nu = \sum_{n=0}^{\infty} \theta \left(\frac{B_1}{B} - \left(n + \frac{1}{2} \right) \right)$$

(c) Hall conductivity



- Chern number of the n -th Landau level:

$$C_n = +1 \quad (n = 0, 1, 2, \dots) \quad (23)$$

- Only the band consisting of extended states can carry the Chern number, which is preserved by the topology of the system.

Hall conductivity of the insulator is

$$\sigma_{yx} = \frac{e^2}{h} \sum_n^{\text{filled}} C_n . \quad (24)$$