

Magnetism of Metals (金属磁性)

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Magnetism of Conduction electron 1 (伝導電子の磁性 1)

Pauli susceptibility (金属常磁性)

Magnetic Impurity in nonmagnetic material (磁性不純物)

Kondo effect 近藤効果

Interaction between atomic magnetic moments

Ferromagnetic or Antiferromagnetic? 強磁性・反強磁性?

Magnetic Alloy (磁性合金)

Magnetism of Conduction electron 2 (伝導電子の磁性 2)

Landau 反磁性, de Haas - van Alphen 効果

quantum Hall effect (2D)

(参考文献)

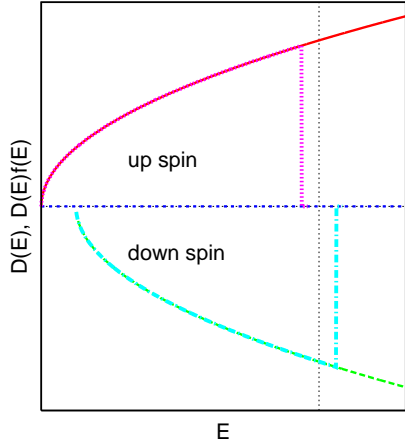
- (1) 金森順次郎著「磁性」(培風館, 1969)
- (2) 斯波弘行著「基礎の固体物理学」(培風館, 2007)
- (3) 斯波弘行著「固体の電子論」(丸善, 1996)
- (4) J. R. Hook & H. E. Hall「Solid State Physics (2nd ed.)」(Wiley, 1991)

(S.I.)

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

1 Paramagnetism in nonmagnetic metal (金属常磁性)

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



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

$$M = \mu_B B \times D(E_F) \times 2 \times \mu_B$$

Paramagnetic susceptibility

in the noninteracting electrons :

$$\chi_0 = \frac{\mu_0 M}{B} = 2\mu_0 \mu_B^2 D(E_F)$$

χ_0 can be obtained by the band structure calculation.

The susceptibility is enhanced, for example,

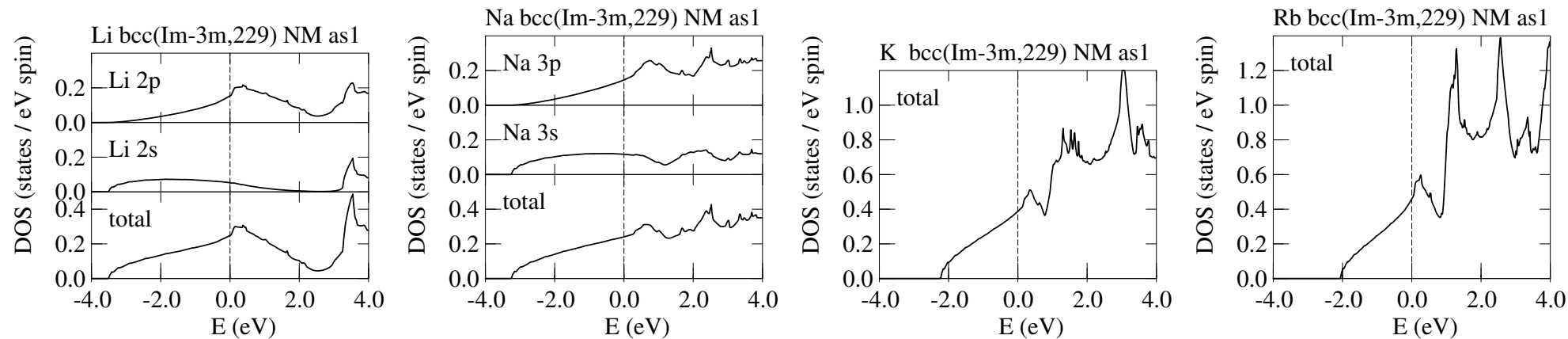
$$\chi_P = \frac{\chi_0}{1 - I\chi_0}$$

due to the electron-electron interaction.

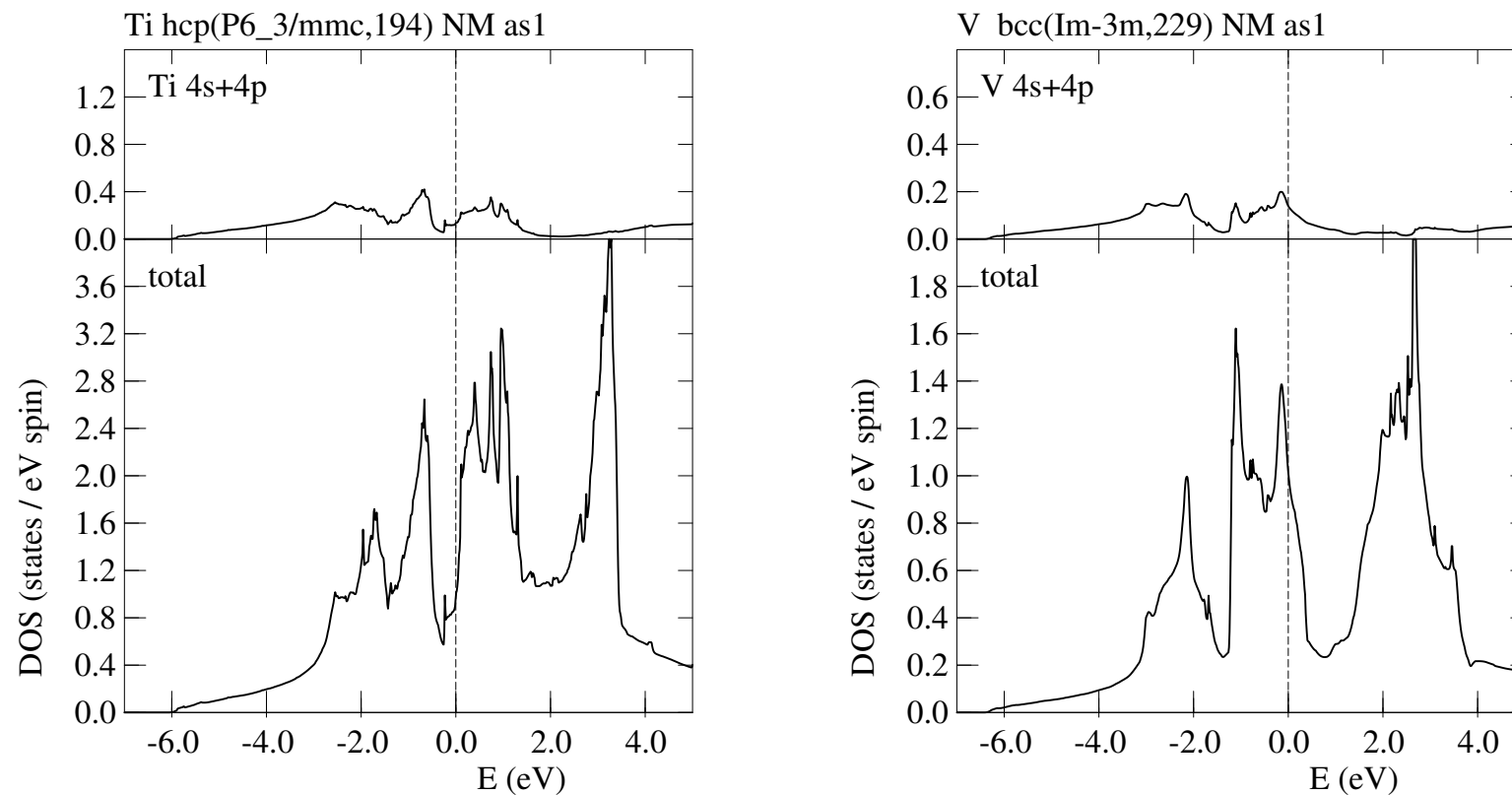
Metal	$\chi/10^{-5}$		
	Free el. χ_0	Band cal. χ_0	exp. χ_P
Li	1.01	1.65	2.5
Na	0.83	0.86	1.4
K	0.67	0.72	1.1
Rb	0.63	0.70	1.0
Ti		3.8	18.1
V		9.9	34.6

The temperature-independent susceptibility is treated as the Pauli susceptibility.

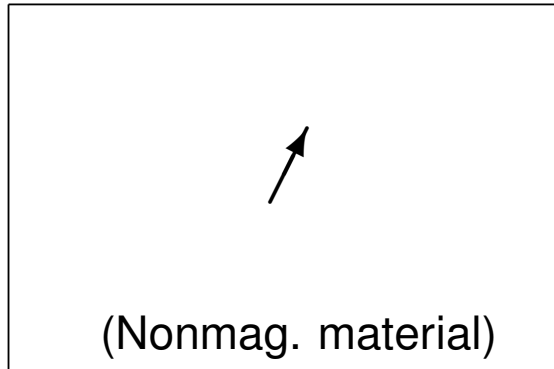
Alkali metals



3d-Transition metals



2 Magnetic Impurity in Nonmagnetic Material



(Example) Fe in Mo

2.1 Anderson Model

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

$$H = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \sum_{\sigma} \epsilon_d n_\sigma + U n_\uparrow n_\downarrow + \frac{1}{\sqrt{N_A}} \sum_{\mathbf{k}\sigma} \{ V_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger d_\sigma + V_{\mathbf{k}}^* d_\sigma^\dagger c_{\mathbf{k}\sigma} \}$$

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

Is the system "magnetic" or "nonmagnetic"?

2.1.1 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 $\langle n_\downarrow \rangle$

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

Virtual bound state

Partial DOS of d state:

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

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

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

2.2 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,

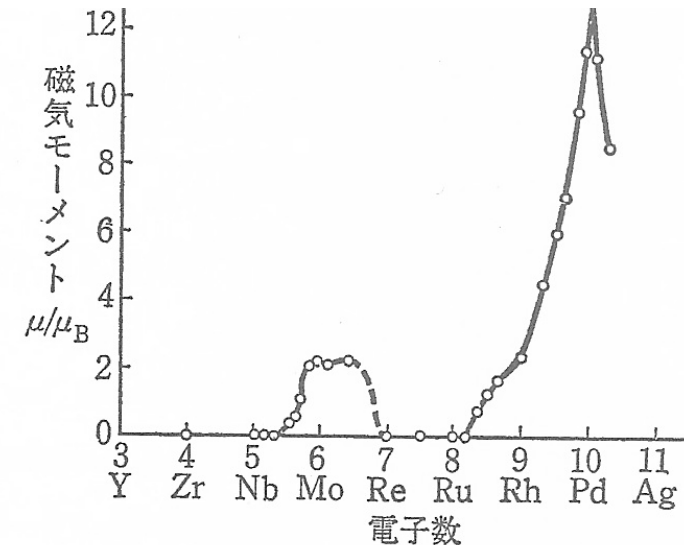
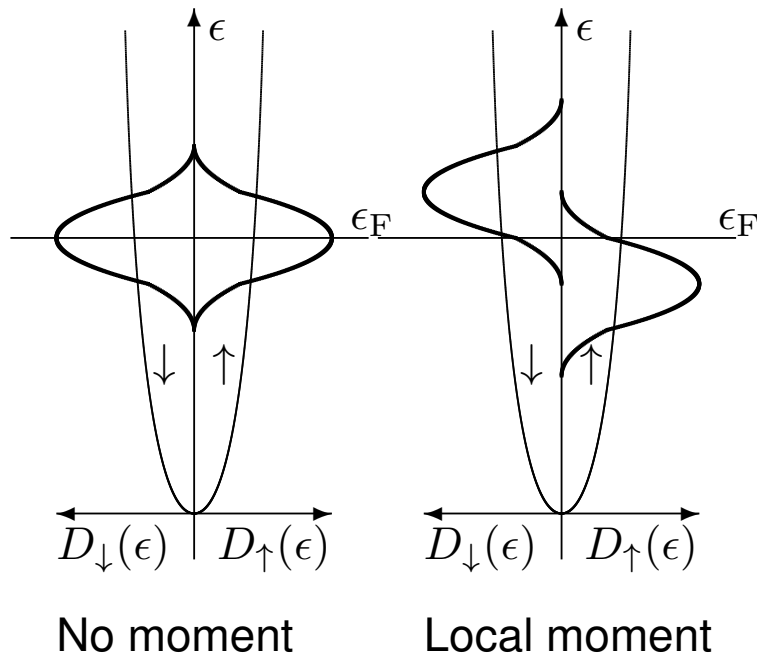


図 11-11 1% Fe を含む合金での Fe の磁気モーメント (Clogston et al)



Virtual bound state

(parameters: E_d, U, Δ)

Starting with no magnetic moment,

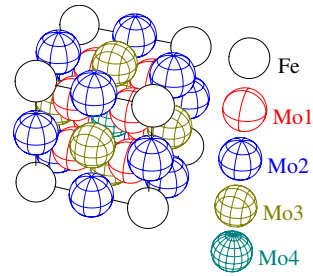
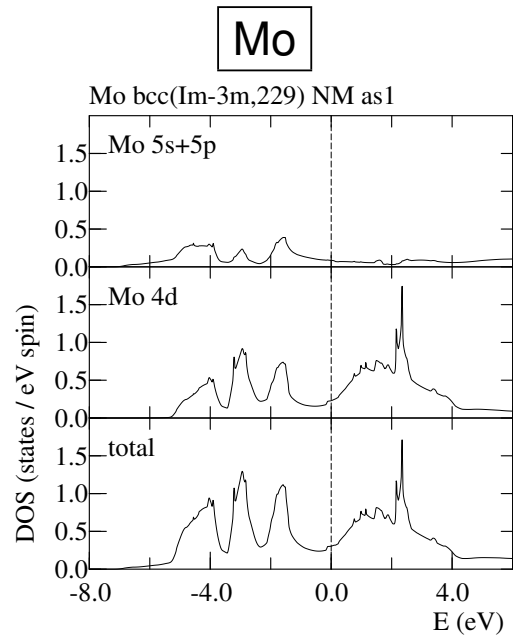
$$D_d(\epsilon_F) \equiv D_{d\uparrow}(\epsilon_F) = D_{d\downarrow}(\epsilon_F)$$

Appearance of local moment:

$$UD_d(\epsilon_F) > 1$$

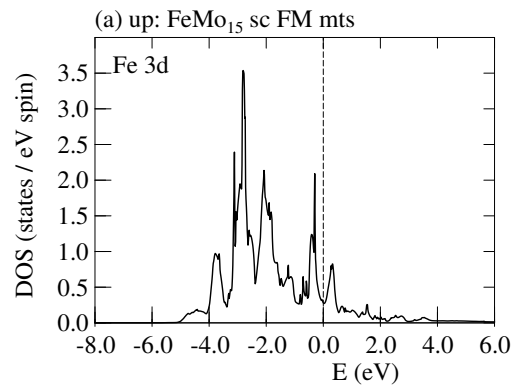
The Fe magnetic moment induces large moment at surrounding Pd atoms.

2.2.1 Band structure calculation: Fe in Mo

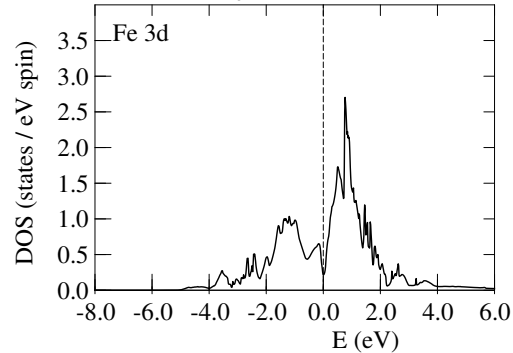


FeMo₁₅ FM

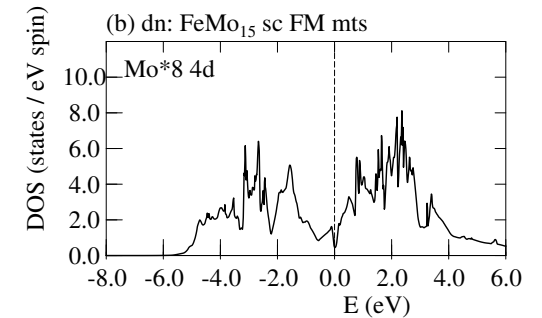
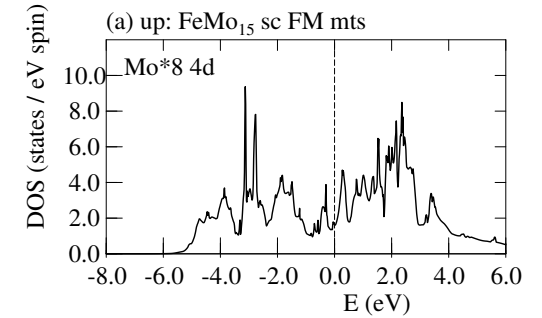
PDOS at Fe site



(b) dn: FeMo₁₅ sc FM mts

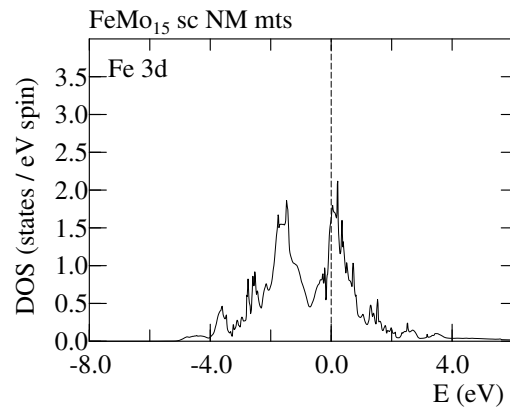


PDOS at Mo1 site



FeMo₁₅ NM

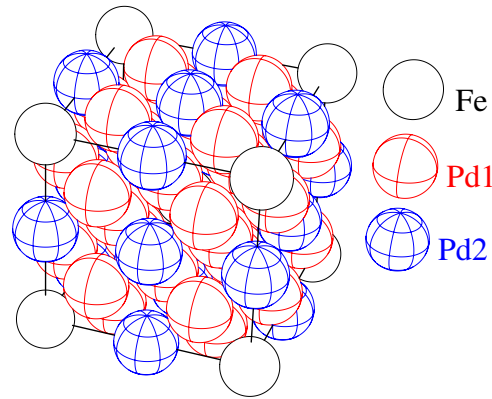
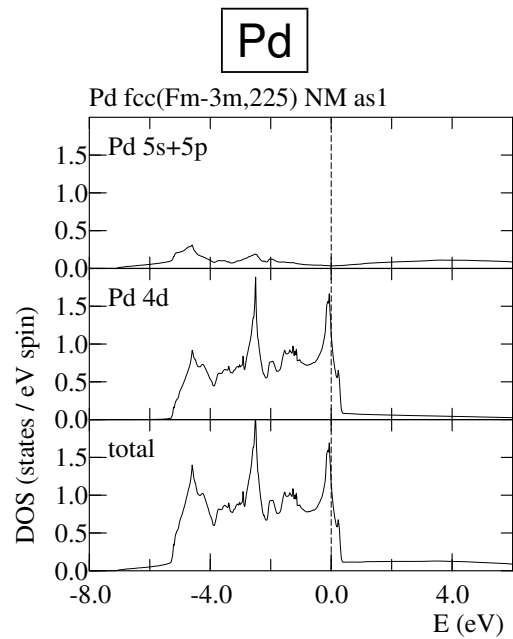
PDOS at Fe site



Magnetic moment [μ_B]

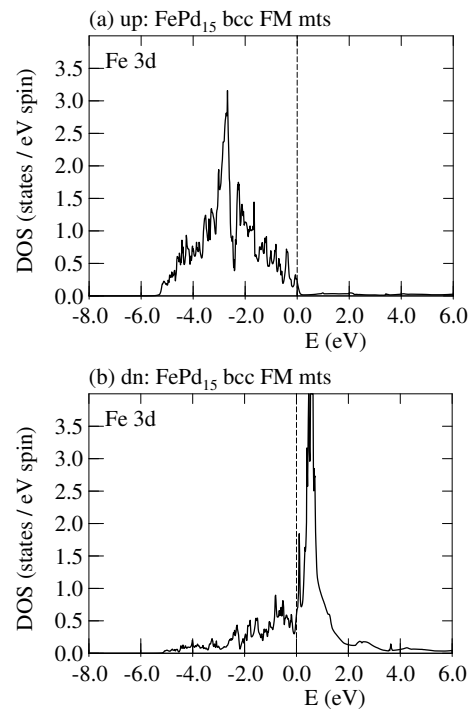
Total	Fe	Mo1	Mo2
2.08	2.12	-0.01	0.02

2.2.2 Band structure calculation: Fe in Pd

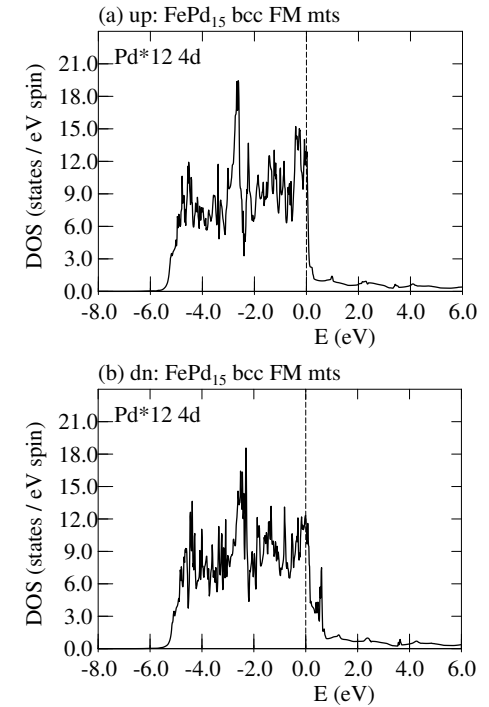


FePd₁₅ FM

PDOS at Fe site

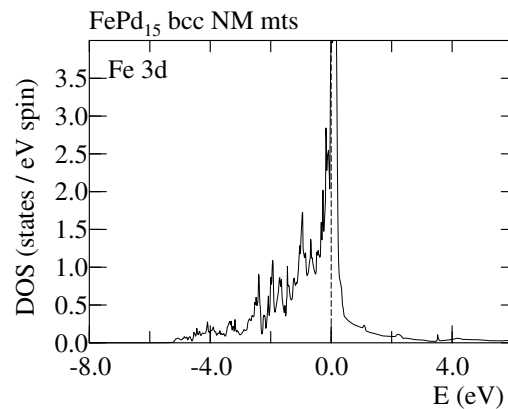


PDOS at Pd1 site



FePd₁₅ NM

PDOS at Fe site



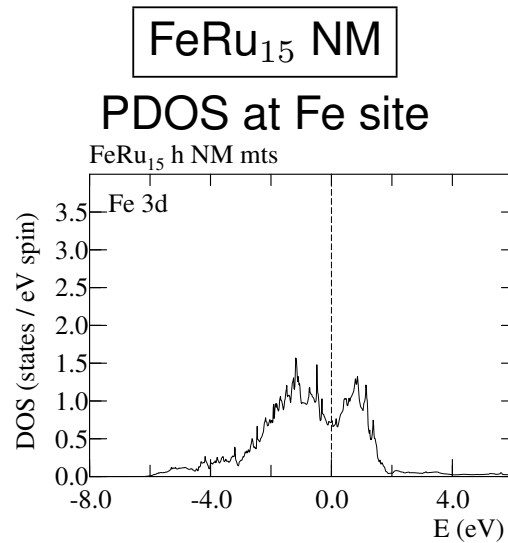
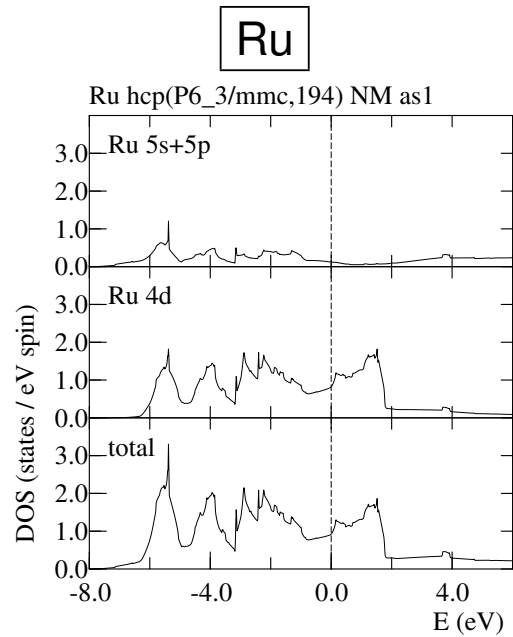
Magnetic moment [μ_B]

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.

2.2.3 Band structure calculation: Fe in Ru



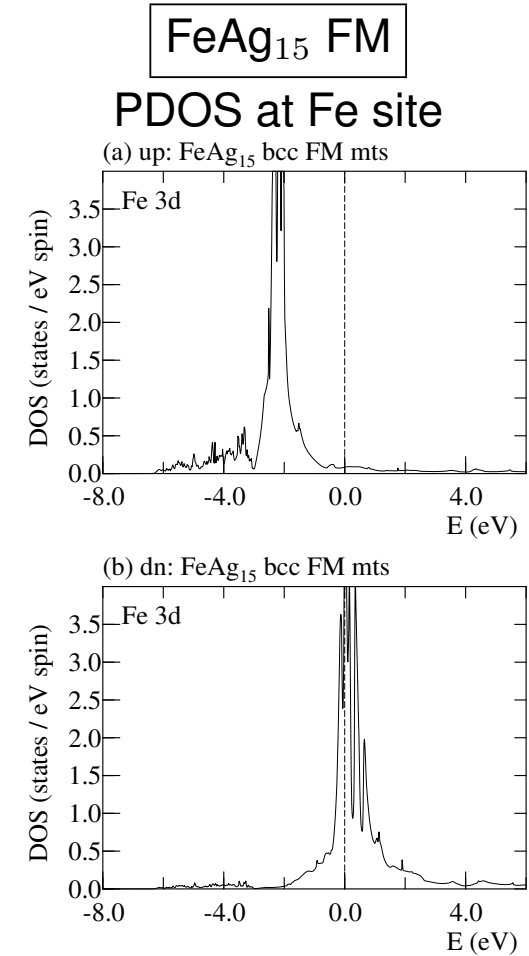
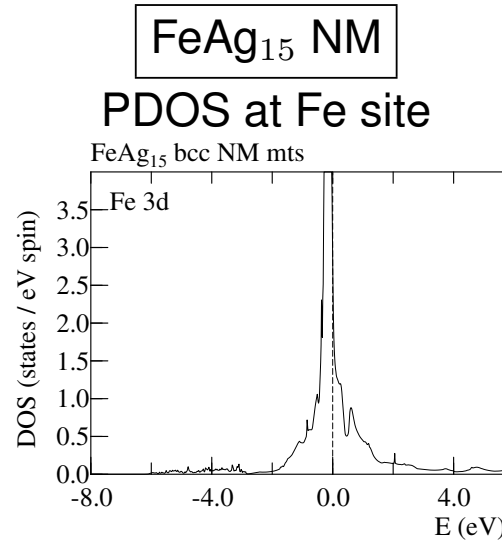
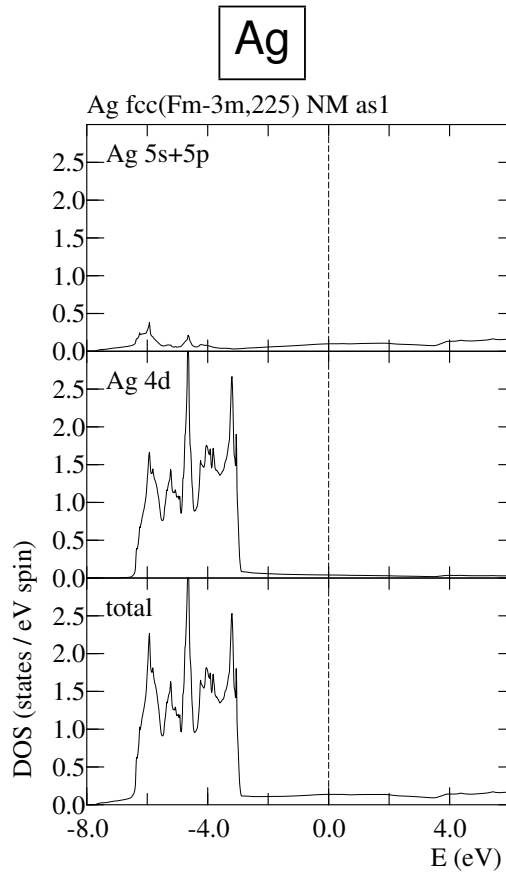
FeRu₁₅ FM

No magnetic solution

The Fe impurity in Ru is really nonmagnetic.

The LDA/GGA calculation works well.

2.2.4 Band structure calculation: Fe in Ag



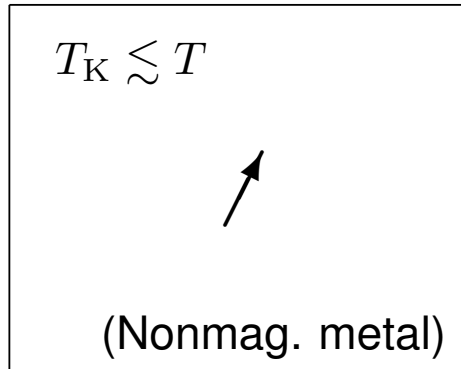
The LDA/GGA calculation has a magnetic solution.

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

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

Kondo effect

3 Magnetic Impurity in nonmagnetic metal (Kondo effect: $T \lesssim T_K$)



(Example) Fe in Cu

At high temperatures

Susceptibility : Curie law

Local magnetic moment



At low temperatures

Susceptibility : → a constant

No local moment

Kondo singlet state

Kondo effect

3.1 Anderson Model

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

$$H = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \sum_{\sigma} \epsilon_d n_\sigma + U n_\uparrow n_\downarrow + \frac{1}{\sqrt{N_A}} \sum_{\mathbf{k}\sigma} \{ V_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger d_\sigma + V_{\mathbf{k}}^* d_\sigma^\dagger c_{\mathbf{k}\sigma} \}$$

For a "magnetic" impurity:

$$V_{\mathbf{k}} \ll U$$



Large U perturbation theory breaks down at low temperatures.

$$(T \lesssim T_K)$$

3.2 Large-U perturbation theory

$|F\rangle$: Free electron ground state ('Fermi sea')

Unperturbed ground states:

$$d_{\downarrow}^{\dagger} |F\rangle, \quad d_{\uparrow}^{\dagger} |F\rangle$$

Perturbation term in Anderson Hamiltonian

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

Approximations:

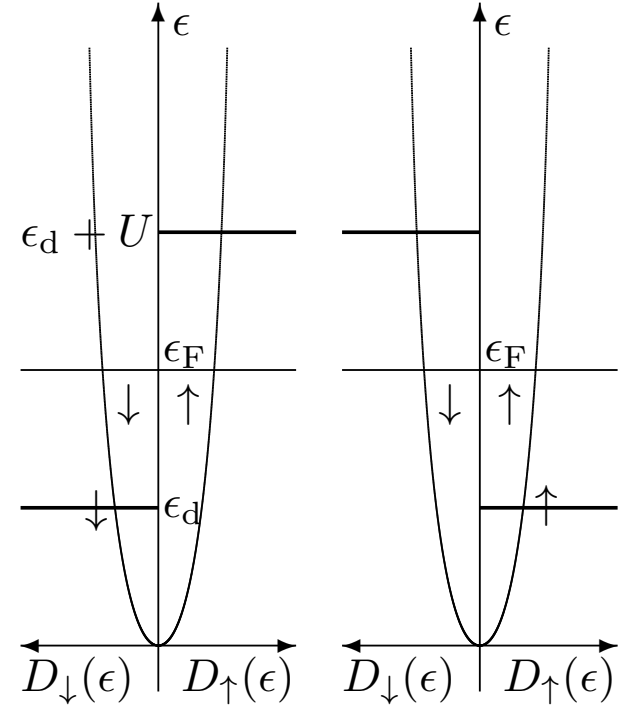
$$\boxed{\begin{aligned} V_{\mathbf{k}\sigma} &= V \quad (\ll U) \\ \epsilon_{\mathbf{k}\sigma} &\sim \epsilon_F = 0 \end{aligned}}$$

↓ (2-nd order perturbation)

Effective Hamiltonian:

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

$$\epsilon_d < 0, \quad -\epsilon_d \sim \epsilon_d + U > 0$$



Unperturbed system

The first term = 0, when $-\epsilon_d = \epsilon_d + U$,

The second term:

(spin-flip scattering of conduction electron)

$$H_K = -\frac{J}{2N_A} \sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'} c_{\mathbf{k}\sigma}^\dagger \boldsymbol{\sigma}_{\sigma\sigma'} c_{\mathbf{k}'\sigma'} \cdot \mathbf{S}$$
$$J = -2V^2 \left(\frac{1}{-\epsilon_d} + \frac{1}{\epsilon_d + U} \right) = -\frac{8V^2}{U} < 0$$

Kondo model

Antiferromagnetic exchange interaction

Local spin S attracts antiparallel conduction spin σ .

\Rightarrow **Kondo singlet** at low temperatures ($T \lesssim T_K$)

Kondo temperature : T_K (W : conduction band width)

Scaling (renormalization of J) theory gives

$$k_B T_K \sim W \exp \frac{1}{JD(\epsilon_F)}$$

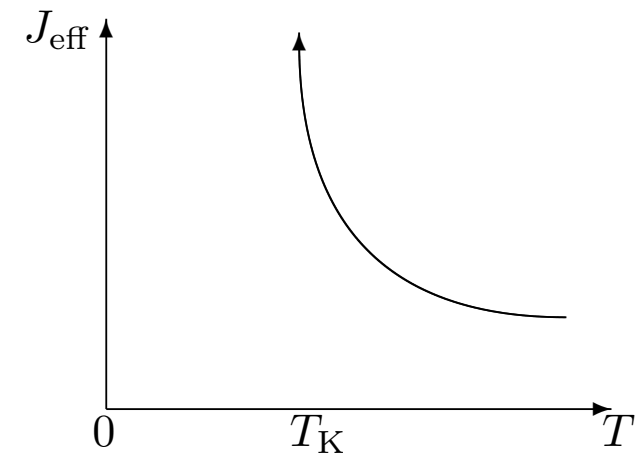
Scaling theory:

$|J_{\text{eff}}| \rightarrow \text{larger}$ ($T \rightarrow \text{lower}$)

$J_{\text{eff}} \rightarrow -\infty$ ($T \rightarrow T_K + 0$)

Kondo singlet state is created.

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



3.3 Perturbation theory from $U = 0$

Unperturbed system: $U = 0$

No local magnetic moment

"Fermi liquid"

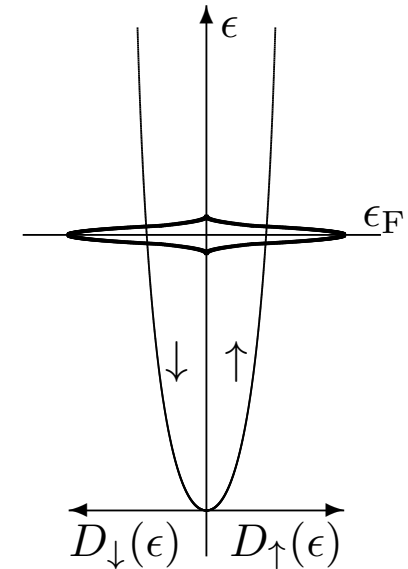
Perturbation: $H' = U n_{\uparrow} n_{\downarrow}$

↓ (even if $U \rightarrow \infty$)

No local moment state is kept.

"Kondo singlet"

This has the property of the "Fermi liquid".



No moment

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

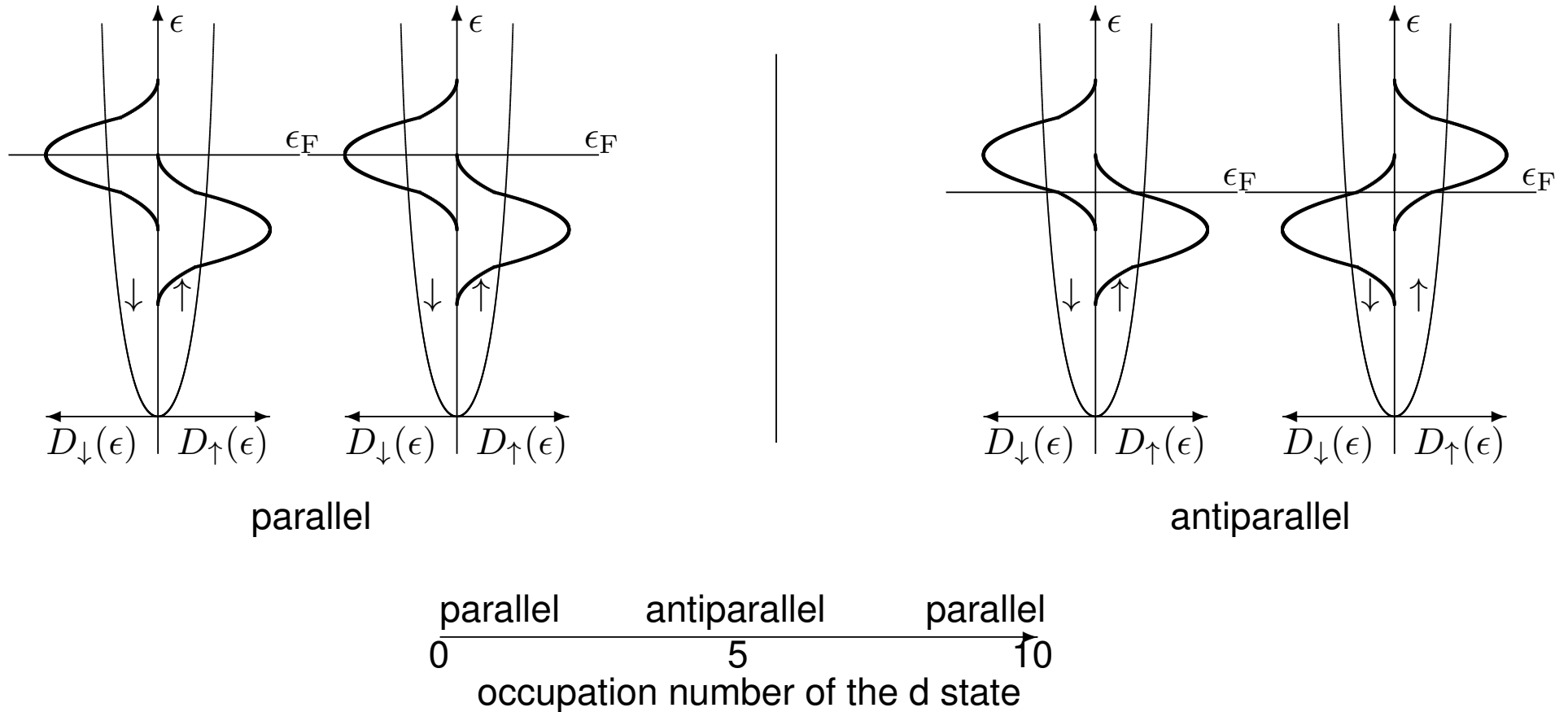
But usual approximation (LDA, GGA, ...) may not express the state appropriately.

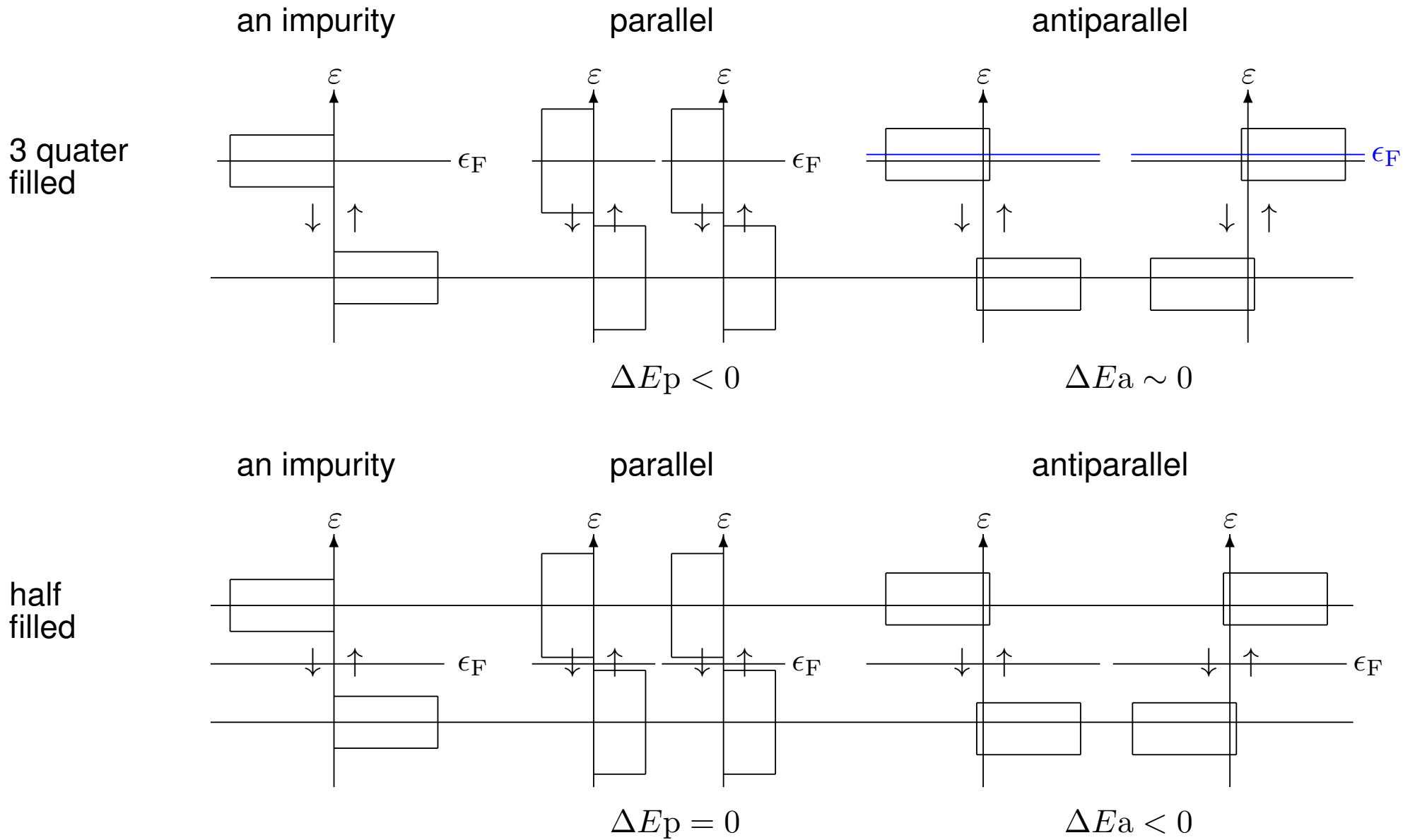
$$E(\text{Kondo}) < E(\text{M}) \ll E(\text{NM}); \quad E(\text{Kondo}) - E(\text{M}) \approx k_B T_K$$

4 Magnetic Interaction between Atomic Moments

4.1 A pair of magnetic atoms

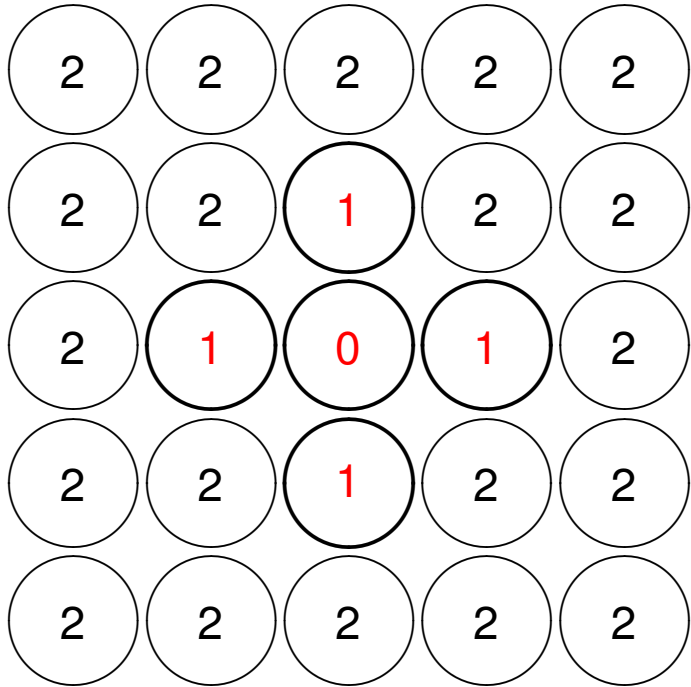
Virtual bound state (parameters: E_d, U, Δ)





The covalent-bond concept is useful for understanding the magnetic interaction.

4.2 Neighbor shells



0: the center, 1: the first neighbors

2: others

4.3 Nonlocal susceptibility

Example) 3d transition metals

Magnetic structure?

- ferromagnetic: Fe, Co, Ni
- antiferromagnetic: Cr, Mn
(spin density wave, etc.)

Local susceptibility: $\chi_{00}(\epsilon_F) = \frac{M_0}{H_0}$

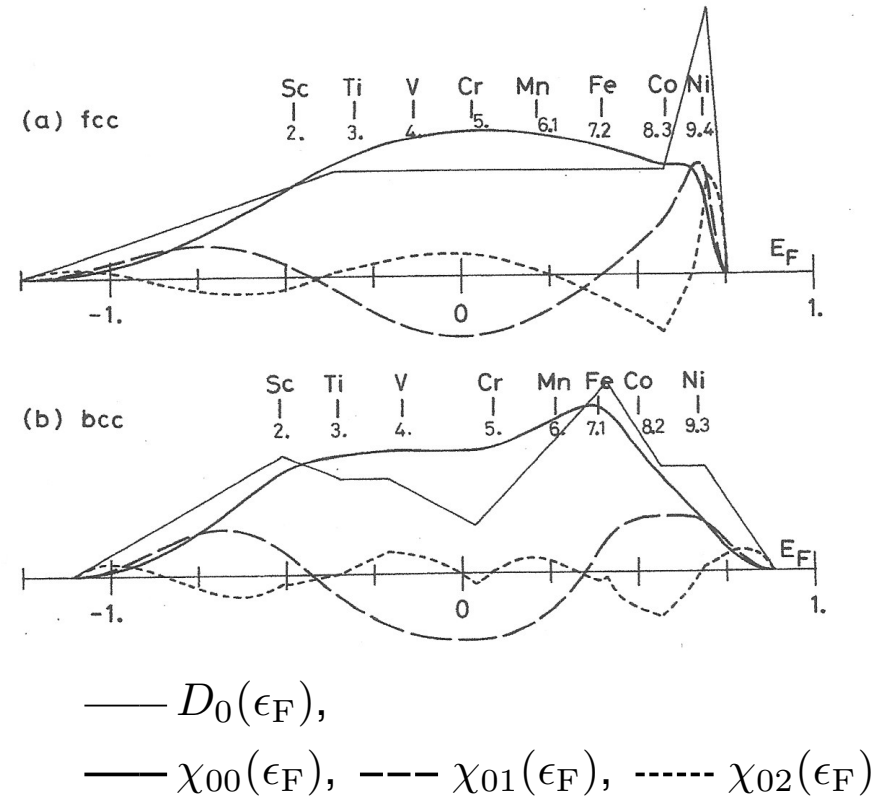
Nonlocal susceptibilities:

$$\chi_{01}(\epsilon_F) = \frac{M_0}{H_1}, \quad \chi_{02}(\epsilon_F) = \frac{M_0}{H_2}$$

PDOS at the center:

$$D_0(\epsilon_F) = \chi_{00}(\epsilon_F) + \chi_{01}(\epsilon_F) + \chi_{02}(\epsilon_F)$$

Local and non-local susceptibilities



$$\chi_{01} > 0 \text{ (FM) for } n_d \lesssim 3 \text{ or } n_d \gtrsim 7$$

$$\chi_{01} < 0 \text{ (AFM) for } 3 \lesssim n_d \lesssim 7$$

The trend is similar for other lattices, although n_d is shifted.

5 Magnetic Alloys (磁性合金)

3d transition-metal alloys

Slater-Pauling curve

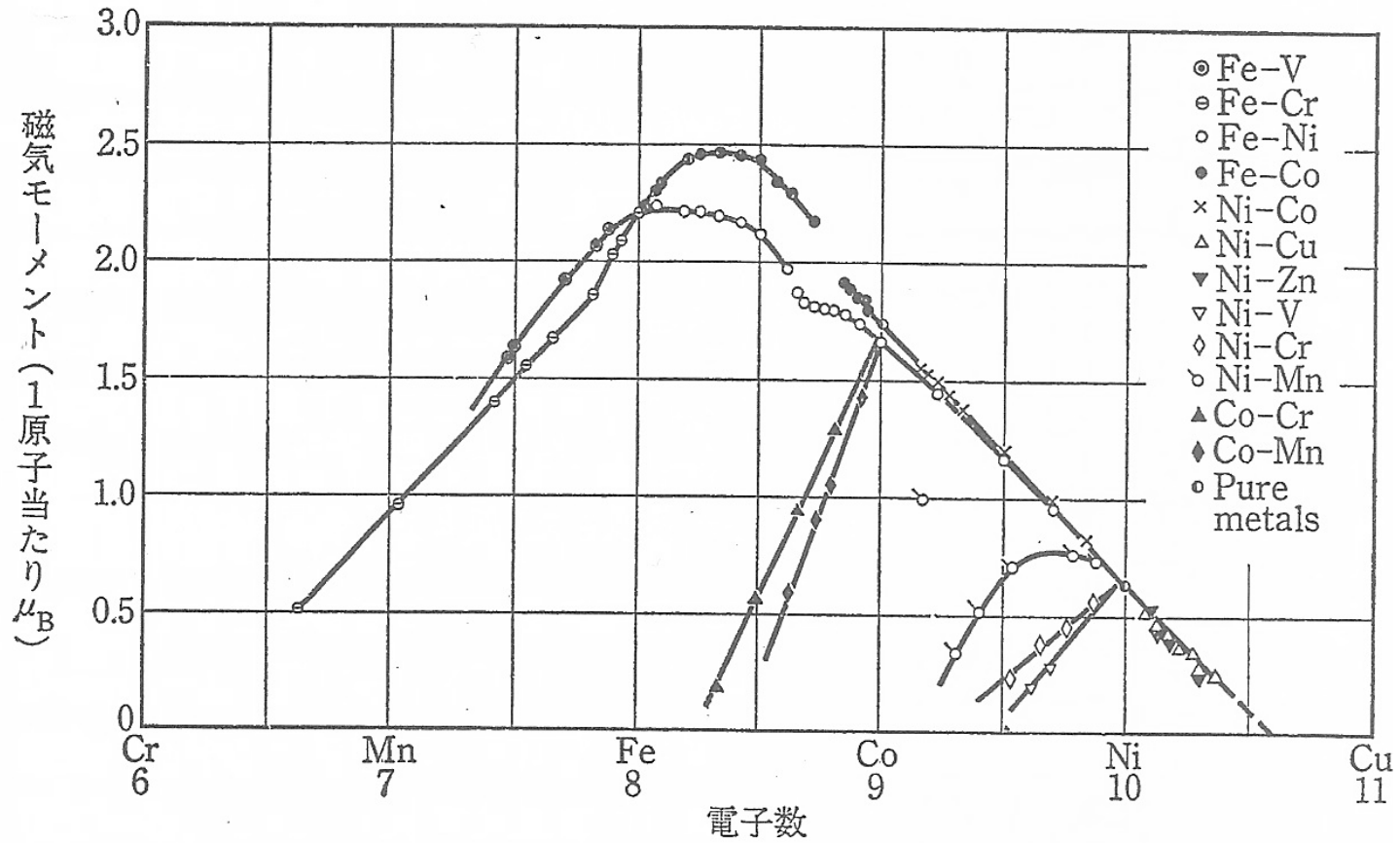


図 11-1 Slater-Pauling 曲線 (Bozorth)

5.1 Hubbard model

Hubbard Hamiltonian:

$$H = \sum_{i\sigma} \epsilon_i n_{i\sigma} + \sum_i U_i n_{i\uparrow} n_{i\downarrow} + \sum_{(i,j)\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma}$$

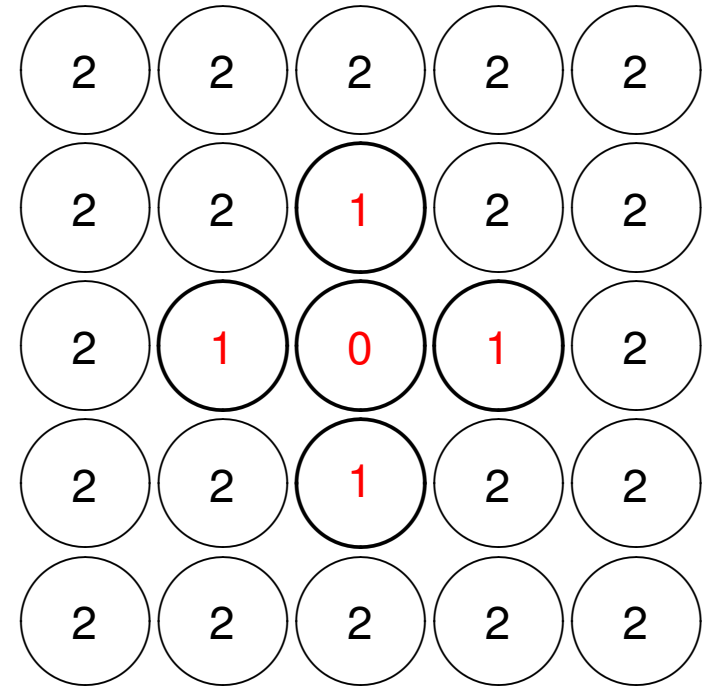
$$n_{i\sigma} = a_{i\sigma}^\dagger a_{i\sigma}$$

Hartree-Fock approximation:

$$H_\sigma = \sum_{i\sigma} \epsilon_{i\sigma} n_{i\sigma} + \sum_{(i,j)\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma}$$

$$\epsilon_{i\sigma} = \epsilon_i + U_i \langle n_{i-\sigma} \rangle$$

A s-orbital at a site



A cluster in metal

0: the center, 1: the first neighbors

2: others

5.2 3d transition-metal alloys

Cluster CPA — 2: coherent potential —

5.2.1 NiFe alloy

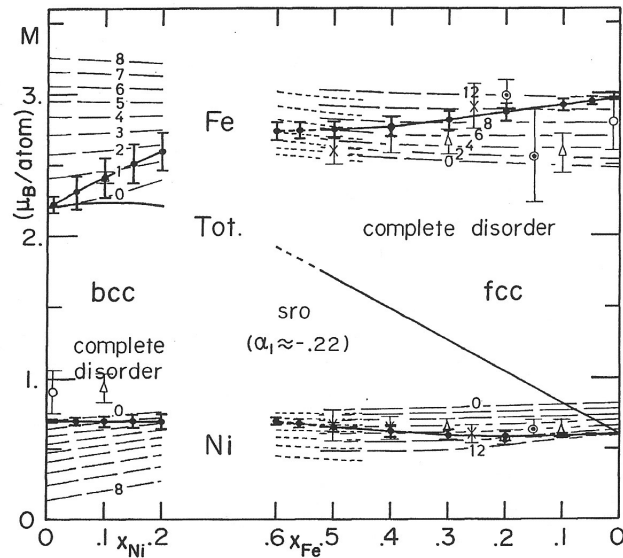
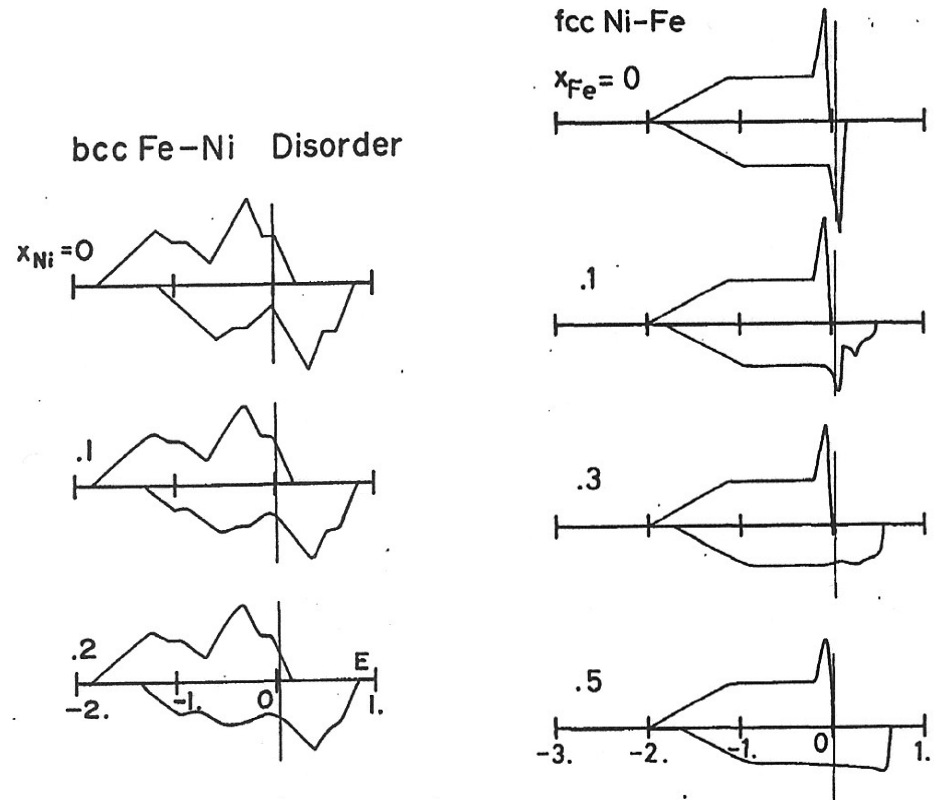


Fig. 4. The Ni and Fe atomic moments in fcc and bcc Ni-Fe. The dashed curves show the Ni and Fe moment for a given number of Ni nearest neighbors as is indicated in the figure. The full lines are the average Ni and Fe moment with the vertical bars representing the root mean square of the deviation of the moment from its average value. The curve labelled Tot. represents the total magnetization per atom. The dotted curves indicate the corresponding moments in alloys with atomic short-range order ($\alpha_1 < 0$). \times , Δ , \triangle , \square , \circ (¹¹) and \odot (¹²) show the experimental data by neutron diffraction.

- Fe: $2.2\mu_B \rightarrow \sim 3\mu_B$
- Ni: $0.6\mu_B$ constant
- Majority-spin band: fully filled?
- Charge neutrality



5.2.2 FeCo alloy

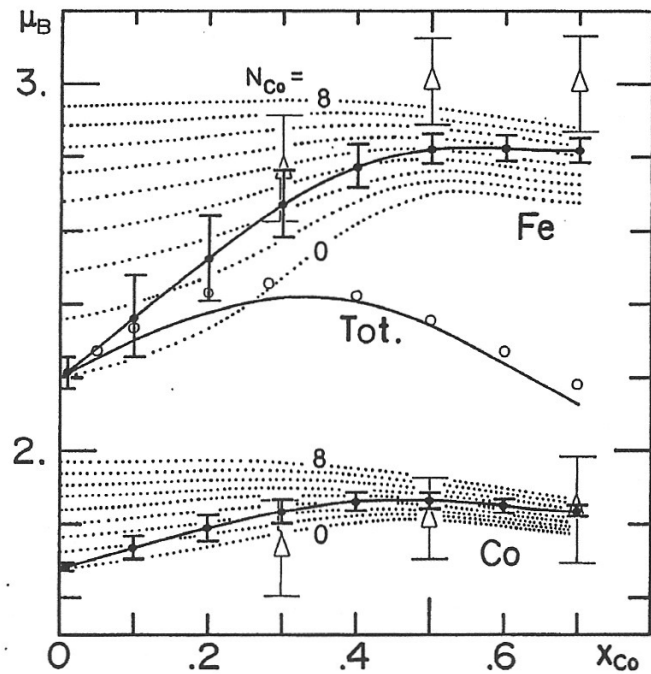


Fig. 12. The Fe and Co moments in bcc Fe-Co alloy with complete disorder. Triangles show the neutron diffuse scattering data for Fe and Co moments.¹⁰⁾ Circles display the experimental magnetization data.¹³⁾

- Fe: $2.2\mu_B \rightarrow \sim 3\mu_B$
- Co: $1.8\mu_B$ constant
- Majority-spin band: fully filled?
- Charge neutrality

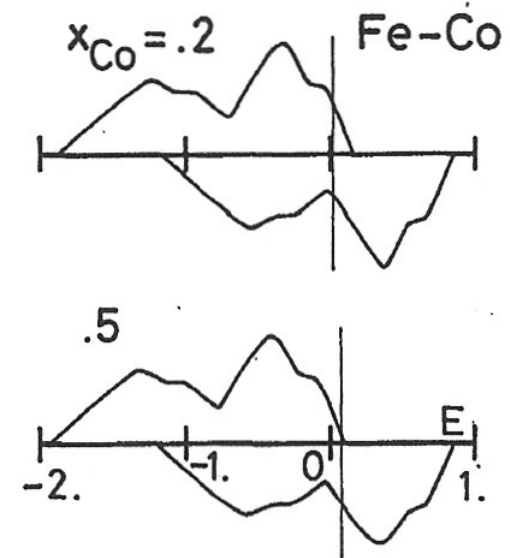


Fig. 9. The total DOS's in bcc Fe-Co.

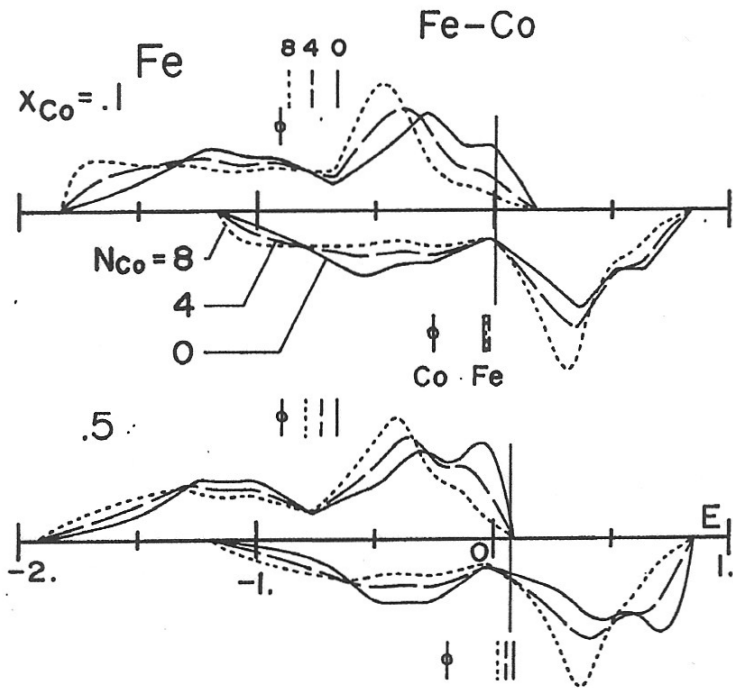


Fig. 10. The local DOS's and the atomic levels of Fe atom in bcc Fe-Co.

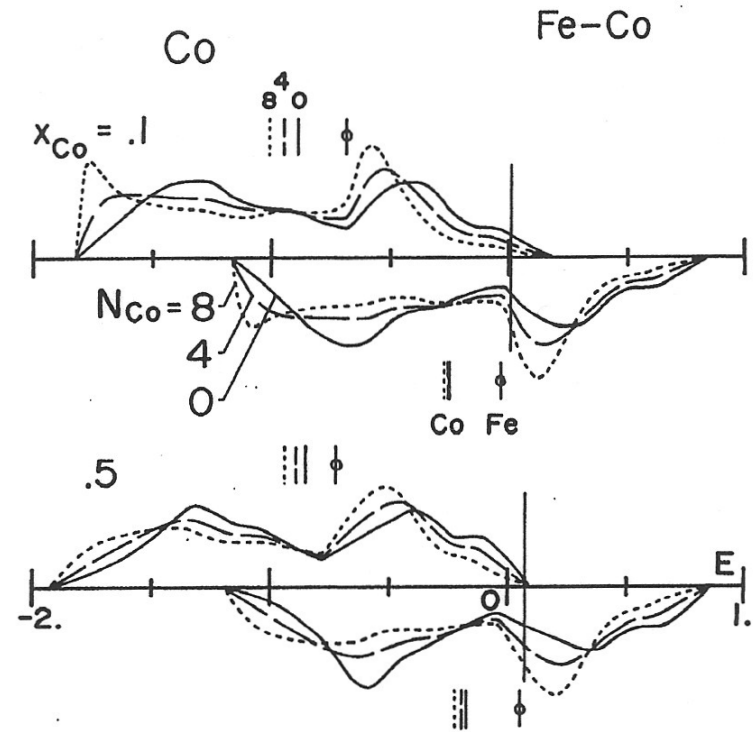


Fig. 11. The local DOS's and the atomic levels of Co atom in bcc Fe-Co.

Neighbor cobaltized Fe makes the Fe moment larger.

⇒ Large magnetization of NdFeB-magnet

5.2.3 FeV alloy

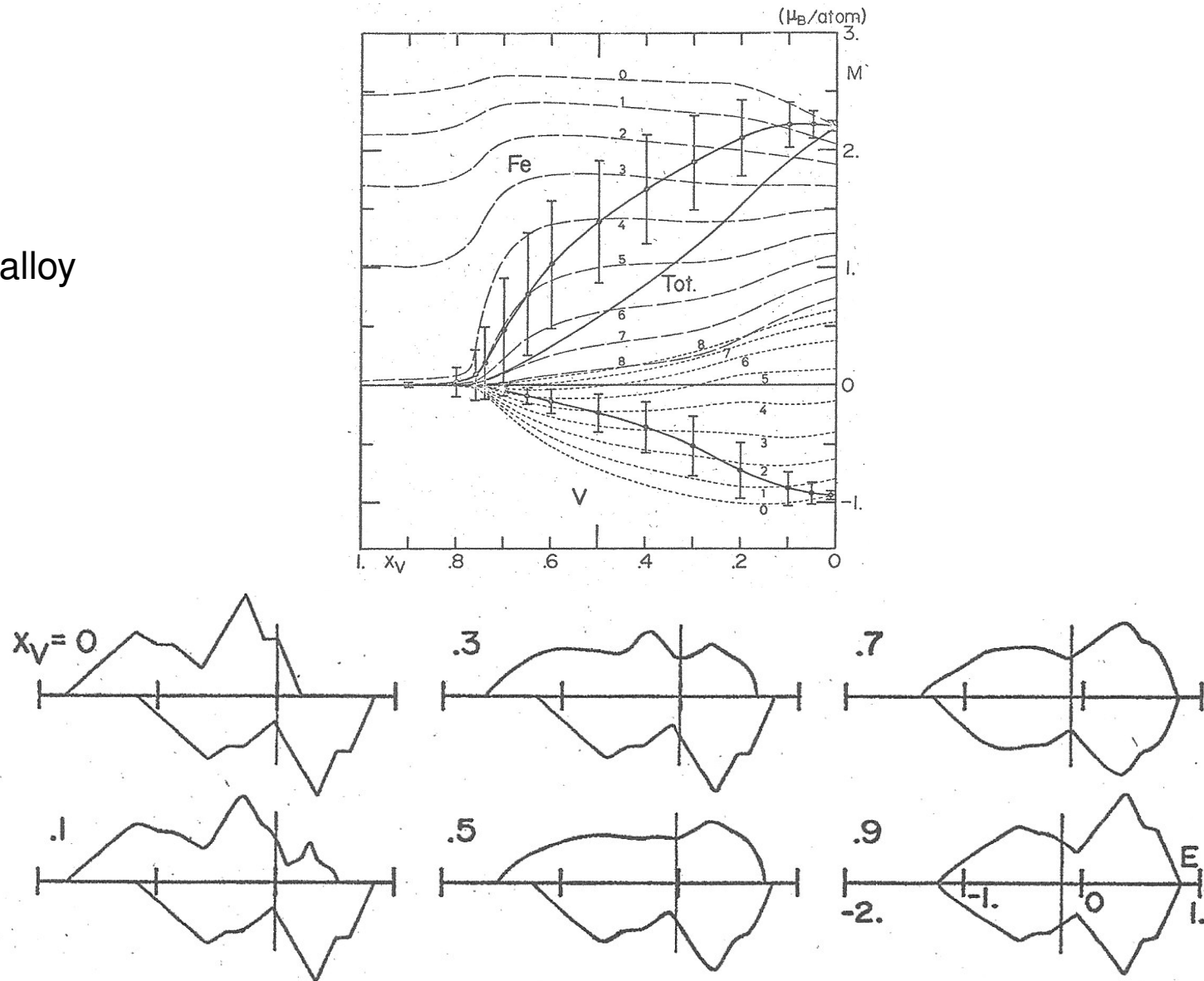
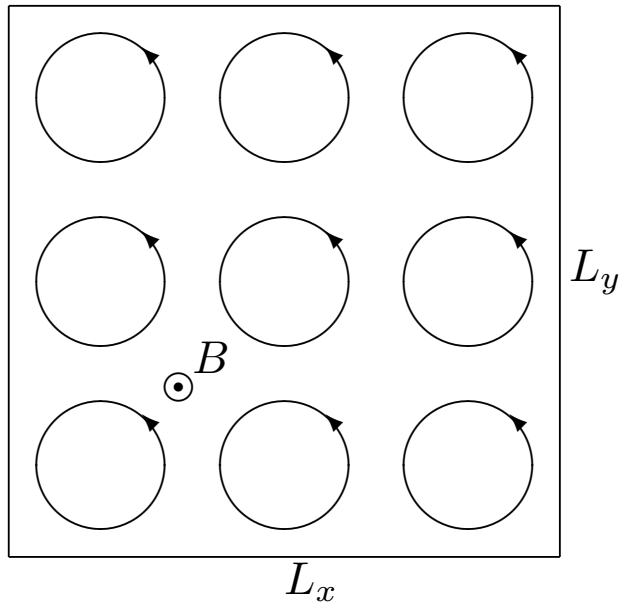


Fig.3. The total density of states for each spin in various V concentrations. The vertical line near $E=0$ is the Fermi level.

6 Free electron under the uniform magnetic field



(Classical picture)

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

$$\boxed{\omega_c = \frac{v}{r} = \frac{eB}{m}} : \text{cyclotron frequency}$$

v, r : arbitrary

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

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

6.1 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:

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

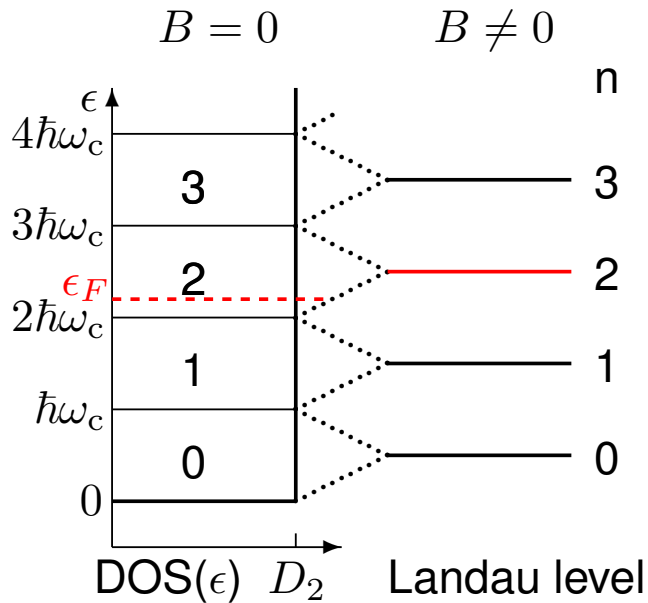
Eigenenergy:

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

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

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) is

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

Cyclotron radius: $l = \sqrt{\frac{\hbar}{eB}}$
 \sim the radius of wavefunction

ϵ_F : Fermi energy in $B = 0$ ($\epsilon_F \sim 1$ eV)

n : Partially-occupied Landau level ($n \sim 10^3$ in $B = 1$ T)

$$n\hbar\omega_c < \epsilon_F < (n+1)\hbar\omega_c$$

Landau level :

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

The increase of energy due to B : $E_2(B)$ ($E = E_0 + E_2(B)$)

$$\begin{aligned} E_2(B) &= \int_{n\hbar\omega_c}^{\epsilon_F} d\epsilon \left[\left(n + \frac{1}{2} \right) \hbar\omega_c - \epsilon \right] D_2 \\ &= \frac{1}{2} [(n+1)\hbar\omega_c - \epsilon_F] [\epsilon_F - n\hbar\omega_c] D_2 \end{aligned}$$

7 Landau diamagnetic susceptibility (Landau 反磁性)

($T \sim 300\text{K}$, $k_B T \sim 30\text{meV}$, $B \sim 10^{-2}\text{T}$, $\hbar\omega_c \sim 10^{-2}\text{meV}$, $\epsilon_F \sim 1\text{eV}$, $n \sim 10^5$)

$k_B T \gg \hbar\omega_c$

average over various Fermi energy : $n\hbar\omega_c \leq \epsilon_F \leq (n+1)\hbar\omega_c$

$$\langle E_2(B) \rangle = \frac{1}{\hbar\omega_c} \int_{n\hbar\omega_c}^{(n+1)\hbar\omega_c} d\epsilon_F E_2(B) = \frac{1}{3} \mu_B^2 D(\epsilon_F) B^2$$

$$M(B) = - \frac{d\langle E_2(B) \rangle}{dB}$$

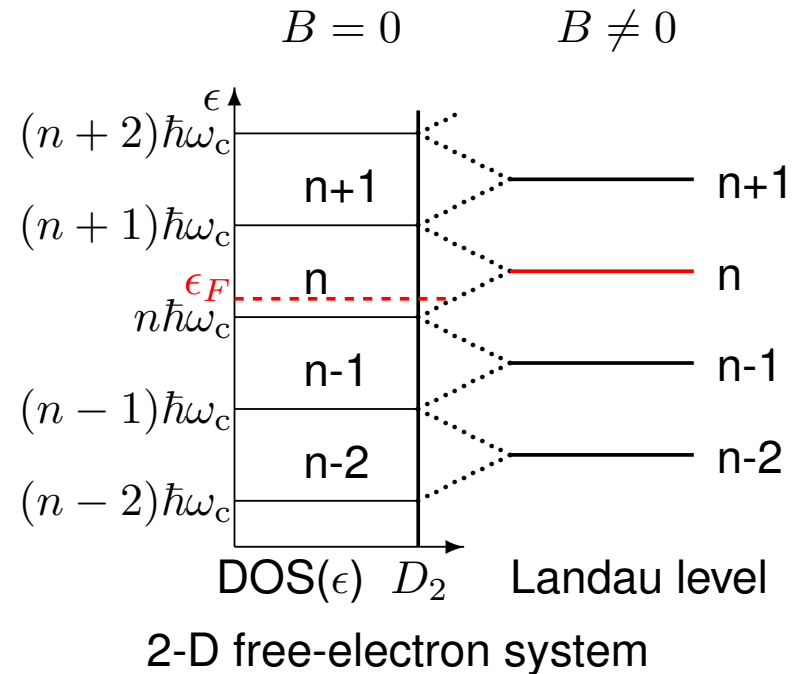
$$\chi_L = \frac{\mu_0 M(B)}{B}$$

$$= - \frac{2}{3} \mu_0 \mu_B^2 D(\epsilon_F)$$

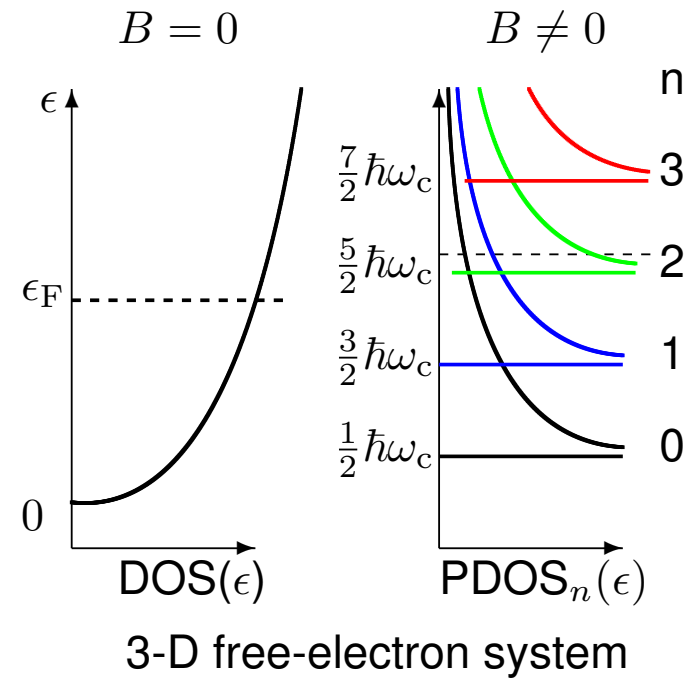
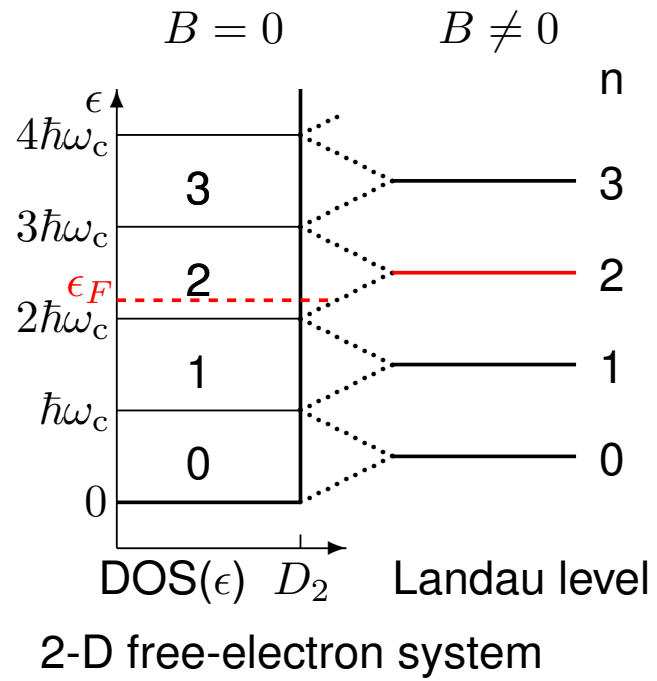
$$= - \frac{1}{3} \chi_P$$

χ_L Landau susceptibility

χ_P Pauli susceptibility



2D vs. 3D



8 de Haas - van Alphen effect

2-D free-electron system

n : Partially occupied Landau level

$$n\hbar\omega_c < \epsilon_F < (n+1)\hbar\omega_c \quad ; \quad \omega_c = \frac{eB}{m}$$

$$n < \frac{B_1}{B} < n+1 \quad ; \quad \frac{\epsilon_F}{\hbar\omega_c} = \frac{m\epsilon_F}{\hbar eB} = \frac{B_1}{B}, \quad B_1 = \frac{m\epsilon_F}{\hbar e}$$

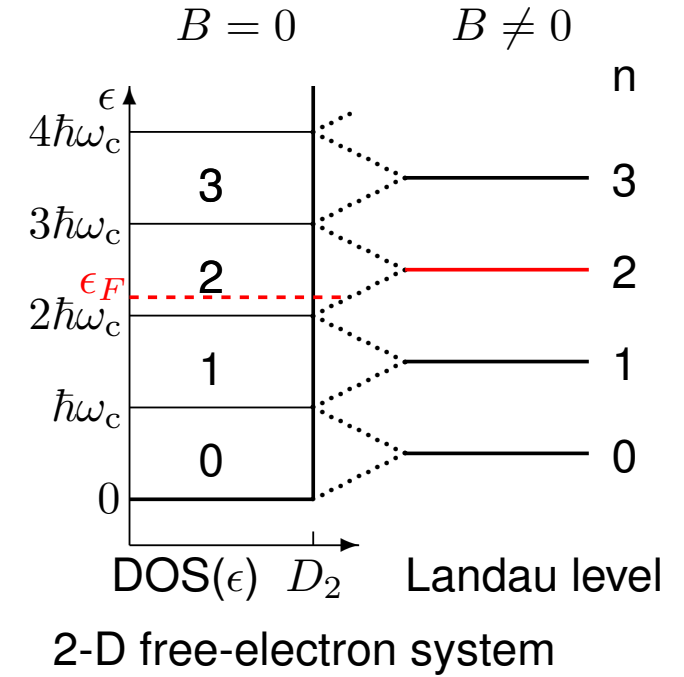
$$\frac{n}{B_1} < \frac{1}{B} < \frac{n+1}{B_1}$$

The increase of energy due to B :

$$E_2(B) = \int_{n\hbar\omega_c}^{\epsilon_F} d\epsilon \left[\left(n + \frac{1}{2} \right) \hbar\omega_c - \epsilon \right] D_2 = \frac{1}{2} [(n+1)\hbar\omega_c - \epsilon_F] [\epsilon_F - n\hbar\omega_c] D_2$$

Magnetization : $\left(\mu_B = \frac{e\hbar}{2m} \right), \quad M_0 = \mu_B \epsilon_F D_2$

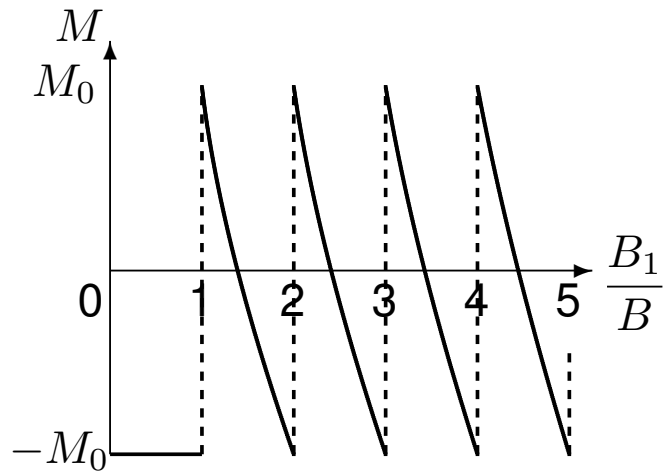
$$\begin{aligned} M(B) &= -\frac{\partial E_2(B)}{\partial B} = -\mu_B [(\epsilon_F - n\hbar\omega_c)(n+1) - ((n+1)\hbar\omega_c - \epsilon_F)n] D_2 \\ &= -\mu_B \epsilon_F D_2 B \left[\left(\frac{1}{B} - \frac{n}{B_1} \right) (n+1) - \left(\frac{n+1}{B_1} - \frac{1}{B} \right) n \right] \end{aligned}$$



de Haas - van Alphen effect

Magnetization oscillates as a function of B.

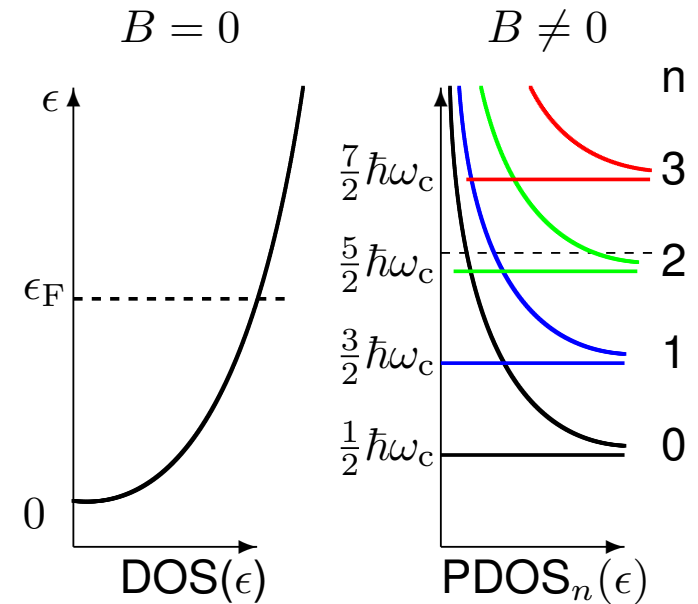
In the 2-D free-electron system,



$$M_0 = \mu_B \epsilon_F D_2$$

$$\hbar\omega_c = \epsilon_F \text{ when } B = B_1$$

In the 3-dimensional system,



DOS($B \neq 0$) : still oscillatory



oscillation of $1/B$ plot

⇒ Fermi surface

(extremal orbit)

$$T \sim 1\text{K}, k_B T \sim 10^{-1}\text{meV}, B \sim 10\text{T}, \hbar\omega_c \sim 10\text{meV}, \epsilon_F \sim 1\text{eV}, n \sim 100$$

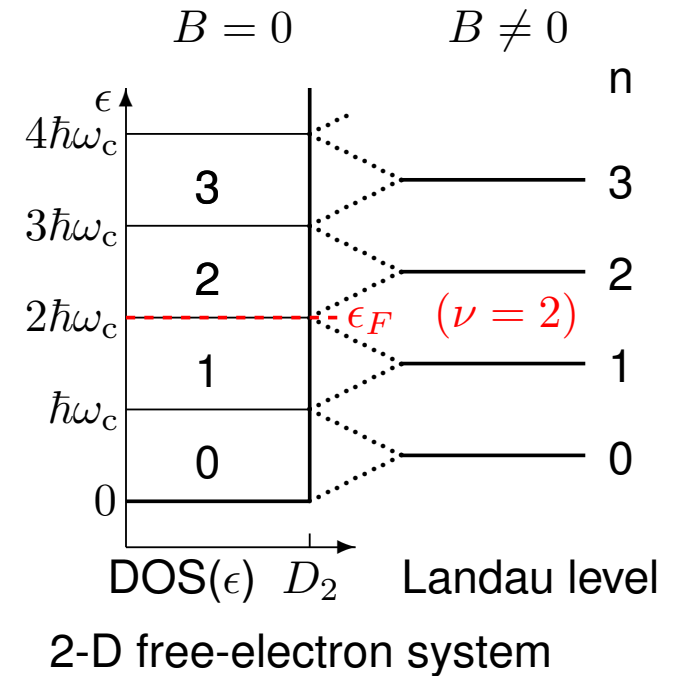
9 Quantum Hall effect (2D)

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 $v_c = \frac{E_x}{B}$, which causes the Hall current

$$J_y = ev_c N_e = \frac{eN_e}{B} E_x ,$$

where N_e is the total electron number per unit

area. Namely, the Hall conductivity is $\sigma_{yx} = \frac{eN_e}{B}$



When $\frac{N_e}{N(B)} = \nu$ ($\nu = 1, 2, \dots$), the system becomes insulator. The condition gives $\frac{N_e h}{eB} = \nu$; namely, $\frac{eN_e}{B} = \nu \frac{e^2}{h}$.

Thus, for the insulating state, the Hall conductivity is quantized:

$$\sigma_{yx} = \nu \frac{e^2}{h} \quad (\nu = 1, 2, 3, \dots)$$

ν : TKNN number (1982), which is proved to be topological invariant.